

SUPPORTING INFORMATION

This supporting information presents some information on how capillary instabilities can prevent the stability of the filaments formed during the shaping process.

The capillary instabilities was first treated by Rayleigh in 1879 for a jet of a viscous fluid in air and extended by Tomotika ¹⁻³ to the case of a single cylindrical viscous thread embedded in a quiescent Newtonian medium (after the flow is stopped). This theory assumes that under affine deformation conditions $Ca / Ca_{(crit)} > 2$, once the droplet has become highly extended, very small sinusoidal disturbances appear on the surface of the fibril. Distortions with a wavelength (λ) larger than the original circumference of the fibril, $2\pi R_0$, will lead to a decrease in interfacial surface area and thus only these distortions can grow (Figure 2).

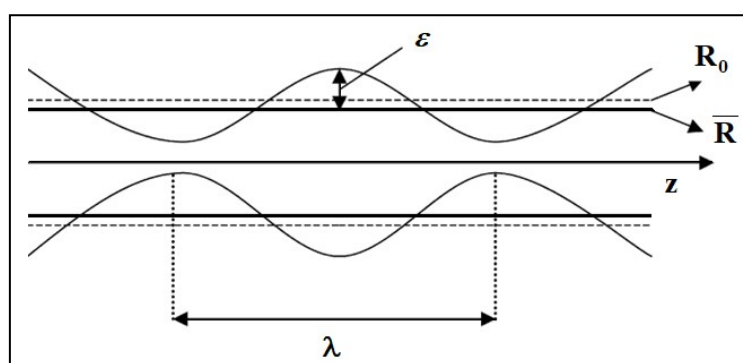


Figure 1. Schematic representation of capillary instability (sinusoidal distortion) appearing during extension of a cylindrical thread with initial radius R_0 . $\bar{R} = \sqrt{R_0^2 - \epsilon^2} / 2$ is the average radius, ϵ is the amplitude of the distortion, λ is the wavelength and z is the Cartesian coordinate along the principal axis of the cylinder.

A dimensionless wave number of distortion, X , is given by $X = 2\pi R_0 / \lambda$ where X varies between zero and unity. The distortion amplitude, ϵ , is assumed to increase exponentially with time, given by:

$\epsilon = \epsilon_0 \exp(qt)$ where ϵ_0 is the amplitude of the distortion at time $t=0$. A lower limit of ϵ_0 , is given by thermal fluctuations and was estimated by Kuhn ⁴:

$$\epsilon_0 = \sqrt{(21\kappa_B T) / (8\pi^{3/2} \Gamma_{d,m})} \quad \text{Eq. 5}$$

Where κ_B is the Boltzmann constant, T is the absolute temperature and $\Gamma_{d,m}$ the interfacial tension.

According to Kuhn ⁴, $\epsilon_0 \approx 10^{-9}$ m for $\gamma_{d,m} = 10$ mN.m⁻¹.

The growth rate of the distortion (q) is given by

$$q = \Gamma_{d,m} \Omega(k, X) / 2\eta_m R_0 \quad \text{Eq. 6}$$

Where η_m is the matrix viscosity, R_0 is the initial radius of the thread and $\Omega(k, X)$ is a complex function of the characteristic wave number, X , of the perturbation and the viscosity ratio, k , of the system concerned. When the function $\Omega(k, X)$ is maximal, the break-up of the thread occurs. Values of $\Omega(k, X)$ can be calculated from Tomotika's original equations². The values of the dominant growth rate $\Omega(k, X_m)$ and the dominant wave number $X_m (X_m = 2\pi R_0 / \lambda_m)$ are plotted against viscosity ratio k in Figure 3 by Janssen and Meijer ⁵. For $0.01 \leq k \leq 10$, Utracki and Shi ⁶ used the following equation to fit the function $\Omega(k, \lambda_m)$:

$$\Omega(k, \lambda_m) = \exp[b_0 + b_1 \log k + b_2 (\log k)^2 + b_3 (\log k)^3 + b_4 (\log k)^4] \quad \text{Eq. 7}$$

where $b_0 = -2.588$, $b_1 = -1.154$, $b_2 = 0.03987$, $b_3 = 0.0889$, and $b_4 = 0.01154$.

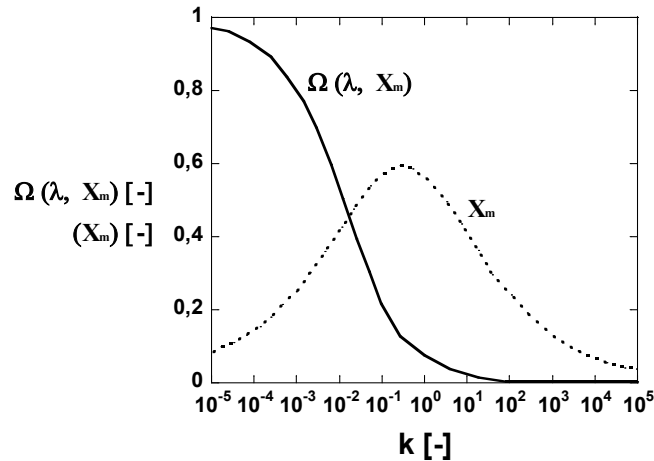


Figure 2. The wavenumber and growth rate of the dominant wavelength (Janssen and Maijer⁵).

Tomotika² estimated that the breakup occurs when the amplitude of the deformation ϵ reached a critical value corresponding to the average radius of the thread where $\epsilon_b = \bar{R} = 0.81.R_0$ and $\bar{R} = R_0^2 - (\epsilon^2 / 2)$ according to the condition of conservation of volume (Figure 2).

References

1. S. Tomotika, Proceedings of the Royal Society A, 1935, 150, 322-337.
2. S. Tomotika, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, 1935, 150, 322-337.
3. S. Tomotika, Proceedings of the Royal Society A, 1936, 153, 302-318.
4. W. Kuhn, Kolloid -Zeitschrift, 1953, 132, 84-99.
5. J. M. Janssen and H. Meijer, Polymer Engineering & Science, 1995, 35, 1766-1780.
6. L. Utracki and Z. Shi, Polymer Engineering & Science, 1992, 32, 1824-1833.