Express Polymer Letters Vol.17, No.2 (2023) 211–217
Available online at www.expresspolymlett.com
https://doi.org/10.3144/expresspolymlett.2023.15

Research article

Size dependence of the elastic modulus of thin polymer fibers – modeling

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Received 14 June 2022; accepted in revised form 21 September 19

Abstract. The problem of the size dependence of physical properties is one of the most intriguing when we transit to the nano-level. Experiments have shown that this effect is characteristic of the elastic modulus of many polymeric nanofibers obtained by electrospinning. Existing explanations of this effect did not offer a general understanding of the physical nature of this phenomenon. In this study, we propose a universal model of this phenomenon. We consider the structure of fibers within the framework of the core-shell model, in which the shell is approximated by a thin elastic surface. The analysis of deformation is based on the fundamental laws of the mechanics of deformation of twisted thin shells and, unlike the theories proposed earlier, does not require any additional artificial arguments. This approach made it possible to obtain a simple analytical expression for the size dependence of the elastic modulus, which represents it as the sum of the bulk modulus of the core and two additional moduli proportional to D^{-1} and D^{-3}, respectively. The resulting model corresponds to all available (from published sources) experimental data, related to polymer of very different chemical structure, and therefore can be considered as universal.

Keywords: *nanomaterials, polymer electrospinning, elasticity, surface tension, surface curvature*

1. Introduction

The problem of the size dependence of the fundamental mechanical properties of materials does not exist in physics and technical applications. However, when we move into the nanoscale world. We see that many important characteristics of the products do depend on their size. One of the intriguing phenomena of this kind is the size dependence of the elastic modulus of polymeric nanofibers obtained by electrospinning from polymer solutions [1–3]. This effect is especially important for the use of nanofibers as a reinforcing component in critical applications in modern technology. This behavior is similar to the analogous effect known for metal and oxide nanowires. For these objects, it was assumed that the concept of surface tension is the dominating mechanism of increasing the modulus [4, 5]. Structure analysis has shown that nanowires can be really treated as a composite of a core-shell structure with cover layers, which penetrate deep into the bulk of a wire depends on its size [6, 7]. This is also applied to polymer fibers, which have a different structure of the volume and outer shell [8–10], which is mainly due to the diffusion process of evaporation of a solvent during their formation from a polymer solution [11]. Indeed, evaporation of the solvent leads to the formation of

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a thin glassy [12] or gel-like [13] film skin on the free surface of the polymer solution, which ensures the formation of the fiber shell.

The primary explanation for the increase in the elastic modulus of ultrathin fibers seems obvious due to their very large relative surface area. However, this approach was rejected [14] due to the fact that a quantitative estimation based on real values of surface tension did not give a reasonable agreement with the experimental data. Meanwhile, in these calculations, the surface tension was considered as a single characteristic of a surface, like in different liquids. However, it is well known that surfaces demonstrate viscoelastic properties [15], and this is especially important for nanoscale objects [16]. Surface elasticity was considered in continuum mechanics of surface/interface layers [17] and was used in constructing the core-shell model of nanowires [18] since nano-size fibers are important not only for organic but also for inorganic objects. In the latter publication, the numerical results have demonstrated the applicability of this model (including two fitting factors related to the surface – the inhomogeneity degree constant and the surface layer thickness) for the elastic modulus of ZnO and Si nanowires in bending and tension loading modes.

The core-shell model has also been used to explain the increase in the elastic modulus for thin fibers due to the deformation and orientation of molecular aggregates within the fiber [19]. This approach shifted the responsibility for the increase in the elastic modulus to the structure of the central part of the fiber.

The purpose of this work is to formulate a simple phenomenological theory based on the two-cylinder core-shell model for fitting experimental data obtained for various polymer nanofibers and explaining the dependence of the total elastic modulus of ultra-fine fibers on their diameter due to the elastic properties of the surface layer associated with its curvature.

2. Theory

Let's start with the simplest model and imagine a fiber in the form of a cylindrical core of the diameter d and the elastic (Young) modulus of E_d, and a shell with an elastic modulus of E_D and a thickness $\delta = 0.5(D-d)$ (D is the total fiber diameter as shown in Figure 1). The core and shell are believed to obey Hooke's law and $E_D \gg E_d$.

The apparent modules of the core-shell fiber E is defined by the Equation (1):

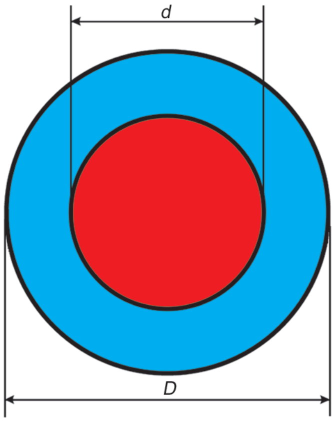

Figure 1. Two-component core-shell model of the cross-section of a fiber.

$$E = \frac{4F}{\pi D^2 \varepsilon} \quad (1)$$

where ε = const is the deformation and the force, F, is the sum of the forces acting in at the core and the shell (Equation (2)):

$$F = \frac{\pi(D^2 - d^2)}{4} E_D \varepsilon + \frac{\pi d^2}{4} E_d \varepsilon \quad (2)$$

Substituting Equation (2) into Equation (1), we arrive at the Equation (3):

$$E = E_D \frac{D^2 - d^2}{D^2} + E_d \left(\frac{d}{D}\right)^2 \quad (3)$$

which can be written as Equation (4):

$$E = E_D \left[1 - \left(\frac{d}{D}\right)^2\right] + E_d \left(\frac{d}{D}\right)^2 \quad (4)$$

Then, as a first approximation, we assume that the shell thickness weakly depends on the fiber diameter, *i.e.* δ = const, and $\delta/D \ll 1$. In this case, the $E(D)$ dependence is expected to be Equation (5):

$$E = E_d + (E_D - E_d)\frac{4\delta}{D} \quad (5)$$

The results of comparing the curve calculated by Equation (5) with experimental data for various polymer nanofibers are included in Figure 2 (blue dots line), which presents the general picture of our approach. (A more detailed analysis of the experimental data is given below.) Despite the fact that formula (5) indicates an increase in the elastic modulus with decreasing fiber size, the predicted effect is rather weak and does not allow one to describe the experimental data (except poly(vinyl alcohol) (PVA), Figure 2d).

The model considered above does not fully take into account the structure of the shell and, in particular, its anisotropy: macromolecules in the shell have a higher orientation than in bulk since in the process of spinning the fiber and evaporation of the solvent, a polymer-enriched surface layer with more pronounced viscoelastic properties is formed. In addition, side groups attached to the polymer backbone can also be ordered due to the surface effect. Therefore, the elasticity of the shell must be characterized by several elastic moduli, and this complicates the consideration of the core-shell model in the general case. To simplify further consideration, we replace the shell with an elastic surface and use the phenomenological approach based on the analysis of the general expression for the surface energy. At the same time, we continue to assume that the elasticity of the core is described by Hooke's law.

Consider again a thin cylinder having an elastic surface. The cross-section of fiber was shown in Figure 1. The elastic properties of the shell (surface layer) will be determined based on the surface energy. The initial length of the cylinder is L, and its deformation is $\varepsilon = \Delta L/L$, where ΔL is the elongation of the cylinder. Accordingly, the radius of the cylinder $R = D/2$ decreases and is equal to $R - \Delta R$, $\Delta R > 0$. The volume of the cylinder is assumed to be constant. Then ΔR is found from the volume conservation equation $V = \pi R^2 L = \pi(R - \Delta R)^2 L(1 + \varepsilon)$, (Equation (6)):

$$\Delta R = R\left(1 - \frac{1}{\sqrt{1+\varepsilon}}\right) \cong \frac{1}{2}R\left(\varepsilon - \frac{3}{4}\varepsilon^2\right) \tag{6}$$

Change in the surface area of the cylinder in extension is Equation (7):

$$\begin{aligned}\Delta A &= 2\pi(R - \Delta R)(L + \Delta L) - 2\pi RL = \\ &= A_0\left(\sqrt{1+\varepsilon} - 1\right) \cong \frac{1}{2}A_0\left(\varepsilon - \frac{1}{4}\varepsilon^2\right)\end{aligned} \tag{7}$$

where $A_0 = 2\pi RL$ is the initial surface area of the cylinder.

Let us accept that the bulk elastic modulus of the cylinder is E_d. The change of the elastic energy in extension therefore is Equation (8):

$$\Delta F_\mathrm{core} = \frac{1}{2}E_\mathrm{d}\varepsilon^2 V \tag{8}$$

Then we write the energy of the shell by analogy with the energy of the lipid layer as the sum of two terms [22–24], Equation (9):

$$F_\mathrm{shell} = F_\mathrm{surf}[A] + F_\mathrm{curve}[C_1, C_2] \tag{9}$$

Here the first term depends only on the area of the surface and is associated with a change in the energy due to its stretching, and the second term reflects the curvature of the surface and depends on the principal curvature values, C_1 and C_2. For a straight cylinder of radius R, $C_1 = 1/R$, $C_2 = 0$.

Upon small elongation of the cylinder, the change of the surface term in Equation (9) is written in the following form (Equation 10):

$$\begin{aligned}\Delta F_\mathrm{surf} &= F_\mathrm{surf}[A_0 + \Delta A] - F_\mathrm{surf}[A_0] = \\ &= A_0\left(\gamma\frac{\Delta A}{A_0} + \frac{1}{2}\mu\left(\frac{\Delta A}{A_0}\right)^2\right) \cong \\ &\cong \frac{1}{2}A_0\left(\gamma\varepsilon + \frac{1}{4}(\mu - \gamma)\varepsilon^2\right)\end{aligned} \tag{10}$$

where γ is the surface tension and μ is the elastic modulus of stretching of the surface. Since the radius of curvature of the shell is much larger than the width of the shell, the expression for the second term in Equation (9) can be expanded in a series with respect to the curvature (Equation (11)):

$$\begin{aligned}&F_\mathrm{curve}[C_1, C_2] = \\ &= -\kappa\int C\,\mathrm{d}A + \frac{1}{2}K\int C^2\,\mathrm{d}A + K_\mathrm{G}\int C_1C_2\,\mathrm{d}A\end{aligned} \tag{11}$$

where $C = C_1 + C_2$ is the total curvature of the surface. Here we introduce additional moduli κ, K and K_G, resulting from the change of curvature [20–22]. Obviously, in our case of uniaxial tension, the last term in Equation (11) is equal to zero ($C_2 = 0$) and $C = C_1$.

Now consider the change in the energy F_curve, Equation (11), due to extension. The total curvature after deformation is $C = 1/(R - \Delta R)$, therefore Equation (12):

$$\Delta F_\mathrm{curve} = -A_0\varepsilon\frac{\kappa}{R} + \frac{3A_0}{4}\frac{K}{R^3}\left(\varepsilon + \frac{1}{4}\varepsilon^2\right) \tag{12}$$

The total change in the energy ΔF_tot, of the cylinder due to extension is determined by the sum Equation (13):

$$\Delta F_\mathrm{tot} = \Delta F_\mathrm{core} + \Delta F_\mathrm{surf} + \Delta F_\mathrm{curve} \tag{13}$$

Finally, we can find the effective modulus of elasticity as Equation (14):

$$E = \frac{1}{V}\frac{\partial^2 \Delta F_{\mathrm{tot}}}{\partial \varepsilon^2} = E_{\mathrm{d}} + \frac{\mu-\gamma}{2R} + \frac{3K}{4R^3} \qquad (14)$$

Thus, when a straight cylinder is stretched, the effective modulus does not depend on the curvature moduli κ and K_G. It is interesting to note that surface tension makes a negative contribution to the elastic modulus. Comparing the formula of Equation (14) with Equation (5) we can conclude that when $\gamma = 0$ and $K = 0$ we come to our previous model with $\mu = 4\delta(E_D - E_d)$. Thereby, the additional input into the elastic modulus of the nanofibers includes two terms proportional to $1/R$ and $1/R^3$, respectively. Besides, it is reasonable to assume that $\mu - \gamma > 0$. The final fitting can be presented as Equation (15):

$$E = E_{\mathrm{d}} + \frac{K_1}{D} + \frac{K_2}{D^3} \qquad (15)$$

where the coefficients K_1 and K_2, in accordance with Equation (9), have the following physical sense (Equations (16) and (17)):

$$K_1 = \mu - \gamma \qquad (16)$$

$$K_2 = 6K \qquad (17)$$

i.e. K_1 is mainly determined by the stretching modulus of the surface and K_2 – by the curvature elastic modulus.

3. Experimental and discussion

We examined five available sets of experimental data for the $E(D)$ dependences, which were found in current publications. The size dependences of the elastic modulus $E(D)$ were described for: poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) [23], Nylon-66 (PA66) [24], polypirrol (PPy) [25], poly(vinyl alcohol) (PVA) [26], polyacrylonitrile (PAN) [27]. The nanofibers were obtained by the electrospinning technique using different polymer-solvent systems.

Experimental data on the $E(D)$ dependencies are always obtained and presented in original publications with a wide scatter. We have shown the fields of experimental data and usually have used averaged points for calculations unless otherwise stated. Fitting equation constants will be found by the standard RMS procedure after presenting them in linearized log-log coordinates. In some cases, we presented fitting lying in the experimental field but not as the averaged curves (that will be noted separately). For comparison, we also presented the results of calculations for the simplest two-cylinder model, which included only elastic stretching moduli.

Figure 2 demonstrates the results of the comparison of the dependences calculated by Equation (15) with the experimental data for various polymer nanofibers (red dash lines), and Table 1 collects the obtained values of the constants K_1 and K_2.

The analysis of Figure 2 shows that Equation (5) does not give satisfactory results, except for one case of PVA (Figure 2d). In the latter case, the increase in the modulus of this polymer occurs rather smoothly. Indeed, the $E(D)$ dependence for this polymer is approximated by a power law with the power is –0.7, which is much less than in other cases. This result can be explained by a very pronounced core-shell structure of the PVA crystalline fibers with a rigid anisotropic outer layer, observed in the original publication [26]. Thus, this structure is the most equivalent to a scheme in Figure 1, and the influence of surface curvature elasticity does not appear. It leads to the zero-value of the $1/D^3$ term in Equation (15). Then the latter equation also fits these data. The difference in the lines in this figure is explained by the fact that when calculating according to Equation (5), we took into account the free term.

For three polymers - PAMPS (Figure 2a). Nylon 66 (Figure 2b), and PPy (Figure 2c), the developed two-term model (Equation (15)) provides quite a fairly good quantitative agreement with experimental data. The agreement of the theoretical model with experimental data for PAN (Figure 2e) should be treated as qualitative. The increase in the modulus with a decrease in the fiber diameter occurs more sharply than $1/D^3$. Perhaps this indicates the need to take into account the higher terms in the expansion (Equation (10)).

Based on the results obtained, we assume that the core-shell model and the concept of the outer surface elasticity is a reasonable assumption about the strong

Table 1. Values of the parameters used for fitting.

Polymer	**$4\delta(E_D - E_d)$ [nm·GPa]**	**K_1 [nm·GPa]**	**$K_2 \cdot 10^{-6}$ [nm^3·GPa]**
PAMPS	11	30	0.26
Nylon	185	200	8.5
PPy	110	250	2.0
PVA	800	1100	0
PAN	100	800	20

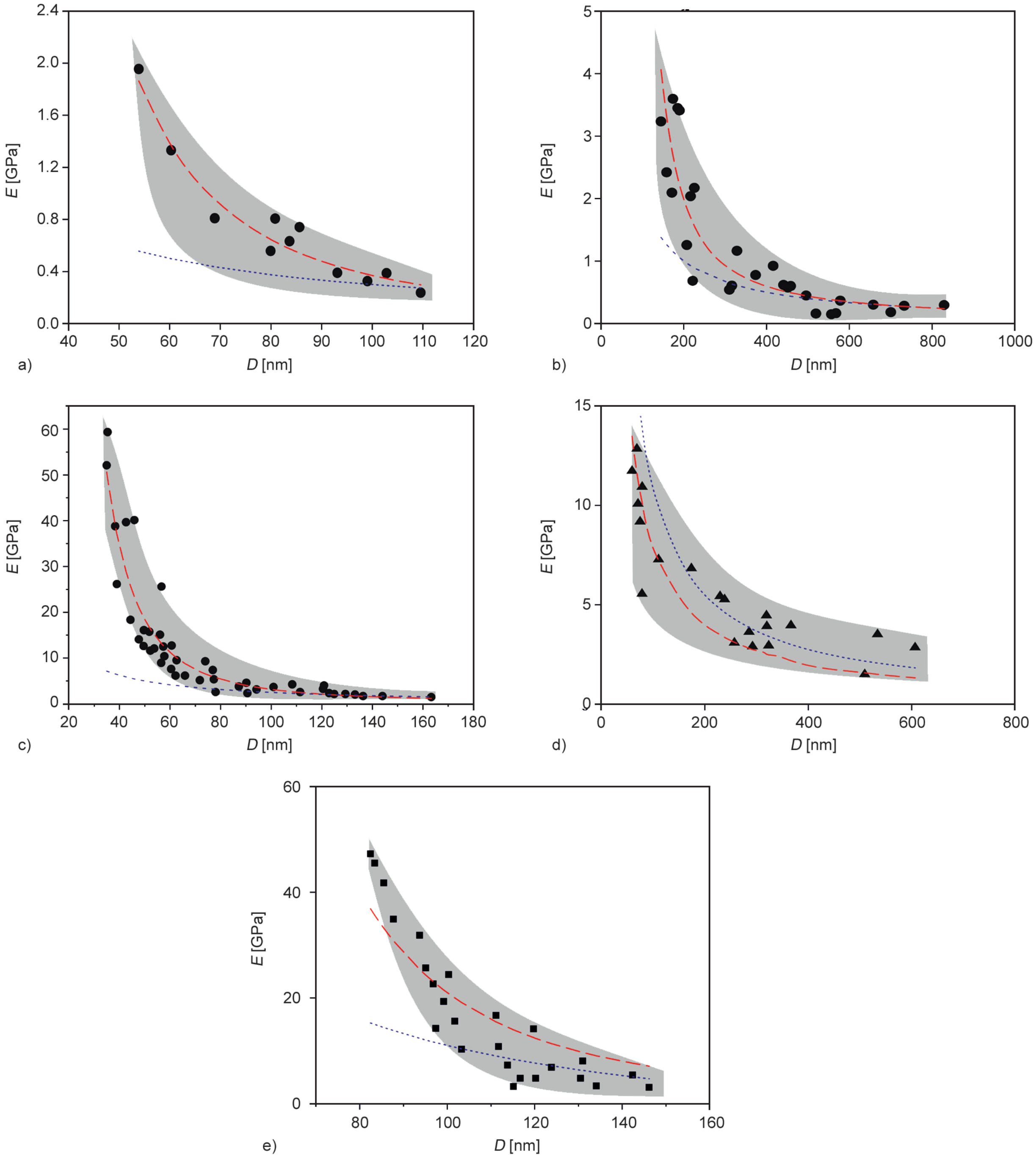

Figure 2. Comparison of the results of fitting by Equations (5) (blue dots) and (15) (red dash lines) with experimental data for various polymers: a) PAMPS [23]; b) Nylon 66 [24]; c) PPy [25]; d) PVA [26]; e) PAN [27]. Grey fields are areas of spreading experimental results. All experimental data were reproduced with permission.

increase in the elastic modulus of electrospun nanosize polymer fibers with a decrease in their diameter. Of course, more experimental evidence would be welcome.

4. Conclusions

In summary, we showed that the size dependence of the elastic modulus of electrospun nanoscale fibers from various polymers in all cases could be quantitatively described in terms of a core-shell model with a shell characterized by the stretching and curvature elasticity. This model turns out to be applicable to various polymer nanofibers and can be considered as a universal physical explanation of the phenomenon under discussion. The role of the shell (surface layer) was estimated on the base of a phenomenological consideration of the change in the surface free energy due to elastic deformation. This approach leads to a two-term equation describing the size dependence of the elastic modulus of nanofiber. The fitting parameters used in theory are reduced to the surface stretching modulus and the surface curvature elastic modulus.

The shell-core morphology is characteristic of all fibers spun from polymer solutions by the wet or dry-wet methods. The main reason for the difference in the structure of the shell and core is the mutual diffusion of the coagulant inside and the solvent outside the spinning jet/fiber. According to X-ray diffraction data in transmission and reflection modes [28], the shell is more ordered than the core, and the final fibers show the dependence of mechanical properties on diameter, increasing with decreasing thickness.

Acknowledgements

We acknowledge funding from Ministry of Science and Higher Education of the RF (Agreement # 175-15-2020-794. The authors are grateful for permission to use experimental data from Ref. [23, 24] to APS, from Ref. [25] to AIP, from Ref. [26] to Elsevier., and from [27] to ACS.

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