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¹ Plastic Deformation Mechanisms of Semicrystalline and Amorphous ² Polymers

³ Sara Jabbari-Farouji,^{*,†} Joerg Rottler,[‡] Olivier Lame,[§] Ali Makke,[∥] Michel Perez,[§] and Jean-Louis Barrat^{†,⊥}

4 [†]Université Grenoble Alpes, UJF Liphy, F38041 Grenoble, France

- ^s [†]Department of Physics and Astronomy, The University of British Columbia, 6224 Agricultural Road, Vancouver, British Columbia
 V6T 1Z1, Canada
- 7 [§]INSA Lyon, MATEIS, UMR CNRS 5510, Université de Lyon, F69621 Villeurbanne, France
- 8 ^{II}EPF école d'ingénieur Institut Charles Delaunay, LASMIS UMR CNRS 6279, F10004 Troyes, France

9 [⊥]Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, F-38042 Grenoble, France

10 ABSTRACT: We use large-scale molecular dynamics simu-11 lations to investigate plastic deformation of semicrystalline

12 polymers with randomly nucleated crystallites. The strain-

13 softening regime is dominated by deformation of crystallites

via reorientation of chain-folded lamellae toward the tensile

15 axis, fragmentation of largest crystalline domains, and a partial

16 loss of crystallinity. The strain-hardening regime coincides with

17 unfolding of chains and recrystallization as a result of strain-



¹⁸ induced chain alignment. These observed deformation mechanisms are consistent with experimental findings. We compare the

19 tensile behavior of semicrystalline polymers with their amorphous counterparts at temperatures above and below the glass

20 transition temperature.

eformation mechanisms in the plastic flow regime of 21 ²² D amorphous polymers (either rubbery or glassy) have ²³ been widely investigated¹⁻⁵ and are rather well understood. 24 However, the underlying mechanisms of deformation in their 25 semicrystalline counterparts are still controversial.^{6,7} Under 26 stretching, semicrystalline polymers undergo a complete 27 molecular rearrangement of the chain-folded lamellae, typically 28 of isotropic spherulitic morphology, into a highly oriented 29 chain-unfolded fibrillar microstructure at high strains. It has 30 been suggested that yielding is controlled by nucleation and the 31 motion of screw dislocations in the crystalline domains,⁸ and it 32 depends on density of stress transmitters.⁹ The crystallographic 33 slip mechanisms within the lamellae are thought to be an active 34 deformation mechanism at all strain levels.⁶ At large 35 deformations, strain-induced melting and recrystallization 36 processes have been proposed to be the dominant mechanism 37 of the structure transformation¹⁰ as confirmed by recent 38 experiments.¹¹

³⁹ Because of the small length scales involved, it is not possible ⁴⁰ to observe experimentally local mechanisms of plastic ⁴¹ deformation and to disentangle the deformations in ordered ⁴² and amorphous parts. The few simulations that exist on this ⁴³ matter^{12,13} focus on deformation of a stacked lamellar ⁴⁴ configuration which mimics a small part of the spherulite ⁴⁵ structure. Our aim is to fill this gap by performing large-scale ⁴⁶ molecular dynamics simulations of semicrystalline polymers ⁴⁷ and by analyzing the evolution of polymer conformations and ⁴⁸ crystalline domains along the stress–strain curve. We employ a ⁴⁹ coarse-grained model representing polyvinyl alcohol (CG-⁵⁰ PVA).¹⁴ By changing the cooling rate, we can tune the degree of crystallinity and observe both crystallization and glass ⁵¹ formation. The semicrystalline samples obtained by this ⁵² method are dominated by homogeneous nucleation and ⁵³ correspond to a microstructure of randomly oriented small ⁵⁴ crystallites (<100 nm) in contrast to the spherulitic structures ⁵⁵ with a lateral size of a few micrometers. Nevertheless, it is ⁵⁶ remarkable that the CG-PVA model reproduces most of the ⁵⁷ mechanical behavior of real semicrystalline polymers. ⁵⁸

Molecular dynamics simulations of the CG-PVA model¹⁴ 59 were carried out using LAMMPS¹⁷ of systems up to 4.3×10^6 60 monomers obtained from replications of smaller samples (9 \times 61 10^4 monomers). The chain length is set to N = 300, which 62 corresponds roughly to 9-10 entanglement lengths as 63 determined by Primitive-Path Analysis.¹⁶ Distances are 64 reported in length units σ = 0.52 nm, and the bond length is 65 $b_0 = 0.5\sigma$. The range and strength of 6-9 Lennard-Jones 66 potential for nonbonded interactions are given by $\sigma_{\rm LI}$ = 0.89 σ 67 and $\varepsilon_{LJ} = 1.511 k_B T_0$ where $T_0 = 550$ K is the reference 68 temperature of the PVA melt.¹⁴ The Lennard-Jones potential is 69 truncated and shifted at $r_{LJ}^c = 1.6\sigma$. The time unit from the 70 conversion relation of units is $\tau = 1.31$ ps, and the temperatures 71 and pressures are reported in reduced units $T = T_{real}/T_0$ and P 72 = $P_{\text{real}}\sigma^3/\varepsilon_0$. We apply periodic boundary conditions in the 73 NPT ensemble using a Berendsen barostat (P = 8) and a Nose-74 Hoover thermostat. The time step in our simulations is 0.005τ . 75

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76 To characterize the crystallites, we use the notion of 77 crystalline domains which are defined as a set of spatially connected regions with the same orientation.¹⁸ To identify the 78 crystalline domains, we divide the box into cells of size about 79 so 2σ , and we compute the nematic tensor $Q_{\alpha\beta} = 1/N\sum_t (3/2b_{\alpha}^i b_{\beta}^i)$ $-1/2\delta_{\alpha\beta}$) of unit bond vectors of polymers \hat{b}^i within each cell. 81 82 The largest eigenvalue and the corresponding eigenvector of 83 the nematic tensor determine the order parameter S and the ⁸⁴ preferred orientation of bonds, i.e., director \hat{n} in each cell. The so volume fraction of cells with S > 0.8 defines the degree of $_{86}$ crystallinity $X_{\rm C}$. We perform a cluster analysis by merging two 87 neighboring cells if they are both crystalline, and their directors ss share the same orientation within the threshold $\hat{n} \cdot \hat{n}' \ge 0.97$. We 89 determine the volume distribution of crystallites as a function of 90 $V_{\text{domain}} = nv_{\text{cell}}$ where *n* is the number of cells with volume v_{cell} in 91 a domain, and we normalize it to the volume of the box V. 92 Thus, we obtain $(d\phi/dV) = [(nv_{cell}N(n))/(V\Delta n)]$ where N(n)93 is the number of domains which comprise between n and n + 94 Δn crystalline cells.

Equilibrated melts at density $\rho\sigma^3$ = 2.35 at *T* = 1 are cooled 96 to the desired temperature with cooling rates in the range 2 × 97 10⁻⁷ < \dot{T} < 10⁻³τ⁻¹ as presented in Figure 1. For $\dot{T} ≤ 10^{-5}τ^{-1}$,



Figure 1. Volume per monomer *v* as a function of *T* for 3600 chains of 300 monomers obtained at different reduced cooling rates \dot{T} . The inset shows T_{crys} (black squares) and T_g (red discs) versus \dot{T} .

98 we observe an abrupt change of volume and slope of the v-T99 curve around a certain temperature. These sharp changes are attributed to the partial crystallization of polymers, ^{14,15} and the 100 temperature marking these changes defines the crystallization 101 temperature T_{crys} . For faster cooling rates, the slope changes of 102 $\nu-T$ curves are less abrupt, and the polymers retain their 103 amorphous configurations during cooling. The system under- 104 goes a glass transition, and the temperature at which the slope 105 of the cooling curve changes gives us an estimation of the glass 106 transition temperature T_g . The inset of Figure 1 shows T_{crys} and 107 T_g as a function of cooling rate. Note that T_g can only be 108 defined for the samples obtained with the fastest cooling rates, 109 when the crystallinity vanishes even at the lowest temperatures. 110

We now turn to the mechanical response of polymers under 111 uniaxial tension. In tensile tests, the samples are deformed in 112 the *y*-direction with a constant true strain rate of $10^{-5}\tau^{-1}$, and a 113 pressure of P = 8 (the same pressure as the nondeformed 114 sample¹⁴) is imposed in the *x*- and *z*-directions. Concomitant 115 with stretching of the box in the tensile direction, the samples 116 shrink in the perpendicular directions. The volume increase is 117 at most 6% for the semicrystalline polymers at lowest 118 temperature T = 0.2, while for the amorphous polymers, the 119 volume increase is less than 2% at all *T*. Therefore, PVA 120 polymers behave nearly as an incompressible fluid. 121

Figure 2a and Figure 2b present the stress-strain curves 122 f2 obtained for different crystallinities at two temperatures above 123 and below the glass transition temperature, i.e., T = 0.7 and T = 124 0.2. In all samples, we observe an elastic regime at low 125 deformations and a strain-hardening regime at very large 126 deformations. The elastic regime of deformation is followed by 127 an overshoot typical of yield-stress fluids for semicrystalline 128 polymers and low-temperature amorphous samples. We define 129 the yield-stress σ_y as the maximum value of stress in the 130 overshoot region. We have plotted σ_y against crystallinity at 131 each temperature in the insets of Figure 2a and Figure 2b. 132 Young's modulus *E* is extracted from the linear response 133 regime.

At $T = 0.7 > T_{gy}$ where the amorphous part is in the rubbery 135 state, *E* and σ_y rise strongly upon increase of crystallinity, 136 presumably due to formation of a percolating crystalline 137 network. Samples with largest crystallinity exhibit a stress 138 plateau before entering the strain-hardening regime. At T = 0.2 139 $< T_{gy}$ where the amorphous part is glassy, we find that all the 140 samples are stiffer than their high-temperature counterparts, 141 and *E* shows a similar trend as at T = 0.7. Interestingly, σ_y is a 142 nonmonotonic function of crystallinity and has the lowest value 143



Figure 2. Stress-strain curves obtained from uniaxial tensile tests at (a) T = 0.7 and (b) T = 0.2 for different crystallinities. The corresponding $X_{\rm C}$ values are shown in the legends, and the cooling rates from the highest to the lowest crystallinity correspond to $2 \times 10^{-7} \tau^{-1}$, $10^{-6} \tau^{-1}$, $10^{-5} \tau^{-1}$, $10^{-4} \tau^{-1}$, and $10^{-3} \tau^{-1}$, respectively. (c) Young modulus *E* versus $X_{\rm C}$. Here, $\varepsilon/\sigma^3 \approx 54$ MPa.

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144 at the highest $X_{\rm C}$. Furthermore, all the samples show a strain-145 softening regime.

146 Next, we focus on the mechanisms of plastic deformation 147 beyond the yield point, i.e., the strain-softening and strain-148 hardening. Figure 3 shows the conformation of semicrystalline



Figure 3. Snapshots of semicrystalline polymers at T = 0.2 obtained for $X_{\rm C} = 0.425$ at different stages of deformation.

149 polymers at different stages of plastic deformation. At strains 150 beyond the yield point, the chain-folded structures align 151 partially in the direction of tensile stress. At larger deformations 152 in the strain-hardening regime, chains in crystalline domains are 153 unfolded as a result of tensile stress, and both chains in 154 amorphous and crystalline domains are stretched and aligned. 155 To quantify our visual observations, we characterize the 156 volume fraction distribution of crystalline domains $d\Phi/dV$ 157 (Figure 4), crystallinity X_C , and global nematic order parameter 158 S_{global} (Figure 5) upon increase of deformation. In the plastic 159 flow region, we recognize the following regimes:



Figure 4. Volume distribution function of crystalline domains $d\Phi/dV$ in semicrystalline samples obtained for $X_{\rm C} = 0.425$ at (a) T = 0.7 and (b) T = 0.2 at different strains.



Figure 5. (a) Crystallinity and (b) the global nematic order parameter S for the semicrystalline sample obtained at $X_{\rm C}$ = 0.425 and amorphous polymers.

160 Strain softening/stress plateau regime: coincides with 161 strains in the range $0.1 < \varepsilon_{yy} < 0.75$ for T = 0.7 and 0.1 <162 $\varepsilon_{yy} < 1.1$ for T = 0.2. Figure 4 reveals that the volume fraction 163 of the largest crystalline domains decreases and that of the 164 smallest ones increases. This implies fragmentation of the larger 165 crystalline domains that leads to a partial loss of crystallinity as 166 also evidenced by Figure 5a. We also find that the population of 167 bonds along the tensile axis in both ordered and disordered regions increases although reorientation is dominated by the 168 bonds in the crystalline regions. By examining pair distribution 169 functions (not shown) in the direction perpendicular to the 170 tensile deformation, we recognize a correlation between the 171 rotation of crystallites and the decrease of nearest neighbor 172 distance between nonbonded monomers in the perpendicular 173 direction in the crystalline regions. These observations lead us 174 to conclude that the strain softening/plateau regime is 175 dominated by reorientation of crystallites in the direction of 176 tensile axis and fragmentation of some of the larger crystalline 177 domains. 178

Strain hardening regime: corresponds to $\varepsilon_{yy} > 0.7$ (T = 0.7) 179 and $\varepsilon_{yy} > 1.1$ (T = 0.2). This regime is delineated by the onset 180 of an increase in $X_{\rm C}$. It results from alignment of chains as 181 evidenced by $S_{\rm global} > 0.5$ (Figure 5b). Notably, the volume 182 distribution of crystalline domains in Figure 4 changes 183 dramatically at such large strains. $d\Phi/dV$ comprises a set of 184 small domains and a large domain of aligned chains. Chains 185 both in crystalline and disordered parts align along the tensile 186 axis as verified by inspection of pair distribution functions. 187 Hence, a majority of chains contribute to formation of a large 188 crystalline domain. 189

We finally discuss changes of conformation of amorphous 190 polymers under tensile deformation as presented in Figure 2. At 191 T = 0.7 where the polymers are in the rubbery state, we observe 192 a crossover from an elastic regime of purely entropic origin¹ to 193 the strain-hardening regime at $\varepsilon_{yy} \approx 0.45$. Strain hardening 194 occurs when chains align with the tensile axis and $S_{\text{global}} > 0.4$ 195 (Figure 5b).¹ At T = 0.2, glassy polymers show a markedly 196 different tensile response from their amorphous counterparts at 197 T = 0.7. We observe a strain-softening regime similar to 198 semicrystalline polymers although the origin of yielding is 199 different and results from overcoming free energy barriers.^{4,5} 200 Similar to rubbery polymers, the onset of strain hardening 201 corresponds to S_{global} > 0.4, and it is accompanied by a strain- 202 induced crystallization (Figure 5a) at large deformations. The 203 strain hardening is shown to be related to the work needed to 204 reorient the chains along the tensile axis.^{4,5} 205

Comparing our simulations with experiments, we notice 206 some differences that are due to limitations in the simulations 207 and the coarse-grained nature of the polymer model. Indeed, to 208 crystallize in an accessible number of MD steps, it is necessary 209 to use a rapidly crystallizable model like CG-PVA. The reduced 210 cooling rates in simulations correspond to 8.4 imes 10⁷ K s⁻¹ $\dot{\rm T}$ 211 $<4.2 \times 10^{11}$ K s⁻¹ and are much faster than the most rapid 212 cooling rates in experiments. A high number of nuclei appear in 213 a relatively small number of MD steps for the slowest cooling 214 rate. As a result, the semicrystalline microstructures differ from 215 the classical spherulitic structures observed in real polymers. 216 Nonetheless, it is striking that most of the obtained trends 217 qualitatively agree with the main features of semicrystalline 218 polymers. More quantitatively, the Young modulus values for 219 temperatures above and below $T_g \approx 320$, $E(T = 0.7 \equiv 385 \text{ K}) \approx 220$ 0.8 GPa and $E(T = 0.2 \equiv 110 \text{ K}) \approx 3 \text{ GPa}$, are comparable to 221 the values reported for PVA polymers.²¹ The yielding occurs at 222 strains of about 10% which is consistent with typical values 223 from polymers.11 224

The plastic deformation mechanisms observed in our 225 simulations are also in line with experimental findings. For *T* 226 > $T_{\rm g}$ where the amorphous phase is in the rubbery state, the 227 model clearly captures the increase of *E* and $\sigma_{\rm y}$ as a function of 228 crystallinity. In terms of microstructure evolution during 229 deformation, this model accounts for the progressive fracture 230

231 of the larger crystallites to obtain smaller ones in the stress-232 plateau regime. The existence of a crystalline network and the 233 predominant deformation of crystalline domains in the stress-234 plateau regime are in accordance with experiments where 235 semicrystalline polymers are found to behave as two inter-236 penetrated networks of a hard crystalline skeleton and an 237 entangled amorphous phase.^{19,20} Thus, at relatively small deformations, the hard crystalline skeleton dominates, whereas 238 the entangled amorphous network is predominant in the strain-239 240 hardening regime as amorphous polymers reorient along the tensile axis. The additional crystallinity observed at large 241 deformations beyond the melting/recrystallization proc-242 ess^{10,11,22,23} is due to alignment of amorphous chains and is 243 also observed for amorphous polymers in Figure 5a. This 2.44 explains the stronger strain-hardening behavior for fully 245 amorphous polymers. For the low-temperature case $T < T_{o}$ 246 where the amorphous phase is in the glassy state, the stress-247 strain curves as well as the evolution of *E* with crystallinity agree 248 with the experimental trends. Here, we also observe 249 250 reorientation and fragmentation of crystallites in the strainsoftening regime similar to the plateau regime of the $T > T_{a}$ 251 252 sample. However, it seems that the amorphous glassy network 253 also plays a role in plastic deformation as the yield stress of purely amorphous polymers is higher than that of semicrystal-254 line polymers with the highest $X_{\rm C}$. Indeed, the strain-stress 255 curves for glass and semicrystalline polymers are quite similar. 256 257 Hence, as strain softening only exists for low-temperature samples, it is most probably correlated with yielding of glassy 258 regions. The nonmonotonic behavior of $\sigma_{\rm v}$ versus crystallinity 259 has so far not been observed and raises interesting open 260 questions about the interplay between plasticity of glassy and 261 crystalline regions operative at the yield point. 262

In conclusion, simulations of coarse-grained semicrystalline 263 polymers allow us to observe directly the mechanisms of plastic 264 deformation at length scales smaller than 100 nm which are not 265 accessible by experiments. The similarity of plastic deformation 266 mechanisms and trends for a very disordered arrangement of 267 crystallites in our simulations and the experimental structures 268 demonstrates that the spherulitic structure is not the main 269 feature that generates the dominant mechanical features of 270 271 semicrystalline polymers, and the underlying lamella at smaller 272 length scales dominate the mechanical properties.

273 **AUTHOR INFORMATION**

274 Corresponding Author

275 *E-mail: sara.jabbari@gmail.com.

276 Notes

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