

**CARBON NANOFIBRE- POLY(VINYLDENE FLUORIDE) NANOCOMPOSITES: EFFECT OF THE CARBON NANOFIBRE CONCENTRATION ON THE  $\alpha$  TO  $\beta$  PHASE TRANSFORMATION AND THE DEGREE OF CRYSTALLINITY**

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The present study is based on the use of Carbon Nanofibres (CNF) instead of Carbon Nanotubes (CNT) in order to increase the dielectric constant of polymer materials and/or the electrical conductivity. The main advantage of the CNF with respect to the CNT from the scientific point of view is that their structure and dimensions potentially reduce the Van der Waals forces acting between them, thus facilitating their dispersion during composites preparation. Furthermore, CNFs can be easily functionalised to improve interaction with the surrounding matrix due to a better accessibility to the graphene planes inherent to their ‘stacked cup’ structure. [1, 2]

In this work CNF/PVDF nanocomposites have been prepared by a solution method with different amounts of CNF (0.1, 0.5, 1, 2, 5%) dispersed in the polymeric matrix. The crystalline phase of the matrix was the apolar  $\alpha$ -PVDF. Further, the nanocomposites are uniaxially stretched in order to achieve the phase transformation  $\alpha$  to polar  $\beta$ -phase within the polymeric matrix. The influence of the CNF on the amount of the crystalline part of the polymer, morphological properties, mechanical and electrical properties and thermal stability of the composites were studied.

The SEM micrographs of the samples showed that the composites crystallise in a spherulitic structure, similar to the one of pure  $\alpha$ -PVDF [3], with a random distribution of the CNF along the surface of the sample.

The insertion of CNF within PVDF increased the elastic modulus with respect to the polymer matrix. The elastic modulus of the composites nearly doubles for a small incorporation of CNF (lower than 1%) and remains almost constant for higher concentrations.

The  $\alpha$  to  $\beta$  phase transformation was studied for the pure polymer and for the nanocomposites and it was concluded that the maximum amount of  $\beta$ -phase is obtained by stretching ratios of 5 or more at a temperature of 80 °C [3, 4] (see Fig. 1).

The DSC thermograms showed that the incorporation of CNF in the polymeric matrix has a direct influence thermal stability of the nanocomposites, increasing the melting temperature ( $T_m$ ) of the composites. This behaviour is observed for the polar and non-polar polymeric matrix,  $\alpha$  and  $\beta$ -phase of PVDF, respectively. The  $T_m$  of the nanocomposites appears at higher temperature when compared to the pure samples of PVDF, as the well dispersed CNF within the PVDF matrix promotes heterogeneous nucleation and act as nucleation agents for the polymer crystallites, increasing the crystallinity fraction of the matrix [5].

The electrical response in the polymer/CNF composites was evaluated by measuring the bulk resistivity and the dielectric constant. The bulk resistivity for the  $\alpha$ -phase composites changes from  $4.35 \times 10^{10} \Omega\text{m}$  for the sample with 0.1% CNF to  $9.0 \times 10^6 \Omega\text{m}$  for the sample with 5% CNF, the threshold being at CNF concentrations of about 1.5%, where the resistivity undergoes a change of three orders of magnitude (see Fig. 2). When the samples are stretched in order to achieve the  $\beta$ -phase, the resistivity remains for the lower CNF concentrations within the same range.

Dielectric measurements reveal, in general, an increase of the dielectric constant with increasing CNF concentration. The dielectric constant increases further by the stretching process, i.e. by achieving the polar  $\beta$ -phase through the  $\alpha$ - to  $\beta$ -phase transformation.

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## References:

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## Figures:

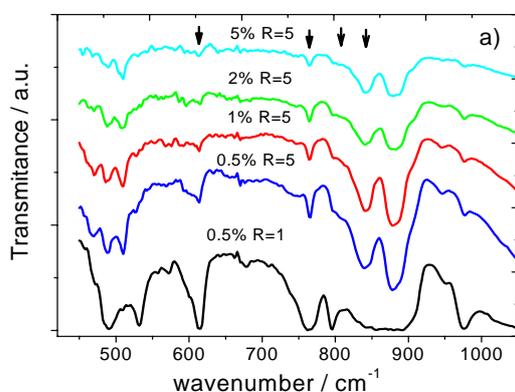


Figure 1. FTIR spectra of PVDF-CNF nanocomposites with different CNF concentrations.

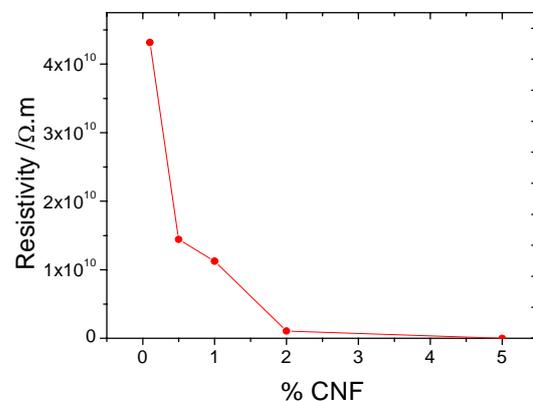


Figure 2. Electrical bulk resistivity of the CNF-PVDF nanocomposites as a function of CNF volume concentration.