ORIGINAL ARTICLE

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Graphical modeling and computer animation of tensile deformation in polymer liquid crystals (PLCs)

Abstract We create polymer liquid crystals (PLCs) on a computer and subject them to constant-force tensile deformations. Molecular dynamics simulation procedure is used and graphical models and animations of crack formation and propagation as a function of time are generated. Special attention is given to realistic rigid LC island geometry and the island spatial distribution in the material. Internal fracture processes can now be easily studied. As a result of the numerous animations recorded, clear patterns in PLC crack initiation and propagation emerge. With the help of the animations, the structure of PLCs may be understood without having to resort to costly laboratory experimentation.

Introduction and previous work

Polymer liquid crystals (PLCs) represent relatively new and insufficiently explored materials. Unlike traditional purely flexible polymers, PLC macromolecules consist of flexible segments united with rigid LC sequences by primary chemical bonds. Thus, in PLCs we do not have insufficient adhesion between the flexible constituent and the reinforcement, the main drawback of traditional heterogeneous composites (HCs, e.g. carbon-fiber reinforced materials) [1–5]. Furthermore, it has been found by scanning electron microscopy (SEM) that the rigid LC segments inserted into a polymeric material do not disperse homogeneously throughout the material, but tend to aggregate into domains of aligned rigid units, or *islands* [6]. The islands, also characterized by diffractometry [7], may vary in magnitude but tend to conform to a uniform spherical or ellipsoidal pattern.

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We know that the response of materials to tensile stress yields significant insight into the performance of the material. In most engineering applications, materials are subjected to a certain degree of stress. If deformation and crack propagation occur at relatively low levels of stress, the applications of the material will be severely limited. When a tensile force is applied to a polymeric material, either the energy may be relaxed within the material, or the force may cause fracture and initiate crack propagation throughout the material [5, 8, 9]. Therefore, in order to construct an optimal material, it is necessary to fully understand at what level of stress the crack initialization occurs in the material. Since PLCs contain at least two phases [4, 6, 7], it is also necessary to understand in which phase the cracks initiate.

Due to the unique geometrical distribution of rigid LC molecules, the study of crack initiation and propagation is especially advantageous for dealing with the PLCs. Given the multi-phase character of PLCs, the structure of these materials can be altered relatively easily. Since the rigid LC constituent is not homogeneously dispersed throughout the material, it is possible within the PLC material that certain spatial arrangements of the islands provide higher mechanical stability than others when the material is subjected to stress. For a given PLC, it is possible to have a large concentration of LC islands in one area and a relatively low concentration in another. Therefore, in order to develop the strongest material, a comprehensive understanding of the connection between the material structure and its behavior during deformation becomes necessary. We need to vary the LC units overall concentration as well as the spatial distribution of the LC islands.

Significance of results: experimentation vs. simulation

Laboratory experimentation has a number of intrinsic shortcomings when dealing with fracture mechanics. The first problem pertains to the information that experiments provide. Laboratory experimentation provides observations

at the broad macroscopic level and electron microscopy can be used to gather information on fracture surfaces. However, pinpointing microscopically *where* cracks are initiating is not possible – an essential feature missing if one is to fully understand the nature of the PLC deformation. The second problem with studying PLCs exclusively via traditional laboratory techniques is the high cost in terms of required time, manpower, and equipment. Varying PLC morphology is possible, but it is a guessing game as to which morphology will provide the strongest material and repeated experiments are again costly as well as time consuming. Performing the needed experiments to generate reliable conclusions involves long hours of hand-generating materials in addition to having to routinely purchase fairly costly materials. Finally, the third problem is that laboratory experimentation is always prone to experimental and human inaccuracies. Inserting LC structures into precise locations is tricky regardless of the caution exercised. This situation behooves us to look to other methods of evaluation of tensile deformation in PLCs.

The development of computer technology has provided us with the tools that make possible a flexible and comprehensive understanding of a variety of physical systems that have previously been very difficult to study. O'Brien, Hodgins, and coworkers at the Georgia Institute of Technology in Atlanta used fracture dynamics with the help of computer technology to develop graphical animations of glass shattering, bowls breaking, and fireballs exploding [10, 11]. Especially in the area of fracture and deformation, computer animations break the process down into multiple time-steps, thereby providing step-by-step analysis of material failure that is impossible with laboratory experimentation. The Atlanta group has demonstrated that their computer-generated materials deform and fracture quite like real materials [10, 11]. The materials they studied, however, are ceramics, whilst we seek to acquire knowledge on polymers.

As mentioned earlier, the high geometric alterability that the rigid LC islands provide within a PLC make computer simulations and animations particularly useful in investigating PLC deformation. Unlike purely flexible polymers, metals, or most ceramics, the structures of PLCs are relatively complex. Thus, computer simulations provide us with an inexpensive and quick way of creating complex structures and investigating them at the *molecular* level, a level hardly accessible to laboratory experimentation.

Using simulations, PLCs can be readily generated and their mechanical properties understood with a high degree of reliability and with no cost of materials. Instead of having a simple number which corresponds to the point at which a tensile force induces failure of a material, now it is possible to see at exactly what level of tensile stress a crack initiates, at what location it appears in the material, and how it propagates through the material. This provides a virtually complete understanding of the origin and development of the mechanical failure processes. Using computer simulations, we can establish what does and what does not ultimately bring about the fracture of a given material.

Overview of simulation procedure

While in computer simulations experimental inaccuracies are eliminated, it is absolutely necessary that the simulation realistically reflect the essential features of the system it is modeling [12]. This sounds like a truism, but is far from being achieved automatically. We are, in a way, continuing earlier work on PLC simulations [13], but now paying special attention to realistic rigid LC island geometry and location.

We have conducted molecular dynamics (MD) computer simulations of PLCs under tensile deformation. MD simulations accompanied with an understanding of single and double-well potential intermolecular interactions (see below) make possible the study of flexible polymers [14], and also PLCs. Such simulations include time as an explicit variable, ultimately allowing all particles (here segments of macromolecules) in the program to 'run' at once. This particular aspect allows for the simulation of time-dependent properties, since the motions of polymer chains constitute the key to understanding the mechanical properties of polymers [13–15].

In our simulations, we have attempted to keep the model as simple as possible, while still maintaining the essential features of the system. Therefore, we have utilized the model previously developed by Blonski and one of the authors [13], and extended it to the more realistic study of polygonal rigid LC island configurations. The model includes three key features that ensure a reflection of a real PLC: (1) two kinds of segments, rigid and flexible, have been defined; (2) to allow for bond failure at relatively large extensions, a Morse-like potential has been defined; (3) rigid LC molecules have been plotted on a triangular lattice, thereby resulting in realistic polygonal island geometries which are near two-dimensional equivalents of spheres and ellipsoids.

The PLC materials have been modeled as sets of chains, with each chain consisting of a linear sequence of particles. Within each chain, the position of each particle is given a single co-ordinate on an axis running parallel to the chain direction. All chains have been arranged in a two-dimensional way such that all chains are parallel and each chain has two neighboring chains (one above it and one below it), with periodic boundary conditions being applied in the direction perpendicular to the chains. Motion of the particles within each chain is determined by three different kinds of forces: bonding forces between adjacent particles along the chain, repulsive forces between neighboring particles on different chains, and external tensile forces acting directly on the end particles of each chain.

Interaction potentials

Potentials for interactions involving both rigid and flexible segments have been considered. For the rigid bonds, we have incorporated a Morse-like potential with a relatively narrow well (see Fig. 1(a)), namely:
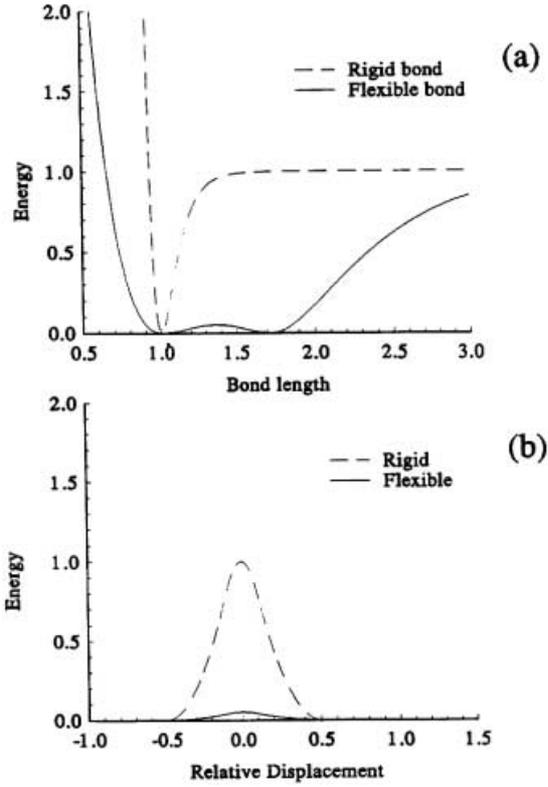
Fig 1a, b Potential energy of (**a**) bonding interaction between adjacent segments along a chain, and (**b**) repulsive interaction between neighboring particles on different chains

$$u(R) = \left\{1 - e^{(\gamma_R(1-R))}\right\}^2 \tag{1}$$

R is defined in our case as the distance between two adjacent segments on the same chain and γ_R is the parameter that defines the width of the well for the rigid bond. In order to represent correctly the conformational transitions in a real polymer chain, a spliced double-well potential has been introduced for flexible bonds, thereby allowing the bond to pass over a barrier during either extension or compression. The *cis-trans* transition in carbon containing chains is a case in point. The potential has been defined by a Morse-like function for the case when the bond is shorter than the first minimum energy position or longer than the second energy position. For intermediate bond lengths between these two extremes, a continuous symmetric barrier has been constructed from the second-order polynomials:

$$U_f(R) =$$
$$\begin{cases} \left\{1 - e^{[\gamma_f(1-R)]}\right\}^2, & R \leq 1 \\ 8U_0[(1-R)/\Delta]^2, & 1 < R \leq 1+0.25\Delta \\ U_0\{1 - 8[(1+0.5\Delta-R)/\Delta]\}^2, & 1+0.25\Delta < R \leq 1+0.75\Delta \\ 8U_0[(1+\Delta-R)/\Delta]^2, & 1+0.75\Delta < R \leq 1+\Delta \\ \left\{1 - e^{[\gamma_f(1+\Delta-R)]}\right\}^2, & R > 1+\Delta \end{cases} \tag{2}$$

Here, U_0 is the energy barrier height for a conformational transition, Δ is the distance between potential wells,

and γ_f is the parameter that defines the width of the well for the flexible bond.

For particles on neighboring chains, interactions between particles are represented by a potential that depends only upon relative displacements of the particles. A system of spliced second-order polynomials defines this type of potential, namely:

$$U_f(R) =$$
$$\begin{cases} 0, & R < -1 \\ (2.5)(U_H)(R/\delta)[0.5(R/\delta)+1], & -\delta \leq R < -0.2\delta \\ U_H[1 - 5(R/\delta)^2], & -0.2\delta \leq R \leq 0.2\delta \\ (2.5)(U_H)(R/\delta)[0.5(R/\delta)-1], & 0.2\delta < R \leq \delta \\ 0, & R > \delta \end{cases} \tag{3}$$

Here, R is the distance between the particles on different chains, U_H is the height of the energy barrier for a relative motion of particles, and δ is the range of the interaction. The shape of this external potential is illustrated in Fig. 1(b). The potential has accommodated for repulsive interaction between parts of neighboring chains, thereby realistically emulating the excluded volume effect. By allowing for these types of interactions, there is a resistance to relative motion of particles from two neighboring chains. This is an important aspect of behavior of polymeric materials, caused by means of chemical cross-links, entanglements and frictional forces between chains.

Units and parameters

Units and parameters within the simulation are similar to those previously used [13]; we have found these quantities sufficient in reflecting realistic materials. As is illustrated in the defining potential formulae, a non-strained bond is defined as one unit of length; similarly, the energy needed to dissociate a bond is defined to be one unit of energy. In our simulations all particles have identical mass, and therefore we have defined a unit of mass to be the mass of one chain segment. A unit of force is given by the ratio of the bond energy (one energy unit) to the rigid bond length (one unit of length).

Quantifying a unit of stress is slightly more complicated. We do not determine the cross-sectional area of the material since that area remains constant during the deformation. Therefore, values of the external force have been substituted as a measure of the stress. The values of the parameters used in the simulations are listed below in Table 1.

The parameters in Table 1 have been defined in such a way as to make the simulated material as general as possible while still maintaining the essential characteristics of the polymer liquid crystal. Experimental data suggests that the conformational transition barrier U_0 should be 5% of the bond dissociation energy. Previous simulation runs have concluded that a realistic value for the energy barrier U_H located between two rigid bonds, or at the chain ends, should be equal to the bond dissociation

Table 1 Parameters for potentials used in the simulations

Parameter	Value	Unit
U_0	0.05	Bond energy – conformational transition
U_H	0.05 or 1	Bond energy – relative motion of particles
γ_r	10	(Rigid bond length)$^{-1}$
γ_f	2	(Rigid bond length)$^{-1}$
Δ	0.732	Rigid bond length
δ	0.5	Rigid bond length

energy, and therefore $U_H = 1$ in this case. If the energy barrier is not located between two rigid bonds, or at the chain ends, then $U_H = U_0$ as the initial results would suggest. The parameter γ_f has been considerably smaller than γ_r in order to obtain broader wells for the flexible bonds. The range of the interactions between chains, δ, has been tuned so that at the start of the simulation this interaction has vanished for non-strained bonds, as one would necessarily expect.

Details of molecular dynamics simulations

Molecular dynamics (MD) computer simulations were first developed by Alder in 1957 [16]. Two other possibilities for simulating polymeric materials under stress are possible, namely Brownian dynamics (BD) and Monte Carlo (MC) methods. The problem with MC simulations is that only one particle is allowed to move at a time, thereby making it a primary tool for obtaining thermodynamic equilibrium properties including phase transitions [17]. Similarly, BD is not appropriate for simulating PLCs because, to study non-thermal sources of polymer fracture, it is necessary to avoid an effect of stochastic thermal forces – which BD simulations require in their procedure. MD simulations appear to be the most reliable in simulating PLC fracture since they allow all particles within the material to 'run' at once and also do not involve unnecessary stochastic thermal forces.

For our simulations, the Newtonian differential equations of motion have been transformed into difference equations, with a finite time step of Δt. Using the positions of the particles at an arbitrary moment and also before the last time step, and applying the forces calculated by summation of potential interactions and external forces we imposed upon the material, the positions after the next time step have been calculated using the so-called 'leap-frog algorithm' [18]. The equations of motion have the form:

$$x_j^i(t + \Delta t) = x_j^i(t) + \lambda(t)\left[x_j^i(t) - x_j^i(t - \Delta t)\right] + f_j^i(t)(\Delta t)^2 \quad (4)$$

where x^i_j (t) is the position co-ordinate of the jth particle in the ith chain, $\lambda(t)$ is a temperature coefficient described below, and $f^i_j(t)$ is the force acting on the particle.

In order to keep the temperature constant, the velocity of each particle has been multiplied by the factor $\lambda(t)$ in each time step:

$$\lambda(t) = \left\{1 + \left[U_{k0} / U_k(t) - 1\right](\Delta t / \tau_T)\right\}^{1/2} \quad (5)$$

where U_{k0} is the given reference value of kinetic energy, $U_{k(t)}$ is the actual value of kinetic energy, and τ_T is the time constant of the thermal relaxation. The kinetic energy per particle has been calculated according to the formula:

$$U_k(t) = \left[\sum_{i=1}^{N}\sum_{j=1}^{N}\left[x_j^i(t) - x_j^i(t - \Delta t)\right]^2\right] / \left[(2)(N)(M)(\Delta t)^2\right] \quad (6)$$

where N represents the number of chains simulated and M is the number of particles in a chain.

The following formulae have been used to calculate the forces acting on the particles:

$$f_j^i(t) = -\delta V\left[x_{j-1}^i(t) - x_j^i(t)\right] / \partial x_j^i(t)$$
$$-\delta V\left[x_{j+1}^i(t) - x_j^i(t)\right] / \partial x_j^i(t)$$
$$-\sum_{k=1}^{M}\partial U\left[x_k^{i+1}(t) - x_j^i(t)\right] / \partial x_j^i(t)$$
$$-\sum_{l=1}^{M}\partial U\left[x_l^{i+1}(t) - x_j^i(t)\right] / \partial x_j^i(t) \quad (7)$$

for $j \neq M$ and $j \neq 1$;

$$f_1^i(t) = -f_{ext}$$
$$-\delta V\left[x_2^i(t) - x_1^i(t)\right] / \partial x_1^i(t)$$
$$-\sum_{k=1}^{M}\partial U\left[x_k^{i-1}(t) - x_1^i(t)\right] / \partial x_1^i(t)$$
$$-\sum_{l=1}^{M}\partial U\left[x_l^{i+1}(t) - x_1^i(t)\right] / \partial x_1^i(t) \quad (8)$$

$$f_M^i(t) = -f_{ext}$$
$$-\delta V\left[x_{M-1}^i(t) - x_M^i(t)\right] / \partial x_M^i(t)$$
$$-\sum_{k=1}^{M}\partial U\left[x_k^{i-1}(t) - x_M^i(t)\right] / \partial x_M^i(t)$$
$$-\sum_{l=1}^{M}\partial U\left[x_l^{i+1}(t) - x_M^i(t)\right] / \partial x_M^i(t) \quad (9)$$

where f_{ext} is the external tensile force applied to the material.

The summations are applied to all particles on a chain, thereby accounting for all possible dynamical changes that could potentially lead to fracture of the material. Periodic boundary conditions in the direction perpendicular to the direction of the chains pose a potential difficulty and have been addressed in the following manner. For chains numbered 1 through N, the forces have been calculated from the formulae stated above, but for chain 1 the neighboring particle of i–1 has been replaced with chain N, and similarly for chain number N the neighboring particles have been in the chain 1 instead of i+1. This compensation allows for top and bottom chains within the material to be realistically simulated and not simply avoided, once again reflecting the nature of real materials.

Creation of islands on the lattice

Reasonable simulation times require that the simulated polymer be constructed on a two-dimensional lattice that

is representative of the three-dimensional real polymer. Forces developing between neighboring particles on the same chain as well as forces resulting from neighboring particles on different chains are incorporated. The rigid LC island configurations we have created correspond to a three-dimensional island. The overall concentration of the LC segments varies from 15 to 80%. Since the emphasis of the present paper is on output information and its animation, we shall describe the details of computer generation of the PLC materials in a later paper.

Simulation procedure

The size of the material undergoing simulation is arbitrary; however, simulation times can become quite long for very large materials. In our studies, we have constructed systems of 30 chains with each chain containing 50 particles (each particle may be either rigid or flexible). In order to avoid breakdown of the material when stress is first applied, two end segments on each side of the chain have been made rigid. No external stress is initially applied. After a specified number of time steps, the current status of the material is checked and saved, at which time a tensile force is applied. For each later time step, the applied tensile force was increased, thereby simulating realistic tensile action. For each force step, co-ordinates of each molecule within a chain are catalogued in separate output files. By plotting these points on a co-ordinate axis, a representation of the material at each point in the tensile deformation process is obtained, thus creating an animation of material failure. Needless to say, the stress σ (force in our system), versus strain ε diagram is generated at the same time.

Animation examples

Since coordinates of molecules are obtained for each force step in the simulation, one can use a variety of techniques to analyze exactly where crack initiation occurs, in which direction(s) cracks propagate, and at what time and force values ultimate failure of the material occurs. We have provided examples of ways to analyze cracks within a chain as well as ways to analyze how cracks propagate through the entire material.

We have analyzed data in such a manner that the entire material is animated by a 'flip-book'-like process, with rigid LC segments appearing as dark circles and flexible molecules appearing as white circles. Consider a PLC comprised of randomly scattered 3×3 rigid LC islands of 15% concentration, as shown in Fig. 2.

An initial snapshot of the material is provided in Fig. 2(a), which illustrates the initial configuration of the material. At a later force step, Fig. 2(b), about midway through the deformation process, it is clear that cracks are beginning to form and also the material is becoming elongated. Finally, a picture of the material once fracture has occurred is shown in Fig. 2(c). It is clear
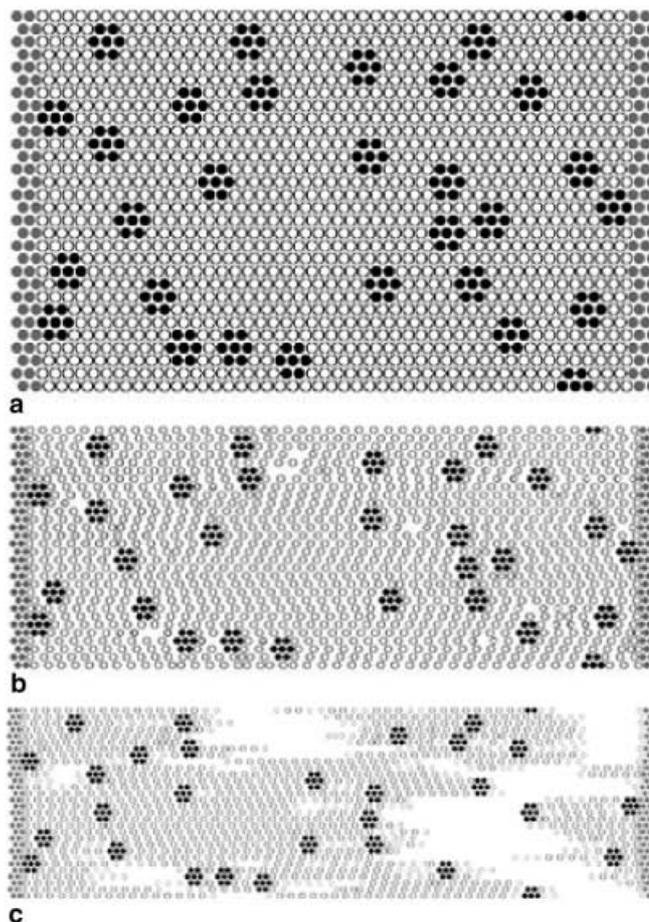
Fig 2a, b, c Arrangements of rigid (*dark*) and flexible (*light*) segments for (**a**) at the initial force step, (**b**) at the force step 29/50, and (**c**) at the force step 50/50

here which smaller cracks previously formed developed into larger cracks. Similarly, it is possible to see where failure of the material does *not* occur (that is, the distances between neighboring molecules remain small). Similar images are produced for intermediary force step values.

By altering the initial configuration, other simulation runs may be easily conducted as well, see Fig. 3.

This is another randomly distributed 3×3 LC island material, with 15% LC concentration. The material generator program used ensures that islands are randomly placed in different spatial locations for each material. A snapshot from the initial configuration, the configuration midway through the simulation, and the final configuration has been taken. Notice also how islands in the bottom and top row correspond, since the program considers them as neighboring islands. Constructing different island sizes and inserting them in different locations alters the deformation process, but we are now able to graphically model how this process occurs.

We are also easily able to construct visual diagrams of the deformation occurring along a selected chain; see Fig. 4.
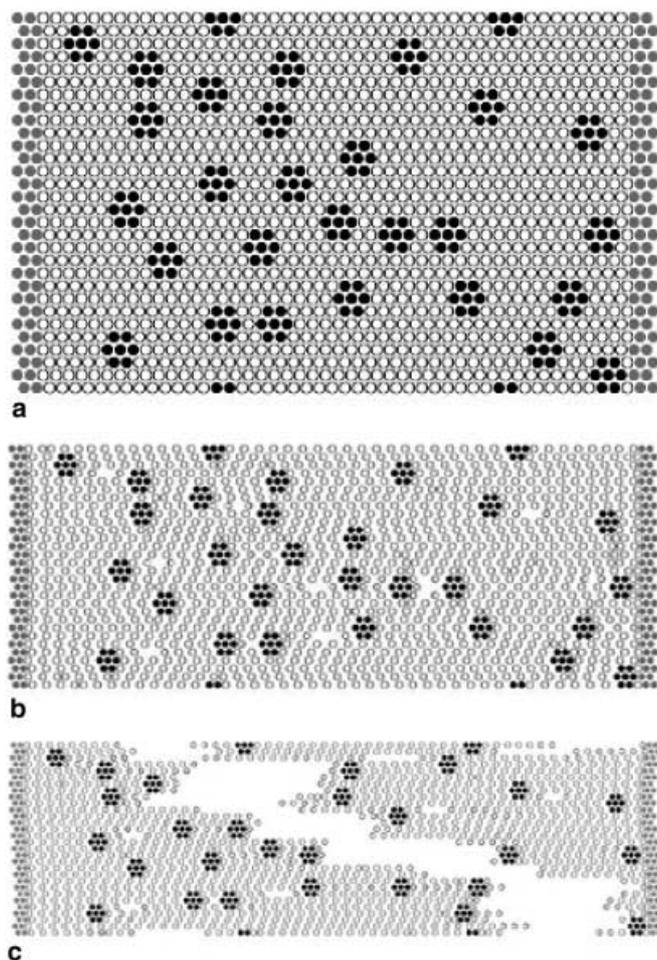
Fig 3a–c Arrangements of rigid (*dark*) and flexible (*light*) segments for (**a**) at the initial force step, (**b**) at the force step 28/51, and (**c**) at the force step 51/51

Fig 4a–c Intersegmental distances in chain 4 (See Fig. 2) for (**a**) the force step 15/50, (**b**) the force step 29/50, and (**c**) the force step 50/50

Here, we animate the intermolecular distances between neighboring segments (bond lengths) as a function of the bond number, thus demonstrating at what time and at what location the distance between molecules is sharply increasing (crack initiation). The animations show precisely how nearby molecules react to stress, thus allowing us to easily compare and contrast intermolecular distances as a function of time. This method gives greater insight into exactly what is occurring along a chain at each value of the force, information that is not sufficiently shown in Figs. 2 and 3.

Finally, three-dimensional graphs of bond vs. time step vs. intermolecular distance provide another way of understanding crack formation. Consider once again the initial 3×3 island configuration, see Fig. 2(a). By making a time-dependent plot of bond length vs. intermolecular distance, a clearer understanding of interchain deformation may be achieved; see Fig. 5.

Figure 5 represents the simulation results in a different manner than Fig. 4. By jointly making use of all these techniques, a surfeit of information pertaining to PLC deformation is provided in a quick, cost-effective manner, thereby providing much more helpful data than could be obtained through laboratory experimentation only.

Concluding remarks

The unique characteristics of PLCs may be utilized to the development of new polymeric materials, more durable than the ones currently manufactured. However, in order to create the best materials for a variety of engineering applications, a comprehensive study of the materials reaction to tensile deformation becomes necessary. Computer simulations provide a realistic way to easily and comprehensively analyze on a molecular level how a PLC responds to tensile deformation.

In the future, computer simulations will be able to provide information that will precisely locate crack initiation and predict propagation patterns in materials. With the help of computer simulations and graphical animations, PLCs and their relatively unexplored mechanical properties may be effectively studied. With this information, it should be possible to develop optimal materials by strengthening demonstrated weaknesses in the materials structure and achieving different LC island geometries.
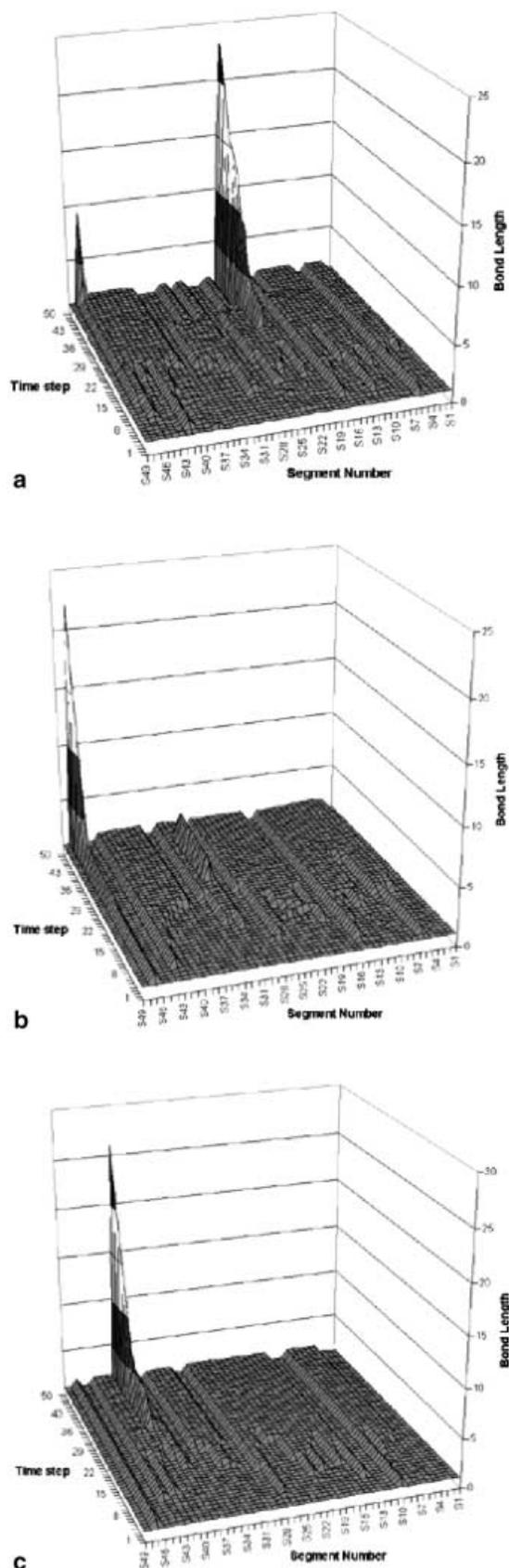
Fig 5a–c Segment number vs. time vs. intersegmental distance for (**a**) chain 4, (**b**) chain 13, and (**c**) chain 24 for the material shown in Fig. 2

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