Effect of the Molecular Structure of Semicrystalline Polyethylene on Mechanical Properties Studied by Molecular Dynamics

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ABSTRACT: We present results from molecular dynamics simulations for an all-atoms model of a semicrystalline polyethylene under uniaxial tensile test. Our model has a realistic semicrystalline organization of two high molecular chains which are involved in two crystalline and two amorphous phases. The tie-molecules link these phases. A high content of tie-molecules is compatible with the stability of the semicrystalline organizations in the initial state. The main objective of the study is to check the effect of some molecular parameters, poorly known from experiments, on the mechanical properties under uniaxial tensile test. It is a way to have an insight on the value of the probable molecular parameters. We show that the number of tie-molecules mainly acts on the elastic modulus and the lamellar thickness acts on the yield stress. A nearly constant stress, a plateau, results from the narrow length-distribution of tie-molecules. This plateau is not observed during mechanical experiments. This plateau is the direct result of isomolecular tie-molecules. The only way to predict the progressive increase of the stress up to the yields stress observed experimentally is to consider a large length-distribution of tie-molecules. This progressive increase of stress implies a progressive deformation of the crystalline phase. The basic mechanism of plastic deformation is the pull-out of crystalline chain segments by the tie-molecules in extended conformation. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: molecular dynamics; polyethylene (PE); semicrystalline; mechanical properties; elasticity

INTRODUCTION

The mechanical properties of solid-state polymers, and especially of polyethylene, are the subject of numerous experimental and theoretical investigations from more than 50 years. These properties depend on their chemical structure and internal organization. The prediction of mechanical properties under large deformation involves a multiscale approach. Most semicrystalline polymers, and in particular polyethylene, crystallize with a spherulitic morphology. Their diameter of the order of tens or hundreds of micrometers is far beyond the usual accessible length scale for atomistic simulations, that is, few nanometers scale. However, when a tensile experiment is performed on a spherulitic system, the equatorial region of the spherulites is first strained.[1] The deformation is heterogeneous inside the spherulites. The properties of the spherulitic system at small strain can, therefore, be approximated by the properties of the equatorial region of one spherulite.[1] This limits the scope of our study to a lamellar system, with layer thickness of the order of 10 nm. It is possible to study such a system with atomistic simulations. The sample preparation, however, is tricky. The limited time-scale of such simulations does not allow the creation of a semicrystalline sample by crystallization from the melt. This is possible only for short chains (maximum a few hundreds of carbons) with a loss of chemical details, by the use of united atoms[2–4] or coarse-grained models.[5,6] In that case, however, the polymer crystallizes in a close-packed pattern, rather than in the orthorhombic crystallographic phase found experimentally. Moreover, these pseudo-crystals are distributed randomly in space and do not form lamellae.

A possible way to overcome this difficulty is to bypass the crystallization step and to build a semicrystalline organization. Few authors have tried to model by this way the mechanical response of semicrystalline polymers at a molecular scale. Indeed, creating a realistic sample representative of the experimentally observed polymer morphology is particularly difficult. Some advances in that field involve the semicrystalline microstructure at a mesoscopic level to explain these unusual mechanical

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properties.[7,8] They model semicrystalline spherulites by a random orientation distribution of crystalline domains embedded inside an elastic polymer network. They are able to predict mechanical properties under large deformation but not the direct effect of the chemical structure. As a main conclusion, the semicrystalline organization is a key parameter to predict the mechanical properties of polymer in the solid state. This is why most authors prefer studying the crystalline phase alone[9] or the amorphous phase alone.[10] Some authors, however, have simulated the mechanical strain of lamellar systems, but either the two phases were uncoupled[11] or they were partially coupled with no possible chain sliding.[12,13] Besides, these models were very limited in terms of chain length. We have shown in the first paper the way to build a fully coupled semicrystalline organization with an all-atoms description.[14] Two polyethylene chains couple the amorphous and crystalline phases with the possibility for the chains to slide through the crystal. A molecular dynamics simulation predicts the mechanical properties of the equatorial zone of spherulites during the first steps of elastic and plastic deformation.[14] It predicts the first steps of cavitation inside the amorphous phase. The cavitation is the result of the extension of the amorphous phase with lateral dimensions constrained by the crystal. The mechanical response under small strain and relaxation strongly depends on the tie-molecules.[14] The strain-rate effect is necessary to match the predicted and experimental mechanical properties.[14]

We propose in this article to analyze by molecular dynamics simulation the separate effect of its structural parameters (tie-molecules content, length distribution of tie-molecules, short-chain branching content, and lamellar thickness) on the mechanism of deformation and the mechanical properties. The tie-molecule content is the fraction of emerging molecules from a crystalline surface which go to the neighbor crystal through the amorphous phase. A narrow distribution of tie-molecules leads to a plateau in the elastic domain which is not observed from experiments.[14] The main objective of this article is to find the molecular parameters which can predict the experimental stress–strain evolution. The origin of this elastic plateau needs to be clarified.

The effect of some other molecular parameters (lamellar thickness, chain branching content) is analyzed with all the other molecular parameters maintained constant. From experiments it is impossible to modify a molecular parameter and to maintain all the others constant. For example, the nature and the distribution of chain branching along the chain strongly influence material's morphology (e.g., crystallinity, number, type, and distribution of crystallites)[15] and the macroscopic properties of polymeric materials.[16]

REFERENCE SYSTEM

The all-atoms model presented in our previous study[14] is used as a reference in this article and is labeled System 1. It describes with details the complete procedure to create and to relax to equilibrium state a semicrystalline organization with two high molecular weight polyethylene chains.

The model is composed of two crystalline lamellae separated by two amorphous layers (Fig. 1). The size of the reference simulation box size is: 3.7 nm (x direction), 3.944 nm (y direction), and 26 nm along the z direction, for two lamellae and two amorphous layers. All the dimensions of the box are more than two times of the cut-off of the intermolecular force field (cut-off radius = 1 nm). It contains two chains (M_w = 108,656 g/mol; i.e., 7761 CH_2), that can fold tight folds and loops in the system and pass through several lamellae and amorphous layers (tie-molecules), in the way mixing the chain folding[17] and the switch board model.[18] This implies that the chain segments exiting a crystalline lamella can either return directly to the same lamella (tight folds), or explore the amorphous space before returning to the same lamella (loops), or enters the next lamella (tie-molecules) or end in the amorphous phase (end). Most of the tight folded chains are oriented along the [110] plane, that is, the growth front plane (Fig. 1). No entanglement is considered in this model to focus only on the effect of tie-molecules on elastic-plastic deformation.

The two crystalline phases and the two amorphous phases are created separately with a connection rule which defined in Figure 1. The four interfaces describe the pass of the two molecules from a crystal to an amorphous phase. We have chosen a high content of tie-molecules to know if a stable semicrystalline organization can be obtained. It is usually considered that a high content leads to high constraints at the amorhous-crystal interfaces and leads to instability. All the semicrystalline organizations created with a high content of tie-molecules are stable. The tie-content is poorly known from experiments and we do not argue that a high content is obtained from experiments. We can conclude that it is possible to have semicrystalline organizations with a high content of tie-molecules. The choice of a high contents is also a way to study more easily the effect of the tie-molecule content on the mechanical properties.

The lamellae have been built by duplicating 5×8 crystallographic orthorhombic unit cells in the x–y plane and duplicating this plane 36 times in the z direction (lamellar thickness $\sim$ 9 nm). These crystals are relaxed at 300 K with a NσT ensemble using an anisotropic Berendsen type barostat.[19] The amorphous phases are created with the connection table:
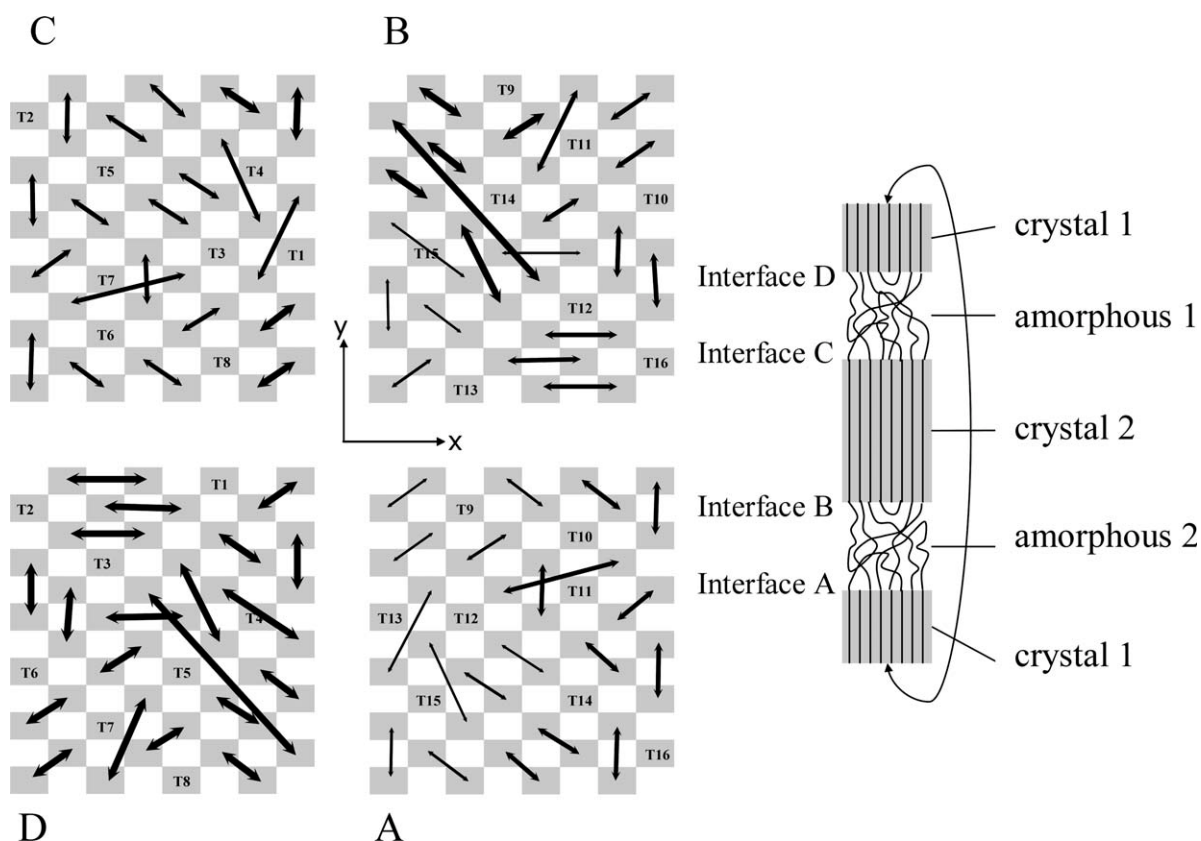
Figure 1 Connectivity sketch for System 2, with 17% tie molecules.

amorphous phase 1 between interfaces C and D and amorphous phase 2 between interfaces A and B (Fig. 1). The four chain ends are not shown, they are included inside the amorphous phases. The two amorphous phases are relaxed separately to minimize their energy by compressing them along the z direction. The atoms at the interfaces are fixed in the x y plane. The energy is minimized during a process of 1.5 ns, the force field parameters and simulation details are explained in the next section. The final densities are close to the experimental value (850 kg/m^3). Then the two crystalline and two amorphous phases are concatenated to build a semicrystalline system. Then the semicrystalline system is first simulated in the NVT ensemble during 300 ps to stabilize the pressure. Then the simulations are done with the NσT ensemble (anisotropic barostat) during 1.4 ns to stabilize the dimensions of the box and to minimize the energy of the molecular system.[14] This procedure was applied for each modification of molecular parameters (tie-molecule content, tie-molecule length distribution, chain branching) or organization (lamellar thickness).

The first model includes tie-molecules with the same length.[14] This simple approximation is a significant characteristic of this model. The mechanical response of this system under tensile strain is described (Fig. 2, 47% tie-molecules). Under small strain, the stress shows a short rise, corresponding to the system's elastic domain, followed by a plateau. After a second stress rise, a maximum appears. This maximum corresponds to the yield observed experimentally. The plateau is representative of the mechanical response of the amorphous layer and is reversible.[14] Then, it is possible to check the effect of the different structural parameters on mechanical properties. The fraction of tie-molecules and their
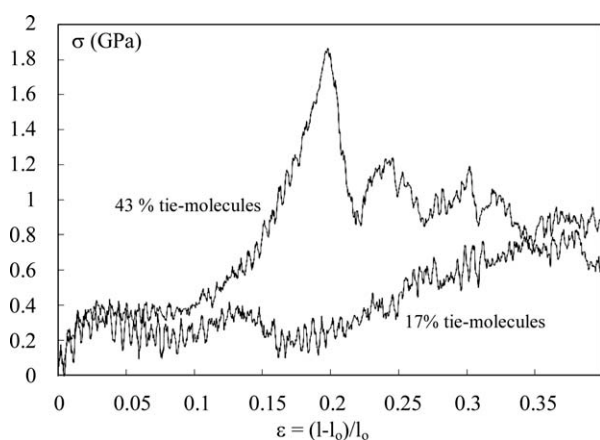

Figure 2 Stress–strain curves for lamellar System 1 (43% ties) and System 2 (17% ties) with a narrow length-distribution of tie-molecules.

length distribution in the amorphous layer can be modified from the initial model (System 1). Branching can be added, with different contents, in special locations on chain segments inside the amorphous phase. The thickness of the lamellae is also modified. It directly acts on the polyethylene crystallinity. All these parameters are modified separately from the initial model. We study their individual influence on the predicted mechanical response and have an insight of the most probable structure of experimental samples by comparing their simulated and experimental stress–strain curves.

SIMULATION DETAILS

The simulations were carried out with the program DL_POLY.[19] We have slightly modified this program in order to perform a continuous tensile test in the z direction, that is, normal to the interface crystal/amorphous domains. The simulation box is scaled anisotropically, according to the pressure calculation, by a Berendsen type barostat, to allow anisotropic cell variations.[19] The simulation box, according to the calculations of the main components of the anisotropic stress tensor, is now linearly scaled in the z direction at a rate specified by the user, while still scaled in the x and y directions according to the stress calculation. This corresponds to a variable external stress in the z direction and a 1 bar stress applied normal to the x–z and y–z planes. The strain-rate is 4×10^9 s^{-1} for all simulations done in isothermal condition.

The time-step used in all our simulations is 1 fs. Berendsen thermostat and anisotropic barostat were used with coupling constants, respectively, 0.5 and 10 ps. The target temperature was fixed to 300 K. The force field is the same in our previous study.[14] van der Waals interactions are truncated above a cut-off distance of 1 nm. No electrostatic interactions were calculated in our simulations, as no partial charges have been attributed to the atoms.

Elastic moduli (TABLE I) are calculated by fitting the stress–strain curve with a function of type:

$$\sigma = \sigma_0(1 - \exp(-\beta\varepsilon)) \qquad (1)$$

where σ is the stress, σ_o is the stress at elastic limit, ε is the true strain [ln (l/l_0)] in small deformation.

The parameter β is calculated by a linear fitting of the curve $\ln\left(\frac{\sigma_0 - \sigma}{\sigma_0}\right)$ versus ε. The value of the elastic modulus is then $\beta\sigma_0$. In our reference system, σ_0 have been set to 0.37 GPa and β have been calculated to 90.3. The resulting elastic modulus is then 33 GPa.

This value is at least one order of magnitude larger than what would be expected experimentally.

This is a consequence of the very high strain rate (4×10^9 s^{-1}) used in our simulations.

Experimental strain rate are usually of the order of 10^{-3} s^{-1}. The effect of strain rate ($\dot{\varepsilon}$) on stress (σ) can be expressed by a power law.[20]

$$\sigma = \sigma_1\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_1}\right)^m \qquad (2)$$

The value of m for polyethylene has been estimated experimentally in the range of 0.06–0.09.[20] We have found the value 0.088 in our previous simulations.[14] Supposing that this law is valid under large range of strain-rates, we expect that the stress obtained with strain rate 4×10^9 s^{-1} would be 13 times larger (considering $m = 0.088$) than a stress measured on the same sample at strain rate 10^{-3} s^{-1}. Therefore, only the equivalent moduli, calculated at experimental rates with eq. (2), should be compared to the experimental moduli. The extrapolated value, 2.53 GPa, is in a reasonable agreement with the experimental value.

The comparison with experimental data at room temperature also requires that the amorphous polymer is still in the rubbery state during simulations. The experimental glass transition temperature is a subject of controversy. It is widespread from $-128°C$[21,22] to $-30°C$[23] and depends on the mechanism considered for this transition. Both γ ($< -100°C$) and β ($\sim -30°C$) relaxations have some of the properties normally associated with the glass rubber transition.[24] From experimental arguments it is difficult to argue if molecular dynamics simulations done at 300 K are in the glassy or the rubbery state. Molecular dynamics results on amorphous polyethylene with different molecular weights are able to answer this question.[25,26] Two methods, by the variation of dilatation coefficient and from the trans-gauche kinetics, are applied to observe the glass transition. A glass transition temperature near 279 K is deduced from specific volume change for a high molecular weight polyethylene during a high cooling–rate 10^{11} K/s.[25] This very high cooling-rate implies a shift of T_g to a higher temperature than observed during experiments. Thus the apparent activation energy seems directly related to the gauche-trans energy difference.[27] The transition rate from gauche to trans conformations leads to a lower glass transition (~ 230 K) in the same conditions.[25] Similar simulations with short polyethylene chains ($N = 70$ carbons) leads to $T_g = 225$ K $\pm$ 10 K and an activation energy $E_{GT} = 825$ J/mol.[26] The cooling-rate applied during these simulations for T_g prediction are done at shorter time-scale, that is, higher cooling-rate, than our simulations. The amorphous phase is in the rubbery state during the present molecular dynamics simulations. This rubbery state implies that experimental and simulations can be compared, then the stress can be scaled by the strain-rate factor.

Values of the Parameters Modified from the Initial Model (System 1) and Resulting Properties (Crystallinity and Mechanical Properties)

System	1	2	3	4	5	6	7
% Tie-molecules	43	17	43	43	43	43	43
Tie-molecule length distribution	Narrow	Narrow	Large	Large	Large	Large	Large
Branching content (branches ‰ carbons)	0	0	0	1	9	10	9
Crystalline lamellae thickness (Å)	90	90	90	90	90	90	50
Crystalline density (kg/m^3)	1047	1026	1045	1013	1035	1016	1025
Amorphous density (kg/m^3)	922	929	919	912	958	941	942
Total density (kg/m^3)	1012	1005	1010	985	1012	993	988
Crystallinity (%)	72	79	72	72	70	70	55
Yield strength (GPa)	1.9	0.8	1.3	1.2	1.4	1.2	0.7
Modulus measured at 4×10^9 s^{-1} (GPa)	33	35	36	23	33	32	27
Modulus estimated at 10^{-3} s^{-1} strain rate (GPa)	2.5	1.6	2.8	1.8	2.5	2.1	2.5

The modified parameters are: tie-molecule fraction, tie-molecule length, short chain branching content, and crystal thickness.

The molecular and structural parameters and the main mechanical results of the molecular dynamics simulations are put together in Table I. Initial system densities are calculated through the following process. First, the crystalline parameters are measured to define the crystal density (ρ_{CRY}). From the number of carbons in the crystal stems and the crystalline parameters, the crystal thickness, volume and mass are deduced. The amorphous thickness, amorphous mass and then the amorphous density (ρ_{AM}) are deduced from the previous parameters. The total density (ρ_{TOT}) is the ratio of the total mass over the total volume. Crystallinity (χ) is calculated from the densities (ρ_{TOT}, ρ_{AM}, and ρ_{CRY}) via the following equation:

$$\chi = \frac{\rho_{TOT} - \rho_{AM}}{\rho_{CRY} - \rho_{AM}} \qquad (3)$$

THE FORCE FIELD

The force field developed for crystalline polyethylene is used in our simulations.[28] This force field is derived from the Dreiding force field[29] and has been optimized in order to reproduce the crystalline parameters and the conformational statistics of amorphous chains of paraffins and polyethylene.[28] Especially, it is able to predict an orthorhombic crystalline phase for paraffins with even numbers of carbons and monoclinic for odd numbers of carbons.[28] Its functional forms and parameters are:

The bond stretching is described via a harmonic potential:

$$V(r) = 1/2\ k_B(r - r_0)^2 \qquad (4)$$

where k_B is the force constant, equal to 167.2 kJ/mol/Å^2 for CC and CH bonds; r_0 is the equilibrium bond length, equal to 0.153 nm for CC and 0.109 nm for CH.

The angle bending is also represented with a harmonic cosine potential:

$$V(\theta) = 1/2\ k_\theta[\cos(\theta) - \cos(\theta_0)]^2 \qquad (5)$$

where k_θ is the force constant, equal to 26.9 kJ/mol/rad^2 for all angles; θ_0 is the equilibrium angle value, equal to 109.47° for all angles.

The torsions are represented with a cosine form:

$$V(\phi) = k_\phi[1 + \cos(m\phi - \delta)] \qquad (6)$$

where k_ϕ is the force constant, equal to 40.6 J/mol for all torsions; m is the multiplicity, equal to 3 and δ is the phase shift, equal to 0.

The van der Waals interactions are described with a Buckingham formalism:

$$V(r) = C_e \exp(-r/\rho) - C_6/r^6 \qquad (7)$$

where C_e is equal to 1610.4 kJ/mol for CC interactions, 1340.23 kJ/mol for CH interactions, and 351.93 kJ/mol for HH interactions; C_6 is equal to 186.6 kJ/mol·Å^6 for CC interactions, 32.106 kJ/mol·Å for CH interactions, and 6.236 kJ/mol·Å for HH interactions; the equilibrium distance of interaction ρ is equal to 0.3571 nm for CC interactions, 0.2857 nm for CH interactions, and 0.2778 nm for HH interactions. These values imply a sufficiently high repulsive maximum for each component to avoid the catastrophic collapse known for this potential. van der Waals interactions are truncated above a cut-off distance of 1 nm. No electrostatic interactions were calculated in our simulations, as no partial charges have been attributed to the atoms.

EFFECT OF THE NUMBER OF TIE-MOLECULES ON MECHANICAL PROPERTIES (SYSTEMS 1 AND 2)

The tie-molecules are the chain segments located in the amorphous phase that link two different crystalline lamellae. The tensile strength of a semicrystalline material is directly connected to the number of tie-molecules between the crystallites. The content of tie-molecules is defined as the ratio of the number of tie segments over the number of stems inside the crystallites. In System 1, the crystalline lamellae are composed of 80 chain segments and the amorphous phase contains 34 tie-molecules. The tie-molecules content is therefore 43%. In order to study the effect of the tie-molecules content, we have prepared a new sample (System 2) with only 17% of tie-molecules. System 2 has been built in the same way than System 1,[14] but with a different connectivity sketch and longer tie-molecules to maintain the crystallinity. This sketch, shown in Figure 1, represents the four interfaces between crystalline and amorphous layers in the system. From this sketch, the conformation of the two chains through the lamellar system can be deduced. In the Systems 1 and 2 all the tie-molecules are isomolecular.

The stress–strain curve of Systems 1 and 2 are superposed on Figure 2. Under low strain, from 0.03 to 0.1, both systems show a first stress rise followed by a plateau corresponding to a stretching of the amorphous phase response. Then a second rise corresponds to a full extension of all the tie-molecules up to the beginning of the chain sliding in the crystalline lamellae. However, the yield stress and the elastic modulus increase with the number of tie-molecules (TABLE I). The yield stress seems directly proportional to the ties content. It increases from 0.8 GPa ($\varepsilon \sim 0.18$) to 1.9 GPa ($\varepsilon \sim 0.4$), that is, multiplied by 2.4, while the ties content increases from 17% to 43%, that is, multiplied by 2.5. The elastic modulus is multiplied by only 1.4. The strain to reach the yield stress is multiplied by 2.2 as an effect of the longer tie-molecules in System 2 (17% tie-molecules) than in System 1 (43% tie-molecules). The length of the tie-molecules is the key parameter to explain the mechanical properties.

A more detailed analysis of the conformation of molecules at the plateau in both systems gives the answer. In the initial state, the amorphous tie-molecules are relaxed as an effect of entropic force. During the traction up to the end of the plateau, the chains are progressively extended along the z direction which roughly corresponds to the direction of their connectivity points with the two crystals (Fig. 1). All the tie-molecules have almost the same length and they are extended in the same way. The stress – strain response in this elastic domain is the sum of the individual identical response of the tie-molecules. During a part of the extension the stress of applied by the tie-molecules to the amorphous/crystal interface remains constant and leads to the plateau. Under higher extension each tie-molecule is similar to a finite extensibility of a short Langevin's chain fixed at the two ends.[30] The sliding of the chain segments in the crystal connected to the tie-molecules begin to slide out the crystal at almost the same strain value. The pulling of the chains from the crystal, that is, the yield strain, starts when the stress due to the chain extension of tie-molecules is equal to the critical shear stress applied on the chain segments embedded inside the crystal. In the experimental curves, the first stress rise leads directly to the yield, therefore the plateau does not exist. We expect that a narrow length distribution of tie-molecules should not be present inside the real semicrystalline polyethylene.

EFFECT OF LENGTH DISTRIBUTION OF TIE-MOLECULES ON MECHANICAL PROPERTIES (SYSTEM 3)

In System 1, the tie-molecules have almost the same length (47 ± 1 CH_2 per tie-molecule). The simulations predict a plateau before yield which is not observed on experiments. This disagreement must be explained. Monte-Carlo simulations predict a large length distribution of tie-molecules.[31] The main hypothesis of Monte-Carlo simulation is the molecular segments inside the amorphous phase follows an equilibrium distribution of chain segments. This hypothesis may be questioned when the amorphous phase results from a kinetic effect, that is, out of thermodynamic equilibrium. We follow the results of results of Monte-Carlo simulation to modify the System 1. The narrow distribution is replaced by a large distribution with the same location of tie-molecules on the crystal surfaces (Fig. 3). The shorter chains are nearly extended chains when the longer chains are nearly fully relaxed as an effect of entropy.

The evolution of stress with strain for a large distribution of tie-molecules is completely different to those observed for a narrow distribution (Fig. 4). The plateau disappears and is replaced by a progressive increase of the stress up to the yield stress. The yield stress is slightly reduced from the value measured on a narrow distribution with the same lamellar thickness (Table I). The elastic modulus deduced from the initial increase of the stress is slightly lower for a large distribution than for the narrow distribution (Table I). The effects of a large distribution on the decrease of elastic modulus and yield stress can be explained by the same mechanism. The shorter tie-molecules are very early stretched and strain-
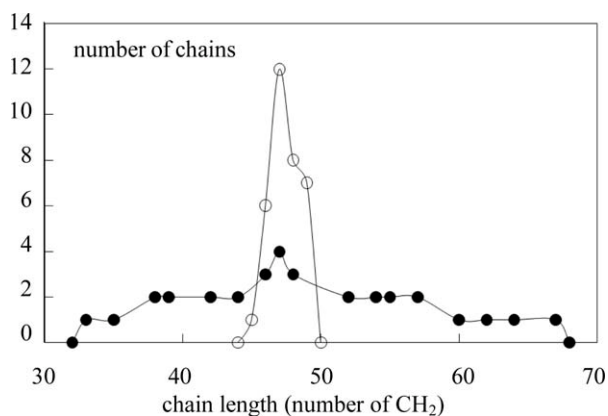
Figure 3 Two distributions of tie-lengths: narrow distribution (System 1) and large distribution (System 3).

hardened. Their low content among all the tie-molecules lead to a weak effect on elastic modulus and to a decrease from the behavior of System 1. The narrow distribution of System 1 of middle-size chains induces an entropic elasticity of the constrained chains on both ends in the rubbery state. These short chains are the first to stretch the corresponding segments inside the crystals. The chain-segments are progressively pull-out from the crystals. As an effect of the tie-molecules distribution, the next tie-molecules by length are then stretched and pull-out the segments inside the crystals. This is why the stress progressively increases and the plateau vanishes. The progressive pull-out of the chains locally disturbs the crystals by steps. At the yield-strain only part of the tie-molecules are involved in the mechanism of plastic deformation of the disturbed crystal. This mechanism explains the decrease of the yield-stress value. Following this analysis the elastic is no more completely separated to the plastic deformation. The plastic deformation should appear very early as an effect of the length distribution of the tie-
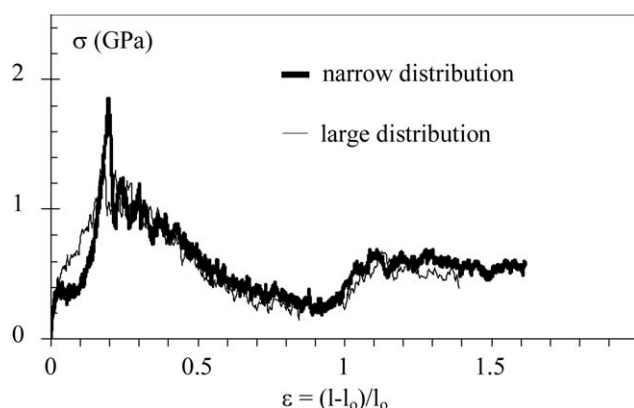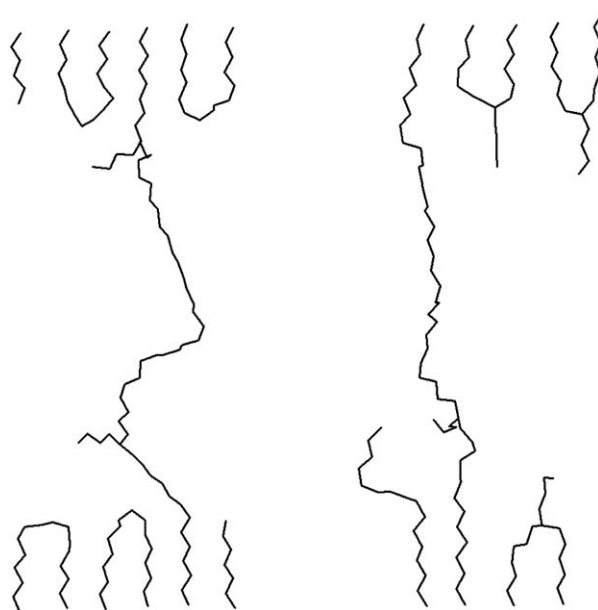

Figure 5 Different branching locations inside the amorphous domain. On the left, the branches (butyl groups) are placed only on the tie molecules, rather near the interfaces with crystallites (System 5). On the right, the branches are placed also on the tight folds at the interfaces (System 6).

molecules. The basic mechanism of plastic deformation should be a pull-out of the chains from the crystals.

EFFECT OF SHORT CHAIN BRANCHING ON MECHANICAL PROPERTIES (SYSTEM 4–6)

The low and medium density polyethylenes are copolymerized with a comonomer. This comonomer (butene-1, hexene-1, or octene-1) leads to a linear chain with from time-to-time short chain pending (ethyl, butyl, or hexyl, respectively). Their distribution along the chain depends of the polymerization process. A Ziegler-Natta polymerization incorporates
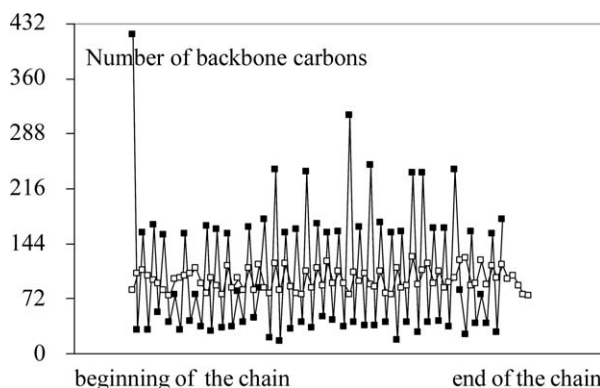

Figure 4 Effect of the distributions of tie-length on the stress–strain curves: narrow distribution (System 1) and large distribution (System 3).

Figure 6 Branching frequency along the chain expressed in term of number of backbones carbons between two branches for System 5 (—■— 9‰) and System 6 (–□– 10‰).
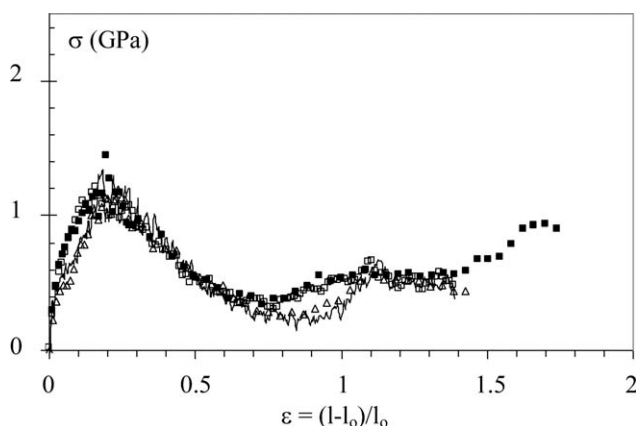
Figure 7 Stress–strain curves for lamellar systems with four different branching contents: System 3 (— linear PE); System 4 (△ 1‰); System 5 (–■– 9‰); System 6 (–□– 10‰).

Figure 9 Stress–strain curves for System 8 at two temperatures: 10 K (—); 300 K (✗).

almost randomly the comonomer along the chain. A metallocene polymerization incorporates more regularly the comonomer inside the chain. As an effect of the size of these segments, these short branches are difficult to incorporate inside the crystals. Some ethyl group can be partly included while hexyls are totally excluded from the crystals. Usually as an effect of crystallization mechanism these short branches limit the thickness of the lamellae and reduce the crystallinity. These short branches are located at the surface or near the surface of crystalline lamellae. There is a coupling between branching content and their distribution with the lamellar thickness of the solid polymer. By simulation we are able to separate the effect of lamellar thickness and of branching content on the mechanical properties. The system with a large length distribution of tie-molecules is modified by incorporating either 1, 9, or 10 butyl branches per 1000 carbons on the chain segments inside the amorphous phase (Fig. 5). In the sample with one group per 1000 carbons, the butyl-
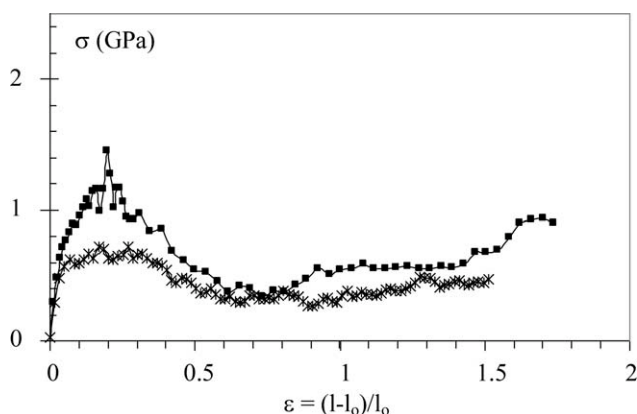

Figure 8 Effect of the thickness of crystalline lamellae on the stress–strain curves: System 5 (■ lamellar thickness = 9 nm); System 7 (✗) lamellar thickness = 5 nm).
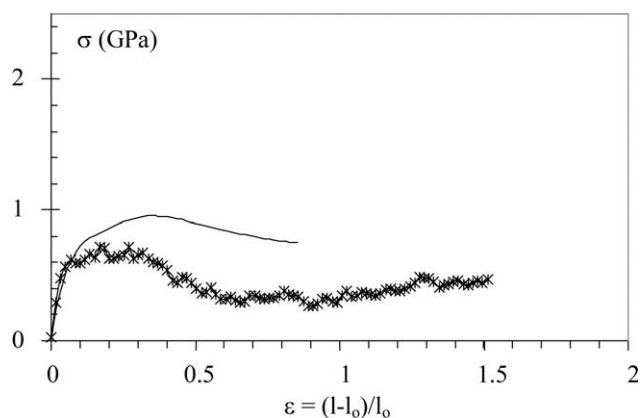
groups are randomly distributed along the chain but only on tie-molecules. The systems with 9 and 10 carbons differ by their distribution of branches along the molecules. The branching frequency along the chain is defined by the number of backbone carbons between two branches. A bimodal distribution is applied on the system incorporating 9‰ butyl (Fig. 6) while a more periodic incorporation is chosen on 10‰ butyl copolymer. It is possible to check the effect of copolymerization statistics on mechanical properties. As an effect of path statistics of the chains inside crystal and amorphous phase, these butyl-branches can be located on tie-molecules near the crystal surface, on large loops or on chain foldings (Fig. 5).

The stress–strain evolution of these copolymers can be compared to the linear polyethylene with the same large length distribution of tie-molecules (Fig. 7). Almost the same trend is observed. The yield strain and stress values seem unmodified by the chain branching. The stress of branched polyethylene increases more regularly up to the yield stress than for the linear polyethylene. These predicted evolutions of mechanical properties are very similar to experimental observations. This more progressive increase of the stress with strain before the yield stress can also be explained by the extra-stress needed to pull-out chain segments from the crystal. Sometimes a branching is located in a place where the pulling-out of a chain segment requires its incorporation inside the crystal. The entrance of the short branch requires an extra-stress as observed on stress–strain curves (Fig. 6). This effect strongly depends on the chain-branching content (Fig. 6).

EFFECT OF THE LAMELLAR THICKNESS ON MECHANICAL PROPERTIES (SYSTEM 7)

Basically the mechanism of deformation involves a pull-out process of chain segments from the crystals.

This phenomenon appears under a very low deformation for a large length distribution of tie-molecules and chain-branching. The process acts when the stress applied by a tie-molecule in an extended conformation is larger than the 1D critical resolved shear stress applied by the crystal on the embedded segments of the polymer chain. This stress should in first order proportional to the lamellar thickness. A new model was built with the lamellar thickness reduced to 5 nm. This thickness corresponds to the lower bound of the experimental range of polyethylene lamellae thickness 5–40 nm.[32] We have applied the large length distribution of tie-molecules, 9‰ of chain-branching and the chain path from the crystals to the amorphous phases. After equilibration, the crystallinity is 55% and its density is 988 kg/m^3. The same strain was applied with the same strain-rate. Figure 8 shows-out the effect of the lamellar thickness on mechanical properties. The main effect is a reduction of the yield stress by a factor ($\sim$ 1.7) almost proportional to the lamellar thickness ratio (1.8; Table I). In the same way, the elastic modulus decreases slightly from 33 GPa to 27 GPa. This is explained by the easier pulling-out of chain segments from the thin crystals.

EFFECT OF THE TEMPERATURE ON MECHANICAL PROPERTIES (SYSTEM 8)

The simulations up to now were done with a rubbery amorphous phase (300 K). A simulation was done at 10 K where the amorphous phase is glassy. This attempt was only to check the effect of amorphous phase on mechanical properties. The simulation was done with a thin crystal system (crystal thickness = 5 nm) after equilibration at 10 K (Fig. 9). The yield stress decreases when the temperature increases from 0.95 GPa (10 K) to 0.7 GPa (300 K). The elastic modulus decreases in the same way from 32 GPa (10 K) to 27 GPa (300 K). The main effect of the glassy state of the amorphous phase is an increase of the yield strain at low temperature $\varepsilon =$ 0.35 (10 K) whereas all the simulations at 300 K have done $\varepsilon = 0.18$ with a large length distribution of tie-molecules. A glassy state of the amorphous phase seems to modify some details in the mechanism of deformation but not the pulling-out of chain segments from the crystal. This first attempt on the thermal effect on mechanical properties needs to be analyzed in more details in a next future.

CONCLUSIONS

The mechanical properties of semicrystalline polyethylene are important to understand. The elastic to plastic transition strongly depends on the molecular organization of molecules inside the crystalline and the amorphous phases. Molecular dynamics simulations have been used to characterize the mechanisms of deformation of chain segments inside amorphous and crystalline phases for various possible molecular organizations and their consequence on the stress evolution. Starting from the semicrystalline polyethylene sample, described in a previous article,[14] we have performed a series of structural modifications and studied their influence one by one.

The main conclusion is the crucial role of the length distribution on the stress–strain evolution under low deformation. These models give a clear insight on the necessity of a large length-distribution of tie molecules to be consistent with the stress/strain experimental results. The chain branching induces a higher stress increase prior to yield. These general results can explain the effect of structural parameters (chemical and organization) on mechanical properties. The effects of these parameters are very difficult to reach from experiments.

We have thus showed that the yield stress is sensitive to the number of tie-molecules, the lamellar thickness, and temperature. The tensile modulus, however, seems hardly affected by any of the structural parameters studied here. The crystallinity may influence the modulus value, but the large uncertainties on the modulus measurement make this assumption difficult to assert for the moment.

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