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A COMPUTATIONAL MODEL DEVELOPED TO DEMONSTRATE THAT DURING THE SPIDER SILK SPINNING INTERNAL DIFFUSION GOVERNS WATER REMOVAL – A PROCESS CENTRAL TO THE GENERATION OF SPIDER SILK'S EXCEPTIONAL MECHANICAL PROPERTIES

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Abstract

Solvent removal by diffusion from a polymer solution occurs in various technological processes, such dry spinning of synthetic silk-like fibers. There, it is important to determine the diffusion coefficient which is dependent on the solvent concentration, assuming the validity of Fick's law. In order to prove the internal diffusion within the dope while traveling through the spider canal, we performed the experimental investigation and developed specific finite element models. We first summarize our methodology of the numerical computation of such diffusion coefficient, published in our reference (Kojić et al., 2006). The diffusion coefficient is determined by matching the mass of the solution computed by the finite element (FE) model, and the mass measured using a pan-weighing experiment, in which a small amount of the polymer solution is placed in a pan and allowed to evaporate into the air. The second part of this report, according to our reference (Kojić et al., 2004), is devoted to exploring the process in which a spider generates a fiber with the extraordinary strength of several orders higher than any technologically produced fiber. It was hypothesized that the governing process within the spider canal where the elongation flow of the dope occurs is the radial diffusion of the water with zero concentration at the canal wall. The computational model for the water diffusion from the dope is developed with the corresponding boundary conditions to confirm our hypothesis.

Keywords: fiber spinning, diffusion, elongation flow, spider fiber, pan-weighing experiment

1. Introduction

Diffusion is one of the governing processes in many chemical engineering applications, such as solvent removal during the dry spinning of fibers out of a polymer solution. It is also the governing process in living organisms. The commonly used is Fick's law for the mathematical description of diffusion (Kojić et al., 2022) where we have that mass flux is proportional to the concentration gradient and is directed from the higher to the lower concentration. The material parameter, as the proportionality factor between the mass flux and concentration gradient is the diffusion coefficient which, in the case of the solvent diffusion from polymer solutions can

change significantly with the solvent concentration. Here, we considered water diffusion from the spinning of synthetic fibers with the elongation material flow and determined the dependence of the diffusion coefficient on the water concentration experimentally and by our computational model (Kojić et al., 2006). The important finding of our study in (Kojić et al., 2006) was that the mechanical characteristics of these fibers, Young's modulus and toughness, significantly increase with the decrease of the fiber diameter (thin fiber has the elastic modulus of 100 MPa and toughness of 15 MJ/m3, about 5 times larger than in case of thick fiber).

Following these findings regarding fibers, we considered a spinning of a solid protein fiber out of a concentrated water solution, occurring in the channels of spiders for millions of years (Shear et al., 1989) (Selden, 1989). The resulting spider-silk fiber has mechanical properties that are superior to any known material (modulus of 10 GPa and toughness of 150 MJ/m^3). Although the chemical composition and genetic basis of the proteins have been established, the spinning process by which the fiber is formed remains a mystery. The fact is that during this process most of the solvent (water) is removed and simultaneously the protein chains are stretched due to the elongational flow through the progressively tapered spinning canal. We assumed that the water removal from the solution is governed by diffusion, with the diffusion coefficient determined by the pan experiment and diffusion model, for Nephila clavipes major ampullate gland (obtained ex vivo).

2. Numerical determination of the solvent diffusion coefficient Numerical determination of the solvent diffusion coefficient in a polymer solution

We consider the polymer solution (Kojić et al., 2006) which consists of 35% polymer and 65% solvent by weight. The solution was placed in a Seiko TG=DT machine, which was used to record mass as a function of time for 12 240 s (3.4 h). The experimental setting of our pan experiment is schematically shown in Fig. 1, and other details are given in (Kojić et al., 2006). The mass change and the fitted curve (used in the computational model) are also shown in the Figure 1.

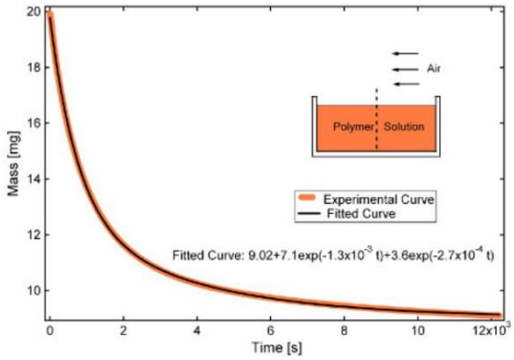

Fig.1. Schematics of the pan weighing experiment and mass change due to solvent evaporation from the polymer solution (according to (Kojić et al., 2006)).

The computational finite element (FE) model is shown in Fig. 2. As shown in the figure, we use the 1D finite element model for diffusion of the solvent, with the boundary conditions: no flux at the bottom (x=0) , and concentration at the top is equal to zero (ρS=0). Detailed analysis of the boundary condition at the top – the boundary between diffusion and convection domains, showing the large B_{iot} number B_{im}, is given in (Kojić et al., 2006).

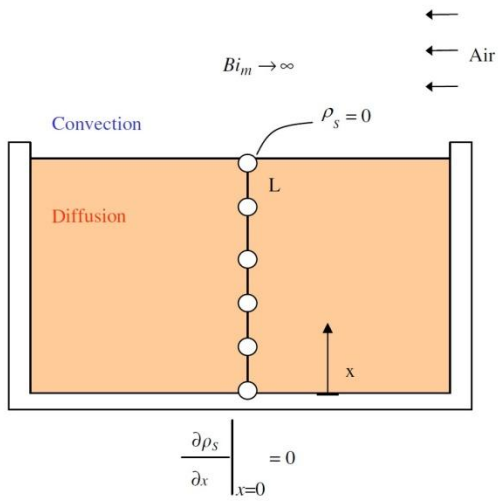

Fig.2. Finite element model of the pan experiment. (according to (Kojić et al., 2006))

The governing balance equation for 1D diffusion can be written as (Kojić et al., 2006),

$$\frac{\partial \rho}{\partial t} - \frac{\partial}{\partial x}\left[\rho D \frac{\partial}{\partial x}\left(\frac{\rho}{\rho}\right)\right] = 0 \tag{1}$$

where ρ_S and ρ_T are concentrations of the solvent and the solution, respectively; and D_{SS} is the solvent diffusion coefficient which is taken to be dependent on the ρ_S. Using the standard Galerkin method (Kojić et al., 2008), this equation is transformed into the FE form, so that the mass balance equation for a 1D finite element, time step Δt, and equilibrium iteration "i", can be expressed as

$$\left(\frac{1}{\Delta t}\mathbf{M} + \mathbf{K}\right) \Delta\boldsymbol{\rho} = \left(\frac{1}{\Delta t}\mathbf{M} + \mathbf{K}\right) \boldsymbol{\rho} \tag{2}$$

where ρ_S is the vector of the nodal concentration, and the matrices **M** and **K** are

$$M_{IJ}^{(i-1)} = A \int_{L^{(i-1)}} N_I N_J dL, \quad K_{IJ}^{(i-1)} = A \int_{L^{(i-1)}} \frac{\bar{\rho}_p}{\rho_T^{(i-1)}} D_{SS}^{(i-1)} N_{I,x} N_{J,x} dL \tag{3}$$

where A is the cross-sectional area of the pan; NI and NJ are the interpolation functions, and the element length is

$$L^{(i-1)} = L_p + \frac{1}{\bar{\rho}_S} \int_{L^{(i-2)}} \rho_S^{(i-1)} dL \tag{4}$$

Here, $L_p = \left(\rho_p^0 / \bar{\rho}_p\right) L^0$ where ρ_p^0 and L_0 are the initial polymer concentration and element length. The computational procedure is as follows: for a time step, we have the mass of the solution and then iterate on the diffusion coefficient, updating solvent concentration and element lengths according to equations (2) and (3), until we reach the value of the solution mass. More details are given in (Kojić et al., 2006). The computational procedure was built into the FE program PAK-T (Kojić et al., 1997). Using the above procedure follows directly the

dependence of the mean diffusion coefficient on the mean concentration. In order to find the dependence $D_{SS}(\rho_S)$ of the diffusion coefficient on the solvent concentration, an error function was introduced in reference (Kojić et al., 2006) (details are given in that reference), and the resulting relationship is shown in Fig. 3. The data are as follows:

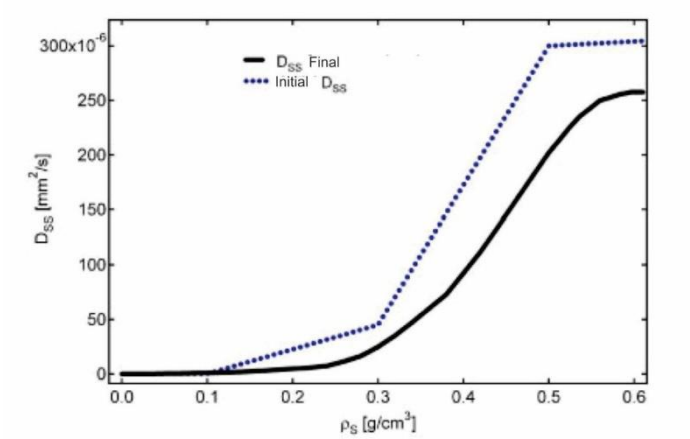

Fig.3. Dependence of the solvent diffusion coefficient on the solvent concentration (according to (Kojić et al., 2006)).

Densities in [g/cm^3], lengths in [cm]

$$\bar{\rho}_S = 0.894,\ \bar{\rho}_p = 1,\ \rho_S^0 = 0.609,\ \rho_p^0 = 0.325\ \ L^0 = 0.112 \tag{5}$$

It can be seen that dependence $D_{SS}(\rho_S)$ is highly nonlinear.

The motivation for exploring the process of spider fiber spinning within the channel was the findings that the mechanical strength of the synthetic fibers, obtained by the spinning procedure, increases with a decrease in the fiber diameter. This is shown in Fig. 4.

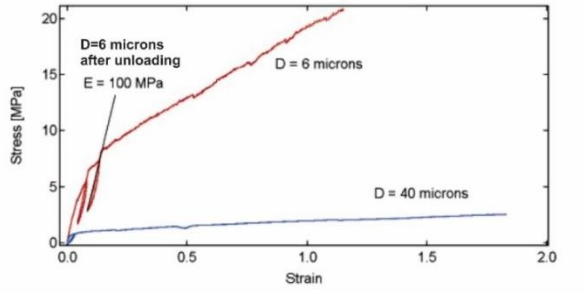

Fig.4. Constitutive curves for synthetic fibers obtained by fiber sinning. The strength increases with a decrease in the fiber diameter.

3. Fiber spinning within the spider canal

In accordance with the above model of diffusion within the polymer solution and the pan experiment, a computational procedure was developed to explore the process of the fiber

spinning within the spider channel (Kojić et al., 2004). This process leads to the generation of spider fibers with extraordinary mechanical characteristics. The research reported in (Kojić et al., 2004) was conducted at the Hatsopoulos Microfluids Laboratory with Professor Gareth McKinley. It was first shown, by the FE modeling of synthetic fiber spinning, that the fibers with smaller diameters are stronger than the fibers with larger diameters (details are given in (Kojić et al., 2004)). Then, using ex vivo dope from the *Nephila* clavipes spider major ampullate gland, and the pan experiment described in Section 2, it was found that the diffusion coefficient of the water evaporating from the dope, was constant and equal to $D_{wd(wtare\text{-}dope)}$= $2.15x10^{-5}$ mm^2/s.

Further, it was measured the geometry of the spider chanal shown in Fig. 5b. It was stated in (Kojić et al., 2004) that: "Unlike the synthetic material, the Nephila water diffusion coefficient was a constant, i.e., it was independent of the water concentration. A possible benefit of the constant diffusion coefficient could be the constant resistance to water motion from the inside of the fiber to the surface. In other words, although the fiber becomes drier the resistance encountered by the escaping water remains constant and does not increase as in the synthetic case." This was one of the main findings in the effort to elucidate the physical process of spider fiber generation.

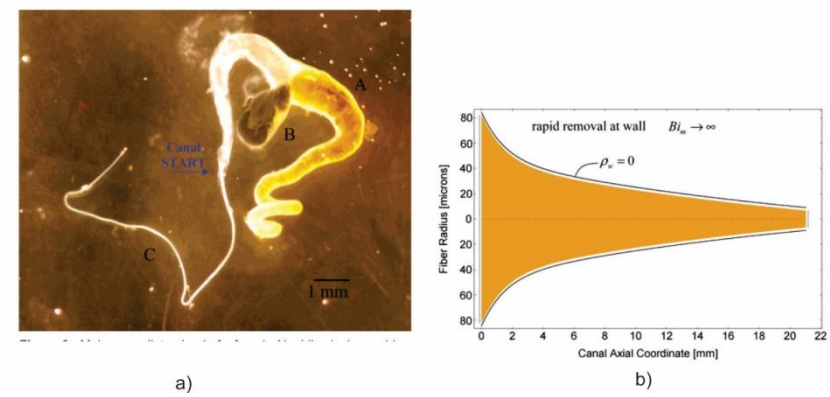

Fig.5. a) Major ampullate gland of a female *Nephila* clavipes spider. A. Ampulla, dope reservoir. B. A blob of dope was used in the pan-weighing experiment. C. Spinning canal, S-duct. b) Measured radius profile of the Nephila spinning canal, with zero concentration boundary condition at the canal wall (corresponding to the high B_{iot} number B_{im}). (according to (Kojić et al., 2004))

$$\frac{\partial \rho_{wd}}{\partial t} - \frac{1}{r}\frac{\partial}{\partial r}\left[r \rho_T D_{wd} \frac{\partial}{\partial r}\left(\frac{\rho_{wd}}{\rho_T} \right) \right] = 0 \tag{6}$$

where ρ_{wd} is the water concentration in the dope solution. This equation is transformed into the 1D FE model of the form (2) and applied to a material element (in close vicinity of a cross-section initially at the entrance to the spider canal) traveling through the canal from the gland to the exit over time, as schematically shown in Fig. 6. Boundary condition of this model is the zero concentration at the canal wall. Besides the zero concentration at the wall, an additional condition is imposed, i.e. the canal must be filled with the dope material, which can be expressed by the following equation:

$$\Delta t v_1 A_1 - \Delta t v_2 A_2 - \frac{\Delta m_d}{\bar{\rho}_w} = 0 \tag{7}$$

where Δt is the time step during the traveling time of the material, v_1 and v_2 are velocities and A_1 A_2 are cross-sections at the elementary distance Δx; and Δm_d is water loss for time Δt computed from the 1D FE model. The elementary length Δx corresponding is computed as $\Delta x = 0.5\left(v_1 + v_2\right)$.

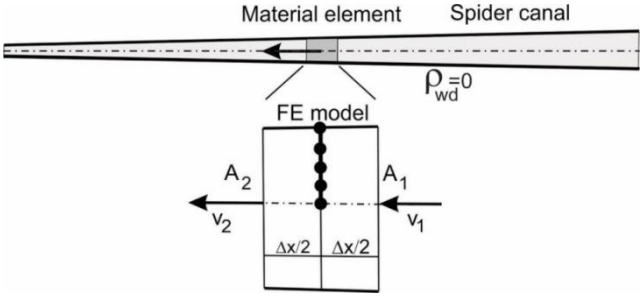

Fig.6. One-dimensional FE model for the internal diffusion within the material element traveling through the spider canal

The computational procedure has the following steps within a time step:

1. Assume velocity v_2 and compute $\Delta x = 0.5\left(v_1 + v_2\right)$
2. Iterate on the mass balance of the FE model
3. Compute Δm_d and then v_2 from (8)
4. Compute new Δx and check for convergence of Δx
5. If convergence is not reached go to step 2.
6. Time step completed. Set: $v_1=v_2$, $A_1=A_2$; new coordinate of the section A_1. Go to step 1

We used the following material densities (in g/cm^3):

$$\bar{\rho}_w = 1 \quad \bar{\rho}_p = 1$$
$$\rho_w^0 = 0.7 \; \rho_p^0 = 0.3 \tag{8}$$

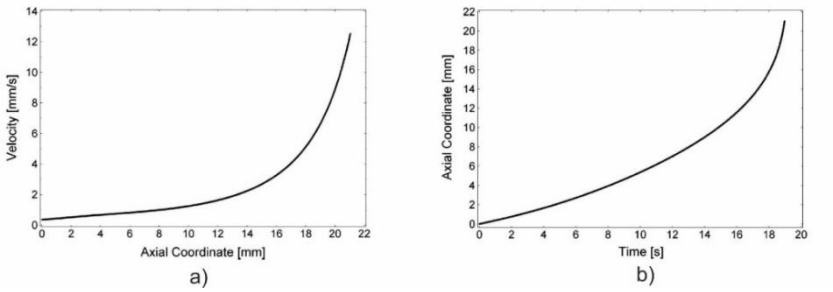

Fig.7. a) Velocity of traveling material element along the spider canal; b) Axial coordinates of the material element in terms of time. (According to (Kojić et al., 2004))

We have adjusted the velocity of the first cross-section, at time t=0, as $v_1 = V_{enetering} = 0.37$ mm/s in order to obtain zero water concentration at the canal exit, $(\rho_w)e_{xit}=0$. The exit velocity was

found to be (at a distance of 21 mm from the canal entrance) 12.5 mm/s, which is within the observed velocity range. The velocity of a material element (cross-section) while traveling along the spider canal is shown in Fig. 7a, and the axial coordinate in terms of time is displaced in Fig. 7b. It can be seen that the velocity increases from a small value to very high values as the material approaches the exit. The material needs 19s to flow to the exit and needs more time for traveling in the region of larger diameter. The water loss during material flow through the canal, shown in Fig. 8, illustrates the hypothesis that the process of the spider fiber generation is governed by the internal water diffusion from the dope.

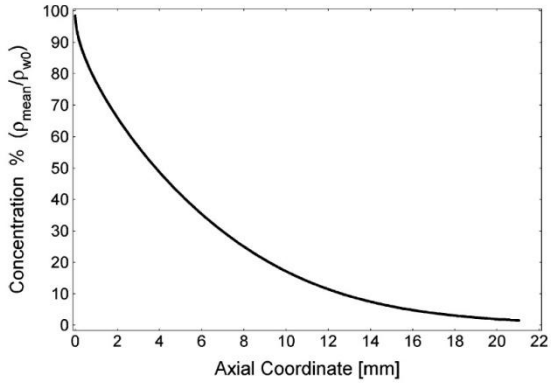

Fig.8. Water concentration along the spider fiber during fiber spinning within the spider canal

4. Concluding remarks

We have summarized in this report our research in the past in references (Kojić et al., 2006) and (Kojić et al., 2004). Experiments were realized within Professor McKinley's lab at MIT, while the numerical methodology was built into the FE program PAK-T (Kojić et al., 1997) for heat conduction, modified for these specific diffusion processes. The designed pan weighing experiment was modeled by the formulation of a challenging FE model, to determine the diffusion coefficient while the solvent was evaporating and diffusing within the solution. Further, a computational model was developed to model the synthetic fiber spinning where the elongation flow is accompanied by the solvent diffusion. It was found that the diffusion coefficient is a nonlinear function of the solvent concentration. Experiments showed that the strength of the fibers increases with a decrease in the fiber diameter. These findings for the synthetic fibers served as a basis for the investigation of the hypothesis that the generation of spider fibers, with extraordinary strength, is governed by internal diffusion while the dope material is subjected to the elongation flow within the spider canal.

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