Kinetics of fiber solidification

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Edited by Noel A. Clark, University of Colorado, Boulder, CO, and approved August 31, 2010 (received for review April 4, 2010)

Many synthetic or natural fibers are produced via the transformation of a liquid solution into a solid filament, which allows the wet processing of high molecular weight polymers, proteins, or inorganic particles. Synthetic wet-spun fibers are used in our everyday life from clothing to composite reinforcement applications. Spun fibers are also common in nature. Silk solidification results from the coagulation of protein solutions. The chemical phenomena involved in the formation of all these classes of fibers can be quite different but they all share the same fundamental transformation from a liquid to a solid state. The solidification process is critical because it governs the production rate and the strength that fibers can sustain to be drawn and wound. An approach is proposed in this work to investigate the kinetics of fiber solidification. This approach consists in circulating solidifying fibers in the extensional flow of a surrounding liquid. Such as polymers in extensional flows, the fibers break if resultant drag forces exceed the fiber tensile strength. The solidification kinetics of nanotube composite fibers serves as a validation example of this approach. The method could be extended to other systems and advance thereby the science and technology of fiber and textile materials. It is also a way to directly visualize the scission of chain-like systems in extensional flows.

diffusion | elongational | microfluidic | rheology

Several fiber production technologies are based on so-called wet-spinning processes (1, 2). These processes can be subdivided in various methods depending on the used materials. Natural or synthetic polymer solidification can indeed result from various phenomena including dehydration, injection in poor solvents, pH variations, temperature variations, phase transitions, etc. (2–9). The kinetics of solidification is primarily limited by the diffusion of the solvent, additives, and polymer molecules. Such mechanisms can be quite complex and differ from a system to another as a function of the specific chemical, physical, and structural features of the used materials (2). Indirect experiments on macroscopic and static pieces of acrylic polymer gels allowed information on diffusion of solvent and nonsolvent molecules to be gained (3). Nevertheless, most of the experimental accessible knowledge on the kinetics of fiber formation is essentially based on observations of the initial and final fiber materials (2). The intermediate stages of solidification remain elusive in spite of their critical importance. A reason for our lack of knowledge is due to the technical difficulty of probing the mechanical strength of a material that is continuously moving and solidifying in a very short time. We propose in this work to use the circulation of fibers in extensional flows to overcome this difficulty and assess the in situ solidification of wet-spun fibers. Extensional flows have already been shown to be efficient at inducing the scission of polymer chains at a molecular scale (10–14). Even though the scission of a chain in an extensional flow has not yet been directly visualized, this phenomenon has been the topic of several previous studies. Extensional flows are also used, for example, to apply mechanical stress on living cells (15) or pressure variations around emulsion droplets (16). A similar approach is explored in this work at a macroscopic scale using filaments of several tens of microns in diameter and indefinite length. These are the typical dimensions of actual synthetic textile and natural fibers. The fibers experience a tensile stress due to viscous drag

forces arising from velocity gradients of the surrounding fluid along the fiber axis. The fibers break when the stress exceeds the fiber tensile strength, thereby allowing the direct visualization of the scission of a chain in an extensional flow. This approach is validated with the example of the solidification of polyvinyl alcohol (PVA)-carbon nanotube composite fibers (17). Nanoparticles based wet-spun fibers are currently being developed to achieve fibers with unique or enhanced properties and functionalities (4, 17–24).

Results

The presently investigated fibers are produced by injecting an aqueous dispersion of nanotubes in the coflowing stream of an aqueous PVA solution. This experiment is achieved by using coaxial pipes as sketched in Fig. 1. The nanotubes coagulate when they are in contact with the PVA solution. The coagulation mechanism, which is known as “bridging coagulation,” results from the adsorption of polymer chains at the interfaces of the nanotubes (17, 25). This process does not involve any actual chemical reactions with the formation or disruption of covalent bonds. After some time, the fiber becomes “solid” and can be extracted from the coagulating liquid. It can then be treated, washed, drawn, etc. by classical methods of fiber technologies (1).

The extensional flow used to probe the fiber solidification is achieved in a pipe with a diameter constriction. The constriction can be located at various places along the pipe. This variation allows the progressive solidification to be probed at different stages of the process. When the constriction is close to the spinneret from which the liquid dope is injected in the coagulation medium, the fiber is still weak and breaks easily. By contrast, when the constriction is placed further down along the line, after the fiber has spent a longer residence time in the coagulating fluid, the fiber can sustain a much greater stress. This increase of mechanical strength reveals a more advanced stage of solidification. The practical and basic interests of this approach are validated by testing the efficiency of different polymers at inducing the coagulation of carbon nanotube fibers. As discussed further, it is observed that long PVA chains are more efficient than shorter ones at solidifying the fibers. In spite of a faster diffusion that promotes a fast coagulation, short PVA chains do not lead to strong fibers and are less suitable for the spinning process.

The nanotubes and the polymer form a gel-like solidifying structure which is transported along a line by the surrounding PVA solution. Related colloidal gels made of polymers and solid particles usually exhibit a shear or compressive yield stress with magnitudes which range from a few pascal to a few kilopascal (26–28). Here the systems are deformed in extension but the deformations involve similar forces and physical bonds. The latter arise from the adsorption of polymer chains onto the colloidal particles. An experimental device to probe the deformation

Author contributions: C.M., A.D., C.Z., and P.P. designed research; C.M., A.L., S.M., and M.M. performed research; C.M., A.L., A.D., and P.P. analyzed data; and C.M., C.Z., and P.P. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1003302107/-DCSupplemental.

Fig. 1. Schematics of the experimental setup used to induce an extensional flow around a fiber. As shown in the upper drawing, the fiber is translated by the surrounding fluid at the center of the pipe at a controlled velocity. The extensional flow is achieved with a diameter constriction of the pipe. The constriction can be located at different distances L from the spinneret, which allows estimating the fiber strength at different residence times T_{res} . The lower drawing shows the geometry of the constriction and the notations used in the text to model the drag forces experienced by the fiber. The fiber is transported at velocities, respectively, V_1 and V_2 upstream and downstream the constriction. The fluid is continuously accelerated from V_1 to V_2 in the conical section of the constriction. The fiber is assumed to be translated in this section at a mean velocity V_M with $V_2 > V_M > V_1$. The fiber experiences a net tensile stress in response to viscous drag and breaks at a distance X_R from the entrance of the constriction. The drag forces pointing to the left and to the right are respectively named F_l and F_r .

and failure of the present fibers should therefore have the capability to induce stresses up to at least a few kilopascal. Such a device is actually presently made of a line of transparent glass pipes connected with joints. The mean velocity V_1 of the PVA solution is of $0.5 \text{ m} \cdot \text{min}^{-1}$ at the center of the pipe. In the above conditions, the coagulating fibers have a diameter of approximately $130 \text{ } \mu\text{m}$. Diameter constrictions used for generating extensional flow consist in a diameter reduction from $d_1 = 2.4 \text{ mm}$ down to $d_2 = 1.5 \text{ mm}$ over a distance L_A of 6 mm . Those dimensions have been optimized for the presently investigated fluids and fiber materials. The corresponding extensional strain rate is given by dV_X/dx where V_X is the fluid velocity at the center of the pipe at a point of x coordinate. From mass conservation, $V_X d_X^2 = V_1 d_1^2$, which yields $dV_X/dx = \frac{2\beta V_1}{(1-\beta x)^3}$ where $\beta = \frac{d_1 - d_2}{L_A d_1}$. The extensional strain rate varies from approximately 1.0 to 4.3 s^{-1} in the present experimental conditions. But stronger or weaker extensional flowfields can simply be achieved by using other diameter constrictions. The location of the constriction along the spinning line is changed by placing the diameter reduction in between different joints of the line. This variation allows the behavior of the fiber to be probed at different times after the nanotube dispersion has been injected in the PVA solution. The time spent by the forming fibers in the coagulating PVA solution before it reaches the constriction is called the residence time and is noted T_{res} . This time corresponds to the distance L from the tip of the spinneret to the location of the constriction divided by the velocity V_1 of the PVA solution at the center of the pipe.

The fluid accelerates along the axis of the pipe at the entrance of the constriction, which induces the development of an extensional flowfield. The gel-fiber transported by the fluid is stretched in response to the acceleration of the supporting fluid. As a result, parts of the fiber upstream of the constriction are drawn and circulate faster than the supporting liquid. As sketched in Fig. 1, the velocity difference results in a drag force F_l pointing upstream. By contrast, parts of the fiber downstream of the constriction circulate more slowly than the surrounding fluid because they are still bound to the rest of the fiber. The velocity difference

on this side leads to a drag force F_r pointing downstream. The combination of these viscous forces result in a tensile stress with a maximum at a well-defined point where $F_l = F_r$. The fiber breaks at this point if the maximum stress exceeds the tensile strength of the fiber. The strength of the fiber evolves rapidly as the nanotubes remain in contact with the coagulating polymer solution. Indeed the polymer chains diffuse throughout the fiber and bind the nanotubes together. Assessing the kinetics of this solidification becomes possible by using different extensional flow geometries and by placing the constriction at different locations along the spinning line. The fiber strength is found to increase with the residence time. This increase is actually confirmed with the observation of three different regimes. When the residence time is too short, the fiber systematically breaks when it passes through the constriction. [Movie S1](#) shows this phenomenon in real-time. By contrast, for a longer residence time the fiber can sustain the hydrodynamic stress induced by the same extensional flow and pass through the constriction without breaking. [Movie S2](#) shows the system in this regime. For an intermediate residence time, in between the two above regimes, the fibers break only occasionally. This intermediate minimum residence time is taken as T_{resmin} . Of course T_{resmin} depends on the used constriction and flow conditions. Examples of these different regimes $T_{\text{res}} > T_{\text{resmin}}$ and $T_{\text{res}} < T_{\text{resmin}}$ are shown in Fig. 2.

Several important features can be deduced from these experiments. When $T_{\text{res}} > T_{\text{resmin}}$, the fiber is stretched upstream of the constriction but undulates downstream. The glass pipe having the same diameter far from the constriction on the right and left sides, the surrounding fluid is flowing at the same velocity in the cylindrical sections. The fiber is first stretched and then compressed as it circulates through the constriction. In other words, it exhibits a positive strain followed by a negative one. The levels of positive and negative strains are similar because the diameter of

Fig. 2. Experimental realization of fiber scission in an extensional flow. (A) The residence time of the fiber in the PVA solution is 8 s . The molecular weight of the PVA is $M_w = 195 \text{ kg} \cdot \text{mol}^{-1}$. The fiber is still too weak to sustain tensile forces induced by the extensional flow in the diameter constriction of the glass pipe. The fiber is cut into small fragments of uniform length. After 14 s (B) and 24 s (C), the fiber is cut into longer fragments. It is observed that the length of the fragments increases with the residence time, which reflects its gradual solidification. (D) The constriction is placed further from the spinneret to set the residence time at 60 s . The fiber is stronger and can pass through the constriction without breaking. We note that the fibers buckle after the diameter constriction, which reflects that they have experienced an irreversible elongation while passing through the constriction.

the pipe and the fluid velocity are exactly the same on the right and left sides. If the fiber would have been elastically deformed, it would have recovered the length it had before passing through the constriction. In such conditions, no extra length would have been created and the fiber would have remained straight. The observed undulations indicate that the fiber has undergone an irreversible stretching during its circulation through the constriction. The undulations result from the buckling of the elongated fiber which is compressed after it has been elongated. When $T_{\text{res}} < T_{\text{resmin}}$, the fiber is cut into small fragments of remarkably regular size. This type of scission confirms that the fiber breaks for a well-defined maximum of stress. As shown in Fig. 2, it is also observed that the length of the fragments increases with the residence time. As discussed further, this quantitatively reflects the increased solidification of the fiber with the residence time. Also, as already observed for $T_{\text{res}} > T_{\text{resmin}}$ the monodisperse fragments buckle when they reach the right side after the constriction.

Discussion

To quantitatively estimate the stress experienced by the fiber in the constriction, a model, inspired from models of the scission of polymer chains in elongational flowfields, is proposed (8). No eddies are observed and the flow is considered as laminar. The Reynolds Re number is given by $Re = \rho U d / \mu$, where ρ is the fluid density, U the mean fluid velocity, d a geometric dimension of the constriction, and μ the fluid viscosity. In all experiments, $d \sim 2$ mm, $\rho \sim 1000$ kg/m³, $\mu = 1.310^{-1}$ Pa·s, and $U \sim V_1$, yielding $Re \sim 0.13$. This estimate confirms that the flow remains laminar, which was not always the case in previous experiments related to the scission of polymer chains in constriction channels (11). The coagulating fiber is considered as a rigid rod and the viscous drag of a rod translated along its axis in a liquid is given by (29)

$$F = 2\pi\mu L_F V,$$

where L_F is the rod length and V the speed of the rod relative to the surrounding fluid. This equation is approximate to within a logarithmic term that vanishes for long, slender fibers. We assume that the fiber is circulating in the constriction at an average velocity V_M , with $V_1 < V_M < V_2$, where V_1 is the velocity of the surrounding liquid before the constriction and V_2 is the maximal speed of the liquid at the center of the constriction. The drag force per unit length experienced by the fiber is given by

$$f = \pm 2\pi\mu(V_X - V_M),$$

where V_X is the velocity of the fluid at the center of the line. We assume that the fiber does not affect the flow. We take for V_X the velocity that the fluid would have in the absence of the fibers in a so-called Poiseuille flow at a given x coordinate along the line. In order to provide an estimate of V_M , we analyze the resultant stress at the breaking point of x coordinate X_R . The drag force toward the left is equal to the force toward the right. The length of the cut fragment is named L_F . We take the entrance of the constriction as the origin of the x axis and assume that the drag force toward the left is effective from $x = 0$ to $X = X_R$. Instead the drag force toward the right is effective from $X = X_R$ to $X = L_A + L_B$ where $L_B = X_R + L_f - L_A$. This force balance can be expressed as

$$\int_0^{X_R} (V_M - V_X) dX = \int_{X_R}^{L_A} (V_X - V_M) dX + \int_{L_A}^{L_A+L_B} (V_2 - V_M) dX. \quad [1]$$

V_M is deduced from the above equation:

$$V_M = \frac{V_2}{L_A + L_B} \left(L_B + L_A \frac{d_2}{d_1} \right).$$

Having an estimate for V_M , it is now possible to integrate Eq. 1 and obtain the tensile force experienced by the fiber in the constriction:

$$F = 2\pi\mu V_2 X_R \left[\left(\frac{L_B + L_A \frac{d_2}{d_1}}{L_A + L_B} \right) + \left(\frac{L_A \frac{d_2^2}{d_1^2}}{X_R(1 - \frac{d_2}{d_1}) - L_A} \right) \right]. \quad [2]$$

The strength of the fiber can be deduced from Eq. 2 by measuring the length of the cut fragments and dividing the force by the cross-sectional area of the fibers. This method is used in the following to quantitatively investigate the coagulation of PVA-nanotube fibers.

The molecular weight of the coagulating polymer is one of the main factors in the spinning process because it is expected to strongly affect the strength of the fiber and the coagulation kinetics. Indeed, small polymer chains diffuse more rapidly than longer ones. They can thus allow a faster coagulation and a greater production rate. However, longer chains are expected to promote stronger bonds between the nanotubes and thereby a more efficient solidification. It is difficult to predict a priori what would be the dominant effect and what kind of polymer would be the most suited for increasing the production rate of such fibers. The approach proposed in this work is shown to be useful to actually select the best conditions. Indeed, the minimum residence time needed for the fiber to go through the constriction without breaking varies substantially as a function of the PVA molecular weight. Different polymers have been tested. As detailed in *Materials and Methods*, the concentration is varied in order to keep the same viscosity for all the systems. The molar concentration of short polymers is greater than that of longer polymers. Therefore diffusion of solvent molecules is also expected to be faster in the short polymer systems. In such conditions, both the size of the polymer and the molar concentrations promote faster diffusion mechanisms in the short polymer systems. In spite of this faster diffusion process, it is found that fibers made of polymers of high molecular weight solidify more rapidly. For $M_w = 195$ kg·mol⁻¹, the fiber does not break in the used constrictions after 30 s of residence time. For $M_w = 145$ kg·mol⁻¹, the fiber does not break until only after 110 s. For polymers of lower molecular weight, the minimum residence time is found to exceed 110 s. The length of the cut fiber fragments is plotted as a function of the residence

Fig. 3. Length of fiber cut fragments as a function of time for different molecular weights of coagulating PVA. Fibers made with PVA of 195 kg·mol⁻¹ and 145 kg·mol⁻¹ don't break in the used constrictions after, respectively, 30 and 110 s (black vertical bars). Instead, fibers made with shorter polymers are still broken in the same constriction and flow conditions even after 110 s of residence time (horizontal arrow).

Fig. 4. Strength of the fibers as a function of the square root of time for different molecular weights of coagulating PVA. The data can be fitted by linear functions, suggesting that the solidification is limited by diffusion. It is observed that the slope of the linear function increases strongly with the polymer molecular weight. In spite of an expected slower diffusion, longer polymer chains induce a much faster and effective solidification of the fibers.

time in Fig. 3. The length of fragments of fibers made of high molecular weight polymer is found to increase rapidly. These data qualitatively suggest that high molecular weight PVA is more efficient than short polymers at quickly solidifying the fibers. More quantitatively, it is possible to estimate the strength of the forming fibers from the data shown in Fig. 3 and Eq. 2. The results are shown in Fig. 4 and reveal how the solidification and mechanical strength of the fibers increase with the residence time. It is observed that, in spite of an expected slower diffusion, the longer polymer chains induce a faster and more effective solidification. This solidification is probed in the present conditions up to a typical stress of about 20 kPa. Only fibers that exhibit a tensile strength greater than this value can pass through the constriction without being cut.

Assuming that the kinetics of fiber solidification is primarily limited by the diffusion of solvent and polymer molecules, one can expect the properties of the solidifying fiber to roughly scale as $T_{\text{res}}^{1/2}$ (2, 3). The values of the applied stress are not sufficient to individually cut polymer chains or carbon nanotubes at the molecular level. The failure of the fibers involves the disruption of physical bonds between the polymer chains and the nanotubes. The number of physical bonds is expected to increase with the molecular weight of the polymer. In order to test the validity of these expectations, the fiber strength is plotted as a function of $T_{\text{res}}^{1/2}$ in Fig. 4. The data exhibit some scattering but can still be reasonably linearly fitted, which suggests that the solidification kinetics is actually limited by diffusion mechanisms. Nevertheless, even if the solidification is limited by diffusion, the strength of the fibers still strongly depend on the molecular weight of the polymer. As shown in Fig. 4, the slope of the linear curves increases with the polymer molecular weight. The exact dependency of this slope cannot be easily discussed in depth because it results from the coupling of several factors, including efficiency of polymers at bridging nanotubes and diffusion mechanisms that are driven by unknown gradients of chemical potentials. Nevertheless, the efficiency of the polymer at bridging nanotubes seems to be a critical factor. Indeed, the slower system, i.e., the system with the greatest polymers, is the one that exhibits the fastest solidification in spite of slower diffusion mechanisms. One can deduce that diffusion is not sufficient to counterbalance the strength increase provided by the size of the large polymer chains in the solidification kinetics of the present fibers.

Materials and Methods

Single walled nanotubes (batch no. PR0925) provided by Thomas Swan are used. The diameters of such nanotubes are in the range of 0.8–1.7 nm (30, 31). Their length exceeds a few microns in the raw material. The nanotubes are dispersed at a weight fraction of 0.3 wt% in an aqueous solution of SDS. SDS is a surfactant that stabilizes the nanotubes in water. The dispersions are homogenized by a sonication treatment during 90 min using a Branson S-450D tip sonicator operating at 40 W. Sonication induces the scission of the nanotubes (32–35) and the average length of the nanotubes after the present treatments is about 500 nm. The quality of the dispersion is assessed before fiber spinning. This assessment is done by checking the absence of aggregates visible at the optical resolution of an optical microscope (Leica DM 2500P equipped with a 40× objective). The PVA was obtained from Sepic-France. Different molecular weights are tested, from 27 to 195 kg·mol⁻¹. The hydrolysis ratio of all the investigated polymers is 99%. The PVA is dissolved in water at 90 °C. The concentration of the PVA is adjusted so that all the solutions exhibit a viscosity of 125 cPs at room temperature. The following concentrations are used for PVA: 195 kg·mol⁻¹ at 5.0 wt%, 145 kg·mol⁻¹ at 6.5 wt%, 61 kg·mol⁻¹ at 10 wt%, and 27 kg·mol⁻¹ at 15 wt%. The solutions are Newtonian in the experimental conditions of the work. These conditions (shear rate up to a few hundreds of seconds⁻¹) are considered as “low shear rate conditions” according to the literature (36). We experimentally checked this rheological behavior by measuring the shear viscosity of the solutions up to 1,000 s⁻¹ and found the viscosity nearly constant at room temperature. The fibers obtained by the coagulation of the nanotube dispersion into the coflowing stream of the PVA solution (14) exhibit a composite structure with a large fraction of nanotubes (>15 wt%) embedded in a PVA matrix. The nanotube dispersion is injected through a syringe needle with a conical tip that has a 300 μm internal diameter. The injection rate of the dope is 50 μL·min⁻¹. The glass pipes have an internal diameter of 2.4 mm. The total length of the line is 2 m. The PVA solution is injected with a pump (Labotron LDP-4) in the pipe and circulates along the line at a controlled flow rate of 150 mL·h⁻¹.

Conclusion

The solidification process is an essential feature of the formation of synthetic and natural fibers. The approach proposed in this work allows a first assessment of the kinetics of this solidification process. It has been validated with the example of fibers formed via the bridging coagulation of carbon nanotubes in the presence of PVA polymers. It was observed that long polymer chains that form strong bridges between the nanotubes are better suited to quickly achieve solid fibers than small polymer chains. Nevertheless, different conclusions could be drawn for other systems. The kinetics of each system depends on the involved chemistry and coagulation mechanisms. The present method can be directly applied to probe other factors such as the influence of salts, cross linkers, pH, etc. to further improve the spinning process of nanotube fibers. This approach may be extended to other classes of fibers which are made by wet-spinning processes. For example, experiments are currently being developed in millifluidic experiments to mimic the spinning of spider silk (6). Implementing extensional flows in such devices could be particularly helpful to gain more insights into the complex solidification processes of various polymers including proteins or synthetic materials. From a more general point of view, the present experiments also demonstrate that synthetic microfibers can be used as models to investigate the flow-induced scission of polymers, such as colloids which can serve as models for atomic systems.

ACKNOWLEDGMENTS. We gratefully thank Dr. Sébastien Chevalier for the figure art. The Direction générale de l'armement, the Arkema group, and the Conseil Régional d'Aquitaine are acknowledged for financial support of this work.

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