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Computer simulations of the early stages of crystal nucleation of linear and short chain branched polyethylene on carbon nanotubes



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ABSTRACT

We have used molecular dynamics simulations to study the process of macromolecular organisation of single chain linear and branched polyethylene on the surface of carbon nanotubes. These systems can be considered as good models for the study of the mechanism of polymer folding at the early stage of crystal formation on carbon nanotubes. The mean-squared radius of gyration, the stem length, the bond orientation order parameter and the radial distribution have been used to describe the organisation process and the structure of the chains at the carbon nanotube surface. When compared to the process of organisation of isolated single chains, interesting results are observed: (i) two different mechanisms of chain organisation give rise to different morphologies; lamellar thickening and lateral crystal growth lead to mono- and multilayered structures, independently of the presence of short chain branching; (ii) lamellar thickening is however hindered, but still present, in the case of polymer chains with short chain branches; (iii) both the stem length and the order parameter increase in the nanocomposites with respect to those obtained for isolated chains under the same conditions; (iii) the reorganisation process of thickening is accelerated by the presence of the carbon nanotubes, which act as nucleating agents; and (iv) the presence of short chain branching in polymer chains delays the onset of nucleation and growth of the crystalline structure, suggesting that the process is quite sensitive to the local chain chemistry.

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1. Introduction

The incorporation of carbon nanotubes (CNTs) into polymeric matrices has attracted great attention in the scientific community. When CNTs are adequately dispersed, interesting polymeric nanocomposites can be prepared

with enhanced mechanical properties and ease of processing [1–8]. These polymer/CNT nanocomposites are characterised by a combination of intrinsic properties associated to each of the components, but the dispersion of the CNTs and their interaction with the polymeric chains play also a key role in their final properties [9]. Indeed, there are synergistic effects that arise from this interaction, which may lead to the organisation of the long polymeric chains onto the CNT surface. This is particularly attractive in the case of

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crystallisable polymeric matrices. In these cases CNTs are considered as nucleating agents, as they can provide an adequate surface to promote polymer crystallisation. Notwithstanding, crystallisation behaviour of nanocomposites is sensitive to many factors, including the molecular architecture of the polymeric matrix, the dimensions and the surface features of the CNT, and the method of preparation of the nanocomposites [10]. It is very difficult to experimentally observe the dynamics of the structural changes driven by the crystallisation of polymers onto CNTs through experiments. For this reason, computer simulation can be regarded as a valuable tool for exploring the dynamics of polymers, including the crystallisation process of semicrystalline polymers. The organisation of single polymeric molecules onto CNT surfaces has been studied by some authors using computer simulations [11–16]. From these studies one can extract that the structure of a polymer on a CNT surface is determined by three main factors: the dimensions of the CNTs, the cooling program and the molecular architecture of the matrix (that eventually controls chain conformation and flexibility). Wei implemented Molecular Dynamics (MD) simulations to explore the conformational features of linear polyethylene (PE) chains on CNT and found a dependence of the wrapping angle of the polymer on the radial dimension of the CNT [11]. Kumar and co-workers have recently studied the effect of the radius of the CNT and the method of cooling [12]. They found that both absorption and arrangement of linear PE chains onto CNT are strongly affected by these two factors. The quenching process leads to a straight lamellar arrangement of the polymeric chain on the CNT surface, while the orientation is independent of its radius. However, during stepwise cooling a helical wrapping arrangement of the polymer chain is observed on the CNTs of moderate radii, while a straight lamellar arrangement is observed on the CNT with the smallest radius of around 2.0 Å. The effects of molecular architecture of the polymer matrix have also been explored. For instance, Yang and co-workers studied the organisation of linear PE molecules with different molecular weight on a fixed size CNT [13]. They cooled the systems from a high equilibrated temperature to room temperature and analysed the effect of the polymer length on the crystal size and its evolution along the simulation. They found that the CNT surface offers an effective support for the crystallisation, and that the van der Waals components of the potential were identified as the driving force of the process. Gurevitch and Srebnik [14] and Tallury and Pasquinelli [15,16] carried out computer simulations to study the conformational behaviour of polymeric chains of different stiffness on CNTs at a fixed temperature. They found that the conformation of an adsorbed chain depends on its stiffness, ranging from the randomly adsorbed conformations of flexible chains to the helical conformations in the case of rigid macromolecules.

Conformational features and chain flexibility can be easily modulated in PE by means of the incorporation of a comonomer, or, in other words, short chain branches (SCBs). Recently, we have studied in depth by experiments and computer simulations the effect of SCB in both the conformation and dynamics in the melt [17–23], and the structure and crystallisation process [24–28] of model

polyolefins and n-alkanes but in the absence of an absorbing surface. The role of SCB in the physical properties of polyolefins has been widely explored from the experimental point of view, and now simulations are giving us interesting information which is not possible to obtain experimentally [19–23,26–28]. In these works, it has been shown that the SCB number and composition has considerable influence on the crystallisation process. In general, SCB is excluded from the crystal and causes a progressive reduction in crystal size and stem length. Thus, we consider of great interest to explore the role of the SCB of the polyolefinic matrix in the organisation of the chains when they are absorbed onto a CNT. In this paper, we examine the effect of SCB on the structural evolution of single chains with different molecular architecture during the crystallisation process onto a single CNT. These simulations are compared with equivalent systems in the absence of the CNT, and also with experimental data available from the literature [29–32].

2. Molecular models and simulation methods

The procedures of our computer simulations were adopted from Ref. [13]. However, we have studied not only linear but also polyolefins with SCB, as in these systems the effect of molecular architecture on the interaction between macromolecules and CNTs has not been explored either experimentally or by means of computer simulations. We have used the graphical interface of *Materials Studio* software package from Accelrys Inc., for the construction of all our molecular models. The single wall CNT has a length of 122.98 Å and a radius of 6.78 Å. We have also constructed a series of flexible PE backbones with a variable number of randomly placed butyl side groups (ethylene/1-hexene copolymers). The polymeric chains consisted of 0, 5 and 10 butyl branches randomly distributed in a chain containing 1000 methylene units. The polymers have been denoted as PE00, PE05 and PE10. In each molecular model, a randomly generated PE chain was placed randomly surrounding the CNT (see Fig. 1). The CNT length was supposed to be much longer than the PE chain length. The structure of the CNT was made periodic along the z-axis and the positions of CNT atoms restrained to their initial values along the MD simulations. Previous studies also imposed such a limitation in the degrees of freedom of this element of the model [14–16]. Before the MD simulations, 500 steps of energy minimization have been performed to relieve unfavourable conformations. For the MD simulations, we have used a NVT ensemble at a temperature of $T = 325$ K, using the Dreiding force field. The parameters used in the Dreiding force field are those listed in Ref. [33]. A united atom model with methyl ($-\text{CH}_3$), methylene ($-\text{CH}_2-$) and methyne ($-\text{CH}-$) groups represented as individual interaction sites has been used to simplify calculations. The total potential energy E_{total} consists of four terms: (1) the bond stretching energy E_{stretch} for two adjacent united atoms, (2) the bond-bending energy E_{bend} among three adjacent united atoms, (3) the torsion energy E_{torsion} among four adjacent united atoms, and (4) the 12–6 Lennard–Jones potential E_{vdw} (van der Waals) between

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