Fabrication of Multilayered Hollow Nanofibers and Estimation of Its Young’s Modulus

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Hollow multilayered polyelectrolyte (PE) fibers were fabricated by the combination of the electrostatic layer-by-layer (LBL) and electrospinning methods. The influence of the deposition conditions on the structure of the obtained hollow multilayered PE fibers was studied systematically. The results showed that the formation of multilayered PE films on polystyrene (PS) fiber surface was strongly influenced by the number of repetitions of deposition and the pH value. The spaces among the adjacent fibers in fibrous mats were blocked by 15 poly(allylamine hydrochloride) (PAH)/poly(styrenesulfonate) (PSS) bilayers. The film growth speed was the highest in a strongly acidic solution. The theoretical Young’s modulus of such a hollow multilayered PE nanofiber was also obtained to be around 21.6 GPa, which is much larger than that of normal synthetic organic fibers but is similar to that of human bone fibers. [DOI: 10.1143/JJAP.46.6790]

KEYWORDS: hollow fiber, layer-by-layer, electrospinning, multilayer, Young modulus

1. Introduction

Silver ragwort Senecio cineraria growing around the Mediterranean Sea is a white-color plant. Its color is not due to any dye substance but is related to trichomes on the plant surface. Some scientist have studied its leaf surface by scanning electron microscopy (SEM) and found that the surface was strongly influenced by the number of repetitions of deposition and the pH value. The spaces among the adjacent fibers in fibrous mats were blocked by 15 poly(allylamine hydrochloride) (PAH)/poly(styrenesulfonate) (PSS) bilayers. The film growth speed was the highest in a strongly acidic solution. The theoretical Young’s modulus of such a hollow multilayered PE nanofiber was also obtained to be around 21.6 GPa, which is much larger than that of normal synthetic organic fibers but is similar to that of human bone fibers. [DOI: 10.1143/JJAP.46.6790]

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1. Introduction

Silver ragwort Senecio cineraria growing around the Mediterranean Sea is a white-color plant. Its color is not due to any dye substance but is related to trichomes on the plant surface. Some scientist have studied its leaf surface by scanning electron microscopy (SEM) and found that the plant was densely covered with a layer of woven hollow fibers with diameters of 1–10 μm. These hollow fibers are responsible for the white color of the plant. One of the characteristics of the trichomes is that it is highly resistant to the strong irradiation of sunlight and therefore they protect the plants from damage due to strong sunlight. Because of the existence of these hollow fibers, the leaf temperature can be several degrees lower than that of other nearby plants under strong sunlight, and overheating can be avoided in the summer. In order to imitate and reproduce the functions of these hollow fibers, scientists in the material and chemical fields have developed a number of methods to produce hollow fibers. For instance, organic tubular nanostructures have been fabricated by the self-assembly of molecular building blocks. Nanotubes of large sizes are usually fabricated by templating against nanowires, nanofibers, or channels in porous membranes. Another novel method is to obtain hollow fibers by exploiting electrohydrodynamic forces that form coaxial jets of liquids with microscopic dimensions by injecting two immiscible or poorly miscible liquids through a pair of concentric needles to which a high voltage is applied. Such hollow fibers can also be used in filters, sensors, biocatalysts, protective clothing, wound dressings, artificial blood vessels, controlled drug delivery systems, filters, and tissue engineering.

2. Materials and Methods

2.1 Materials

The sources of chemicals were as follows: poly(styrene-sulfonate) (PSS; Mn 70,000), poly(allylamine hydrochloride) (PAH; Mw 70,000), and tetrahydrofuran (THF) were obtained from Aldrich. All these materials were used as received. NaCl and polystyrene (PS) were bought from Saiji Company (Nanjing).

The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18.2 MΩ·cm⁻¹.
2.2 Fabrication of polystyrene nanofiber mats by electrospinning

PS particles were dissolved in N,N-dimethylformamide (DMF) at concentrations of 10, 15, 18, and 24%. Then the solution was quickly loaded into a syringe equipped with a five gauge stainless-steel needle that was connected to a high-voltage supply capable of generating voltage up to 10.3 kV. The feeding rate of the precursor solution was controlled to 1.0 ml/h using an automatic syringe pump. A plate used as the collector was placed 15 cm from the tip of the needle for the collection of the nanofibers. The electrospinning apparatus is shown in Fig. 2. The solution was ejected as fibers from the tip of the needle were ejected as fibers under a strong electric field towards the collector. PS fibrous mats used to study the effects of the number of deposited films and pH were made from 15% PS solution.

2.3 Construction of hollow multilayered PE nanofibrous mats

PSS and PAH solutions used for the adsorption of the template were prepared in Milli-Q water at a concentration of 1.0 mg/mL in 0.5 M NaCl. An agglomerate of PS fibrous mats was selected as a template and immersed alternatively in PAH solution and PSS solution. After every step, to allow the adsorption of the polyelectrolyte, 30 min. was left and then rinsed with liberal amounts of water. When the expected (PAH/PSS)$_n$ bilayers numbers was attained, the multilayered polymer-coated PS fibers were immersed in THF (2 mL) solution for 5 min to remove the PS core. To remove the excess solution, the sample was centrifuged at 1000 rpm for 3 min and then washed with THF two times. Finally, the sedimentation was redispersed in water for the next measurement. From our previous results, we know there are very small agglomerates at the bottom and some very small fragments in the supernatant. The small fragments are very short hollow tubes, while the agglomerate at the bottom comprises the hollow multilayered PE fibers. In this work, we only study the hollow multilayered PE fibers.

2.4 Measurements by SEM and material elemental analysis

The obtained hollow multilayered PE fibers and (PAH/PSS)$_n$-coated PS fibrous mats, were observed by SEM (1530 VP, LEO, Germany), with a material elemental analysis device (Oxford Inca-Sight).

2.5 Measurements of Fourier transform infrared spectra

Fourier transform infrared (FTIR) spectra were recorded by time resolved FTIR spectroscopy (IFS66/S, Bruker, Germany) in the wave-number range of 500 – 4000 cm$^{-1}$ under room conditions.

3. Results and Discussion

3.1 Influence of number of multilayered PE films on nanofibers

Typical electrospun nanofibrous mats composed of polymer nanofibers have a three-dimensional (3D) structure with pores of micron or submicron size. Different from other
supports, the amount of deposition space among adjacent nanofibers in PS nanofibrous mats is limited. It is necessary to study the suitable deposition parameters for the fabrication of the desired hollow multilayered PE nanofibers.

To investigate the influence of the number of multilayered PE layers on the morphology of multilayered nanofibers, PS nanofibers were deposited with 2, 4, 10, 15, and 20 PAH/PSS bilayers. SEM images of PS nanofibers coated with various numbers of PAH/PSS bilayers are shown in Fig. 3. From Figs. 3(a)–3(c), one can see that with an increase in the number of deposited PEM layer, the morphology of the fibers was retained even after coating 10 PAH/PSS bilayers. Figure 3(b) shows that some multilayered PE films were sometimes formed in two adjacent fibers, possibly because such fibers are conjointed in fibrous mats. There are some crystals on the fiber surface [Fig. 3(b)]. According to the results of element analysis, they are NaCl crystals that can be removed by increasing the number of wash cycles (shown in Table I). Figure 3(c) shows that although the fiber shape can be maintained after coating 10 bilayer PE films, the surface became much rougher than that with fewer layers.

The fiber looses its shape after coating 15 or 20 PAH/PSS bilayers because the multilayered films formed not only on the fiber surface but also in the region between adjacent fibers. The PS nanofibers were embedded in the hybrid multilayered films, which was largely due to the limited amount of space among the adjacent fibers and the 3D growth of hybrid films along the PS fibers. The tip of the 1, 2, and 4 PAH/PSS bilayer coatings on the fibers are shown in Figs. 4(a)–4(c). In Fig. 4(a), the brushlike part is bare PS, and the part around it is PAH/PSS film. Therefore the tip of the fiber is partly coated by PAH/PSS film. When the number of layers is increased to 2, the PE film can cover the fibrous tip completely [Fig. 4(b)]. However, because the coating layer is very thin, the brushlike part still can be distinguished clearly. When the deposition number is increased to 4, the multilayered PE films completely cover the fibrous part and the brushlike part disappears. Finally, only the smooth multilayered films on the fibrous head part [Fig. 4(c)] are seen. From Figs. 4(a)–4(c), one can see that with an increase in the number of deposition cycles, the multilayered PE film grows.

FTIR spectra of the (a) 2-bilayer-coated PS nanofibers (solid line) (b) 4-bilayer-coated PS nanofibers (three point segment line), and (c) 10-bilayer-coated PS nanofibers (two point segment line) were shown in Fig. 5. The absorption peaks are similar to each other. The peaks at 3445 and 1185.63 cm\(^{-1}\) were assigned to –OH and –S=O stretching, which means that PAH and PSS exist on the fibrous surface. The peaks at 1415, 1467, 1514, and 1612 cm\(^{-1}\) are attributed to the aromatic ring’s characteristic absorptions.

### 3.2 Influence of pH on formation of multilayered PE films on nanofibers

In order to investigate the influence of the pH value on the formation of the hybrid films, the number of layers was kept at four bilayers, and three types of solutions: strongly acidic solution with a pH of about 2.5, neutral solution with a pH of about 7.5, and strong basic solution with a pH of about 10.5
were employed. The SEM images are shown in Figs. 6–8, respectively. The SEM images reveal that the fiber shape was well retained under the three different deposition conditions. The head parts of the three types of multilayered-PE-coated PS fibers are shown in Figs. 6(a)–8(a). Comparing these three images, one can see that the growing speed of multilayered PE films was highest under the strongly acidic condition, intermediate under the strongly basic condition, and the lowest under the neutral condition. This result is similar to that obtained for a plane substrate. 20)

3.3 Fabrication of hollow multilayered PE fibers

In order to study the influence of the number of deposited layers on the shape of the hollow multilayered PE fibers, PS fibrous mats coated with \((\text{PAH/PSS})_n\) \((n = 1, 2, 4, 10)\) were treated with THF to remove the PS fiber and then redispersed in water. The mat was dried and observed by SEM. A typical image is shown in Fig. 9, where \(n = 4\). The obtained hollow multilayered PE fiber is a round tube with some small pores on the fiber surface. The hollow PEM fibers have a shell of about 100 nm thickness while the inner hollow diameter is about 400–500 nm. The inner diameter of the hollow fibers is much smaller than that of the uncoated PS fibers (average diameter of about 920 nm) because it shrinks during the preparation of the sample for SEM measurement. When PSS/PAH was selected as the shell material to construct PEM capsules, the thickness of four PSS/PAH bilayers was about 16–20 nm, as measured by single-particle laser scattering (SPLS) and atomic force microscopy (AFM). In this experiment, the thickness of four PSS/PAH bilayers is about 100 nm, which is much thicker than that of the microcapsules but similar to the result for PSS/PAH nanotubes. 15) One reason may be that some polyelectrolytes can form multilayers in the region between adjacent fibers. Another reason may be that the diameter of the tubes is nearly in the range of the radius of gyration of the polyelectrolyte molecules. Thus, for the molecules, the wall surface is, in effect, somewhat concave, which may lead to stronger polymer adhesion. In contrast, for \(n = 1\) and 2, the obtained hollow multilayered PE fibers will collapse after drying (the shape is similar to that in Fig. 10).

In order to study the influence of pH on the shape of the obtained hollow multilayered PE nanofibers, PS fibrous mats coated with \((\text{PAH/PSS})_4\) under different deposition conditions were treated with THF to remove the PS fibers and redisperse them in water. Then they were each observed by SEM. When the deposition occurred in strongly acidic solution, hollow multilayered PE fibers were not obtained while the hollow multilayered PE fibers were obtained, but there are many fragments under the strongly basic condition. When the deposition condition is nearly neutral, hollow multilayered PE fibers were obtained after removing the PS template (Fig. 10). The particles on the surface are residues
of PS. However, the obtained hollow multilayered PE fibers collapse shortly after drying because the multilayered PE wall is too soft to stand in air.

The above experimental results indicate that although hollow multilayered PE fibers can be obtained under different conditions, their shapes are different after drying. Some obtained fibers retain their round tube structure in air while others collapse, i.e., they buckle. One possible reason is that some films are firm enough to stand while others are too soft in air, similar to PEM capsules which also collapse in air because of evaporation. In order to study Young’s modulus of such hollow multilayered PE fibers, different sizes of the template and different numbers of layers deposited on the fibers were employed. The results are shown in Fig. 11.

The obtained hollow multilayered PE collapse (or buckle) in air because of the evaporation of water, i.e., water induces a swelling pressure that can be estimated as

$$P_c = (t/d)^2[2Y/(1 - \nu^2)],$$

where $t$ and $d$ are the shell thickness and diameter, respectively. $Y$ is Young’s modulus while $\nu$ is the Poisson ratio, which is about 0.3 for most materials. If $\Pi > P_c$, the pipe is unstable; otherwise, it is stable. Thus $\Pi = P_c$ gives the critical ratio of $t$ to $d$:

$$\alpha = (t/d)_c = [\Pi/(2Y(1 - \nu^2))]^{1/3}.$$  

When $t/d > \alpha$, the shell is stable; otherwise it will buckle.

The above experimental results confirm our interpretation, where $\alpha = 0.17$. The samples with the thickness-to-diameter ratio of above 0.17 (circles in Fig. 11) are stable, while the other samples (triangles) buckle. With $\alpha = 0.17$, we estimate Young’s modulus as

$$Y = \rho\Phi RT/[(2\alpha^2(1 - \nu^2))] = 21.6\, \text{GPa}.$$  

As we know, for most organic synthetic fibers, Young’s modulus is about 7.5 GPa, which is much smaller than that of our hollow multilayered PE fibers. This means that after multilayer deposition process, the hardness of the fiber is improved. Young’s modulus for human bone fiber is about 17 GPa. Young’s modulus of our hollow multilayered PE fibers is similar. The combination of the LBL technique with electrospinning may be a new effective way to fabricate artificial human bone when the appropriate biomaterials are employed.

4. Conclusions

LBL-structure PAH/PSS-film-coated PS fibrous mats were successfully produced by a combination of electrospinning and electrostatic LBL self-assembly. The deposition conditions were studied in this work, and the results showed that the formation of multilayered PE fibers was strongly influenced by the number of deposited layers and the pH value. The spaces between the adjacent fibers in the fibrous mats were blocked by 15 PAH/PSS bilayers. The film growth speed was the highest under the strongly acidic condition. Multilayered PE fibers were obtained when the number of deposited layers was less than 10 and the deposition occurred in water. Moreover, hollow multilayered PE fibers were obtained when the deposition occurred in neutral or strongly basic solution. Because the obtained hollow multilayered PE fibers lost their round tube structure and collapsed or buckled in air, different sizes of the template and different numbers of deposited layers were studied in the experiment. We found that when the ratio of the obtained fiber thickness/diameter is larger than 0.17 (i.e., the thickness/radius ratio of is larger than 0.34), the obtained hollow multilayered PE tube will retain its round tube structure. Such a round-tube-structure hollow fiber can be used to carry catalyst and medication. Therefore this kind of hollow multilayered PE nanofiber may have the potential for application to catalyst or drug delivery systems. We also determined Young’s modulus of these hollow multilayered PE nanofibers to be about 21.6 GPa, which is much larger than that for most synthetic organic fibers and similar to that of human bone fibers. Consequently, it is possible to prepare a fiber whose mechanical properties are similar to those of human bone fiber if appropriate biopolymers are employed. Further work on this issue is in progress in our group.
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