CONDUCTIVITY AND DIELECTRIC RESPONSE IN POLY(ETHYLENE OXIDE) – MODIFIED MULTIWALL CARBON NANOTUBES

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Abstract
The electric response of nanocomposites consisted of poly(ethylene oxide) as matrix and modified multiwall carbon nanotubes as reinforcing phase, is investigated. The dielectric response and the conductivity of nanocomposites is examined with parameters the content in MWCNT, the temperature and the frequency of the applied electric field. The dependence of conductivity on the MWCNT content allows the determination of percolation threshold, which governs the transition from the insulating to the conductive behaviour. Moreover, the dependence of conductivity on temperature and frequency offers the possibility to study the charge transport mechanisms. The type of the conductivity is studied by means of Variable Range Hopping model and Symmetric Hopping model. The applicability of both models implies hopping as the main conduction mechanism below percolation threshold. Recorded dielectric relaxations arise from both the matrix and the filler.

1 Introduction

The term nanodielectrics refers to multiphase systems with, at least, one of the constituents' dimension at the nanoscale. The principle categories of nanodielectrics are two: (a) polycrystalline semiconductive or insulating materials with grain at the nanoscale level, and (b) polymer matrix composites with embedded nanoinclusions. The second category exhibits advantages related to both the mechanical and electrical properties. This type of materials can be processed easily, is characterized by enhanced thermomechanical stability, and high dielectric breakdown strength. Polymer matrix nanodielectrics replace conventional insulating materials in many technological applications, because of their ability to diffuse electrical carriers, avoiding thus the concentration of charges at tips inside the bulk material, which may cause an early failure of the component. Moreover, could be exploited in microelectronics as conductive adhesives, circuit elements, and recently in remote energy storing devices.

Polymer nanocomposites represent a new, well promising, class of engineering materials. The idea of nanoreinforcement is to control the structure/interactions at the smallest scale, providing the best possibilities for tailoring the macroscopic performance of the systems. Carbon nanotubes (CNTs) and layered silicates (LS) appear to be the most popular nanofillers, because of their high aspect ratio and reinforcing efficiency in mechanical,

thermal and electrical behavior. Poly(ethylene oxide) (PEO) is a technologically important polymer in solid polymer electrolyte applications (batteries, supercapacitors, fuel cells) [1]. However, its poor mechanical properties act as a limiting factor upon the aforementioned applications. A possible solution could be the integration of CNTs in PEO, targeting both the enhancement in mechanical and electrical performance. The reinforcing efficiency of CNTs is directly related to the quality of their dispersion within the matrix. For this reason different methods of CNTs modification have been proposed [1].

In the present work the electric response of pure PEO and PEO/modified multiwall carbon nanotubes (MWCNT) composites is investigated. The dielectric response and the conductivity of nanocomposites is examined with parameters the content in MWCNT, the temperature and the frequency of the applied electric field. The electrical response of the nanocomposites was assed by means of Broadband Dielectric Spectroscopy (BDS) in the frequency range of 0.1 Hz to 10^7 Hz, and in the temperature range from 25^{o}C to 60^{o}C. An abrupt increase of conductivity with filler content is recorded. The transition from insulating to conductive behaviour can be analysed by means of percolation theory. Percolation threshold or critical concentration diminishes with temperature. Charge transport mechanisms can be studied via the dependence of conductivity on temperature and frequency. For this reason, obtained data are analysed via the Variable Range Hopping model and Symmetric Hopping model. From the analysis, results that in the vicinity of percolation threshold and prior to that the dominating charge transport mechanism is hopping, while at higher filler's concentration conduction via geometrical contacts is also present. Nanocomposites with MWCNTs content lower than the percolation threshold exhibit three dielectric relaxation processes attributed to interfacial polarization, glass to rubber transition of the matrix, and local motions of polar side groups of the polymer chains.

2 Materials and testing methods

2.1 Specimens preparation

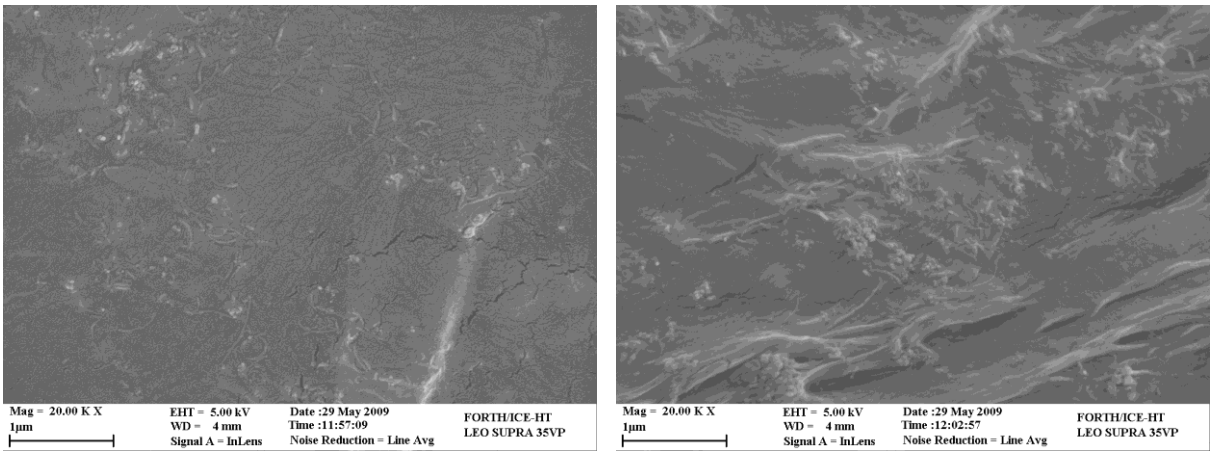
For the specimens preparation the following materials were used: PEO with weight average molecular weight of 300,000 g mol^{-1} (Acros Organics,Geel, Belgium), MWCNT (Baytube® 150P, Bayer MaterialScience AG, Leverkusen, Germany), suberic acid (Aldrich, Steinheim, Germany) and sodium hydroxide (J.T. Baker, Deventer, Holland). Nanocomposites were produced by dispercing MWCNT in the aqueous solution of PEO (5 %w/w) using a sonication method. Analytical description of the preparation procedure and the MWCNTs' modification has been given elsewhere [1].

2.2 Specimens characterization

The morphology of the prepared systems was examined by means of Scanning Electron Microscopy (SEM) via a Leo Supra 35VP instrument. Thermal behaviour of the polymer matrix was recorded in terms of Differential Scanning Calorimetry (DSC) by employing a Diamond DSC instrument supplied by Perkin Elmer. From the conducted thermal analysis were determined, the glass to rubber transition of PEO at -28^{o}C, and its melting point at 73^{o}C. The initiation of melting process at 60^{o}C fixed the condition of maximum applied temperature during the dielectric scans. Electrical characterization of all the tested systems was carried out by means of BDS technique in the frequency range10^{-1}Hz to 10^7Hz, via an Alpha-N Analyser (High resolution dielectric analyzer) supplied by Novocontrol Technologies. Examined specimens were subjected to isothermal scans from 25^{o}C to 60^{o}C, with a temperature step of 5^{o}C. Temperature was controlled via Novotherm system and the used dielectric cell was BDS 1200, both supplied by Novocontrol Technologies.

3. Results

Figure 1 presents SEM images of the examined nanocomposites. The distribution of MCNTs can be considered satisfactory since large agglomerates are absent in the samples with modified MWCNTs. However, smaller clusters as well as nano-dispersions can be detected in all studied systems.



(a) (b)

Figure 1. SEM images of nanocomposites with: (a) 0.25, and (b) 0.50 %w/w in modified MWCNT content

Conductivity as a function of frequency at two temperatures, varying the conductive filler content is depicted at Figure 2. Conductivity increases with MWCNT content at all studied temperatures. Variation of conductivity with frequency appears to be in accordance with the, so called, ac universality law [2], which is expressed via the relation:

$$\sigma(\omega) = \sigma_{DC} + A\omega^{s} \tag{1}$$

where σ_{DC} is the limiting value of conductivity when frequency tends to zero, ω the angular frequency and A and s constants depending upon filler concentration and temperature [3]. In the present study as σ_{DC} is considered the value of conductivity at the lowest measured frequency 0.1Hz.

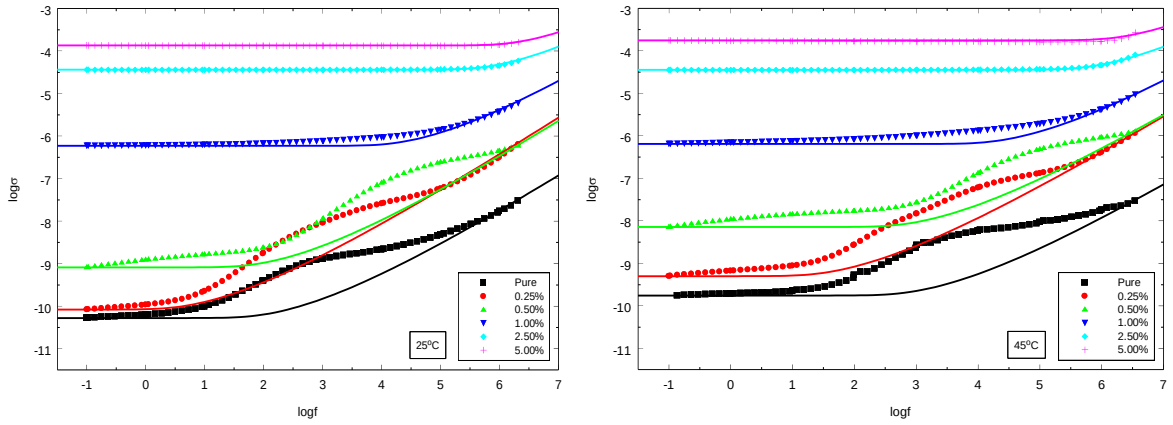


Figure 2. Conductivity versus frequency for all the examined systems at 25 and 45°C. Lines are produced by the random free-energy barrier model.

From Figure 2 becomes evident that conductivity varies with frequency and temperature. However, the influence of these parameters upon conductivity is also related to the conductive filler content. At low frequencies conductivity tends to acquire constant values, in all cases,

approaching thus its DC value. On the other hand, beyond a critical frequency conductivity follows an exponential dependence on frequency. This type of conductivity variation with frequency is considered as an indication that charge carriers migration is conducted via hopping mechanism [4], [5]. At low MWCNT content, that is less than 0.50% w/w, and in the intermediate frequency range a dielectric relaxation process is recorded. At higher MWCNT content the frequency dependence of conductivity becomes weak or even negligible, implying that the critical concentration for the transition from insulating to conductive behaviour has been exceeded.

4. Discussion

The variation of conductivity as a function of the modified MWCNT content and temperature, at two frequencies, is shown in Figure 3. In both graphs, as well as in all the examined cases, an abrupt increase of conductivity in a narrow range of filler content is observed. The alteration of conductivity values by several orders of magnitude, varying the conductive content by less than 2%, signifies the transition from the insulating to the conductive behaviour. Furthermore, it is apparent that the effect of temperature is more pronounced in systems with MWCNT content lower than the percolation threshold. Critical concentration or percolation threshold is a parameter governing the transition from insulating to conductive behaviour. Increasing the concentration of conductive phase results in decreasing of the mutual distance of inclusions. At a critical content a conductive path is formed within the matrix, through which charge carriers can migrate percolating the whole nanocomposite, resulting in the dramatic increase of conductivity. At even higher content of the filler, a three-dimensional network of conductive paths is formed and system's conductivity remains practically constant being independent from variations in conductive phase content [6,7]. In the vicinity of threshold, transport properties exhibit strong non-linear behaviour, which mathematically can be expressed via the relation

$$\sigma \approx (P - P_C)^t \tag{2}$$

where P is the content of conductive phase, Pc the critical concentration or percolation threshold and t the critical exponent, a dimensionless constant related to the dimensionality (1-D, 2-D, 3-D) of the formed conductive path, inside the composite. Critical concentration and exponent can be determined by fitting experimental data via equation (2) in its logarithmic form, as expressed by equation (3)

$$\log \sigma \approx t[\log(P - P_C)] \tag{3}$$

Insets of Figure 3 give characteristic examples of P_C and t determination at 25 and 45 ^{o}C.

Determined values of critical concentration P_C and exponent t were found to vary with both temperature and frequency of the applied field. Percolation threshold varies between 0.46 and 0.35% w/w in modified MWCNTs. Percolation theory predicts also, a huge increase of ε' in the vicinity of the critical concentration, which mathematically is expressed by the relation:

$$\varepsilon' \approx (P_C - P)^{-s} \tag{4}$$

where s is a critical exponent. Equation (4) is valid for conductive phase concentrations lower than the critical one. As can be seen in Figure 4, data obtained in this study are in accordance

with equation (4). The large increment of permittivity values in the vicinity of the percolation threshold has been considered as an artificial method for developing, the so-called, high k materials.

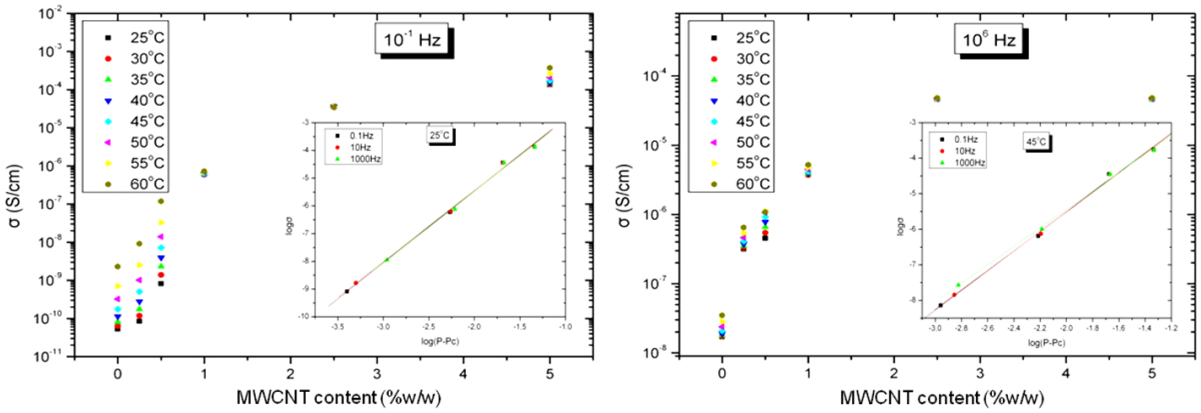


Figure 3. Conductivity versus the MWCNT content, at various temperatures, for two different frequencies. Insets are used for the determination of the percolation threshold.

The examined systems are considered as disordered, since they are not metals and have no crystal structure [5]. Hopping conductivity has been found to be the main charge transport mechanism in many amorphous and disordered materials [4,5]. The term hopping refers to the sudden displacement of a charge from one site to another adjacent one and in generally includes both jumps over a potential barrier and the quantum mechanical effect of tunnelling [8]. The temperature and frequency dependence of conductivity can be employed in order to examine the occurring conductance mechanisms. For this reason the applicability of two conductivity models upon the obtained data has been considered.

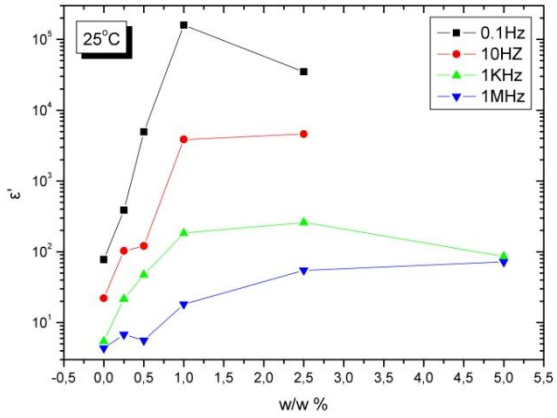


Figure 4. Real part of dielectric permittivity as a function of the MWCNT content at 25°C, for various frequencies.

Variable Range Hopping model (VRH), originally proposed by Mott for amorphous semiconductors [9] is the first one. VRH model considers charge migrations from a localized site level to an adjacent one with higher energy level or to another one far apart but with similar energy level. Neglecting mutual interactions between charge carriers, the temperature dependence of conductivity according to VRH model can be expressed via the following relation:

$$\sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\gamma}\right] \tag{5}$$

where σ_0 is a pro-exponential factor, considered as the limiting value of conductivity when temperature tends to infinity, and T_0 is a characteristic temperature which determines the thermally activated hopping process between localized sites of different energy levels and is considered as the measure of the system's disorder. Further, the term γ is related to the dimensionality of the conduction process via the relation $\gamma = 1/(1+d)$, where d=1,2,3. The applicability of the model is examined by constructing graphs of the form $\log \sigma T^{1/2} = f(T^{-\gamma})$. If data can be satisfactory linear fitted, then the model is able to describe the variation of conductivity with temperature providing direct information for the type of the charge transport mechanism and the dimensionality of the process [5]. Graphs of Figure 5 give evidence for the applicability of VRH model upon the examined systems. The term γ takes value equal to ¼, since all tested samples were in the form of circular disk with average thickness of 2 mm, and the fitting quality factor R was found to approach unity.

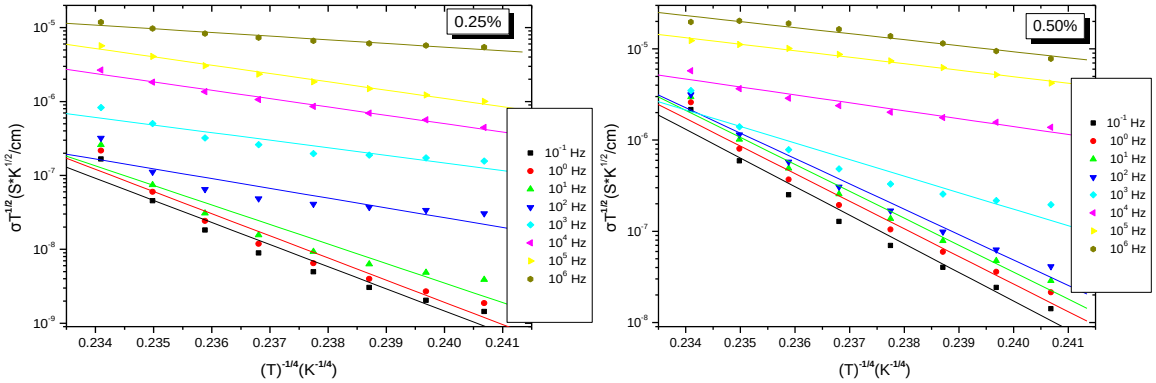


Figure 5. Conductivity of (a) 0.25 and b) 0.50 %w/w in MWCNT as described by VRH model.

The second employed model is the random free-energy barrier model known also as the symmetric hopping model, proposed by Dyre [4]. Dyre's model describes the dependence of conductivity upon frequency, in a wide frequency range, in disordered solids at constant temperature. In this approach ac conductivity is less temperature dependent implying that in ac conductance processes activation energy is lower than the dc corresponding one. Further, charge carriers are considered to remain at sites of minimum energy, without any mutual interactions. Employing a continuous time random walk approximation and suggesting that only hops at neighbor sites are allowed, energy barriers vary randomly, and the probability of hopping between adjacent sites is equal for both directions, Dyre proposed the following equation [4]:

$$\sigma^*_{ac}(\omega) = \sigma_{dc}\left[\frac{j\omega\tau}{\ln(1+j\omega\tau)}\right] \tag{6}$$

where σ_{dc}, ω and τ are dc conductivity, angular frequency, and relaxation time respectively.

In Figure 2 experimental data are described via the real part of equation (6). The resulting curves tend to constant values at low frequencies; while at high frequencies follow the exponential law of equation (1). At systems with conductive phase content lower than the

critical one, data are in accordance with values predicted by equation (6) at low and high frequencies. Nanocomposites with MWCNT content higher than the percolation threshold are in agreement with the produced curves in the whole frequency range. Thus it can be concluded that hopping conductivity is present in all the examined systems. In systems with low or moderate MWCNT content data decline from equation (6) in the intermediate frequency range. This deviation is attributed to the existence of dielectric relaxation processes, in the particular systems, which cannot be described via Dyre's model. These processes are not recorded in the spectra of nanocomposites with higher MWCNT content, and consequently the model's agreement with data is enhanced. It should be noted that the specific model refers to ac conductivity and it was not developed for describing dielectric relaxations.

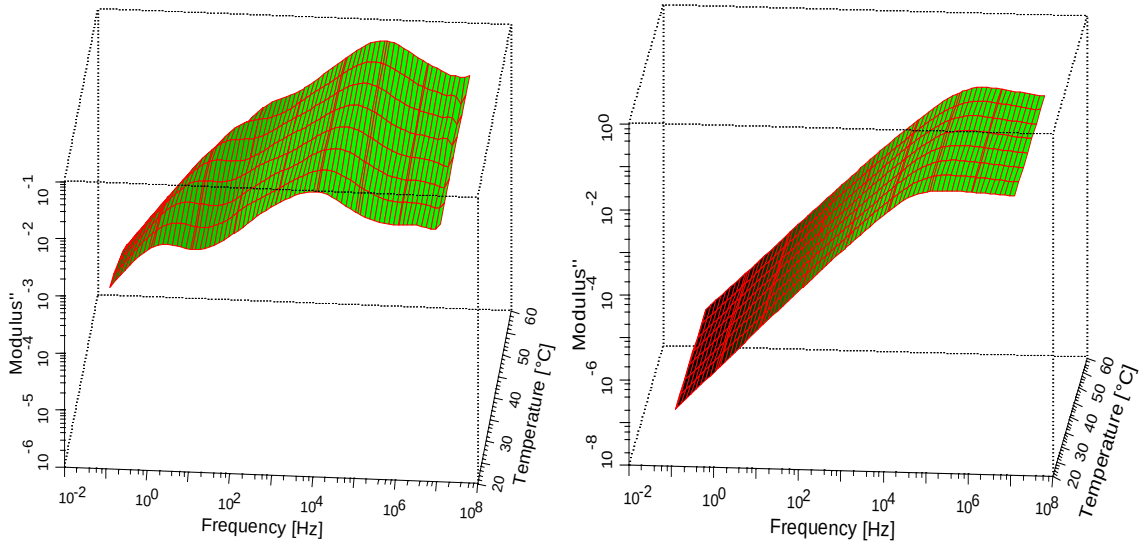


Figure 6. Loss modulus index versus frequency and temperature for the composites with (a) 0.25, and (b) 1.0 (%w/w) of MWCNT.

Dielectric relaxations have been studied by means of electric modulus formalism. The variation of the imaginary part of electric modulus (loss index) as a function of temperature and frequency is presented in Figure 6 for two nanocomposites. PEO is a semi-crystalline polymer [1,10] and thus it is consisted by hard (more rigid) crystalline regions and soft amorphous regions. The relaxation process at the intermediate frequencies, which has been detected via dielectric spectroscopy and dynamic mechanical analysis [10,11], is attributed to relaxation of the amorphous phase, specifically to the glass to rubber transition. The relaxation process recorded at the high frequencies edge is attributed to local motions of small parts of the crystalline chains. In the low frequency range and at relatively high temperatures another dielectric relaxation process is recorded, which is assigned to Interfacial Polarization (IP) effect known also as Maxwell-Wagner-Sillars (MWS) effect. IP is present in heterogeneous systems, since unbounded charges accumulate at the constituents' interface, where they form large dipoles. These dipoles try to follow the alternation of the applied field, however as frequency increases their inertia delays their orientation. IP is recorded in all systems with MWCNT content up to 0.5%w/w. In nanocomposites with filler content higher than the critical concentration IP is absent. Considering that the physical origin of IP is related to the gathering of mobile charges at the interface of the system, it is reasonable to suggest that above percolation threshold IP stops existing. Above threshold, conductive path or paths have been formed inside the nanocomposite and charges no longer remain at the interface, migrate through the whole system participating thus to electrical conduction, cancelling at the same time the occurrence of IP.

Conclusions

Variation of conductivity for all the studied systems as a function of MWCNT content and for all the examined temperatures is in accordance with percolation theory, and can be described via its exponential law. The applicability of two conductivity models (namely Variable Range Hopping model and Symmetric Hopping Model) on the obtained data was examined aiming to study the type of the charge transport mechanism. It was found that the main conduction mechanism in the vicinity of critical concentration and prior to that is hopping conductivity. Above percolation threshold charge transport via physical contacts occurs. The contribution fraction of the latter increases with filer content, although charge transport via hopping is ascertain even at the composite with the highest MWCNT content. Three relaxations are recorded in the dielectric spectra of pure PEO. From low to high frequencies, they attributed to IP between crystalline and amorphous phase, relaxation of the amorphous phase, and to local motions of small polar parts of crystalline chains. IP is present in systems with MWCNT content up to 0.5%w/w and then stops existing. Its absent from the spectra of the systems with conductive filler content higher than the critical one is attributed to the electrical conduction through the whole composite of the mobile charges which are requisite for the occurrence of the effect.

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