

Effect of the carbon nanotube surface characteristics on the percolation threshold and conductivity of carbon nanotube/poly(vinylidene fluoride) composites

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In order to increase the application range of polymers, highly conductive nanoscale fillers can be incorporated into the polymeric matrix. As carbon nanotubes (CNT) present high electrical conductivity (10^3 - 10^4 S/cm), they have been widely used [1]. Therefore, CNT/polymer composites are expected to have several important applications, namely in the field of sensors and actuators [2]. However, in order to properly tailor the composite material properties for specific applications, the relevant conduction mechanisms must be better understood.

The experimental percolation thresholds for CNT composites results on a wide range of values for the same type of CNT/polymer composites [3], being a deviation from the bounds predicted by the excluded volume theory and a dispersion for the values of the critical exponent (t) [4-5]. It was demonstrated that the conductivity of CNT/polymer composites can be described by a single junction expression [6] and that the electrical properties also strongly depend on the characteristics of the polymer matrix [7].

In the present work, commercial multi-walled carbon nanotubes (Nanocyl - 3100) have been used as received (sample CNTs) and functionalised through oxidation under reflux with HNO₃ (7 M) for 3 h at 130°C, followed by washing with distilled water until neutral pH, and drying overnight at 120 °C (sample CNTox). The CNTox material was heat treated under inert atmosphere (N₂) at 400 °C for 1 h (sample CNTox400) and at 900°C for 1h (sample CNTox900). The obtained samples were characterised by adsorption of N₂ at -196°C and by temperature programmed desorption (TPD). The results obtained are shown in Table 1. The different surface oxygenated groups created upon oxidising treatments decompose through heating, releasing CO and/or CO₂ (Figure 1). As this release occurs at specific temperatures, identification of the surface groups is thus possible [8]. In nanotubes, the oxygenated groups (Figure 2) are formed at the edges/ends and defects of graphitic sheets [10]. The total amounts of CO and CO₂ evolved from the samples were obtained by integration of the TPD spectra and are also presented in Table 1. The peaks were deconvoluted using the nonlinear least-squares procedure, assuming a multi Gaussian peak shape [8-9]. It is clear that the treatment with HNO₃ produces a large amount of acidic oxygen groups, like carboxylic acids, anhydrides and lactones, which decompose to release CO₂. Part of these groups (carboxylic acids) are removed through heating at 400°C. A treatment at 900°C removes all the groups, so that the obtained sample is similar to the original, but with an increase of the surface area (Table 1).

CNT/poly(vinylidene fluoride) composites were prepared using the above CNT samples, with different filler fractions up to 0.5 %wt. It was found that oxidation reduces composite conductivity for a given concentration and shifts the percolation threshold to higher concentrations. The theoretical analyses of these facts help to get interesting insights on the conduction mechanism of these composites.

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Table 1 - BET surface areas (m^2/g) obtained by adsorption of N_2 at $-196^\circ C$ and amounts of CO_2 and CO ($\mu mol/g$) obtained by integration of areas under TPD spectra.

Sample	CNTs	CNTox	CNTox400	CNTox900
BET surface area (m^2/g)	254	400	432	449
CO_2 ($\mu mol/g$)	70	778	230	24
CO ($\mu mol/g$)	193	1638	1512	204
CO / CO_2	2.76	2.11	6.57	8.50

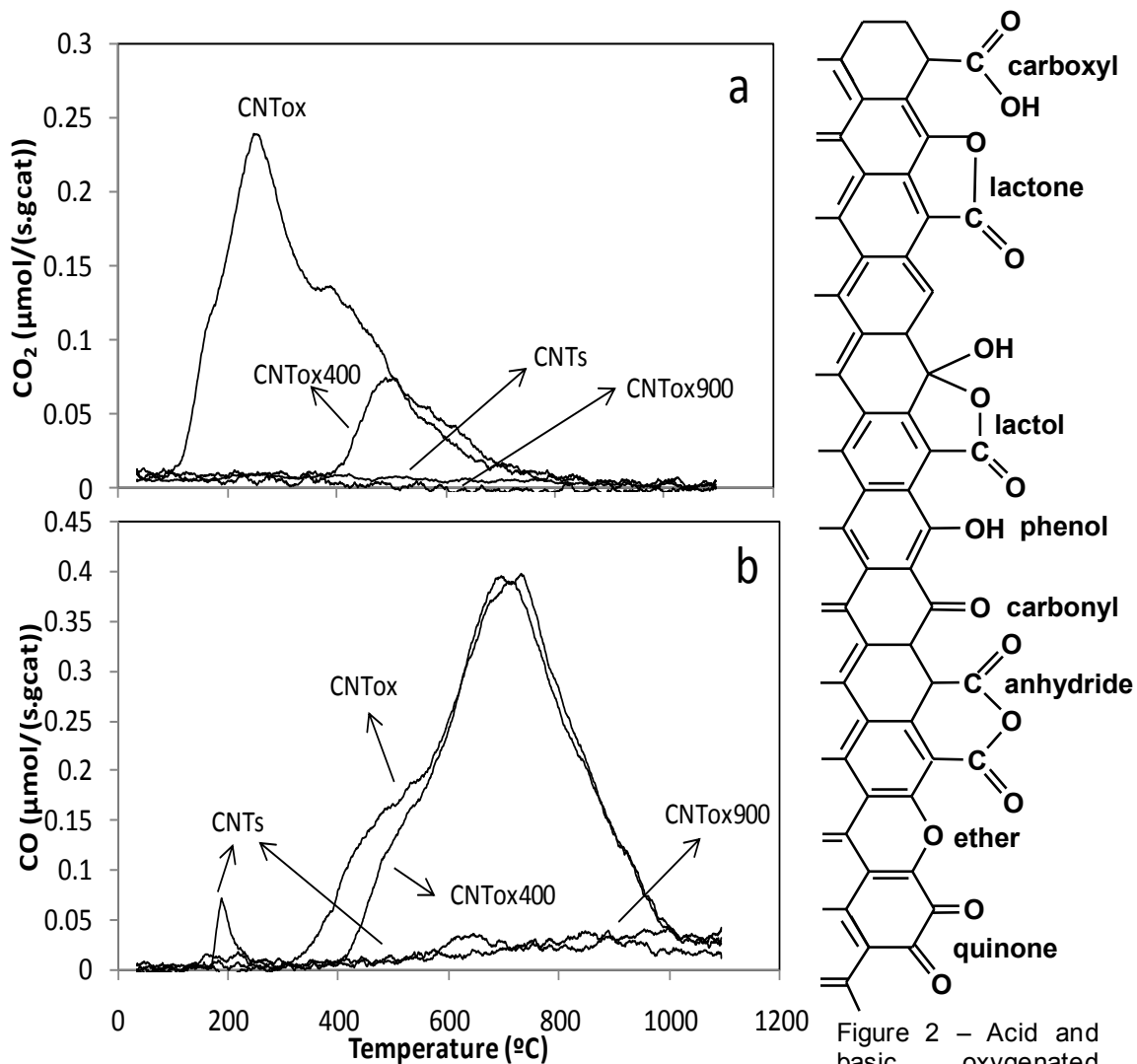


Figure 1 - TPD spectra of the CNT samples before and after the oxidizing treatments: CO_2 (a) and CO (b) evolution.

Figure 2 - Acid and basic oxygenated groups on CNT surface.