SELF-ASSEMBLY OF MACROMOLECULES IN A LONG AND NARROW TUBE

by

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Many nature materials have hierarchical structure, and its last cascade is always on a molecule scale, e. g., double-stranded DNA, making the hierarchy effective with minimal building blocks. Now artificial hierarchy can begin with a nanoscale level to embody the material with remarkable and fascinating properties which can be never achieved using non-hierarchical structure. A strong desire to fabricate some biomimicking hierarchies from a molecule level has been stimulating scientists. Herein we show that molecular structure can be easily controlled by a long and narrow tube, and self-assembly of macromolecules can be achieved to improve its crystallinity with plenty of excellent properties. We anticipate this paper to be a starting point for more sophisticated fabrication of fibers with self-assembly of macromolecules.

Key words: *biomimetic materials, spider silk, fractal, nanofiber, nanoscale porous materials, electrospinning, fractal harmonic law, math-biomimics, Angstrom technology*

Introduction

Spider silk is a protein fiber, which is extremely strong and extraordinarily flexible [1-4], its hierarchical structure with an approximate 3-fold symmetry plays the key role in the nature fiber's excellent properties [5, 6]. There is a very long extrusion duct to convert the protein into the thousands of spinnerets, the duct serves as a molecular switch to control fiber assembly [7, 8], additionally, the pH value changes along the duct, which is another factor to control the self-assembly of spider silk proteins [9].

It is astonishing that the nature silk consists of only very limited number of building blocks called *spidroins* and their geometrical structures are responsible for the nature silk's highly specialized properties, for example, a double-stranded DNA is of remarkable structure stability and excellent mechanical and thermal properties [10, 11]. Geometrical potential [12, 13] can explain many natural phenomena geometrically, and the intermolecular interactions (chain entanglement, geometrical potential, friction, and hydrogen bonds) between repeat building blocks provide strength and elasticity [10, 11].

A strong desire to bio-mimic new materials has been attracting attentions from material community, and various attempts have been made, but many failed. For example, the spidroin or spider silk protein was extracted to fabricate nano/micro fibers by electrospinning, but the artificial fibers have nothing to do with their natural partner [14].

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So far, no research has been attempted to improve the mechanical properties of artificial fibers by mimicking molecule structures because of neither theory nor technology that can make the macromolecules in a needed order in the spinning process, a suitable molecule matrix can greatly enhance the artificial fiber's mechanical property. This report aims at intentionally organizing a molecule matrix in an artificial fiber using a simple theory in fluid mechanics.

Laminar flow

In fluid mechanics, a laminar flow admits a parallel layer motion with different velocity profile. We assume that a flow in a long and narrow tube is laminar, and the velocity profile on the tube section can be expressed [15]:

$$u(r) = \frac{\Delta P}{4\mu L}(R^2 - r^2) \tag{1}$$

where r is the distance from the tube axis, R – the tube radius, ΔP – the pressure difference imposed at the two ends of the tube, L – the tube length, and μ – the viscosity coefficient.

Equation (1) reveals that the velocity on the tube boundary ($r = R$) is zero, and it reaches maximum at the tube center ($r = 0$). Macromolecules in the laminar flow will gradually straightened along the tube and then will be organized in a good order. Consider a macromolecule in a laminar flow, which locates randomly in a tube, the part near to the center moves fast than the left part near to the boundary, as a result the macromolecule is stretched, and gradually macromolecules are arranged periodically.

Experimental design and experimental results

In order to control the self-assembly of macromolecules by laminar flow, polyvinyl alcohol (PVA) solution was used to fabricate nanofibers by electrospinning, the set-up is same as that in our previous publications [16, 17]. The PVA is a macromolecule with chemical formula $[CH_2CH(OH)]_n$. It is widely used in nanotechnology, energy, tissue engineering, textile engineering, papermaking, and a variety of coatings.

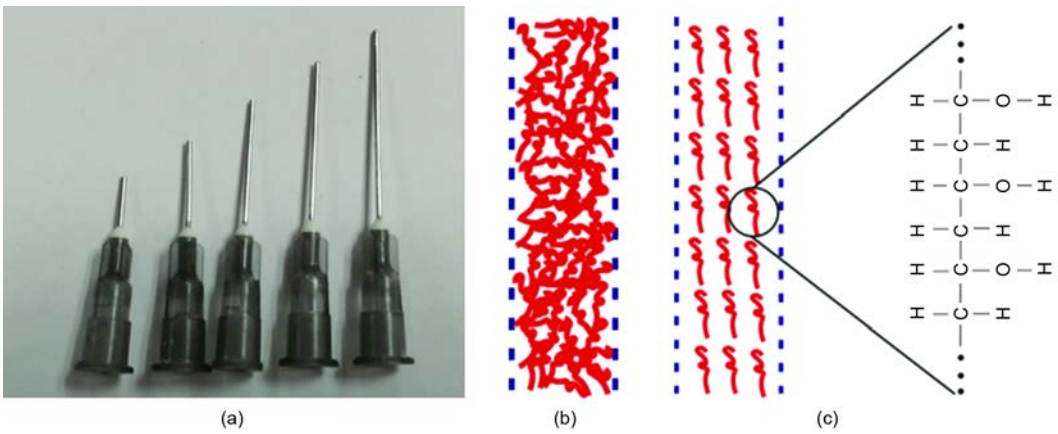

Figure 1. Tube samples (a) and chain distribution of PVA solution in the tube, (b) amorphous chains in a short tube, and (c) periodic chains in a long tube

In our experiment, all spinning conditions are kept unchanged except the tube length. We use the tube length to control the laminar flow, an infinite long tube produces a fully developed laminar flow for macromolecules as shown in fig. 1(c), while we assume that macromolecules are distributed randomly on a very short tube.

The tube length in our experiment varies gradually from 6 mm to 26 mm, and mechanical property and wetting property of the obtained nanofiber membranes are measured. Experimental results show that tube length affects greatly the mechanical property but has little effect on wetting property.

A tearing test was carried out to measure the mechanical property of the obtained nanofiber membranes, the experimental set-up is illustrated in fig. 2(a) and the stress-strain relationship is given in fig. 2(b). It is shown that the tear strength and toughness are greatly improved for the long tube where the self-assembly of PVA macromolecules is achieved. The periodicity of PVA chains as illustrated in fig. 1(c) will greatly enhance the tear strength. During the tearing process, the parallel chains are entangled with each other, this will remarkably increase the intermolecular interactions, as a results the tear strength increases for a long tube as illustrated in fig. (2b). Toughness is conferred by the presence of controlled interfacial features (geometrical potential, chain entanglement, friction, hydrogen bonds). During the tearing process, the friction among chains, the entanglement of chains and geometrical potential between adjacent chains will extremely increase toughness. The parallel molecules under the tearing force will be entangled with each other, this greatly increase intermolecular interaction. Therefore, a longer tube predicts a better toughness of the obtained nanofiber membrane.

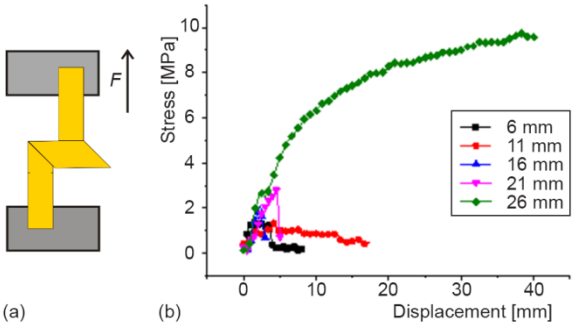

Figure 2. Tearing process (a) and the stress-strain relationship for different tube lengths from 6 mm to 26 mm (b) (*for color image see journal web site*)

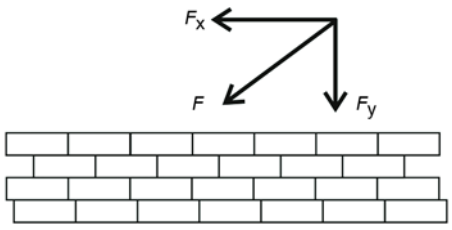

Figure 3. Periodic molecular chains under force

The mechanical property can be explained by assimilating molecular chains to wall bricks, and fiber to wall, see fig. 3. The bricks have rather meager properties, but the wall is stable under different forces.

Wetting property can be described by the contact angle (CA). Each sample was measured five times and its average value was used in our experiment. The wetting property of each sample was given in fig. 4.

It is obvious that the tube length also affects nanofiber membrane's wetting property. The main effects affecting the CA are fiber diameter and fiber's surface morphology. Smaller fibers predict a larger CA, while the parallel molecules on the fiber's surface will introduce a geometrical potential, and a boundary-induced force is produced alone the fiber axis acting on the water drop, as a result a larger CA is predicted. While the tube length affects

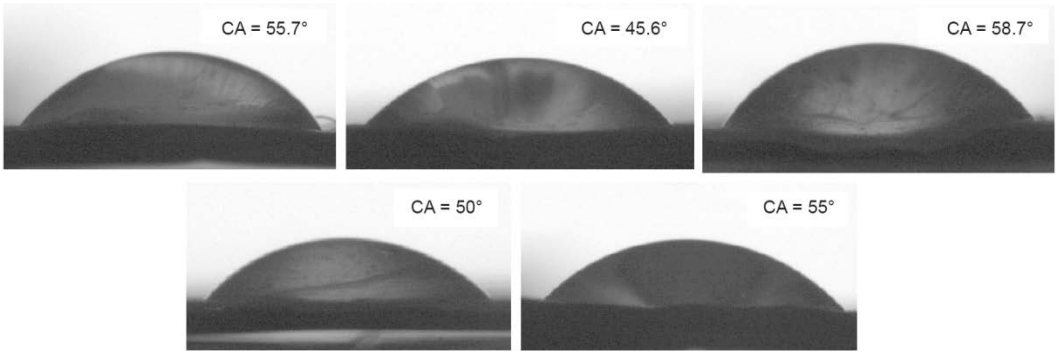

Figure 4. Wetting property of each sample with different tube lengths from 6mm to 26 mm

both factors in the electrospinning process, the combined effect of fiber's morphology and fiber's diameter on wetting property makes the theoretical analysis much complex, and a more sophisticated experiment is still needed for further theoretical and experimental analyses.

Hierarchical structure *vs.* fractal structure and math-biomimetic materials

Nature materials with hierarchical structure always behave excellently, a hierarchical structure should have at least three cascades, and it can be considered as a fractal structure, see fig. 5. If an artificial material has exactly same hierarchical structure with the nature one, we call it as a replication material, which should have the same properties with those of the nature one. Such replication is always very difficult, because each cascade might have special structure which can not be realized by any modern technologies. For example, the hierarchical structure of a gecko foot consists of main three cascades: a gecko toe, setae, and spatula. On the other hand, the last cascade of a natural hierarchy is always on a molecule scale or Angstrom scale, so to replicate each cascade to fabricate an artificial material is almost impossible. A hierarchy beginning from a molecule scale cascade can save much building blocks.

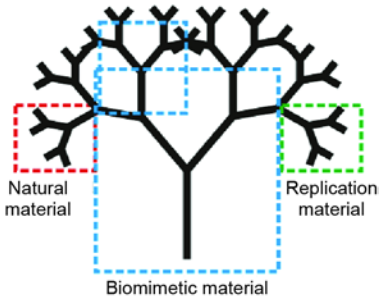

Figure 5. Hierarchical structure *vs.* fractal structure; the middle two closed hierarchies imply biomimetic materials on different scales

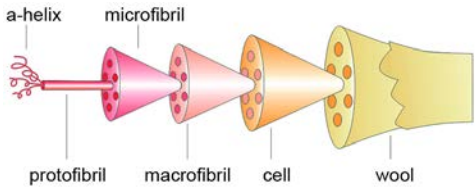

Figure 6. Hierarchy of a wool

For design of a biomimetic material, it is important to have same cascade number and same fractal dimensions with its natural partner, this is required by the fractal harmonic law [18, 19], and we call such biomimics as math-biomimics. Figure 5 shows two hierarchical structures on different scales to bio-mimic the natural hierarchy. As an example, we consider the hierarchical structure of a wool [20, 21] as illustrated in fig. 6, the fractal dimension of the hierarchy is 1.618, the golden meaning. This hierarchy has excellent thermal property for

the excellent one-way heat conduction. For math-biomimics, we should design a hierarchy with same fractal dimension of 1.618 [18, 19].

Conclusions

This paper gives a new trend from nanotechnology to molecule scale technology or Angstrom technology by controlling molecule's structure in the spinning process. If a hierarchy begins with a molecule level, the materials requires extremely less building blocks than that beginning with a higher level. In this view, nature hierarchical structures are optimal to achieve a needed property, and the math-biomimicking is to design a hierarchy with same fractal dimension with that of the natural one.

In nature, molecule structures are always incorporated in the protein structures of some biomaterials as the last cascade of the hierarchy, leading to unusual mechanical, thermal, electronic and light properties. The self-assembly of macromolecules in many biomaterials serve as the simplest material blocks, though the molecular blocks have meager properties, the hierarchy always has outstanding bio-functional properties. Nanotechnology provides scientists with a nanoscale block to fabricate artificial hierarchies, by controlling nanofiber's diameter or nanoporous size on the fiber's surface [20-25]. Now the Angstrom technology sheds a new light on controlling molecule structure in the spinning process like that in the extrusion duct of a spider, and bio-inspired hierarchical structural materials with needed properties can be fabricated.

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