CONFINEMENT MECHANISM OF AS-SPUN POLYMER NANOFIBER REINFORCEMENTS

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A model describing a mechanism resulting in size-dependent behavior of electrospun polymer nanofibers under small deformation is proposed. According this model, the nanofiber polymer matrix contains anisotropic regions consisting of directional-correlated wormlike subchains, partially orientated along the fiber. These ordered regions have no clearly delineated boundaries and smoothly transfer one into another. Nevertheless, in order to introduce an effective internal structure of as-spun polymer nanofibers, these ordered regions can be approximated by ellipsoids with one long, $l_{||}$, and two short, d_f. These ellipsoids, separated from neighboring ones by thin amorphous layers, play the role of elements reflecting the supermolecular structure of polymer matrix of as-spun nanofibers. Note that the properties of the introduced ellipsoids are anisotropic: in direction of the long axis the elastic modulus, $E_{||}$, is much higher than in perpendicular directions, E_{am} ($E_{||} >> E_{am}$), and this fact is of great importance for our concept.
Assuming these ellipsoids as structural elements of the polymeric matrix, one can depicture the following effective internal structure of as-spun nanofibers. The nanofiber can be considered as a composite consisting of anisotropic particles (the above effective ellipsoids), surrounded by a binder (thin amorphous polymer layers) (see Fig. 1).

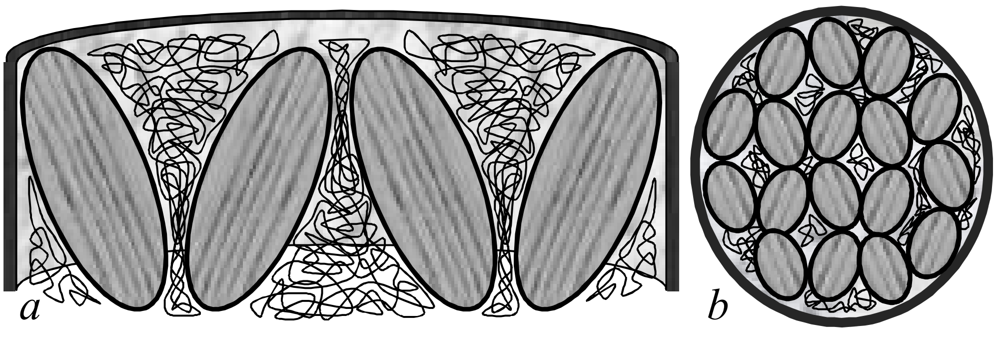

Fig. 1. Schematic internal structure of as-spun polymer nanofibers: a cross-section along a fiber (*a*); and a cross-section across a fiber (*b*).

A fiber elongation under external force is accompanied by relative rotations of the above ellipsoids. The ellipsoid rotation occurs because of a moment arising due to local stress. This moment strives to decrease the angle between long ellipse axis, $l_{||}$, and fiber axis. At the same time, the relative displacement of neighbor ellipsoids results in arising of a moment having the opposite sign, so the rotation angle corresponds to the equality of these two moments. Confinement effect is that the above rotations are hindered by the fiber surface layer; and this fact is to be taken into account by boundary conditions. As a result the elastic modulus depends on the diameter of the deformed fiber. In case of small fiber diameters this restriction is dominant while the effect decreases with increase of fiber diameter, and tends to zero for large fiber diameters according to square-law and such behavior is in good agreement with the experimental dependences.