

Study of electrical / dielectric and thermomechanical properties of polymer – carbon nanotubes nanocomposites.

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Abstract: - The influence of multi-walled carbon nanotubes (MWCNT) on electric/dielectric, thermal and mechanical properties of CNT – reinforced polymer nanocomposites is studied. The nanocomposites under study was polyamide-6 polymer matrix filled with MWCNTs (PA-6/MWCNT), and polypropylene polymer matrix filled with MWCNTs (PP/MWCNT). The investigation is focused on electrical and dielectric properties in relation to percolation : ac and dc conductivity above the percolation threshold p_c and dielectric permittivity, ϵ' , below p_c . To that aim, broadband dielectric relaxation spectroscopy (DRS) was used. In addition, the effect of MWCNT on the thermal transitions and thermomechanical properties (storage modulus, loss tangent) of the nanocomposites was examined by dynamic mechanical analysis (DMTA) measurements.

Key-Words: - polyamide-6, polypropylene, carbon nanotubes, thermal transitions, dielectric properties, electrical properties, percolation threshold, thermomechanical properties.

1 Introduction

The reinforcement of polymers with nano-scaled fillers developed a new class of advanced multifunctional materials with improved properties, used in many fields ranging from microelectronics to aerospace. Conductive composites based on carbon nanotubes (CNT) in polymeric matrices offer many functional applications in the manufacture of sensors, microelectrodes, electromagnetic shielding materials, parts for automotive engineering, etc. CNTs are an especially attractive class of inclusions because of their exceptional mechanical, thermal and electrical properties. Apart from mechanical reinforcement, one key interest is the development

of conductive polymer composites, preferably at low concentration of CNT taking advantage of their high aspect ratio (~ 1000) for numerous applications, which include antistatic devices, capacitors, materials for electromagnetic interference shielding and sensors [1, 2]. A homogeneous dispersion and good interfacial adhesion are crucial for the successful preparation of nanocomposites. Due to the intermolecular van der Waals interactions and entanglements between the nanotubes, destruction of primary agglomerates is not easily to obtain. In context with industrial applications the preferred method is the preparation of composites using melt mixing. Melt-mixing of CNT into thermoplastic polymers using conventional processing techniques

are particularly desirable, because of the speed, simplicity, and availability in the plastic industry [2].

In this study composites of polyamide 6 / multiwalled carbon nanotubes (PA6/MWCNT) and polypropylene / MWCNT (PP/MWCNT) were prepared [3, 4]. Dielectric relaxation spectroscopy measurements were performed to study both the electrical and dielectric properties of the nanocomposites. Special attention is paid to percolation aspects by ac conductivity measurements [5]. Percolation threshold is the critical concentration of the filler where conducting pathways are formed by CNT and consequently a transition from the insulating to conducting phase is observed. Dynamic mechanical analysis measurements were performed in order to study the thermomechanical properties of the nanocomposites.

2 Experimental

2.1 Nanocomposites preparation

2.1.1 Polyamide-6 / MWCNT nanocomposites

A masterbatch of 20 wt% MWCNT in PA6 was obtained from Hyperion Catalysis International, Cambridge, MA in pellet form. The nanotubes are produced from high purity, low molecular weight hydrocarbons in a proprietary, continuous, gas phase, catalyzed reaction. The outside diameter of the tube is approximately 10 nanometers and the length is over 10 microns, giving a very high aspect ratio of ≥ 1000 . Their density is approximately 1.75 g/cm^3 . The masterbatch was diluted with the same PA6 as used in the masterbatch using melt mixing in a Plasti-Corder kneading machine PLE 331 (Brabender, Germany) at 240°C , for 15 min at a mixing speed of 60 rpm. Slabs with a thickness of 1 mm were formed by compression moulding of the mixed components using a laboratory hydraulic press SRA 100 (Fontijne, Netherlands) at 2.4 MPa and at 240°C for 2 min. Prior to mixing, the materials were dried at 80°C in a vacuum for a minimum of 12h. The final concentration of the samples in CNT was varied from 2.5 to 20 wt.%. According to the material densities (1.15 g/cm^3 for PA6 and 1.75 g/cm^3 for CNT) the corresponding volume concentrations are 1.6 to 13.1 vol.%. It is noted that the same procedure was followed for both the pure PA and the masterbatch of 20 wt.% MWCNT, in order to be all the samples directly comparable.

2.1.2 Polypropylene / MWCNT nanocomposites a. Multi-Walled Carbon Nanotubes (MWCNTs)

Two different kinds of MWCNTs were used for the fabrication of PP hybrid materials: nanotubes of $\sim 95\%$ purity and nanotubes dispersed in a PP master batch. The 'pure' MWCNTs were bought from Nanothinx (Greece) and had been made by a CVD process. They were used as received, as they are organophilic and thus, they can be dispersed in olefinic polymers. However, prior to their use, they were dried in a vacuum oven for at least 1 h. The master batch MCNTs were 20% w/w in the PP matrix and were bought from Hyperion Catalysis International. These were also dried in a vacuum oven for at least 1 h prior to their use. No other treatment were they received before use.

b. Polypropylene (PP) matrix

Both isotactic (iPP) and syndiotactic PP (sPP) were purchased from Aldrich Polymer Products and were used as received. Following, though, the same protocol as with the CNTs, they were dried in a vacuum oven for at least 1 h prior to their use. iPP with the following characteristics was used: $M_n=50000$ with a degree of dispersion $M_w/M_n=3.8$, MFI = 35.00 gr/10 min ($230^\circ\text{C}/2.16 \text{ Kg}$, ASTM D 1238). The sPP used had the following characteristics: $M_n=54000$ with a degree of dispersion $M_w/M_n=2.35$, MFI = 4.50 gr/10 min ($230^\circ\text{C}/2.16 \text{ Kg}$, ASTM D 1238). The PP used had a density of 0.9 gr/cm^3 and iPP was the one to be closer to the PP matrix of the master batch, since the latter had a MFI = 30.00 gr/10 min ($230^\circ\text{C}/2.16 \text{ Kg}$, ASTM D 1238). That's why, it was iPP that was mixed with the master batch, while sPP was mixed with the pure MCNTs. Thus, two types of hybrid materials were prepared: sPP/MWCNTs(pure) and iPP/MWCNTs(masterbatch). A ThermoHaake 'MiniLab' Micro - Compounder / Extruder was used for the preparation of the PP/MCNTs nanocomposites through the melt blending technique. The various samples of PP/MCNTs were prepared in this machine by operating it as a compounder at first and then, as an extruder. A home-made thermal press was employed for the production of circular 10 cm disks made of the nanocomposites materials.

2.2 Experimental techniques

2.2.1 Dielectric Relaxation Spectroscopy

Dielectric relaxation spectroscopy (DRS) measurements were carried out isothermally in the

frequency range 10^{-2} - 10^6 Hz and temperature range -150 to 100°C by means of a Novocontrol Alpha analyzer.

2.2.2 Dynamic Mechanical Analysis Measurements (DMTA)

For DTMA in bending mode, a polymer laboratories apparatus (Model PL-MK II) was used in the frequency range 0.1-100 Hz from -100 to $+100^\circ\text{C}$.

3 Results and discussion

Figures 1 and 2, 3 shows the temperature dependence of storage modulus E' and mechanical losses tangent $\tan\delta$ ($=E''/E'$) of DMTA measurements of the PA6/MWCNTs and iPP/MWCNTs nanocomposites respectively.

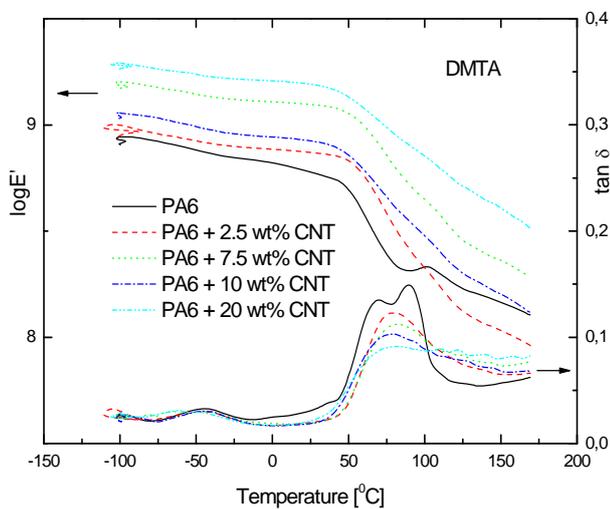


Figure 1: Storage modulus E' and loss tangent ($=E''/E'$) vs temperature for series PA6 / MWCNTs

When a polymer goes through an α relaxation, $\tan\delta$ shows a maximum at the α -transition temperature (T_α), and a substantial drop in E' appears, indicating viscous damping due to segmental motion in the polymer. The presence of the nanofiller with 2.5 – 20 wt.% enhances the values of E' up to 30% (Figure 1) and this effect appear in different magnitudes at various temperature ranges, although the glass transition temperature decreases by the addition of MWCNTs in agreement with differential scanning calorimetry results, not shown here. The low temperature mechanism is attributed with secondary relaxations, studied in detail at DRS results, remains unaffected by the addition of CNTs.

The presence of the nanofiller with 2 – 5 wt.% in iPP/MWCNTs enhances the values of E' up to 60% (Figure 2), although the glass transition temperature remains unaffected by the addition of MWCNTs (Figure 3).

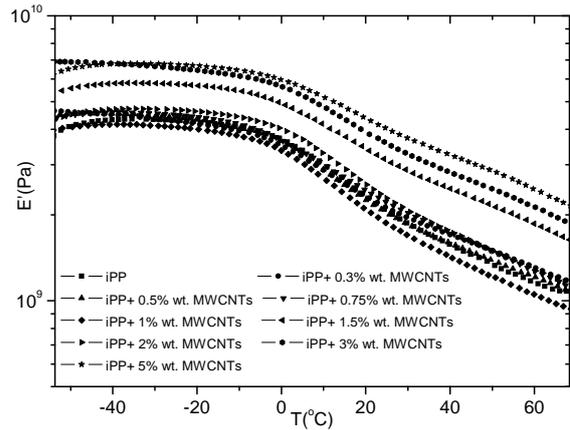


Figure 2: Storage modulus E' vs temperature for series iPP / MWCNTs

Figure 4 shows the ac conductivity (σ_{ac}) at room temperature as a function of frequency for the samples indicated on the plot.

The frequency dependence of the ac conductivity follows a power law behaviour and can be expressed by the following equation :

$$\sigma'(\omega) = \sigma(0) + \sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s \quad (1)$$

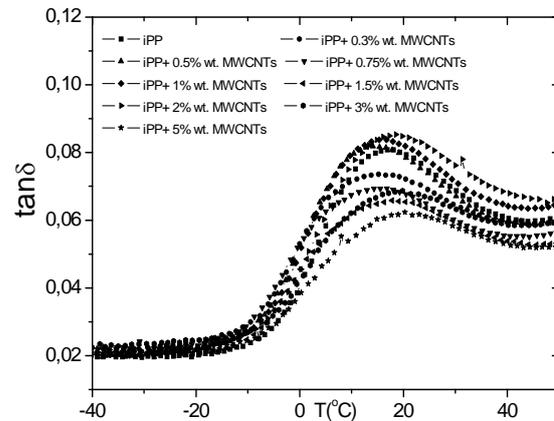


Figure 3: Loss tangent vs temperature for series iPP / MWCNTs

where ω is the angular frequency, σ_{dc} is the dc conductivity (at $\omega \rightarrow 0$), A is a constant which depends on temperature T , and s is an exponent dependent on both frequency and temperature with values in the range 0-1. This is a typical behaviour for a wide variety of materials and is called 'universal dynamic response' (UDR) [6]. The value of σ_{dc} can be estimated from the plateau values of conductivity. Also, for each composition there is a critical frequency f_c beyond which a power law is followed. Due to space charge polarization a hump is appeared at the crossover region and the results cannot be further analyzed with the UDR theory.

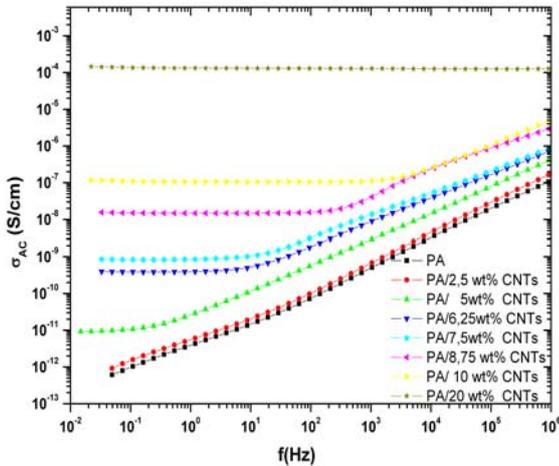


Figure 4 : Conductivity vs frequency for PA6/MWCNTs samples

For the pure PA and PA/2.5 wt.% MWCNT, ac conductivity increases approximately linearly with the frequency in a logarithmic scale, exhibiting a typical capacitor behaviour. At loadings in excess of 5 wt.% a dc plateau, where conductivity is independent of frequency, appears up to the critical frequency f_c . For these composites the value of the crossover frequency f_c increases with increasing MWCNT content. For the sample PA/20 wt.% MWCNT the dc plateau spreads to the whole frequency range. Thus, the dc conductivity plateau is clearly achieved above 2.5 and below 5.0 wt.% CNT indicating that percolation threshold (p_c), the transition from the insulating to the conducting phase, is located between 2.5-5.0 wt % (or 1.6-3.3 vol.%) MWCNT.

Figure 5 shows the extrapolated values of the dc conductivity ($\sigma_{dc} = \sigma'(\omega \rightarrow 0)$) versus the MWCNT volume content (p) for the nanocomposites above the percolation threshold. In order to get an estimate for p_c the well known scaling law [5]:

$$\sigma_{dc}(p) \sim (p - p_c)^t \quad (2)$$

was fitted to the experimental σ_{dc} data for $p > p_c$, where t is a critical exponent which is related with the dimensionality of the investigated system. A value of $t \approx 2.0$ is predicted theoretically for a statistical percolation network in three dimensions [6]. The best linear fit for σ_{dc} vs. $(p - p_c)$ data on a log-log scale was found for $p_c = 1.7 \pm 0.1$ vol.% and critical exponent $t = 8.4 \pm 0.4$ (see inset in Figure 5). The solid curve in Figure 4 was calculated from Eq. (2) using the fit values of p_c and t .

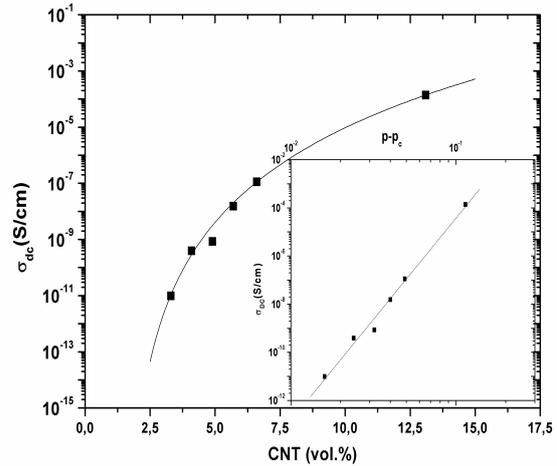


Figure 5 : σ_{dc} vs MWCNTs concentration p for PA6/MWCNTs nanocomposites above p_c . The inset shows a log-log plot of σ_{dc} vs $(p - p_c)$ with $t = 8.4$ and $p_c = 1.7$ vol. %.

Such high values for t have been mentioned before in literature [8]. This discordance probably derives from the fact that, in contrast with the conventional percolation model, there is no physical contact between the fillers but the conducting CNT are connected electrically by tunnelling and, as it has been proposed by Balberg [9], a very wide inter-particle distance distribution can lead to non-universal high t values. The absence of physical contacts between the nanotubes is supported from DSC results, where the formation of a polymer layer around the CNT walls prevents their formation. Also, the interaction between the nanotubes and the polymer matrix is not considered by the classic theory, constituting a second reason for the high value of the exponent in eq. 2.

Figure 6 shows the ac conductivity (σ_{ac}) at room temperature as a function of frequency for iPP/MWCNTs series. The dc conductivity plateau is clearly achieved above 0.75 and below 1.5 wt.% MWCNT indicating that percolation threshold (p_c), is located between 0.75 - 1.5 wt.% (or equivalently, between 0.4 - 0.7 vol.%) MWCNTs.

The best linear fit for σ_{dc} vs. $(p - p_c)$ data on a log-log scale was found for $A = 2.6 \times 10^{-6}$, $p_c = 0.60 \pm 0.05$ vol.% and critical exponent $t = 4.5 \pm 0.5$. Such high values for t have been mentioned before in literature. Mamunya et al. have reported $t = 8$ in polyethylene (PE)/polyoxymethylene (POM) blends filled with iron particles [10]. Also, a value of 6.27 has been mentioned by Ezquerro et al. in polyethylene-graphite composite materials [8].

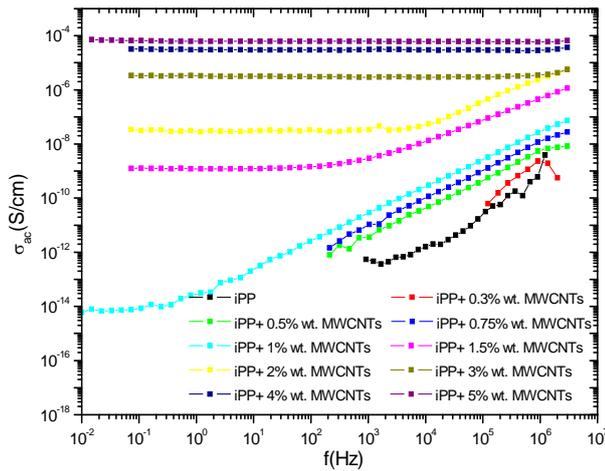


Figure 6: Conductivity vs frequency for series iPP / MWCNTs and for the samples indicated on the plot.

Figure 7 shows the real part of dielectric permittivity for different MWCNT loadings in iPP. Due to the high ac conductivity of the samples with contents higher than 1 wt.% MWCNTs, it was not possible to measure reasonable values of ϵ' for these compositions. However, it is clearly seen in Figure 7, that the curves can be distinguished between two groups. The composites with less than 1.0 wt.% MWCNTs have nearly constant ϵ' value and composites with MWCNTs loading higher than 1.0wt.% show a significantly different behaviour. This significant difference between the two groups was also visible in dc conductivity (see Figure 6), which is a measure of the long range movements of the charge carriers.

A second dc quantity that can be derived from the experimental data is the static permittivity $\epsilon_s = \epsilon'(\omega \rightarrow 0)$. Static permittivity is expected to increase with increasing filler content when approaching p_c for small concentrations and to decrease above the percolation threshold due to equation 3 :

$$\epsilon_s(p) = A \cdot (p - p_c)^{-s} \quad (3)$$

The composition dependence of the static permittivity was found [7] to follow equation 3 for both $p > p_c$ and $p < p_c$. According to equation 3, the static permittivity is expected to diverge at the percolation threshold. The solid line in the inset at Figure 7 are calculated from equation 5 with $A = 2.52$, $p_c = 0.70$ vol.% and $s = 0.20$. The calculated percolation threshold is in good agreement with that calculated from dc conductivity values, $p_c = 0.60$ vol.%. Conventional percolation model predicts theoretical value of $s \approx 0.7$ for percolation network formed by a random mixture of complex resistors [7].

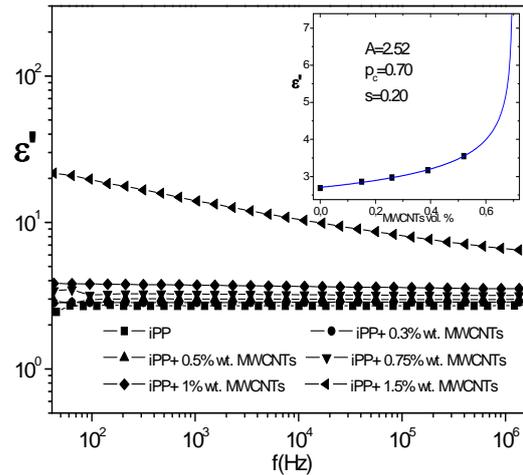


Figure 7: Real part of the dielectric function (ϵ') vs frequency for series iPP / MWCNTs. The inset shows static permittivity ϵ_s vs MWCNTs concentration p for nanocomposites below p_c . The line is a fit of eq. (3) to the experimental points.

The observed deviations ($t = 4.5$ instead of $t \approx 2.0$ and $s = 0.20$) indicates the absence of physical contacts between the fillers [5]. The conducting MWCNTs are connected electrically by tunnelling and, as it has been proposed by Balberg [9], a very wide inter-particle distance distribution can lead to non-universal high t and s values. From the evaluation of conductivity measurements on sPP/MWCNTs nanocomposites, not shown here, we found the percolation threshold between 2.5 – 3.0 wt.% (or equivalently 1.3 – 1.6 vol.%) in MWCNTs. The higher p_c values for sPP matrix nanocomposites, as compared with those for iPP matrix, reflects the different structure of the polymer matrix (sPP is more viscous).

Figure 8 shows the dependence of the imaginary part (ϵ'') of the dielectric function with the temperature (T), at a fixed frequency of 1.19 Hz, for the pure PA6 and PA6/2.5 wt.% MWCNT. The dielectric properties are investigated in these two samples, as the rest are above the percolation threshold. The two peaks at about -120 and -50°C , correspond to the γ and β secondary dielectric relaxation mechanisms of PA6 respectively, and are related with local dipolar motions. In particular, γ relaxation is attributed to a rotational motion of the CH_2 segments, while β relaxation is considered to be related with motions of the amide bonds [11]. Furthermore, β relaxation is more pronounced because it stems from the motion of polar bonds in contrast with γ relaxation. Due to the effect of water on the β relaxation of PA6, it is mentioned that the samples were dried, prior to the measurements, at 110°C for 24h. The main α relaxation mechanism of PA6, which is associated with the glass transition

temperature, is expected to be a few degrees higher to the T_g derives from DSC. The high ϵ'' values at high temperatures (above 40°C) are due to the onset of conductivity and covers the α relaxation. As a result, it is not possible to distinguish the α relaxation as a separate peak and to study it in detail. As concerns the effects of CNT on molecular mobility of the polymer matrix, the addition of CNT does not seem to influence the secondary relaxation mechanisms. Either their position or their strength (mind the log scale) remains unaffected by the addition of nanotubes and the only change is an overall increase of the dielectric losses (ϵ'') by one order of magnitude.

Supplementary to the above discussion Figure 9 shows the frequency dependence of ϵ'' at -40°C . The peaks in the low and high frequency region attributed to β and γ relaxation respectively. Coming back to the ϵ'' enhancement in the nanocomposite, this can be attributed to an enhancement of the internal field which is induced by the presence of CNT [12].

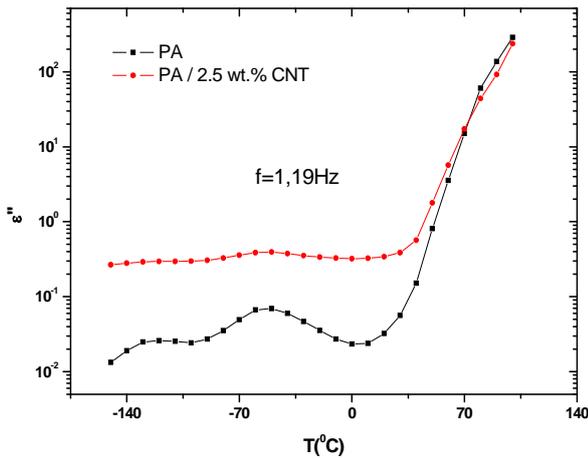


Figure 8 : Imaginary part of the dielectric function (ϵ'') versus temperature at a frequency of 1.19 Hz for the samples indicated on the plot.

In Figure 10 ϵ' and ϵ'' versus frequency at room temperature and for the samples below p_c are presented. In this frequency range none of the dielectric relaxation mechanisms is appeared, as the secondary β and γ relaxations, we discussed above, have been moved to higher frequencies, or in case of β is covered by the conductivity, whereas the main α relaxation is below the 10^{-2} Hz and is also out of our frequency window.

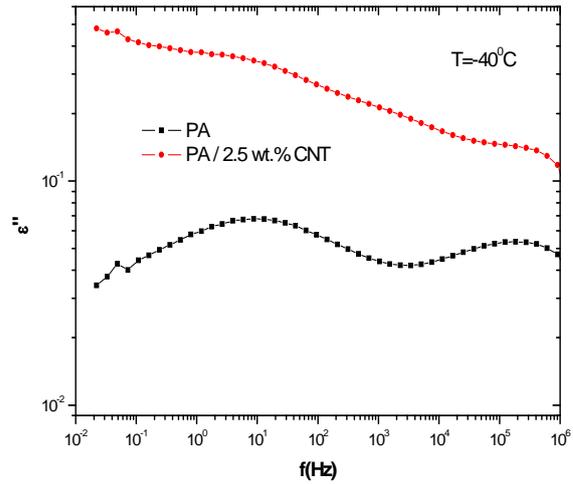


Figure 9 : Imaginary part of the dielectric function (ϵ'') versus frequency at -40°C for PA6/MWCNTs

Consequently, the ϵ' and ϵ'' increase, at the low frequency region, is due to space charge polarization and conductivity effects.

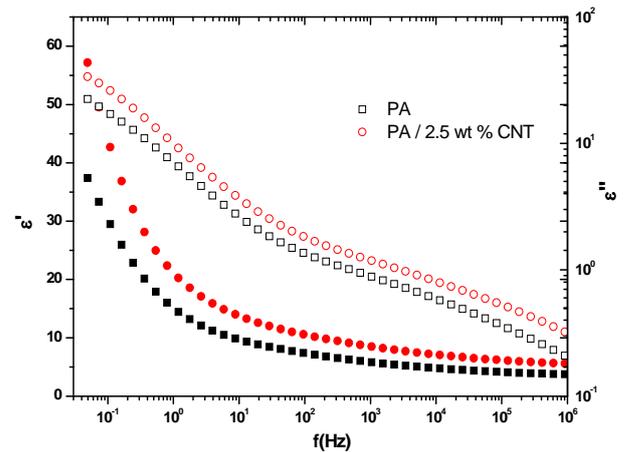


Figure 10 : Real part (ϵ') (filled symbols) and imaginary part (ϵ'') (open symbols) of the dielectric function versus frequency at room temperature for the samples indicated on the plot.

Additionally, the real part of the dielectric function is approximately constant, at the high frequency region, and increases by the addition of MWCNT. This fact can be attributed to the polarization of the nanofillers which contributes to the dielectric function, and is very interesting as there is an increasing need for the development of new materials with high ϵ' values.

4 Conclusions

i) PA6/MWCNTs nanocomposites

By performing ac conductivity measurements the percolation threshold and critical exponent values were calculated ($p_c=1.7$ vol.% and $t=8.4$). The high exponent values indicate the absence of physical contacts between the nanotubes in agreement with DSC findings. Furthermore, the presence of CNT does not influence significantly the molecular mobility of the PA6 matrix. Also, the real part of the dielectric function increases as the amount of nanotubes increases.

ii) PP/MWCNTs nanocomposites

Similar values for the percolation threshold (p_c is about 0.6-0.7 vol. % were found from both conductivity and permittivity measurements. Conventional percolation model predicts $t=2$ and $s=0.7$. The observed deviation ($t=4.5$ and $s=0.2$) indicates the absence of physical contacts between the nanotubes. The reinforcing effect of filler on the nanocomposites also reflected in dynamic-mechanical measurements, while the α -relaxation of the matrix does not affected systematically by the filler.

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