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Molecular simulations demonstrate how the skin-core structure of polymer fibers can be tuned for bio-inspired optimization of their mechanical performance.



# Tuning bio-inspired skin-core structure of nascent fiber via interplay of polymer phase transitions

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The properties of polymer fibers are determined by their inner structures. We performed dynamic Monte Carlo simulations of early-stage solidification in the fluid filaments of stretched polymer solutions after extruded into a coagulation bath upon fiber spinning. We observed that the radial temperature gradient dominates polymer crystallization to form an oriented crystalline skin (from single to multiple layers), while the radial non-solvent influx dominates phase separation to form a concentrated but less oriented core. The skin-core structure offers fibers a balanced performance between strength and toughness similar to plant stems, which can be tuned by the interplay of phase transitions. Our molecular-level observations facilitate a systematic understanding on the microscopic mechanism of fiber-spinning, which will pave a way towards making excellent polymer fibers.

## I. Introduction

Polymer spin-fibers have brought deep impact to human civilization since last century.<sup>1</sup> The achievement is mainly attributed to a high mechanical strength of oriented polymer crystals.<sup>2-4</sup> A few of ultra-strong fibers have been produced, such as Dyneema (a brand of DSM products) by super-stretching the gel of high-molar-mass flexible polyethylene, and Kevlar (a brand of DuPont products) by spinning the liquid crystalline solution of low-molar-mass rigid polyaramid.<sup>4</sup> However, vast commodity of polymer fibers between these two extreme cases are processed via conventional spinning from solutions or melt, whose Young's modulus and tensile strength are still far below the theoretical maxima of polymer crystals.<sup>4</sup> Therefore, tuning fiber structures for optimized properties accounts for significant attention in the spinning processing of polymer fibers. So far, our knowledge about fiber structure formation mainly rests at the level of industry know-how, and systematic investigations on its microscopic mechanism towards know-why are still rare.<sup>2-4</sup>

For structure formation upon the conventional spinning of polymer fibers, the key instant is presumably the early stage of solidification as soon as the fluid filament has been extruded into a cold coagulation bath from the hot spinneret, as depicted in Fig. 1a for the dry-wet solution spinning as a general example. The melt spinning can be regarded as its specific case at the higher end of polymer concentrations and the lower end of cooling rates. Various complicated factors, from the structures of polymers, the compositions of polymer, the processing speed, solvent and non-solvent to the filament and bath temperatures, are influencing this solidification process.



**Fig. 1** (a) Schematic illustration of the key solidification process upon dry-wet solution spinning of polymer fibers. (b) The fluid filament of 56×56×80 lattice sites for a polymer solution with polymer volume concentration of 0.1143 (224 stretched chains, each containing 128 monomer units with two ends restricted at the two boundaries of the long axis for a strain around 400%). All the bonds are drawn in yellow cylinders, and the chain ends are labeled in red. (c) A sketch illustrating heterogeneous distributions of temperatures and three components in the cross section of 80×80×80 lattice sites of the sample space (blue dots represent non-solvent, while red strings represent polymer chains in good solvent). Blue arrows indicate the radial directions for non-solvent diffusion and linear temperature gradient.

When the temperature difference between the fluid filament and the cooling bath (or the drying atmosphere) is large, the periphery of the fluid filament reaches the low temperature first, in which the highly oriented polymers crystallize in priority. The solidified skin will take over the resistance to the take-up stress, and allows for central polymers to relax and then to crystallize with less orientations. This behavior often results in a skin-core structure upon fiber spinning.<sup>5,6</sup> The skin-core structure of the viscose rayon (the regenerated cellulose fiber) produced via solution spinning was first proposed by Hall in 1929.7 Carbon fibers inherit this structure from their precursors of rayon or acrylonitrile-based fibers.<sup>8</sup> The skin-core structures of nascent fibers have also been found in the high-speed melt spinning of polyolefin and polyesters under the conditions of fast cooling.9,10 Morehead and Sisson believed that highly oriented crystallites in the dense skin benefited high strength, while less oriented crystallites in the coarse core allowed large elongation; therefore, a combination of mechanical advantages of the skin and the core resulted in both strong and tough performances of rayon fibers.<sup>11</sup> In fact, such a structural feature for an optimized mechanical performance is bio-mimetic to the plant stems that commonly hold a fine shell and a coarse core for an optimized strong-yet-tough performance.<sup>12</sup> Therefore, tuning the a balanced skin-core structure can provide the nascent fibers a balanced performance between strength and toughness.

In solution spinning of polymer fibers, double diffusion occurs simultaneously with the solidification at the periphery of the fluid filament: solvent diffuses from the filament to the bath and meanwhile non-solvent diffuses from the bath to the filament.<sup>13,14</sup> When the compositions of solvent, non-solvent and polymers reach the critical point, phase separation happens. The interplay between phase separation and crystallization will change the course of early-stage solidification, as evidenced in quiescent polymer solutions<sup>15</sup> as well as colloidal suspensions.<sup>16,17</sup> Therefore, interplay of polymer phase transitions upon fiber spinning will help us to tune the skin-core structure of the fiber, and its mechanism is worthy of further investigation.

Industrial spinning of commodity polymer fibers is usually at a high speed, which makes the time window too narrow to an in-situ experimental observation on the early stage of phase transitions and their interplay. Molecular simulations hold their advantages on the study of such a fast process. Recently, Monte Carlo simulations have been employed to investigate the effect of radial diffusion on the cross-sectional morphology upon the phase separation of a ternary mixture during fiber wet-spinning, although polymer crystallization has not yet been considered.<sup>18</sup> Meanwhile, Monte

Carlo simulations have been employed to investigate strain-induced crystallization in a fluid filament of melt polymers, which demonstrated the switching of crystal nucleation from intramolecular to intermolecular preferences upon raising strains.<sup>19</sup> In this report, we put both phase separation and polymer crystallization together, and performed Monte Carlo simulations of fluid filaments of polymer solutions surrounded with a coagulation bath to study their early-stage interplay upon dry-wet solution-spinning (see the sketch in Fig. 1).

We tentatively considered both thermal and mass diffusions along the radial directions of the filament, and adjusted initial polymer concentrations, bath temperatures (supposing linear temperature gradient from the center to the bath at the early instant) and bath non-solvent properties (solvent quality, concentrations and diffusivity under the supposed site-by-site diffusion from the bath) to compare the fiber structures formed under otherwise parallel conditions. The results will demonstrate that polymer crystallization under the radial temperature gradient generates an oriented crystalline skin, while phase separation under the non-solvent influx forms a less oriented and more concentrated core. Our molecular-level observations are consistent with various practical experiences, and bring systematic insights to the fibers spun from solutions as well as from the melt.

## II. Simulation techniques

Monte Carlo simulations of the lattice polymer solutions have been widely applied in the study of polymer crystallization.<sup>20</sup> In the lattice model, a consecutive occupation of 128 monomers represented a bead-stick model of single polymer chains, while single occupied sites stood for solvent or non-solvent molecules. A certain amount of polymer chains were parallel-stacking in a box of 56×56×80 lattice sites, with two ends of each chain separately restricted on the boundary surfaces along the fiber axis (80 sites long). The vacancies in the box stand for athermal solvent. Polymer chains were moving with a micro-relaxation mode of single-site jumping and local chain-sliding.<sup>20</sup> Double occupation and bond crossing were avoided, to mimic the volume exclusion of molecules. Polymer chains were relaxed under athermal conditions into equilibrium coils but maintaining two chain ends restricted on the boundaries of the box to mimic the stretched situation of polymers in fluid filaments (around 400% strain for 128-mers<sup>19</sup>) upon their entering into the coagulation bath during dry-wet spinning (see Fig. 1b). After that, the fluid filament of polymer solution was placed at the center of a larger box (80×80×80 lattice sites), surrounded by the coagulation bath that mixes a certain

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amount of non-solvent with athermal solvent (see Fig. 1c). Since the coagulation bath serves as a huge reservoir with a constant concentration of non-solvent, we redefined those athermal solvent sites as non-solvent sites, once they swapped with non-solvent sites at the boundaries of fluid filaments.

In the viewpoint of statistical mechanics, Metropolis algorithm is based upon the detailed balance,<sup>21</sup> that is equivalent to the Onsager reciprocal relation and therefore allows us to study the out-of-equilibrium processes like phase transitions during the fiber-spinning process. The conventional Metropolis sampling was employed in each step of micro-relaxation, with the total potential-energy change

 $\Delta E/(kT) = (c + p^* E_p / E_c + b^* B / E_c + f^* E_f / E_c) / (kT / E_c)$ (1)

where  $E_c$  is the energy parameter for non-collinear connection in a pair of bonds consecutively connected along the chain (reflecting the static flexibility of the polymers), and c is the net change of corresponding bond pairs after the trial move;  $E_p$  is the energy parameter for parallel-packing interactions between two polymer bonds (reflecting the driving force for polymer crystallization), and p is the net change of such parallel bond pairs; B is the mixing-interaction energy for one pair of monomer and solvent (reflecting the non-solvent for phase separation between polymers and non-solvent, while the solvent here is athermal for both polymers and non-solvent), and b is the net change of the corresponding pairs;  $E_f$  is the frictional barrier for chain sliding in the crystalline phase, and f is the sum of the parallel bond pairs along the local sliding segment.<sup>20</sup> For simplicity, the reduced energy parameter  $E_p/E_c$  was fixed at one for driving crystallization at high temperatures where polymers were still flexible, while a small frictional barrier  $E_f/E_c$  was chosen as 0.01 for a good polymer diffusivity in the crystal like polyethylene. The reduced energy  $B/E_c$  reflects the variable quality of non-solvent, while the reduced temperature  $kT/E_c$  was used to set the variable temperature (k is the Boltzmann's constant and T the temperature. Below we simplified it as T).

Our observations were focused on the fluid filaments after immersed into the coagulation bath and released the chain-end restriction for a period of 800 MC cycles (a short enough period in comparison to the Rouse relaxation time of bulk 128mers around 3200 MC cycles<sup>20</sup>, comparable to the small time window in the industrial spinning processes). One Monte Carlo cycle (MCc) was used as the time unit in our simulations, which was defined as the number of the trial moves equals to the total monomers in the sample system. Since the distance in the lattice space was defined by the number of site-by-site steps along lattice axes or diagonals, the concentric squares in the cross-sectional area of fluid filaments correspond to the concentric circles in the continuous space. We monitored the radial layer-by-layer distributions of monomer concentrations from the concentric squares in the cross-sectional area of the fluid filament.

## III. Results and discussion

We made systematic comparisons of fiber structures by changing one-by-one spinning parameters, with a reference to the fluid filament holding an initially low volume concentration 0.1143 of stretched polymers (224 chains), a high volume concentration 0.8 of bath non-solvent, a small mixing energy between non-solvent and monomers  $B/E_c=0.1$  (but large enough to initiate phase separation in the present temperature range), and a large linear temperature gradient from the center 4.5 to the bath 0.5 (the melting point of bulk 128-mers is around 5.0<sup>20</sup>).



**Fig. 2** Snapshots of the skin surfaces and the (elongation and cross) middle sections (80×80 lattice sites) of the fluid filaments with three initial polymer volume concentrations as denoted. All the bonds are drawn in yellow cylinders. In the elongation and cross sections, only 10 middle lattice layers are shown for clarity.

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### A. Initial polymer concentrations

We start with a change in the initial polymer concentrations. We made visual inspections on the fiber skin, the elongation section and the cross section with three initial polymer concentrations

varied from 0.1143 to 0.3428 and 0.5714, as summarized in Fig. 2. One can see from the fiber skins that many small crystallites (clusters formed by parallel-stacked bonds) are oriented along the fiber axis. In reality, most of the spacing between small crystallites will be squeezed out upon further attenuation of the fiber, forming tiny fibrils. During this process, those amorphous segments at the end of each crystallite can be separated into two parts: the major part will force the crystallite to align into the fibril, and the minor part will connect the crystallites between fibrils. This feature appears consistent with the Swiss-cheese three-phase model proposed to describe the inner structures of nascent fibers.<sup>22</sup> The minor amorphous part was also referred to taut-tie molecules, which might be responsible for the limitation in the achieved strength of polymer fibers.<sup>23</sup> Meanwhile, some voids between the boundaries of fibrils can still be left, which are related to the dye ability of the fibers.

From the elongation and cross sections of fluid filaments shown in Fig. 2, one can clearly see the skin-core structures with an oriented crystalline skin, an amorphous core and a concentration gap between them. Higher polymer concentrations result in thicker crystalline skins and less voids, consistent with parallel experimental observations.<sup>24,25</sup> The results are further confirmed by radial distributions of monomer concentrations shown in Fig. 3a. In addition, a good linear relationship between the skin thicknesses and the initial polymer concentrations could be found in Fig. 3b, reflecting the shifting-up of melting points (the boundary temperatures to enable crystallization) with the increase of the initial polymer concentrations. Polymers in the concentrated core are less oriented, and in reality they will crystallize later-on to form a coarse core upon further proceeding of cooling.

The fluid filaments with higher polymer concentrations exhibit a trend of multiple layers in the thick skins, as clearly shown in the right side of Fig. 2 as well as multiple peaks in Fig. 3a. This trend can be attributed to the concentration wave generated upon the radial development of crystallinity.<sup>26</sup> At the first moment, primary crystal nucleation is initiated at the surface of the fluid filament, where the lowest bath temperature provides the strongest thermodynamic driving force for crystallization. Crystal growth right after nucleation will generate a depletion layer of polymer concentrations along the radial direction inward from the periphery, resulting in the formation of the first skin layer. Later on, if polymer concentrations are high enough and temperatures are low enough behind the depletion layer, primary crystal nucleation will be initiated for the formation of the second skin layer, and so on for even more layers.



**Fig. 3** Radial distributions of (A) monomer volume concentrations of the fluid filaments with three initial polymer concentrations as labeled. (B) Skin thicknesses versus initial polymer concentrations. The skin thickness is defined by the distance between the left and the right minima of skin peaks on the radial distribution curve of monomer concentrations in (A). The straight line results from linear regression, and each data point is averaged over five independent observations.

### B. Bath temperature

Next, we watch at the effect of bath conditions. Figure 4 compares the reference fluid filament to those under no influx of non-solvent or no temperature gradient. The fiber under no influx of non-solvent (set  $B/E_c=0$ , no difference between two kinds of solvents) appears as a hollow fiber, and the crystalline skin contains crystallites much larger than those of the reference fiber, indicating that in the latter case the influx of non-solvent initiates spinodal decomposition to split polymer-rich domains.<sup>27</sup> Apparently, crystallization induced by the temperature gradient is mainly responsible for the formation of the crystalline skin, while phase separation induced by the non-solvent influx appears mainly responsible for the formation of the concentrated core. Two kinds of phase transitions compete with each other, in order to gather

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polymers separately in the skin and in the core, resulting in a concentration gap between them. The fiber under no temperature gradient eliminates the skin-core structure and contains uniformly small crystallites via instantly-initiated homogeneous nucleation. This result confirms again that the temperature gradient is mainly responsible for the formation of the crystalline skin layer.



**Fig. 4** Snapshots of the skin surfaces and the (elongation and cross) middle sections (80×80 lattice sites) of the fluid filaments without any non-solvent influx ( $B/E_c$ =0, the middle case) and without any temperature gradient (constant *T*=0.5, the right case), in order to compare the standard filament with the temperature gradient from 4.5 at the center to 0.5 at the bath and with  $B/E_c$ =0.1 (the left case). The bonds are drawn in yellow cylinders. Only the middle 10 lattice layers of elongation and cross sections are shown for clarity.

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We further made a comparison among three fluid filaments with different bath temperatures (i.e. 0.5, 1.5 and 2.5), in other words, different temperature gradients. We chose a higher polymer concentration 0.3428 in order to watch better at the distributions of polymer concentrations in the fluid filaments. Figure 5 summarizes their morphologies yielded at three bath temperatures. One can see that higher bath temperatures result in thinner skins and more concentrated amorphous cores. The corresponding radial distributions of monomer concentrations are shown also in Fig. 6, along with a linear relationship between the skin thicknesses and the bath temperatures. The linear relationship reflects the shifted locations of the boundary temperatures for the initiation of primary nucleation.



Fig. 5 Snapshots of the skin surfaces and the (elongation and cross) middle sections ( $80 \times 80$  lattice sites) of the fluid filaments with polymer volume concentration 0.3428 and with three bath temperatures as denoted. All the bonds are drawn in yellow cylinders. In the elongation and cross sections, only middle 10 lattice layers are shown for clarity.



Fig. 6 Radial distributions of (A) monomer concentrations under

different bath temperatures as denoted for the fluid filaments shown in Fig. 5. (B) Skin thicknesses versus bath temperatures. The skin thickness is defined by the distance between the left and the right minima of the skin peaks in the radial distribution curves of monomer concentrations shown in (A). The straight line results from linear regression, and each data point is averaged over five independent observations.

The skin-core feature becomes less obvious in smaller temperature gradients. Such a trend is consistent with parallel experimental observations.<sup>28</sup> High bath temperatures make the effect like uniform temperatures at the higher end to eliminate the skin-core structure. This situation corresponds to the practical air-drying of nascent fibers upon high-speed melt spinning to make a homogeneous fiber structure with less oriented crystallites for further hot stretching.<sup>10</sup>

#### C. Bath non-solvent

Finally, we made comparisons of fluid filaments with bath non-solvents variable in solvent quality, bath concentrations and diffusivities, respectively. The reference filament contains the non-solvent quality  $B/E_c=0.1$ , the bath non-solvent concentration 0.8 and a high diffusivity of non-solvent with 100% swaps between solvent and non-solvent. Figure 7 summarizes the snapshots for the fiber skin, the elongation section and the cross section of the fluid filaments with the mixing interaction parameters  $B/E_c=0.5$ , bath non-solvent concentration 0.2 and 1% only swaps for comparison, respectively.

One can see from Fig. 7 that larger  $B/E_c$  value means higher incompatibility between non-solvent and polymers, resulting in a more compact core and a larger void gap between the skin and the core. The result confirms again that the concentrated amorphous core shown in Fig. 2 results from phase separation induced mainly by the non-solvent influx. If the bath concentration of non-solvent is substantially decreased from 0.8 to 0.2, polymers in the core becomes almost completely relaxed. This observation is consistent with both parallel experiments and previous simulations.<sup>29</sup> If the diffusivity of non-solvent becomes substantially difficult (allowing only 1% swaps between solvent and non-solvent), phase separation is almost prohibited, similar to the case shown in the middle of Fig. 4 for the fiber under no influx of non-solvent. One can imagine that upon further attenuation of the fiber, squeezing-out the empty core or the large void gap between the skin and the core will result in the crumpled cross-sectional shapes of the fibers. Large crystallites can be harvested due to the retardation of phase separation, although skin thicknesses appear non-sensitive to the variations of non-solvent properties.



Fig. 7 Snapshots of the skin surfaces and the (elongation and cross) middle sections ( $80 \times 80$  lattice sites) of the fluid filaments separately with non-solvent quality  $B/E_c=0.5$ , bath non-solvent concentration 0.2 and 1% only probability for the swaps between solvent and non-solvent sites as denoted. All the bonds are drawn in yellow cylinders. In the elongation and cross sections, only middle 10 lattice layers are shown for clarity.

#### **IV.** Conclusion

The key process for structure formation upon industrial fiber-spinning processing from solutions is presumably the early stage of solidification under interplay of polymer phase transitions, when a fluid filament of stretched chains is immersed into a coagulation bath. The melt spinning of fibers can be regarded as its specific case at higher polymer concentrations and slow cooling for less orientation. Our Monte Carlo simulations demonstrated that the radial temperature gradient induces crystallization to form a skin layer of highly oriented crystallites, while the radial non-solvent influx from the bath induces phase separation to form a concentrated core of lowly oriented polymers. The radial structure of the fiber can be tuned by the interplay of phase transitions. Although there are still many other parameters, such as the degree of strain, the extensional flow, chain-length distribution, entanglement, chain flexibility and chain mobility in the crystals, as well as the specific case of melt spinning for further investigations along this approach, our preliminary observations presented here have provided a systematic understanding on the structure formation of the fiber processing, which will benefit industry to produce excellent fibers.

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