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Elastic modulus and yield strength of semicrystalline polymers with bond disorder are higher than in atomic crystals

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ABSTRACT

We perform thorough molecular-dynamics simulations to compare elasticity and yielding of atomic crystals and model semicrystalline polymers, the latter characterized by very similar *positional ordering* with respect to atomic crystals and considerable *bond disorder*. We find that the elastic modulus G, the shear yield strength, τ_Y, and the critical yield strain ϵ_c of semicrystalline polymers are higher than (G, τ_Y), or comparable to (ϵ_c), the corresponding ones of atomic crystals. The findings suggest that the bond disorder suppresses dislocation-mediated plasticity in polymeric solids with positional order.

1. Introduction

Elasticity theories [1–4] predict that solid materials respond linearly with elastic modulus G to small shear deformations. Upon increasing strain, amorphous solids show complex and far from linear behavior [5–7]. When a critical yield strain ϵ_c is reached, corresponding to the shear yield strength τ_Y, the transition from the (reversible) elastic state to the (irreversible) plastic state takes place [8–10]. In an ideal elasto-plastic body (Hooke-St.Venant) τ_Y is the maximum stress [8].

It is well-known that plasticity in crystalline solids results from the structure and the mobility of defects (in particular dislocations) [11]. Dislocations do not exist in amorphous polymers, but, under an applied stress, elementary shear displacements can occur in a spatially correlated linear domain which can close on itself to form a loop to be interpreted in terms of classical dislocation mechanics and energetics [8,12–14]. However, even if the model can be used to fit the experimental data, there are conceptual problems to extend dislocation based concepts to glassy polymers [15,16]. That difficulty is part of the complexities involved in the phenomenon of plastic deformation in glassy polymers which is not yet fully understood, in spite of many accurate phenomenological models, see e.g. Refs. [8,15] for comprehensive reviews. In particular, Argon considered a scenario where individual chains are embedded in an elastic continuum [15]. He argued that plastic deformation is caused by the cooperative rearrangements of a cluster of segments with size Ω_f. The latter region is thermally activated under the applied stress to overcome the resistance that is generated from elastic interaction of the polymer chain with its surroundings. Ω_f is significantly smaller than the activation volume of dislocations [8,15]. The concept of localized cooperative rearrangements was proven to be fruitful also to account for the plasticity of non-polymeric glasses [15]. It was found that Ω_f is much smaller in amorphous metals with respect to glassy polymers. In comparison with the plasticity of crystalline solids, where the long-range positional order permits the translation of dislocations, the plasticity of disordered solids is mainly driven by the activation of cooperative rearrangements within the cluster of segments [15,17].

The previous discussion highlights that there are strong differences in the microscopic mechanisms of plasticity of *atomic crystals* and *polymeric glasses*. These two classes of materials differ in two rather distinct aspects, namely the connectivity and the positional ordering. Since these two features cannot be thought of as mutually independent and may exhibit antagonism, singling out the role of each of them is of interest. As a first step along this direction, the present paper aims at elucidating the role of connectivity into the linear and non-linear deformation of solids with *different connectivity* and *rather similar positional order*. Influence of connectivity outside the elastic limit has been recently reviewed [18]. Our study considers atomic crystals and polymer semicrystals, the latter with very similar positional ordering and considerable bond disorder to average out the coupling between connectivity and positional order [19,20]. We find that the elastic modulus G, the shear yield strength, τ_Y, and the critical yield strain ϵ_c of polymeric semicrystals are higher than (G, τ_Y), or comparable to (ϵ_c), the corresponding ones of atomic crystals. The results show that the introduction of disordered connectivity perturbs the

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long-range order, most presumably suppressing dislocation-mediated plasticity, and then increases the shear strength. In this sense, *if positional order is present*, atomic and polymeric plasticity appear to be not reconcilable. It is worth noting that the previous conclusion does not hold for glassy systems where, e.g., the plasticity of polymeric and atomic glasses with different connectivity exhibits similarities [21].

2. Methods

Molecular-dynamics (MD) numerical simulations were carried out on two different systems, i.e. a melt of linear polymers and an atomic liquid.

As to the polymer systems, a coarse-grained polymer model of $N_c = 50$ linear, fully-flexible, unentangled chains with $M = 10$ monomers per chain is considered [19]. The total number of monomers is $N = 500$. Non-bonded monomers at distance r belonging to the same or different chain interact via the truncated Lennard-Jones (LJ) potential:

$$U^{LJ}(r) = \varepsilon\left[\left(\frac{\sigma^*}{r}\right)^{12} - 2\left(\frac{\sigma^*}{r}\right)^{6}\right] + U_{cut} \tag{1}$$

$\sigma^* = 2^{1/6}\sigma$ is the position of the potential minimum with depth ε. The value of the constant U_{cut} is chosen to ensure $U^{LJ}(r) = 0$ at $r \geq r_c = 2.5\,\sigma$. The bonded monomers interaction is described by a harmonic potential U^b:

$$U^b(r) = k(r - r_0)^2 \tag{2}$$

The parameters k and r_0 have been set to $2500\,\varepsilon/\sigma^2$ and $0.97\,\sigma$ respectively [22]. Full-flexibility of the chain is ensured by the missing bending stiffness between adjacent bonds [20]. It must be pointed out that the bond length $\simeq 0.97\,\sigma$ prevents the significant heterogeneity of the monomer arrangements which is seen with longer bond length, see Fig. 6a of Ref. [20].

As to the atomic systems we consider systems of $N = 500$ atoms interacting with the truncated Lennard-Jones potential as in Eq. (1).

From this point on, all quantities are expressed in term of reduced units: lengths in units of σ, temperatures in units of ε/k_B (with k_B the Boltzmann constant) and time t_{MD} in units of $\sigma\sqrt{m/\varepsilon}$ where m is the monomer mass. We set $m = k_B = 1$. Periodic boundary conditions are used. The study was performed in the *NPT* ensemble (constant number of particles, pressure and temperature). The integration time step is set to $\Delta t = 0.003$ time units [23–26] The simulations were carried out using LAMMPS molecular dynamics software (http://lammps.sandia.gov) [27].

Fifty-six polymeric samples with initial different random monomer positions and velocities are equilibrated at temperature $T = 0.7$ and pressure $P = 4.7$, corresponding to number density $\rho \sim 1$. That thermodynamic states allows the polymer melt to equilibrate in the liquid phase for at least three times the average reorientation time of the end-end vector of the chain. After the equilibration, production runs started and proceeded up to the spontaneous onset and the full development of the crystallization of the samples. Fourteen runs failed to crystallize in a reasonable amount of time, while forty-two of them underwent crystallization forming polymorph crystals with distorted body-centered cubic (Bcc) lattices. Additional details, in particular concerning the crystallization process, are given elsewhere [19]. Sixty-four atomic liquid runs were equilibrated with starting temperature $T = 1.5$ and pressure $P = 20.0$. The temperature is higher in the atomic systems to avoid crystallization before the initial equilibration of the liquid phase, as the absence of polymer bonds facilitates the transition to the solid phase. The pressure ensures similar densities in the polymeric and atomic liquids. After equilibration for several relaxation times τ_α in the liquid phase, fifty-one runs spontaneously crystallized into two well defined classes. Seventeen runs formed solids quite close to face-centered cubic (Fcc) crystals and thirty-four runs formed Bcc-like atomic crystals. See sec. 3 for a detailed discussion. The remaining thirteen runs reached a variety of metastable solid-like conformations and were discarded.

After completion of the solidification, all the systems were quenched to temperature $T = 10^{-3}$ and pressure $P = 0$ in a time $\Delta t = 0.003$ and, in agreement with others [29], later allowed to relax with an NPT run to let the total energy stabilize. The latter run lasted for a total time $\bar{t} = 3000$. The final densities of the polymeric and atomic Bcc-like solids are $\simeq 1.11$ and $\simeq 1.052$, respectively. The density offset is due to the different connectivity, having both solids the same pressure ($P = 0$) and temperature ($T = 0$).

Simple shear deformations of the resulting athermal solids were performed via the Athermal Quasi-Static (AQS) protocol outlined in Ref. [29]. An infinitesimal strain increment $\Delta\varepsilon = 10^{-5}$ is applied to a simulation box of side L containing the sample, after which the system is allowed to relax in the nearest local energy minimum with a steepest descent minimization algorithm. The accurate localization of the state corresponding to a local energy minimum ensures force equilibration on each particle, i.e. mechanical equilibration. The procedure is repeated until a total strain of $\Delta\varepsilon_{tot} = 15{\cdot}10^{-2}$ is reached. Simple shear is performed independently in the planes (xy, xz, yz), and at each strain step in the plane $\alpha\beta$ the corresponding component of the macroscopic stress tensor $\tau_{\alpha,\beta}$ is taken as the average value of the per-monomer stress $\tau^i_{\alpha,\beta}$:

$$\tau_{\alpha,\beta} = \frac{1}{N}\sum_{i=1}^{N}\tau^i_{\alpha,\beta} \tag{3}$$

In an athermal system the expression of the per-monomer stress in the atomic representation is [30]:

$$\tau^i_{\alpha,\beta} = \frac{1}{2\,v}\sum_{j\neq i} r_{\alpha ij}F_{\beta ij} \tag{4}$$

where $F_{\gamma kl}$ and $r_{\gamma kl}$ are the γ components of the force between the kth and the lth monomer and their separation, respectively, and v is the average per-monomer volume, i.e. $v = L^3/N$. For each plane a stress-strain curve is collected, an illustrative example of which is given in Fig. 1.

Fig. 1 is quite analogous to what reported for many other systems under athermal conditions [31–36] with an initial linear increase followed by increasing bending and onset of the plastic regime. In particular, similarly to other MD studies of glassy polymers [37], one notices that, in the plastic regime, the stress levels off to a plateau with fluctuations caused by subsequent loading phases and sudden stress drops. We

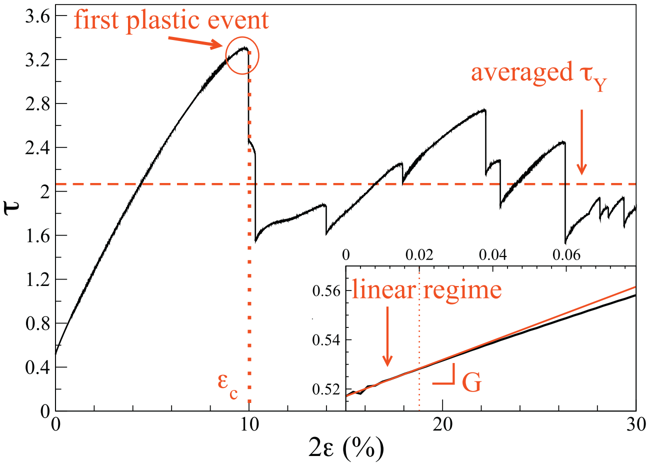

Fig. 1. Typical stress-strain curve under athermal quasi-static shear deformation of the semicrystalline polymer. After a first 'loading' phase, plastic events with macroscopic stress drops become apparent. τ_Y is defined as the average value of τ in the steady state phase [28]. ε_c is defined as the strain at the first significant plastic event with stress drop of at least $\Delta\tau_{th} = 0.1$. The elastic modulus G (see inset) is measured via a linear fit of the stress-strain curve in the linear regime of small deformations $2\varepsilon < 0.02$.

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