Time-resolved Synchrotron X-Ray Study of the Crystalline Transformations in Nylon-6/Carbon Nanotube Nanocomposites

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Polyamides, known as nylons, are important engineering materials widely used in diverse industrial sectors, from medical through transportation to consumer goods, and novel strategies to improve some of their performance characteristics are the subject of many fundamental scientific studies. In recent years, polymer / carbon nanotube nanocomposites have received great interest from researchers because they frequently exhibit unexpected hybrid properties synergistically derived from the two components. The incorporation of CNTs into polymer matrix has remarkably improved the mechanical, electrical, and thermal properties of the resulting composites, compared to other reinforcing agents such as glass fibers, metal flakes, hollow microspheres, and carbon nanofibers, due to their high aspect ratio [1]. The incorporation of some fillers into nylon can have an important influence on the crystallization behaviour of the polymer matrix by acting as nucleating agents. Since the crystalline morphology will affect the mechanical properties of nylon, the investigation of crystallization and melting phenomena in this type of nanocomposite is of great importance.

In most raw nylons, a polymorphic transition is observed on heating. This phenomenon was first found in nylon-66 by Brill in 1942 [2]. Upon heating, the room temperature triclinic crystalline structure (α) transforms into a modified triclinic structure (γ), at the denominated the Brill transition, which is clearly manifested in X-ray diffraction studies where the two strong α-phase reflections at around 20º (100) and 24º (010/110) merge into a single γ-phase reflection at the transition temperature. Besides variable-temperature WAXD, some other techniques have also been adopted to detect the Brill transition, such as real-time FTIR, SAXS, DSC and NMR.

In this work, several concentrations of as-produced (0.1, 0.25, 0.5 and 1wt.% of CNTs) are introduced into a nylon-6 matrix by melt-mixing using a micro-extruder (Thermo-Haake Minilab system), operated at 240 ºC with a rotor speed of 150 rpm for 10 min. The nylon-6 used in this work was supplied by La Seda de Barcelona S.A and single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) were synthesized by the arc-discharge method in the G-CNN group (ICB-CSIC, Zaragoza, Spain).

In order to obtain information on the differences in the crystalline transformations of both neat nylon-6 and nylon-6 in the nanocomposites, the dynamic crystallization of nylon-6/CNT
nanocomposites from the melt was investigated by DSC and time-resolved synchrotron X-ray diffraction. Figure 1 shows the effect of CNT content on the dynamic crystallization behaviour of nylon-6. The crystallization temperature ($T_c$), obtained from the minimum of the exothermic peak, is about 188 °C for nylon-6. The addition of 0.1-1wt.% of CNT led to a shift of the crystallization peak mainly towards higher $T_c$ (e.g. $T_c$,1wt.% SWNT or 1wt.% MWNT = 192°C). The increase of $T_c$ can be explained by the assumption that both the SWNTs and MWNTs act as nucleating agents for the crystallization of the nylon-6 matrix, and the crystallization rate increased compared to that of neat nylon-6. However, the crystallinity value obtained from the crystallization exotherm of nylon-6 is more stable than the nylon-6/MWNT nanocomposites containing 1wt.% SWNT or 1wt.% MWNT.

Additionally, the data presented in Figure 2 using synchrotron radiation indicates that nylon-6 crystallizes first into a pseudo-hexagonal phase from the molten state, and then converts to the monoclinic form during cooling. However, when nylon-6 nanocomposites experience a faster cooling process, alpha-form crystals are generated, which differs from the case for the neat nylon-6 matrix (i.e. formation of the more-disordered phase) as shown by WAXS in Figure 3. This reversible crystal-to-crystal phase transition is a gradual and continuous process typically observed in nylons upon heating from the RT, known as the Brill transition [1]. As an example, Figure 4 presents the WAXS diffractograms for neat nylon-6 and its nanocomposites with 1wt.% of CNTs (SWNTs and MWNTs), and those recorded during a heating cycle at 5°C/min after previously cooling at 10°C/min. The experimental data indicate that the nanocomposites contain more perfect crystals than the neat nylon-6, which results in higher crystalline transition temperatures. Since the α-phase is more stable than the γ-phase, the crystalline transformation in the nylon-6 nanocomposites requires more energy, available at higher temperature, to overcome this restriction. This appears to be independent of the type of nanotube used. However, given that the Brill transition was not found during the heating process in the case of nylon/MWNT nanocomposites prepared by in-situ polymerization [3], its appearance may also be influenced by the processing conditions. In the same way, the results obtained from DSC melting data (not shown) were consistent with those provided by WAXS. The reduction of the width of the double endothermic peaks of nylon-6 as well as the increase in crystallinity with the addition of CNTs (nylon-6 = 37% and nylon-6/SWNT (1wt.% = 42% [4]) were related to the improved stability of the more disordered γ-form crystals. This behaviour was also independent of the type of nanotube used.

![Figure 4: WAXS diffractograms of (a) nylon-6, (b) nylon-6/SWNT and (c) nylon-6/MWNT nanocomposites containing 1wt.% of nanotubes.](image)

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**References**