



Simulation of semi-crystalline polyethylene: Effect of short-chain branching on tie chains and trapped entanglements



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ABSTRACT

A Monte-Carlo simulation method for assessing the tie chain and trapped entanglement concentration in linear polyethylene was extended to enable the simulation of explicitly branched polyethylene. A sub-routine was added to the model making possible the incorporation of different branch lengths and distributions. In addition, the microstructure of branched polyethylene was considered to be made of lamellar stacks of different thicknesses, acknowledging the segregation phenomenon during crystallization. Also, based on complete exclusion of bulky branches from the crystal lattice, a 'pull-out' mechanism was developed for the relaxation of branched parts of polyethylene chains in the vicinity of the crystal layer. Simulations of two series of real polyethylene samples showed the effect of short-chain branching on the concentrations of tie chains and trapped entanglements. Introducing a few branches to an unbranched polyethylene increased the concentration of inter-lamellar connections significantly. This effect decayed if the number of branches was further increased. The tracking of the position of all the carbon atoms during the crystallization process was implemented in the model, making the average square end-to-end distance $\langle r^2 \rangle$ of polyethylene chains calculable. Simulation of chains with the same molar mass but with different branch contents showed a reduction in the average end-to-end distance with increased branching. The use of real molar mass distribution data was also added to the model features.

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1. Introduction

On a sub-micron scale, semi-crystalline polyethylene with a medium to high crystallinity (> 40 wt.%) is typically made up of stacks of crystal lamellae sandwiching intermediate amorphous layers. This applies to both homo-polyethylene and poly(ethylene-co-1-alkene)s with up to 3 mol.% co-monomer (i.e. 15 short branches per 1000 backbone carbon atoms) [1]. The polymer chains in the amorphous regions can form tight folds, statistical loops, loose chain ends (cilia), fully amorphous chains, tie chains or chains connecting via permanently entangled loops to the adjacent crystal layer, the latter being referred to as trapped entanglements [2]. Earlier studies have shown that the trapped entanglements and tie

chains connecting the crystal lamellae are extremely important for the fracture toughness and the resistance to slow crack growth [3–6].

In short-chain branched polyethylene, e.g. linear low density polyethylene (LLDPE), the branches affect the crystallization of the polymer chains and the morphology of the semi-crystalline material. Whereas methyl or ethyl branches can, to some extent, be incorporated into the polyethylene crystal lattice [7,8] albeit as defects, bulkier branches such as butyl or hexyl are known to be almost completely rejected from the crystal lattice [3]. Hence, in the case of bulky branches, the crystallization is limited to the ethylene sequences between the branches. Under given crystallization conditions, this limitation leads to thinner lamellae and a lower crystallinity than in linear polyethylene of the same molar mass [9]. However, it is known that the existence of branches increases the number of inter-lamellar connections leading to a stronger network and enhanced fracture toughness [10–15]. The rejection of branches to the amorphous phase also increases the free volume which leads to increased resistance to slow crack growth [16].

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Considering the importance of inter-lamellar connections in semi-crystalline polymers, several researchers have attempted to assess the concentration of the connections by different theoretical methods. The theoretical models for studying polymers at an atomistic scale are generally based on molecular dynamics or Monte Carlo simulations [17]. When modeling complex materials like semi-crystalline polyethylene, simplifications must necessarily always be introduced due to limited computer capacity and imperfect knowledge of the morphology and physical and chemical properties of the corresponding real-world materials. Even relatively simple computer models can often be useful for predicting material properties under specific conditions, but with the successive removal of simplifications, a greater model applicability and reliability can be achieved. The pros and cons of preceding works were discussed briefly in our previous paper [2], which also describes the Monte-Carlo algorithm, “the Nilsson model”, which is extended in this report.

In this work, the role of short-chain branching in the assessment of inter-lamellar connections in semi-crystalline polyethylene has been the main matter of concern. Previous models have either considered only single values for the crystal and amorphous thicknesses or included fractionation techniques where the tie chain calculations for each fraction have been performed separately [3–5,10,18–21]. Due to the computational efficiency of the Nilsson Monte-Carlo model [2], sufficiently large simulation domains can be constructed to make possible the removal of these simplifications. This was achieved by including the whole crystal thickness distribution in the simulated short-chain branched semi-crystalline polyethylene systems. In fact, inter-branch ethylene sequences of similar length crystallize together and form crystal layers of the same thickness. Thus, due to the presence of an ethylene sequence length distribution, lamellae with different thicknesses co-exist in the semi-crystalline polyethylene.

In a previous study, a Monte Carlo random walk model was developed to simulate the chain structure of amorphous layers in polyethylene and to calculate the concentrations of tie chains and trapped entanglements [2]. The model was able to simulate both linear and branched polyethylene with encouraging results. However, the branches were not explicitly considered and the original model ignored possible segregation effects. The application of the original model to systems with explicit branches not housed in the crystals led to a pronounced overcrowding of the amorphous phase. The present study was therefore aimed to further develop the Nilsson model [2] and to address the aforementioned shortcomings of other works in order to simulate the semi-crystalline structure of the polyethylene more realistically.

2. Experimental

Data from real samples were used as input for our model. Three samples of single-site metallocene-catalyzed homogeneous poly(ethylene-co-1-hexene) with narrow molar mass distributions were supplied by Borealis AB, Sweden. The samples were denoted B-EHX_{but}, where X_{but} is the percentage molar fraction of butyl branches in the polymer. The molar mass data were obtained by size exclusion chromatography (Agilent PL GPC220 equipped with a refractive index and differential pressure detector using 1,2,4-trichlorobenzene with antioxidant as solvent and the universal calibration procedure.). Smithers Rapra Ltd, United Kingdom, carried out the size exclusion chromatography and the calculations of the average molar masses. The branching data were obtained by solution ¹³C NMR (Jeol Eclipse +300 NMR using tetrachloroethane as solvent). ITS Testing Services Ltd, United Kingdom, carried out the ¹³C NMR branching analysis.

The equilibrium melting points of the copolymers were calculated according to the expression [22]:

$$T_m^0(p) = \frac{1}{\left(\frac{1}{T_m^0(p=1)} - \frac{R}{\Delta H_f^0} \times \ln p \right)} \quad (1)$$

where ΔH_f^0 is the heat of fusion per mole of crystallisable repeating unit, which for polyethylene is equal to 8.284 kJ (mole C₂H₄ units)⁻¹ [23], $T_m^0(p)$ is the equilibrium melting point for the copolymer with p molar fraction of crystallisable units and $T_m^0(p=1) = 414.6$ K is the equilibrium melting temperature of 100% crystalline polyethylene [24], and $R = 8.314$ J mol⁻¹ K⁻¹ is the universal gas constant. Eq. (1) assumes that the branches are excluded from crystals, which is a reasonable assumption for the butyl-branched polyethylene samples studied.

Differential scanning calorimetry was used to assess the crystallinity and the melting trace of the samples to obtain information about the crystal thickness distribution. Samples weighing 5 ± 1 mg were encapsulated in 40 μ l aluminium crucibles and placed in a temperature- and energy-calibrated Mettler Toledo DSC 1 using nitrogen as purge gas. The system was calibrated by recording the melting of pure indium at the actual heating rate used. Samples were heated at a rate of 10 K min⁻¹ up to 433 K, kept at this temperature for 5 min and then cooled at a rate of 10 K min⁻¹ to 223 K. The samples were then heated again at a heating rate of 10 K min⁻¹ up to 433 K. The second melting trace was used for the calculations. The heat of fusion Δh_f , determined from the normalized melting peak area of the DSC thermogram, was used to obtain the mass crystallinity w_c of the samples using the total enthalpy method [25] according to:

$$w_c = \frac{\Delta h_f}{\Delta h_f^0 - \int_{T_1}^{T_m^0} (c_{p,a} - c_{p,c}) dT} \quad (2)$$

where T_1 is an arbitrary temperature below the melting range, $c_{p,a}$ and $c_{p,c}$ are the specific heat capacities of the amorphous and crystalline components respectively, and $\Delta h_f^0 = 293$ kJ kg⁻¹ is the heat of fusion for 100% crystalline polyethylene at the equilibrium melting point (calculating this parameter for the equilibrium melting temperatures of the copolymers presented in Table 1 results in negligible error.). Data for $c_{p,a}$ and $c_{p,c}$ from Wunderlich and Baur [26] were used. The calculated mass crystallinities are presented in Table 1.

In addition, data for four quenched single-site metallocene ethylene/1-hexene homogeneous copolymers with narrow molar mass distribution from Ref. [27] were also used as input. The samples were denoted as EHX_{but}, where X_{but} is the percentage molar fraction of butyl branches in the polymer. These samples were chosen since, except for the branching level, they had similar molecular characteristics which made them ideal for this study.

The crystal thickness L_c at the peak melting temperature was calculated according to the Thomson–Gibbs equation [28]:

$$T_m = T_m^0(p) \times \left[1 - \frac{2\sigma(p)}{\Delta h_f^0 \rho_c L_c} \right] \quad (3)$$

where T_m is the peak melting temperature, $\rho_c = 1003.0$ kg m⁻³ is the density of the crystalline polyethylene for the orthorhombic unit cell [29], and $\sigma(p)$ is the specific free energy of the fold surface for the copolymer with p molar fraction of crystallisable units. The use of $\sigma = 93$ mJ m⁻² for linear polyethylene results in a negligible

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