TECHNICAL ARTICLE

Experimental Study of the Mechanical Properties of a Novel Supramolecular Polymer Filament Using a Microtensile Tester Based on Electronic Balance

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Abstract

A novel kind of supramolecular polymer filament with a diameter of 2–5 μm was artificially synthesized, which is in fact a bundle of self-assembled nanotubes with a diameter of about 40 nm. The filament can be drawn from a special alkaline aqueous solution directly and free standing in room temperature, which has never been performed earlier. A microtensile tester was developed with the aid of an electronic balance to investigate the mechanical properties of the new filament. Monotonic and load–unload tensile tests were performed, respectively. The maximum tensile strength and the elastic modulus of the filament were 23.8 MPa and 1.9 GPa, respectively, which were higher than previous supramolecular polymers and comparable to some covalent-linked polymers.

Introduction

Supramolecular polymers are made by the self-assembly of many monomeric units with directional and reversible non-covalent bonds.[1] They have a wide range of applications in biomaterials,[2–4] smart materials,[5,6] medicines,[7–9] electronic devices,[10,11] and optical technologies.[12,13] Because of their highly organized nanostructures, supramolecular polymers present many advantages, such as molecular operability, cycle applicability, self-healing properties, and molecular recognition.[14] However, until now, most supramolecular polymer filaments are not free standing, which may bring out poor mechanical properties and may limit their applications.

In this paper, a kind of free-standing supramolecular polymer filament, with a diameter of 2–5 μm, was artificially synthesized. We have found that an L-histidine-terminated bolaamphiphile could self-assemble into supramolecular polymer filaments in slightly alkaline aqueous solution (pH 8–9). Then, the supramolecular polymer filament could be drawn from the aqueous solution by a needle directly. It is in fact a bundle of hollow nanotubes self-assembled by non-covalent bonding, which may mean a weaker tensile strength. However, the phenomenon of free standing indicates a better tensile strength. Further experimental study is needed to investigate the novel supramolecular polymer filament.

However, the test force should be very tiny (much less than 10^{-3} N), estimated according to the diameter of the filament and the strength of some superpolymers. The commercial material testing machines, such as INSTRON 5848 Micro Tester (INSTRON, Norwood, MA, USA)[15] and SIROLAN-TESTER (CSIRO, Australia),[16] have no sufficient force resolution for this test due to the strain-gaged force transducer.

In order to acquire enough force resolution, more sensitive elastic components are adopted as a substitute for the strain-gaged force transducer, such as the atomic force microscope (AFM) cantilever,[17−20] microelectromechanical system (MEMS)-based cantilever[21−23] and other specially designed film cantilevers.[24,25] These cantilevers have good force resolution and are suitable for the tensile tests of microscale filaments. However, it is difficult to install the specimen because the sensitive elastic component is fragile and small in size.

In addition to the above apparatuses, another kind of apparatus is designed based on electromagnetism. A coil-magnet component is adopted as actuator, as well as force transducer.[26−30] In this way, the tiny force can be easily measured by recording the currents in the coil. In fact, there are two kinds of design, namely moving coil or moving magnet. The former have a better force linearity in a long displacement range than the latter.[26] This technique has been applied commercially, such as MTS NanoBionix[31,32] (now taken over by Agilent, Santa Clara, CA, USA). It has the distinct advantage of perfect force resolution, low hysteresis, and easy control. However, a spring with a stiffness of about 80 N/m is used to support the moving mass in order to avoid bearing friction, which seriously limits the testing ability of small stiffness specimens.[33] In this paper, a new microtensile tester was developed with the aid of an electronic balance in order to test the novel supramolecular polymer filament. This tester is suitable for tensile test of microspecimens with very low stiffness, and is easier to manipulate. Moreover, the electronic balance has ideal force accuracy without additional calibration.

Experiments

Specimen

In slightly alkaline aqueous solution (pH 8–9), EDH (*N*,*N*-eicosanedioyl-di-L-histidine) can assemble into extremely long supramolecular nanotubes with a length-to-diameter ratio of more than 5000. These nanotubes are randomly distributed and nicely separated from each other. The internal diameters and wall thicknesses of nanotubes are about 22 and 10–14 nm, respectively. When a needle is put into the solution and carefully lifted out of the liquid surface, a supramolecular filament with length of about several centimeters can be dragged out directly. More details are described in Ref. 34. The SEM inspections show that the filament has an approximately uniform diameter of 2–5 μm (Fig. 1(a)). The magnified view demonstrates that the filament is constructed by many well-aligned hollow nanotubes. The microstructure is illustrated in Fig. 1(b). Each supramolecular polymer filament is speculated to contain at least 2000 nanotubes as the single nanotube's outer diameter is about 40 nm.

Apparatus

In order to investigate the mechanical properties of the novel supramolecular polymer filaments, a microtensile tester was constructed using an electronic balance (Fig. 2).

The actuator of the tester is a step motor, which has a step of about 1.2 μm per pulse with a stroke of 30 mm. The force is measured by using an electronic balance with a readability of 0.1 mg and a measurement range of 120 g. This means that the force resolution is about 1 μN and the force range is about 1.2 N. More details of force measurement will be described in the following. The displacement of the step motor is measured by a linear variable differential transformer (LVDT) with a resolution of 0.1 μm in 2 mm displacement range. It should be noted that the electronic balance must be isolated from the tester's main frame in order to avoid the motor's vibration.

The upper grip is a metal hook linked to the core rod of LVDT, whereas the lower grip is settled on the electronic balance. Before testing, the filament is attached to the upper and lower grips with a relaxed state. At this time, the reading of the balance is the mass M of lower grip. Then, the step motor drives the upper grip, the filament specimen is stretched, and the reading of the balance will be changed to M_N. The force F applied on the filament can be easily calculated by Eq. (1):

$$F = (M - M_N)\,g \tag{1}$$

where the gravity acceleration g at Beijing, China, 39°55′N and 116°55′E, is 9.8012 N/kg.

At the same time, the displacement of the upper grip is measured by the LVDT, which is regarded as the extension of filament.

Testing procedure

Firstly, the supramolecular polymer filament was drawn from the aqueous solution by using a needle, and then rolled to the grips directly. It should be noted that the filament specimen must be kept relaxed before extension. The gage length of the specimen was about 10 mm. Special care must be taken to align the filament accurately between the two grips.

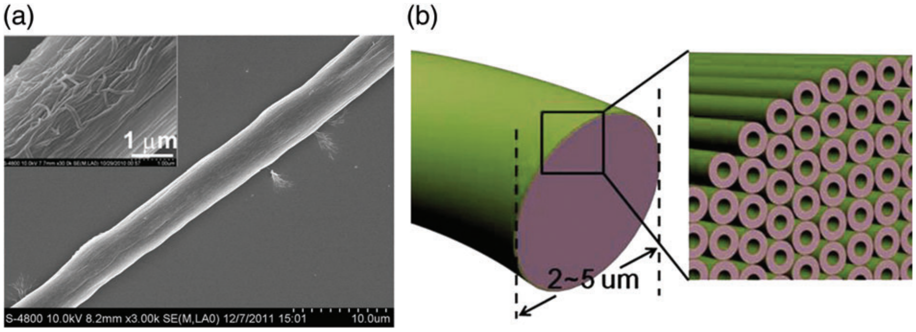

Figure 1 Illustrations of the supramolecular polymer filament. (a) SEM photograph and (b) structure diagram in microscale. The filament is actually constructed by many well-aligned hollow nanotubes.

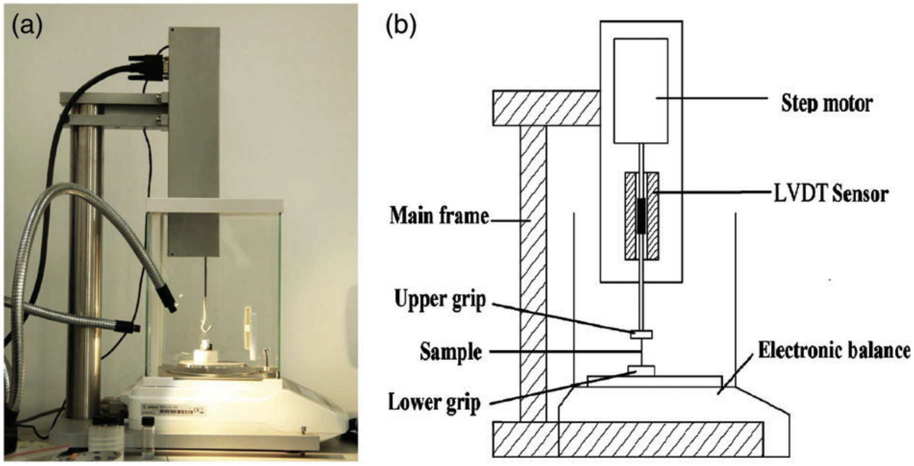

Figure 2 Illustration of the experimental apparatus. (a) Photograph and (b) schematic arrangement. The force is measured by the electronic balance, and the displacement is measured by the LVDT sensor.

Monotonic tensile tests were carried out on the tester. The force–displacement curves were recorded automatically, and then converted to engineering stress–strain curves by taking the cross sectional area and the gage length into consideration. All the specimens were tested at room temperature and a strain rate of 10^{-3}/s. In order to ensure enough balance time, there is 3-s interval between the two steps of motor.

In addition, load–unload tensile tests were carried out at a strain rate of 10^{-3}/s to further investigate the deformation mechanism of the filament. The maximum extension of each load–unload loop was set to increase about 10 µm per loop until the filament broke. Similarly the force–displacement curves were recorded automatically, and the corresponding engineering stress–strain curves were obtained.

Results and Discussion

Monotonic tensile tests

The test results of four specimens are shown in Fig. 3. The results exhibited good linear extension behavior. No plasticity was observed. The slopes of these curves were similar, which indicated the good repeatability of the tests. The mean Young's modulus of about 1.9 GPa was calculated. The maximum tensile strength scattered from 10.9 to 23.8 MPa, which was higher than that of previous supramolecular polymers, such as $PCL_{2000}UPy_2$ (7 MPa),[35] and even closed to some covalent-linked superpolymers, such as polypropylene random copolymer (about 30 MPa).[36] The scatter of the data may be caused by the uncertain defects of the specimen or the damage of grips.

The failure mode of the supramolecular polymer filaments was brittle fracture, different from most superpolymer filaments. The SEM fractography (Fig. 4) clearly showed that almost all nanotubes were fractured at the same cross section, without any necking and longitudinal splitting. This phenomenon is directly related to the self-assembly microstructure of the non-covalent bond.

Load–unload tensile tests

A typical load–unload curve is shown in Fig. 5. The results clearly showed that the load and unload curve coincided very well, which means a good resilience properties of the filaments. Moreover, it can be deduced that the elongation of the filament results

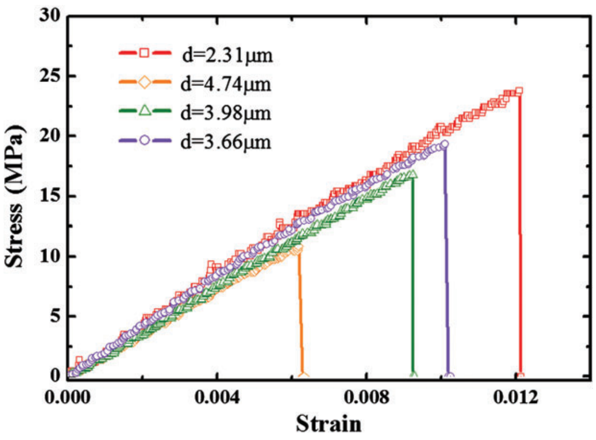

Figure 3 Stress–strain curves of four specimens with different diameters and gage lengths.

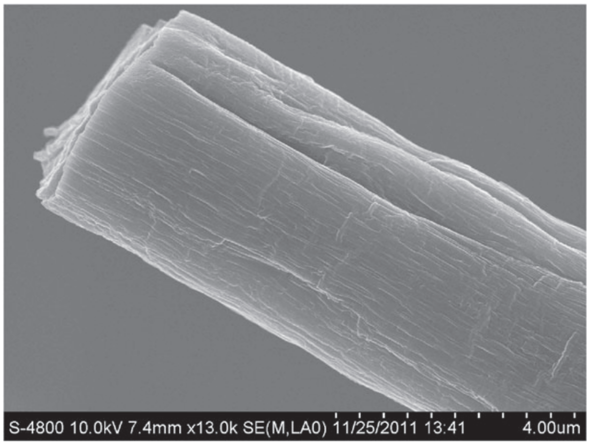

Figure 4 SEM photograph of the fractured specimen.

from the elastic deformation of the nanotubes, rather than sliding among them.

Conclusions

In this study, a novel kind of free-standing supramolecular polymer filament, with a diameter of 2–5 μm, was artificially synthesized. A new microtensile tester was developed with the aid of an electronic balance to investigate the mechanical properties of the filament. Monotonic tensile tests and load–unload tensile tests were performed, respectively. The specimens exhibited good linear extension behavior and good resilience without any plasticity. The failure mode was brittle fracture. Of note was the maximum tensile strength and the elastic modulus of the filament were as high as 23.8 MPa and 1.9 GPa, respectively, which were much higher than previous supramolecular polymers and even comparable to some covalent-linked polymers.

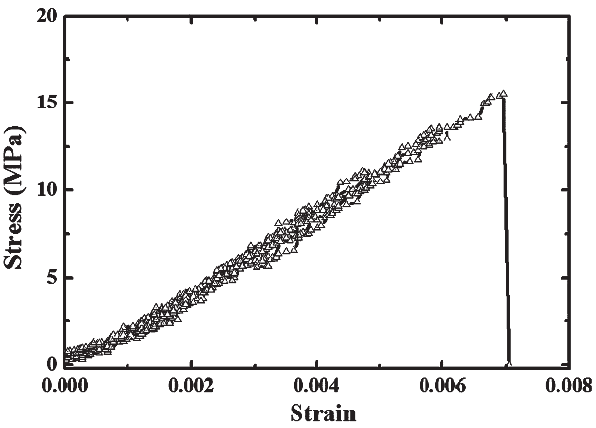

Figure 5 Load–unload tensile test results of the supramolecular polymer filament.

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