

Enhanced Mechanical Properties of Multilayer Nano-Coated Electrospun Nylon 6 Fibers via a Layer-by-Layer Self-Assembly

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ABSTRACT: We reported the mechanical properties of the polyelectrolyte multilayer nano-coated electrospun fiber mats with different number of layers. Multilayer nano-coatings composed of layers of PSS and PAH were successfully deposited onto electrospun nylon 6 fibers via layer-by-layer self-assembly. Compared with pure nylon 6 fibers, the morphology of polyelectrolyte multilayer coated nylon 6 fibers was uniform and smooth. The mechanical properties of polyelectrolyte multilayer coated random and aligned nylon 6

fibers were remarkably enhanced. Moreover, it was found that the higher degree of alignment resulted in higher tensile strength, suggesting the combined effects of the alignment, the surface nanocoating and the formation of internal networks of polyelectrolytes on nylon 6 fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2211–2216, 2008

Key words: polyelectrolyte; layer-by-layer technique; electrospun fibers

INTRODUCTION

Polyamides (nylon) are often used to produce fibers with the diameter in the order of 30 μm by conventional melt spinning.¹ However, the fibers with much smaller diameters are preferred for many industrial applications. For example, the nylon fiber-reinforced composites will have good transparent property if the fiber diameter is lower than that of light wavelength. So the novel spinning methods with the advantages in producing smaller fiber should be developed to fulfill the industrial requirements. Electrospinning is becoming of great interest because not only it can produce polymer fibers with diameters in the range of nano- to a few micrometers, but it also has the advantages of being simple, convenient, and inexpensive as compared with conventional methods.^{2–7} Because of the small size of the electrospun polymer nanofibers, the membranes collected from electrospun nanofibers possess a large surface area per unit mass and a very small pore size.^{8,9} These characteristics make the electrospun nanofibers have many potential applications such as optical materials, sensor materials, nanocom-

posite materials, tissue scaffolds, wound dressing, drug delivery systems, filtration, and as protective clothing.^{10–15} However, because electrospun fiber mats have very poor mechanical properties due to the random orientation within the fibers and broad distribution of fiber diameter, their applications are limited. Hence, an enhancement in both mechanical and physical properties of the electrospun fiber mats is very important from an industrial point of view. So far, most of studies have been focused mainly on the basic principles, the processing parameters, the spinning conditions, the morphology of the electrospun fibers, and the instability zone between the capillary tip and the collector. There have been few studies about the mechanical behaviors of the electrospun fibers themselves. By way of example, Kim and coworkers reported that the electrospun thermoplastic polyurethane elastomer (TPU) fiber mats showed nonlinear elastic and inelastic characteristics which might be due to slippage of crossed fiber (nonbonded or physical bonded structure) and breakage of the electrospun fibers at junctions (point-bonded or chemical bonding structure) and demonstrated that the point-bonded structures of fiber mats played an important role in the load-bearing component as determined in loading–unloading component tests.¹⁵ Fennessey and Farris reported that there were different alignment appearances of electrospun fibers by high-speed rotative collector velocity on electrospinning and found that the ability to orient the polyacrylonitrile (PAN) nanofibers on electrospinning allows for the production of carbon

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nanofibers with mechanical properties comparable with those of carbon fibers prepared by conventional methods.¹⁶

Layer-by-layer (LbL) self-assembly technique has been widely utilized over the past decade for the preparation of ultrathin surface coatings.^{17–19} The technique involves the sequential adsorption of oppositely charged materials to construct a thin film in a step-wise manner. The process is commenced by adsorbing a polyelectrolyte onto an oppositely charged surface, thereby, reversing the surface charge. Further layers are added by repeating the process until the desired film thickness is reached. The sequential adsorption of polycations and polyanions from dilute solutions is a simple, cheap, and robust method allowing a high degree of control over film thickness in the nanometer range. A variety of materials can be assembled via the LbL technique, including charged polymers, biomolecules, nanoparticles, and small molecules, and the method can be applied to a number of different substrates, including planar supports, colloids, membranes, or biomolecules.^{20–22} The primary focus of LbL researches conducted has been on the fabrication of multilayer thin films and microcapsules and their characterization, but studies on the more functionalization-oriented research have also remained. Recently, Caruso and co-workers reported the LbL surface functionalization of high aspect ratio polystyrene (PS) electrospun fibers of various diameters (400 nm or 1.5 μm) with polyelectrolytes by using LbL electrostatic self-assembly technique, and the formation of hollow fibers by dissolving the inner PS fibers with tetrahydrofuran.²³ In this study, we report the mechanical properties of the polyelectrolyte multilayer nano-coated electrospun fiber mats with different number of layers. To the best of our knowledge, no reports have been published on nanoscaled LbL nanocoating of electrospun nanofiber to improve the mechanical properties.

EXPERIMENTAL

Materials

The poly(sodium 4-styrenesulfonate) (PSS, $M_w \sim 70$ kDa), poly(allylamine hydrochloride) (PAH, $M_w \sim 70$ kDa), and polyethyleneimine (PEI, $M_w \sim 25$ kDa) were purchased from Sigma-Aldrich Co., USA. Nylon 6 (Unitika Co., Japan) with relative viscosity of 3.2 was dissolved in formic acid (Showa Ltd., Japan) at room temperature. After the electrospinning, the electrospun nylon 6 fibers were dried in a vacuum oven at 25°C for 1 day to remove the residual solvent. All chemicals were of analytical grade and used without further purification.

Preparation of electrospun nylon 6 fibers

A high voltage power supply (CPS-60 K02v1, Chungpa EMT Co., Republic of Korea), capable of generating voltages up to 60 kV, is used as a source of electric field. Nylon 6 solution of 22 wt % dissolved in mixture (8 : 2, v/v) of formic acid and acetic acid and was supplied through a plastic syringe attached to a capillary tip of about 0.6-mm inner diameter using a micro-syringe pump. The copper wire connected to a positive electrode (anode) was inserted into the polymer solution and a negative electrode (cathode) was attached to a grounded rotating metallic collector. The distance between the capillary tip and the collector was fixed to be 13 cm, and the plastic syringe was placed at an angle of 10° from the horizontal direction. When the applied voltage becomes larger than the surface tension of polymer solution, a charged jet is formed and ejected towards the metallic collector. The jet is triggered by the electrically driven bending instability, alternatively referred to as whipping instability and divided into multiple filaments by radial-charge repulsion, known as splaying. The solvent evaporates in the air and dried fibers are collected in the form of fiber mats. In addition, to produce aligned nylon 6 electrospun nanofibers, nylon 6 solution was electrospun onto the metallic collector capable of rotating up to 3000 m/min. Various degrees of aligned nylon 6 nanofibers were prepared as controlling the linear velocity of collector surface (0, 300, 700, 1000, 1500 m/min).

Assembly of polyelectrolyte multilayers on electrospun nylon 6 fibers

The polyelectrolyte multilayer nanocoating was carried out by LbL assembly of layers of PSS and PAH onto nylon 6 fiber mats as a template. Briefly, polyelectrolyte multilayer coated nylon 6 fiber mats were prepared as follows. For effective dipping procedures in water, nylon 6 fiber mats were sandwiched between PET films as a supporter and then used. The concentration of each polymer solution was 1.0 mg/mL. First, nylon 6 fiber mats were immersed into the PEI solution of 1.0 mg/mL for 20 min to achieve the uniform surface charges for the successive oppositely charged polyelectrolyte, PSS, followed by rinsing at least twice with pure water. The positively charged nylon 6 fiber mats were then dipped in PSS solution (1.0 mg/mL, no salt, pH 6) at room temperature for 20 min, followed by two rinsing cycles. Afterwards, a PAH salt-free solution (1.0 mg/mL, pH 6) was added to the fiber mats. After 20 min given for adsorption, two washing cycles were performed as following above. The PSS and PAH adsorption steps were repeated until the desired

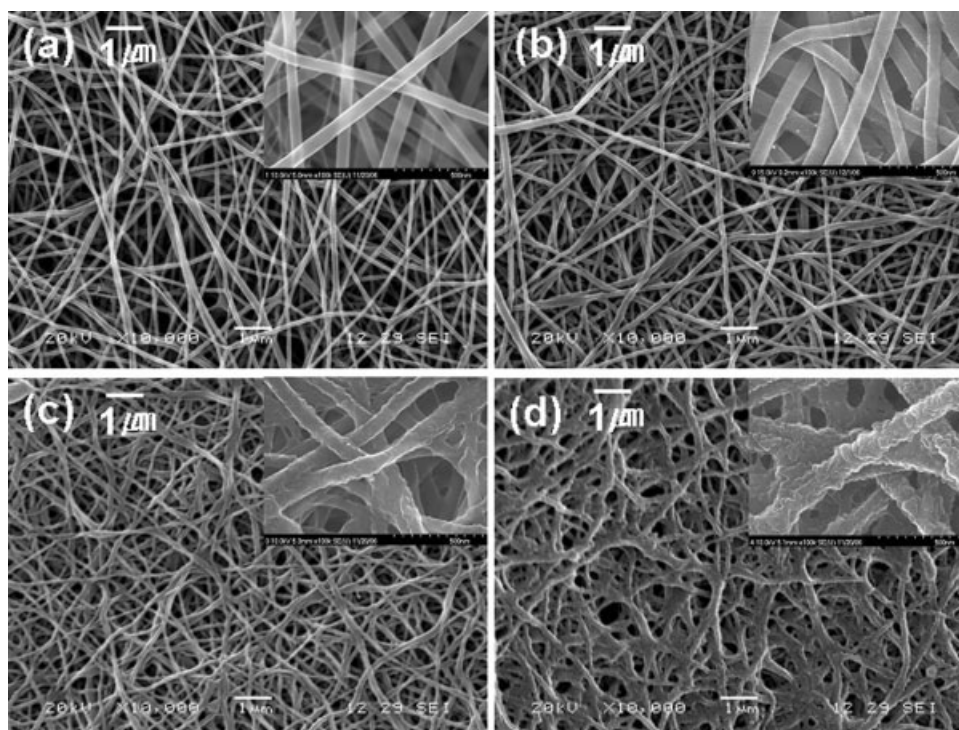


Figure 1 SEM images of polyelectrolyte multilayer-coated nylon 6 fibers with different number of bilayer of PSS and PAH (a) nylon 6 fibers alone (without coating) (b) one bilayer (c) five bilayers, and (d) 10 bilayers (Insets show FE-SEM images of each nanofibrous mats. The solution concentration, applied electric field and tip-to-collector distance were 22 wt %, 15 kV, 13 cm, respectively).

number of bilayer is reached. Each adsorption followed by washing out excess polymer and salt.

Characterization

The morphology of the electrospun nylon 6 nanofiber mats was observed with scanning electron microscopy (SEM, JSM-5900, Jeol Co., Japan) and field-emission scanning electron microscopy (FE-SEM, S-4700, Hitachi Co., Japan) and the fiber diameter and distributions were determined with an image analyzer (Image-proplus, Media Cybernetics Co., USA). The mechanical behavior of the nanofiber mats was investigated at room temperature with a universal testing machine (UTM, AG-5000G, Shimadzu Co., Japan) under a crosshead speed of 10 mm/min. In accordance with ASTM D-638, samples were prepared in the form of a dumbbell-shape and, then, at least five specimens were tested for tensile behavior and the average values were reported. All specimens were dried in a vacuum oven at 25°C for 1 day before use. Three parameters were determined from each stress–strain curve: Young's modulus (E), tensile strength (σ_b), and elongation at break (ϵ_b). Elastic modulus or Young's modulus is the initial slope of the stress–strain curve. Tensile strength is the stress at failure and the strain corresponding to the tensile strength is the failure strain.

RESULT AND DISCUSSION

Build-up and morphology

We studied zeta-potential of polyelectrolyte multilayer coated nylon 6 fiber mats with respect to the number of layers in order to demonstrate the successful polyelectrolyte multilayer deposition on nylon 6 fiber mats. Successive adsorption of negatively charged PSS and positively charged PAH resulted in an alternative negative and positive surface charges of comparable magnitude (data not shown). It was therefore confirmed that LbL assembly approach of PSS and PAH was shown to give the reversal of the surface charge, demonstrating the successful polyelectrolyte multilayer deposition onto nylon 6 fiber mats. Similar results have been shown in numerous articles^{24–26} involving the deposition of a variety of polyelectrolyte systems on various templates. Figure 1 shows SEM images of pure nylon 6 and polyelectrolyte multilayer coated nylon 6 fiber mats. In general, electrospun fibers are deposited as a randomly oriented fiber mats, forming a highly porous structure, which is held together by connecting sites such as crossing and bonding between the fibers. The morphology of pure nylon 6 fibers is regular and a narrow distribution of diameters is observed, with an average diameter of 90 nm. After polyelectrolyte multilayer nanocoating of one bilayer of PSS and

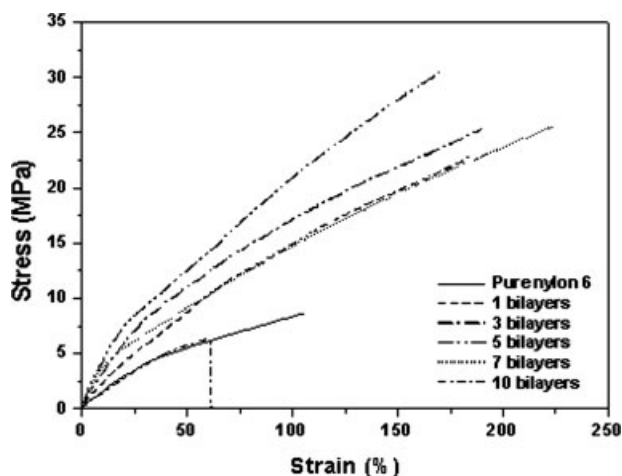


Figure 2 Stress–strain curves of pure nylon 6 fiber mat and polyelectrolyte multilayer coated nylon 6 fiber mats with different number of bilayer of PSS and PAH.

PAH, a regular and smooth fiber surface was observed, indicating a uniform nanocoating of polyelectrolytes on electrospun nylon 6 fibers. Moreover, interestingly the formation of internal network by continuous nanocoating between fibers [inset in Fig. 1(b)] is observed resulting in a similar point-bonded network system.¹⁵ On the other hand, after five bilayers of PSS and PAH, the surface roughness and diameter of the fiber becomes significant. In case of 10 bilayers surface-coating of PSS and PAH, sometimes it happens that nonuniformly coated nanofilms are peeled off, showing a very heterogeneous and irregular nanocoating, thereby giving rise to a poor mechanical property as we will explain later.

Mechanical properties

Figure 2 shows the stress–strain curves of pure nylon 6 and polyelectrolyte multilayer coated nylon 6 fiber mats with different number of bilayer of PSS and PAH under static loading condition. Pure nylon 6 fiber mats show a peculiar characteristic of thermoplastic elastomers, in that the stress–strain behaviors

show linear elasticity as their intrinsic material property. Afterwards, the fiber mats are broken when the maximum amount of tensile stress (tensile strength) applied to them. In contrast, polyelectrolyte multilayer coated nylon 6 fiber mats show not only a continuous elastomeric behavior up to fracture, but also have higher tensile strength than that of pure nylon 6 fiber mat. Therefore, the multilayer coating of polyelectrolyte on the surface of electrospun nylon 6 fibers resulted in an improved tensile strength and Young's modulus. The reason for an enhanced mechanical property may be considered as a dense/hard coating (via protecting of, if any, small cracks or other imperfections in the electrospun fibers) of polyelectrolyte onto electrospun nylon 6 fibers. Here it should be also noted that the average diameters of polyelectrolyte multilayer coated nylon 6 fibers are increased slightly on increasing the number of bilayer of PSS and PAH whereas a tiny increased diameter of fibers does not significantly affect the mechanical properties. As a result, polyelectrolyte layers are found to camouflage substrate defects, yielding a system with many ionic crosslinks and good adhesion properties.^{27–29} Compared with pure nylon 6 fiber mats (tensile strength $\sim 10.6 \pm 2$ MPa), the tensile strength of polyelectrolyte coated nylon 6 fiber mats were largely increased to 23.4 ± 2 and 30.1 ± 3 MPa for one bilayer and five bilayers coated fiber mats, respectively. In addition, the elongation of polyelectrolyte multilayer coated nylon 6 fiber mats dramatically increased as a function of the number of bilayer, suggesting that the rubber elasticity of polyelectrolyte multilayer coated nylon 6 fiber mats was reinforced by polyelectrolyte nanocoating of nylon 6 fibers and formation of internal network. The breaking elongation of the polyelectrolyte multilayer coated nylon 6 fiber mats increased from $(115 \pm 10)\%$ for pure nylon 6 fiber mats up to $(186 \pm 25)\%$ for three bilayers coated nylon 6 fiber mat, respectively. The resulting Young's modulus, tensile strength, and elongation at break are shown in Table I.

The strength and ductility of electrospun fiber mats can thus be greatly modified. Moreover, the

TABLE I
Mechanical Properties of Pure Nylon 6 Fiber Mat and Polyelectrolyte Multilayer Coated Nylon 6 Fiber Mats With Different Number of Bilayer of PSS and PAH

Layer number ^a	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
Pure nylon 6	10.6 ± 1.0	16.0 ± 1.0	115.3 ± 10.0
1	23.4 ± 2.0	29.2 ± 2.0	166.5 ± 20.0
3	25.5 ± 1.0	36.4 ± 1.0	185.6 ± 25.0
5	30.1 ± 3.0	62.2 ± 3.0	160.8 ± 20.0
7	24.9 ± 5.0	41.1 ± 5.0	241.7 ± 20.0
10	8.5 ± 1.0	33.9 ± 1.0	68.5 ± 15.0

^a Layer number indicates the number of bilayer of PSS and PAH nano-coated on nylon 6 fibers.

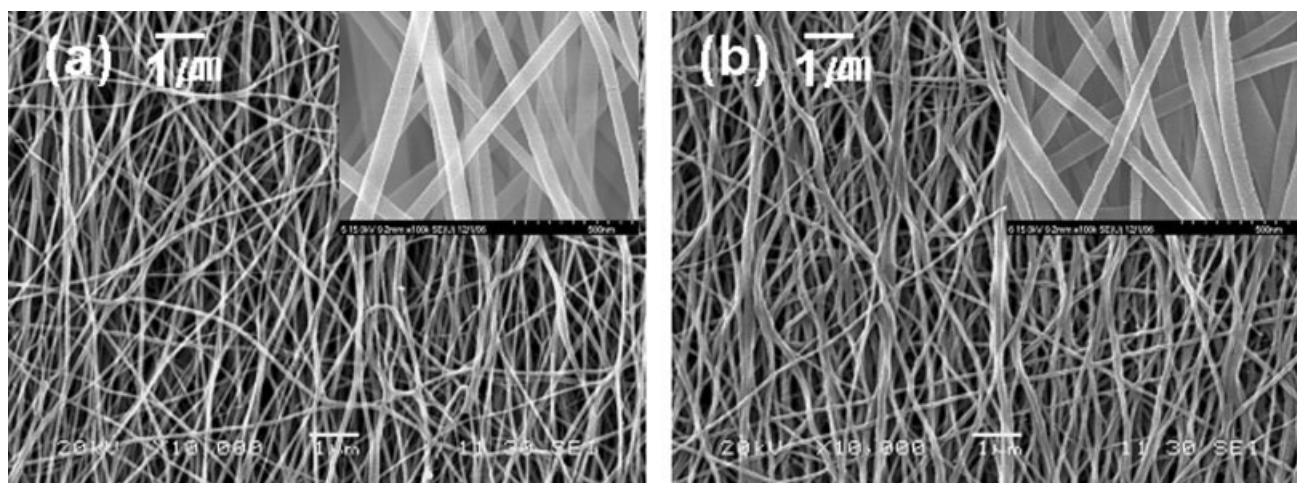


Figure 3 SEM images of (a) aligned nylon 6 nanofibers and (b) one bilayer PSS/APH coated aligned nylon 6 nanofibers. Inserts show FE-SEM images of each nanofibrous mats.

toughness, defined as the energy absorbed by the electrospun nylon 6 fiber mats until breaking, for one bilayer PSS/PAH coated nylon 6 fiber mats has the higher value (0.0494 J) than that of pure nylon 6 fiber mats (0.0258 J). Therefore, the higher amounts of ionic pairs present in the multilayers can serve as the crosslinking units and thereby improve the mechanical properties of fiber mats.

Surface nano-coating and alignment effects on morphology and tensile strength of polyelectrolyte multilayer coated nylon 6 fibers

Recently, it was found that the mechanical properties of electrospun fiber mats depended strongly on the arrangement of fibers (fiber alignment) and drawing (molecular orientation).³⁰ Such aligned nanofibers

were successfully prepared by using the rotating collector enabling to control the linear velocity of metallic collector to induce nanofiber orientation in the electrospun fiber mats during electrospinning. As a result, the degree of alignment was strongly affected by the linear velocity of collector. In this work, we used the linear velocity of 300, 700, 1000, and 1500 m/min, respectively. Figure 3 shows the SEM images of pure aligned nylon 6 fibers (linear velocity \sim 1500 m/min) and its one bilayer PSS/PAH coated nylon 6 fibers. In comparison with the morphological structure of the random nylon 6 fibers [Fig. 1(a)], aligned nanofibers [Fig. 3(a)] exhibit a more orientation of electrospun nanofibers along the rotating direction. Moreover, after one bilayer PSS/PAH coating, a smooth fiber surface was also observed.

It was found that as the linear velocity of collector increases, the resulting tensile strength for aligned nylon 6 fiber mats increased linearly (Fig. 4). Furthermore, as seen in Figure 4, it was observed that the tensile strength for each sample increases dramatically after one bilayer PSS/PAH nanocoating onto aligned nylon 6 fibers.

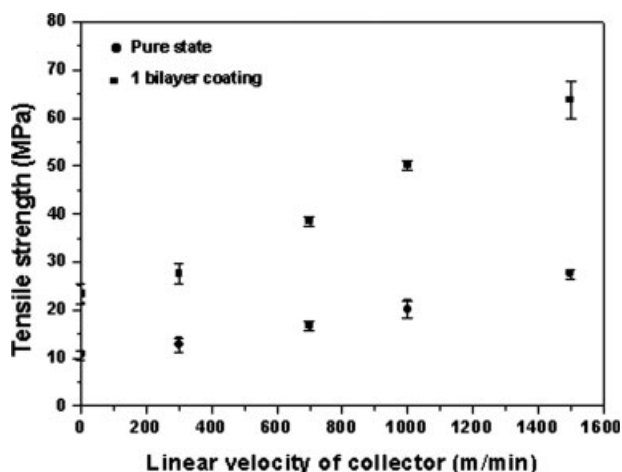


Figure 4 Tensile strengths of pure nylon 6 fiber mats and one bilayer PSS/PAH coated nylon 6 fiber mats as a function of linear velocity of metallic collector during electrospinning.

CONCLUSIONS

Polyelectrolyte multilayer mats composed of layers of PSS and PAH were successfully deposited onto electrospun nylon 6 fibers via LbL electrostatic self-assembly. The morphology and mechanical properties of the polyelectrolyte nano-coated random and aligned nylon 6 fiber mats were examined. Compared with pure nylon 6 fibers, it was observed that the morphology of polyelectrolyte multilayer coated nylon 6 fibers was uniform and smooth, indicating a dense and harder nanocoating of polyelectrolytes onto nylon 6 fibers. The mechanical properties of

polyelectrolyte multilayer coated random and aligned nylon 6 fiber mats were enhanced by surface nanocoating of polyelectrolytes onto nylon 6 fiber mats. Moreover, it was found that the higher degree of alignment resulted in higher tensile strength, suggesting the combined effects of the alignment, the surface nanocoating and the formation of internal networks of polyelectrolytes on nylon 6 fibers.

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