

# Thermal stability and structural study of the poly(3-hexyl thiophene)/HiPCO single walled carbon nanotubes (P3HT/SWCNT) nanocomposites<sup>★</sup>

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**Abstract.** In this work we present the effect of HiPCO single walled carbon nanotubes (SWCNT) introduction into the conjugated polymer matrix poly(3-hexyl thiophene) (P3HT) on the structural and thermal stability of these nanocomposites. The P3HT/SWCNT nanocomposite films were prepared using chloroform and chlorobenzene as solvents and optimised ultrasonication duration. The prepared samples were analyzed by thermogravimetric analysis (TGA), X-ray diffraction and transmission electron microscopy (TEM) to study the effect of carbon nanotubes on the thermal stability and structure of the polymer matrix. The measurements carried out for different SWCNT loadings show that the thermal stability was enhanced for a 0.5 wt.%, but exhibits a decrease with increasing the SWCNT content. Our results prove the structural enhancement which is in favor of a better organisation for both P3HT chains and carbon nanotubes due to their interaction.

## 1 Introduction

The combination of conjugated polymers and fillers such as carbon nanotubes (CNTs) have shown immense potential application in the field of electronics, particularly the fabrication of optoelectronic devices such as organic field effect transistors, light emitting diodes and organic photovoltaics [1–4].

The exceptional electronic properties of carbon nanotubes make it not only an excellent compound favoring the charge separation in organic photovoltaic based on polymers but also a reinforcing agent because it combines a Young's modulus of about 1 TPa and a capacity for elastic deformation of greater than 10%, the CNTs have also a very high breaking strength, the addition of such nanoscale carbon form with different concentrations into the polymeric matrix was found to enhance the thermal stability and structural properties. This enhancement was attributed to the unique characteristics of the nanotubes [5], whereas most polymers exhibit a rather poor thermal stability, and degrade under the effect of temperature, owing to the presence of oxygen which accelerates their degradation [6].

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It is recognised that the dispersion and orientation of the SWCNT in the polymer matrix, as well as the interface interaction between the two components, are important factors influencing the thermal performance and structure of the final materials [7]. The present work report the effect of HiPCO SWCNT insertion on the thermal stability and structure of the poly (3-hexyl thiophene) (P3HT).

## 2 Experimental details

High purity SWCNT (residual iron catalyst 22%) was purchased from Carbon Nanotechnology, Inc., Texas, USA. They were prepared by the HiPCO method and typical diameters were in the range of 0.8–1.2 nm and lengths between 0.1 and 1  $\mu\text{m}$ . The regioregular P3HT (RR-P3HT) used in this study (provided from Rieke) has the following characteristics: average molecular weight  $M_W = 37.680 \text{ g mol}^{-1}$ , PDI = 1.48 (polydispersity) and regio-regularity HT (head-tail) > 98.5%.

A 1 mg mL<sup>-1</sup> polymer solution was prepared by dissolving the P3HT in chloroform (CHCl<sub>3</sub>). The carbon nanotubes, used as received, were dispersed in the same solvent under ultrasound stirring for 30–45 min. Composite solutions were prepared by adding SWCNT solutions to the solubilized matrix in order to achieve the different concentrations, and then stirred in ultrasonic bath for 5 min to ensure homogeneity. We obtained homogenous

solutions, showing that the carbon nanotubes are well dispersed due to the intercalation of the macromolecular chains of the polymer. Thin films were prepared by drop casting for XRD analysis. The TGA samples were obtained by removing the films using a cutter and had weights ranging between 5 and 15 mg. The same preparation procedure with chlorobenzene ( $C_6H_5Cl$ ) as solvent was carried out in order to study the solvent effect.

Thermogravimetric analysis (TG-DTG) was performed with a Thermogravimetric analyser SDT 2960 TA, under air. The samples were heated from room temperature to 800 °C at a heating rate of 2 °C/min and a platinum pan was used. Measurements of X-ray diffraction were carried out using a diffractometer X'Pert PRO powder on Panalatyca equipped with an ultrafast scintillation detector X'Celerator. The transmission electron microscopy (TEM) images were obtained in bright field (BF) using a TECNAI G2/FEI microscope working at a voltage of 120 kV.

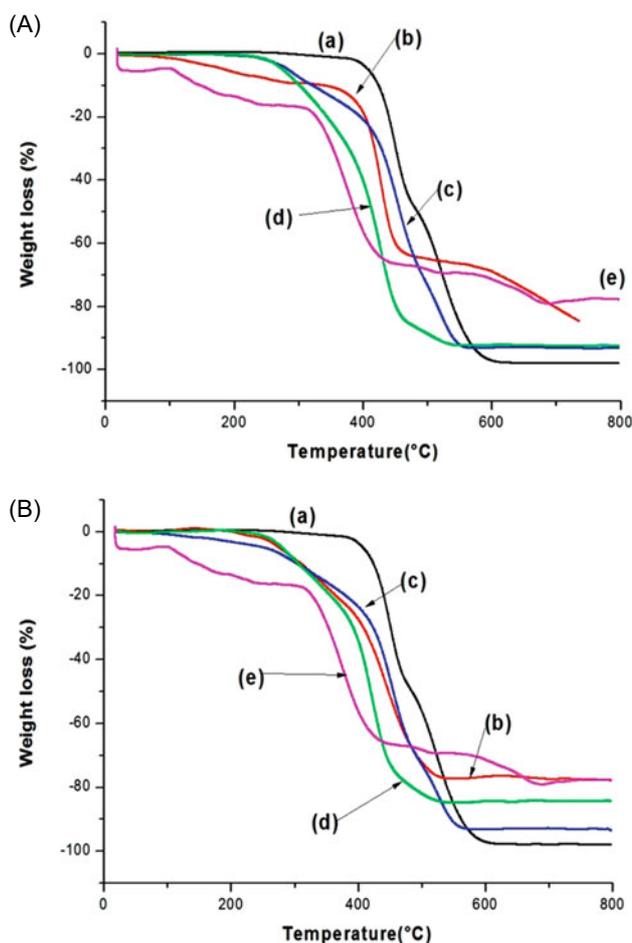
### 3 Results and discussion

#### 3.1 Thermogravimetric analysis

TGA is a powerful analytical technique used to determine the thermal stability of materials and the fraction of volatile components by monitoring the weight loss that occurs when a sample is heated in an inert atmosphere [8].

The TGA results of P3HT and P3HT/SWCNT composites dispersed in chloroform, compared with the pure SWCNT powder, are presented in Figure 1a. P3HT showed good thermal stability because the weight loss began only when the temperature reached 450 °C, and beyond this temperature the mass loss was complete (98%) which is due to the nature of the polymeric chains [9]. In the temperature range below 310 °C, low mass loss of -16% was noted, which can be attributed to synthetic residues with lower degradation temperature than that of carbon nanotubes. At a temperature lower than 370 °C, we note that the mass loss for the 0.5 wt.% composite was 9% and is assigned to the traces of solvents evaporated, which is lower than for the SWCNT. At a temperature of 470 °C the mass loss was of 63%.

In order to compare the effect of solvent on the thermal stability of the composites, the same preparation of materials has been conducted with chlorobenzene. The results are depicted in Figure 1b. It is noted that the behavior of the P3HT and the SWCNT remain the same for both solvents, however for the composites the weight loss was of 11% for the temperatures below 320 °C, which can be attributed to the evaporated traces of chlorobenzene. Above this temperature all the three composites start to show a drastic weight decrease. An overall enhancement of the thermal stability of the P3HT was noted particularly for the 0.5 wt.% composite. This might be due to wrapping effect of the P3HT over the SWCNT network, causing afterward the orientation of the polymeric chains and thus an increase in the crystallinity of the P3HT which contribute also to the enhancement of the thermal stability

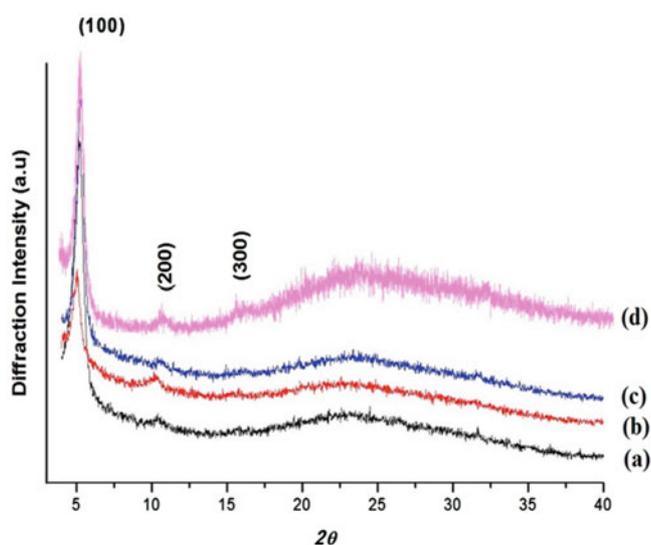


**Fig. 1.** TGA curves of: (a) bulk P3HT, and P3HT/xSWCNT composites: (b)  $x = 0.5$  wt.%; (c)  $x = 1$  wt.%; (d)  $x = 2$  wt.% and (e) SWCNT in (A) chloroform, and in (B) chlorobenzene.

of the composite [10,11]. Such increase in thermal stability has already been reported for different polymer/CNT composites [10,12–14].

#### 3.2 X-ray diffraction

XRD patterns of the P3HT and P3HT/SWCNT composite films drop casted from chlorobenzene solutions are presented in Figure 2. XRD can provide useful information on the structural modifications of the polymer's interchain distance related to lattice parameters, and to the coherence length introduced by SWCNTs. According to what has been reported by several researchers and by our previous work [15–17] the polymer chains association has been described as a lamellar self-organisation of the polymer chains with  $\pi$ -stacking. For P3HT, the strong narrow peak at  $2\theta = 5.34^\circ$  corresponds to  $d = 16.34$  Å, which is the in-plane interchain distance between thiophene rings, two weak peaks at  $2\theta = 10.65^\circ$  and  $15.75^\circ$  are assigned to the second and third order reflections from the interlayer spacing [18].



**Fig. 2.** XRD patterns recorded on the P3HT/SWCNT composite films for (a) P3HT, and P3HT/xSWCNT composites: (b)  $x = 0.5$  wt.%; (c)  $x = 1$  wt.%; (d)  $x = 2$  wt.%.

The XRD patterns of the composite films for the different SWCNT concentrations display a better resolution of the (100) peak compared to the pristine P3HT indicating a better organisation in the composite films. The full width at half maximum (FWHM) of this peak shows a slight decrease in the values; this could be due to the coating of the polymer on the walls of the SWCNT [19].

An amorphous halo of low intensity appears at  $24^\circ$  which can be attributed to the stacking distance of thiophene rings [9]. Therefore, the incorporation of SWCNT improves the crystallization of the composite films and the same behavior was noted in our previous work for the composites using chloroform as solvent [17].

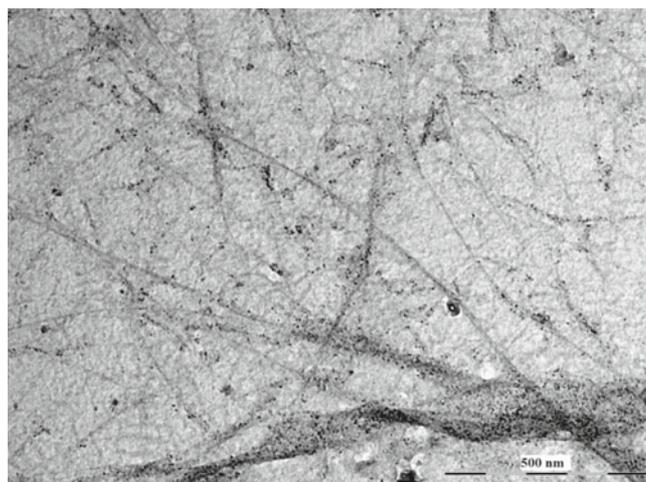
### 3.3 Transmission electron microscopy

We show in Figure 3, a TEM image of the P3HT/SWCNT 2 wt.% film obtained in bright field conditions revealing the aggregation of nano-crystalline domains, around the SWCNT. The crystallites size has been calculated from the XRD data for the different composites by the Scherrer [20] equation (1):

$$t = \frac{K\lambda}{B \cos \theta}. \quad (1)$$

The values of the crystallite size vary between 10 and 20 nm which is consistent with a crystalline structure improvement of the P3HT. The alignment and dispersion of SWCNT in P3HT can be observed in the TEM image. The P3HT wrapping effect around the SWCNT has been noticed for similar composites using other techniques like AFM [21].

Therefore, we can conclude that the crystallinity of the composite films is slightly improved upon the insertion of SWCNTs into the polymer matrix.



**Fig. 3.** TEM image of the P3HT/SWCNT in chloroform 2 wt.%.

## 4 Conclusion

The thermal stability and the enhancement of the structure of the P3HT/HiPCO SWCNT composite have been elucidated by means of thermogravimetric analysis, X-ray diffraction and TEM microscopy. The incorporation of SWCNT leads to an improvement of the thermal stability essentially for the 0.5 wt.% and 2 wt.% for chlorobenzene indicating that the choice of solvent plays an important role in the interaction between the two components [22]. The enhancement of the crystallisation can be explained by a planarisation of P3HT backbone after interaction with the SWCNT. The effect of wrapping the SWCNT with the P3HT chains implies a large contact surface which interacts via  $\pi$  stacking interaction between P3HT and SWCNT. These results obtained for low loadings of SWCNT are very suitable for application in the field of organic optoelectronics and organic solar cells.

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