Broadband Electrical Conductivity of Polymer Nanocomposites with Carbon Nanoadditives

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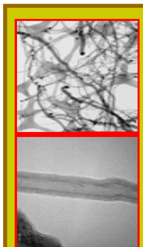
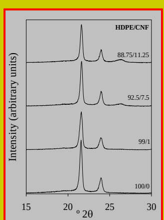
INTRODUCTION

- The electrical conductivity of the composite material varies from that of the polymer matrix to that of the carbon additive due to the formation of a percolative network.
- Recently, polymer composites based on carbon nanoadditives, such as carbon nanofibers (CNF) and carbon nanotubes (CNT), have begun to be intensively investigated[1-3].
- A clear picture about the conduction mechanism is still lacking.
- In this work we attempt to shed additional light to this topic by characterizing the electrical conductivity of polymer nanocomposites based on high density polyethylene (HDPE) as matrix and a carbon nanofiber (CNF) a nanoadditive in a broad frequency range.

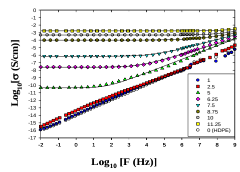
EXPERIMENTAL

- Polymer nanocomposites based on high density polyethylene (HDPE) (Repsol-Química, Spain) and different amounts of carbon nanofiber (CNF) (Grupo Antolín Ingenieria, S.A., Spain) have been prepared by mixing the components in the molten state. Subsequently, films of about 0.1 cm thickness were obtained by compression moulding.
- The complex permittivity was measured as a function of frequency (10^{-2} < F/Hz < 10^{9}) and temperature (-150ºC up to 75ºC), with two different equipments: in the 10^{-2} < F/Hz < 10^{6} range, a Novocontrol system integrating an ALPHA dielectric interface was employed, and in the range 10^{6}-10^{9} Hz, an HP 4291 coaxial line reflectometer.
- Visualization of the inner structure of the nanocomposites was accomplished by Transmission Electronic Microscopy (TEM) and Scanning Electronic Microscopy (SEM).
- Wide angle X-ray scattering (WAXS) measurements were performed by means of a Seifert XRD 3000 θ/θ diffractometer.





- The carbon nanofiber consists of high aspect tubular structures, with a diameter of about 70 nm, made of rolled graphene layers.
- The WAXS diffraction patterns of the nanocomposites show the reflections of the orthorhombic phase of polyethylene, and the graphitic layer structure of the CNF.



- For CNT concentrations below 5 vol%, conductivity follows a linear dependence with frequency with a slope close to 1 characteristic of insulating materials.
- For higher concentrations, it adopts a characteristic behaviour which can be described by[4]:

$$\sigma (F) = \sigma_{dc} + \sigma_{ac} = \sigma_{dc} + A \times F^{s} \quad (1)$$

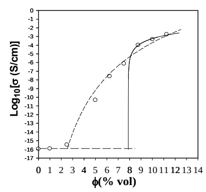
where σ_{dc} is the frequency independent direct current conductivity and $0 < S < 1$. The continuous lines correspond to fits of eq. (1) to the experimental data. From these fits the σ_{dc} values can be extracted.

DC Electrical Conductivity

- The characteristic percolative behaviour is observed. At low concentration of the CNF, around 3 vol%.
- The dc conductivity about the critical concentration can be analyzed in terms of the percolation theory[5] by means of the scaling law given by:

$$\sigma_{dc} \propto (\Phi - \Phi c)^{t} \quad (2)$$

The continuous line shows the fitting with Φ_c= 7.8 vol% and t = 2.

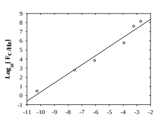


- When electrical conductivity is higher than that of insulating matrix, before a continuous particle network is formed, the existence of a tunneling process can be expected. In this case, the conductivity can be described by[6]:

$$\sigma_{dc} \propto \exp(-Ad) \quad (3)$$

- If a random distribution of particles is assumed, then the mean average distance (d) among particles can be assumed to be proportional to −1/3.
- The dependence between σ_{dc} and Φ is represented by the dashed line.

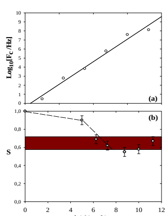
AC Electrical Conductivity



- Eq. (1) introduces a critical frequency, F_c, above which $\sigma (F) = \sigma_{ac} \propto F^{S}$.
- The higher the dc conductivity the higher is the critical frequency, F_c:

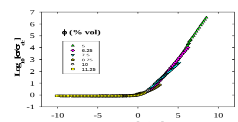
$$F_c \propto \sigma_{dc}^{\ b} \quad (4)$$

the exponent b takes values close to 1.



- F_c increases in a linear fashion with the volume concentration.
- At low CNT concentration, S-exponent = 1, corresponding to insulating specimens.
- As CNT concentration increases, S-exponent decreases linearly S ≈ 0.6. According to percolation theory, S-values for three dimensional materials ranging from S ≈ 0.72, when polarization between particles is considered[7], to S ≈ 0.58 when anomalous diffusion in fractal clusters is considered[8]. The coloured area in Fig. is the region where the percolation theory is fulfilled.

- Master curve generated by normalizing conductivity values by σ_{dc} and frequencies by F_c, with an additional shift in $Log_{10}(F/F_c)$ of ∝ ±0.5.



CONCLUSIONS

✓ At low nanoadditive concentration, HDPE-CNF nanocomposites consist of isolated conducting regions dispersed within the insulating polymeric matrix. Despite the lack of a continuous conducting network between particles, a significant dc electrical conductivity is observed.

✓ As nanoadditive concentration increases, the size of the finite-size cluster tends to increase. In this situation, the frequency dependence of the conductivity reflects the features of anomalous diffusion in fractal structures as expected according to percolation theory.

✓ A master curve can be constructed. However, considering the observed dependence of the exponents describing the ac electrical conductivity, this behaviour should be contemplated rather as a working rule than as a universal law.

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