

MECHANICAL RESPONSES OF COMPLIANT POLYMER NANOFIBERS

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Introduction

Continuous nanofibers produced by electrospinning represent a new class of one-dimensional (1D) nanomaterials [1,2], as shown in Fig. 1. Due to their continuity, high surface area to volume ratio, and tailorable diameter (1-2,000nm), surface morphology and microstructures, electrospun nanofibers have found promising applications in nanocomposites, filtration, protective clothing, biomedical engineering and technologies, nanodevices, etc. [3-4]. Understanding of the mechanical behaviors of these nanofibers is fundamental to their broad applications. Recent high-resolution single-fiber tensile tests have evidenced that polymer nanofibers behaved differently from their large diameter and bulk counterparts [5-7], e.g. apparently size-dependent modulus and tensile strength and unique surface rippling when subjected to stretching. The interpretation and prediction of these unique mechanical properties requires new theoretical investigation.

In this study, the author developed a simple 1D nonlinear continuum mechanics model to take into account the combined effect of surface energy and nonlinear elasticity in the mechanical responses (e.g. deformation, wave propagation, and surface rippling, etc.) of compliant polymer nanofibers. This model can interpret a series of size-related mechanical phenomena as observed in polymer nanofibers, and can predict new surface stability conditions useful to nanofiber fabrication.

Problem statement and solutions

Static tensile deformation subjected to axial stretching

Consider a compliant polymer nanofiber as a circular cylinder at stretch-free state. Two configurations are adopted to describe the motion of a material point of the fiber, i.e. stretch-free configuration (with surface tension ignored) and current configuration subjected to finite axial stretch. The corresponding coordinates of the material point are denoted by (R, Θ, Z) and (r, θ, z) , respectively. Subjected to uniform axial stretching, the axisymmetric deformation can be described as:

$$\begin{aligned} r &= \lambda_1 R \quad (0 \leq R \leq R_0), \quad \theta = \Theta \quad (0 \leq \Theta \leq 2\pi), \\ z &= \lambda_3 Z \quad (-\infty \leq Z \leq +\infty), \end{aligned} \quad (1)$$

where R_0 is the initial radius of the stretch-free nanofiber (with surface-tension ignored), and λ_1 and λ_3 are the transverse and longitudinal stretches, respectively.

The constitutive law of the polymer nanofibers is modeled to follow that of isotropically, incompressible hyperelastic Mooney-Rivlin solid [8], which can be expressed as the Cauchy stress tensor T vs. the left Cauchy-Green tensor B corresponding to deformation (1):

$$T = -pI + 2c_1B - 2c_2B^{-1}, \quad (2)$$

where p is the hydrostatic pressure, and c_1 and c_2 are two material constants. The stress equilibrium equations are:

$$\partial T_{rr} / \partial r + (T_{rr} - T_{\theta\theta}) / r = 0, \quad \partial T_{\theta\theta} / \partial \theta = 0, \quad \partial T_{zz} / \partial z = 0. \quad (3)$$

Two traction boundary conditions (BCs) on fiber surface and along axial direction are evoked:

$$T_{rr} = -\gamma / r_0 \quad (r = r_0), \quad P = 2\pi \int_0^{r_0} r T_{zz} dr + 2\pi r_0 \gamma. \quad (4)$$

In the above, γ (N/m) is the surface energy of the amorphous polymer fiber which is assumed being independent of either the current fiber radius r_0 or the applied axial stretch λ_3 , and P is the axial tensile force. Solving (3) under BCs in (4) yields [9]

$$P = 2\pi R_0^2 (\lambda_3 - \lambda_3^{-2}) (c_1 - c_2 \lambda_3^{-1}) + \pi R_0 \gamma \lambda_3^{-1/2}, \quad (5)$$

which shows the surface/size effect in the axial deformation.

Longitudinal wave propagation in pre-stretched nanofibers

When considering longitudinal wave propagation in a pre-stretched polymer nanofiber, the dynamic motion is dealt with as a small disturbance superimposed on the axisymmetric deformation of the nanofiber given above in (1). The perturbed state is described by coordinates $(\tilde{r}, \tilde{\theta}, \tilde{z})$. Thus, for small disturbance, coordinates of a material point in the perturbed configuration can be described as

$$\tilde{r} = [\lambda_1 + f(Z, t)]R, \quad \tilde{\theta} = \Theta, \quad \tilde{z} = \lambda_3 Z + g(Z, t), \quad (6)$$

where $f(Z, t)$ and $g(Z, t)$ are two small time-dependent disturbance functions satisfying BCs in (4).

The governing wave propagation equation can be derived by using the principle of least action (Hamilton's law):

$$\delta \int_{t_1}^{t_2} L dt = 0, \quad \text{where } L = T - \Pi. \quad (7)$$

In the above, t_1 and t_2 are two arbitrary starting and ending times, L is the modified lagrangian, and T and Π are respectively the kinetic energy and potential energy of the nanofiber segment under consideration which are defined as

$$T = 1/4\pi R_0^4 \int_{t_0}^{t_0} \rho \dot{f}^2 dZ + 1/2\pi R_0^2 \int_{t_0}^{t_0} \rho \dot{g}^2 dZ, \quad (8)$$

$$\begin{aligned} \Pi &= 2\pi \int_{L_0}^{R_0} e R dR dZ + 2\pi R_0 \gamma \int_{L_0}^{R_0} (\lambda_1 + f)(\lambda_3 + g_z) dZ \\ &\quad - P \int_{L_0}^{R_0} (\lambda_3 + g_z - 1) dZ, \end{aligned} \quad (9)$$

in which \dot{f} and \dot{g} are respectively the transverse deformation rate (strain rate) and the axial translational speed of a material point, and ρ is the mass density, e is the strain energy density of incompressible hyperelastic Mooney-Rivlin solid defined by [8]

$$e = c_1 (I_1 - 3) + c_2 (I_2 - 3), \quad (10)$$

with I_1 and I_2 respectively the first and second invariants of the left Cauchy-Green tensor of perturbed deformations given in (6). The three terms in (9) are the contributions due to elastic strain energy, surface energy, and the mechanical work done by the axial force P , respectively. In addition, the integration with respect to Z runs over the entire length L_0 of the fiber segment under consideration.

After several variational operations and eliminating the higher order terms based on small perturbation assumption, the necessary condition for an extremum of functional in (7) leads to a linearized longitudinal wave propagation equation:

$$R_0^2 \rho \ddot{g}_{zz} - 8\lambda_3^3 \rho \ddot{g} - 2(c_1 + c_2 \lambda_3^{-1}) R_0^2 g_{zzzz} + 8(4c_1 + 2c_2 \lambda_3^3 + 6c_2 \lambda_3^{-1} - \gamma / (2R_0) \lambda_3^{1.5}) g_{zz} = 0. \quad (11)$$

To determine the wave dispersion relation, assume the travelling longitudinal wave to carry the mode:

$$g(Z, t) = A_0 \exp[ik(Z - ct)], \quad (12)$$

where A_0 is the complex amplitude of the wave disturbance, k is the wave number, and c is the wave phase speed. Substituting (12) into (11) yields the wave dispersion relation:

$$Ak^2 c^2 + Bc^2 - Ck^2 - D = 0, \quad (13)$$

where

$$A = R_0^2 \rho, \quad B = 8\lambda_3^3 \rho, \quad C = 2(c_1 + c_2 \lambda_3^{-1}) R_0^2, \quad (14)$$

$$D = 8[4c_1 + 2c_2 \lambda_3^3 + 6c_2 \lambda_3^{-1} - \gamma / (2R_0) \lambda_3^{1.5}]. \quad (15)$$

By introducing an *intrinsic length* l_0 [10] and the *reference wave phase speed* c_0 of the polymer material:

$$l_0 = \gamma / c_1, \quad c_0 = \sqrt{c_1 / \rho}, \quad (16)$$

Wave dispersion relation (13) can be recast as

$$\left(\frac{c}{c_0}\right)^2 = \frac{2[1 + (c_2 / c_1) \lambda_3^{-1}] k_0^2 + 8[4 + 2\lambda_3^3 + 6(c_2 / c_1) \lambda_3^{-1} - 0.5(l_0 / R_0) \lambda_3^{1.5}]}{k_0^2 + 8\lambda_3^3}. \quad (17)$$

In the above, if ignoring the transverse motion of the nanofiber in (8), the wave speed can be determined from (17):

$$(c / c_0)^2 = 4\lambda_3^{-3} + 2 + 6(c_2 / c_1) \lambda_3^{-4} - 0.5(l_0 / R_0) \lambda_3^{-1.5}. \quad (18)$$

Besides, in the limiting case of wave propagation in a stretch-free nanofiber ($\lambda_3=1$), i.e. infinitesimal deformation, relation (18) can be further simplified as

$$c = \sqrt{E_T / \rho - \gamma / (2\rho R_0)}, \quad (19)$$

where E_T is the tangential modulus of hyperelastic Mooney-Rivlin solid at $\lambda_3=1$:

$$E_T = 6(c_1 + c_2). \quad (20)$$

Relation (19) covers the case of longitudinal waves propagating in linearly elastic nanowires (with Poisson's ratio $\nu=0.5$) [11].

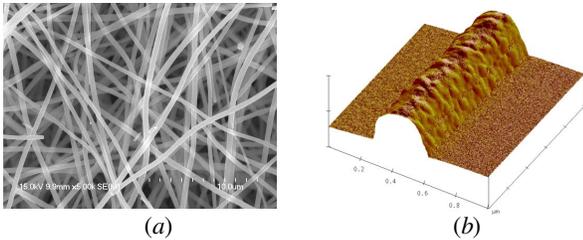


Fig. 1: Polyimide (PI) nanofibers (with diameter: ~ 250 nm) fabricated by electrospinning: (a) SEM micrograph of as-electrospun PI nanofibers and (b) AFM micrograph of a PI nanofiber after imidization, where surface ripples were induced by imidization and thermal stresses (Experiments were performed at University of Nebraska-Lincoln, 2008).

Surface rippling of nanofibers subjected to axial pre-stretch

Governing wave propagation Eq. (11) can be further used to study the surface rippling phenomenon as observed recently in compliant as-electrospun polyacrylonitrile (PAN) nanofibers subjected to axial stretching [4,5]. By eliminating the two inertia terms in Eq. (11), it decays to the equation governing the surface rippling:

$$Cg_{zzzz} - Dg_{zz} = 0, \quad (21)$$

where C and D are defined in (14) and (15). The ripple wave number k can be determined by assuming the rippling modes in the form:

$$g(Z) = B_0 \exp(ikZ), \quad (22)$$

where B_0 is the complex amplitude of wave disturbance similar to that in (12). Substituting (22) into (21) yields the ripple wave number as

$$k^2 = -D / C. \quad (23)$$

For physically meaningful rippling mode, k must be positive. This implies that surface rippling happens only under the condition of $D < 0$. Based on relation (23), the critical condition can be determined for surface rippling in compliant nanofibers:

$$R_0 < (l_0 / 4) / [2\lambda_3^{-1.5} + \lambda_3^{1.5} + 3(c_2 / c_1) \lambda_3^{-2.5}]. \quad (24)$$

Relation (24) can be further used to determine an important geometrical parameter in nanofiber fabrication, i.e. the minimum critical fiber radius $(R_C)_{\min}$, below which surface rippling happens spontaneously without any pre-stretch (i.e., $\lambda_3=1$). By setting $\lambda_3=1$ in relation (24), it yields

$$(R_C)_{\min} = \gamma / (2E_T) = (\gamma / 12) / (c_1 + c_2). \quad (25)$$

For typical rubbery polymer nanofibers, relation (25) gives $(R_C)_{\min} \approx 10-40$ nm. Apparently, below $(R_C)_{\min}$, compliant nanofibers cannot exist due to their surface instability (rippling). This indicates that it is physically impossible to fabricate compliant nanofibers with radius below $(R_C)_{\min}$. Detailed discussions on surface rippling in polymer nanofibers are available elsewhere [12].

Conclusion

The 1D nonlinear continuum mechanics model developed in this study can clarify the dependencies of axial deformation, longitudinal wave dispersion, and surface rippling condition in compliant polymer nanofibers upon the surface energy, nonlinear elastic properties, and fiber diameter. The results obtained in this study can be utilized as the theoretical basis of dynamic characterization of compliant nanowires/nanofibers, nanodevice design, etc.

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