

Flow-induced formation of crystal structures in carbon-nanotube filled polyethylene

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The combined in-situ small-angle synchrotron x-ray scattering in combination with shear rheology setup at the DORIS beamline BW1 was utilized to study the formation of crystal structures in carbon-nanotube (CNT) filled high-density polyethylene (HDPE) nanocomposites. Initially, we were aiming to study the CNT distribution at the interphase of two-phasic polymer blends, but due to a lack of contrast for these materials we carried on to study the crystallization effects in polyethylene-based composites.

The matrix polymer morphology is strongly influenced by CNTs, especially in semicrystalline polymer composites such as HDPE because the CNTs have the potential to nucleate and alter the polymer crystallization.¹⁻³ The mechanical and electrical properties of the final nanocomposite can both be influenced by the type, size and location of the crystals. An interesting question arises for both academia and industry as to how CNTs affect the crystallization of a commodity thermoplastic like HDPE crystals during melt blending and follow-up processing, e.g. for the production of anti-electrostatic fuel tanks investigated within the EU Framework 7 project *HARCANA*.

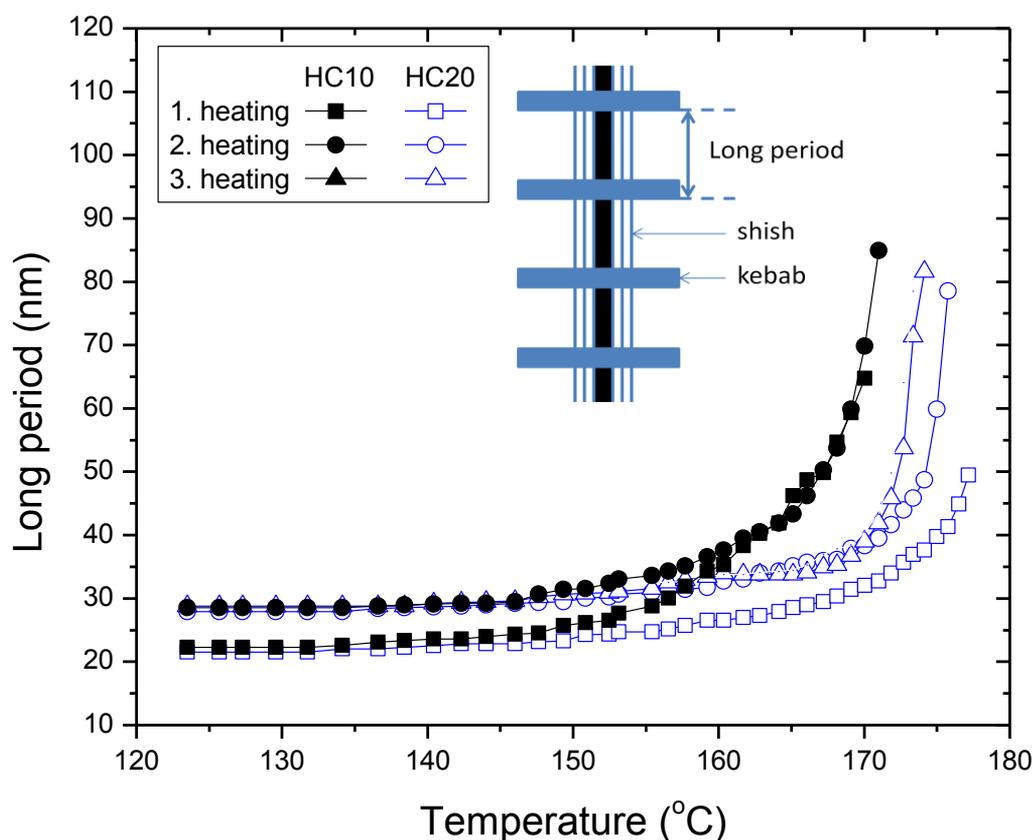


Figure 1. Long period as a function of temperature during heating for three cycles indicating the crystal spacing in the vicinity of CNT fibers. The inserts show a schematic of the shish-kebab crystals morphology next to a CNT.

The nucleation and growth mechanisms of HDPE crystals in the presence of CNT were investigated using the unique vertical Rheo-SAXS setup at BW1.⁴ Various HDPE/CNTs nanocomposites with different pre-blending times have been studied. The angular dependence of the scattering intensity in 2D images shows a flow-induced orientation of kebab lamellae. The peak position of the scattering maximum q_{\max} in the Lorentz-corrected plot is used to determine the average spacing $L = 2\pi/q_{\max}$ (so-called long period) between the adjacent lamella stacks (or so-called kebabs), and its time evolution were examined.

As shown in Figure 1, in repeated non-isothermal melting cycles, the value of L versus temperature is increasing, indicating a disappearance of lamella stacks during melting. In addition, the average spacing L of the nanocomposites with a long pre-blending time have a higher melting temperature, thus suggesting a larger size of lamellar crystals. This change of HDPE crystals grown on CNTs has a significant influence on the electrical properties of the nanocomposites, e.g. the conductivity.

For example, two nanocomposites with exactly the same composition, but different pre-shearing history were studied. HC10 refers to HDPE/CNTs with 10 minute blending time while HC20 20 minutes of blending. For both HC10 and HC20, the spacing L increases dramatically above a certain temperature, indicating gradual melting and disappearance of lamellae. Furthermore L is 22 nm for the first cycle, and thus 6 nm lower in comparison with the following heating cycles (28 nm). This difference is probably caused by the initial thermal history from sample preparation using a hot-press and subsequent cooling.

In general, it takes a higher temperature for HC20 to be fully melted than for HC10. This indirectly suggests that the crystal size (or area of 2D-disks) of HC20 is bigger than that of HC10, since we proved that the lamellae thickness of these two composites is the same. Moreover, after 3 heating and cooling cycles, the highest melting temperature of HC20 is still about 3°C higher. These results are also consistent with the calorimetric data from thermal analysis. They indicate that the lamellar crystal dimensions depend on the blending time and that extended chain layers can be generated during melt processing.

For CNT-filled PE the time-resolved Rheo-SAXS reveals small differences in the crystal morphology, which are strongly influencing the electrical properties, and these insights can help to improve the behavior of such nanocomposites in melt processing as well as in end-use applications.

Financial support by the 7th Framework Program research project “HARCANA”, Marie-Curie IEF fellowship “SUPRADYN”, and the “KETEP” as well as technical support with the beamline BW-1 by Dr. Bernd Struth (DESY) are gratefully acknowledged.

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