Characterization of polymer nanofibers coated by reactive sputtering of zinc

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ABSTRACT

The surface properties of polymer nanofibers are of importance in various applications. In this work, electrospun polyamide nanofibers were used as substrates for creating functional nanostructures on the nanofiber surfaces. The surface functionalization of polymer nanofibers was made by reactive sputtering of zinc (Zn). The surface structures of the sputter-coated nanofibers were examined by atomic force microscopy (AFM) and environmental scanning electron microscopy (ESEM). AFM results revealed the formation of functional coatings on the nanofiber surface. A full energy dispersive X-ray analysis (EDX) mounted on the ESEM confirmed the chemical compositions of the nanofiber surfaces. The electrical conductivity and light transmittance of the functional nanofibers were also investigated. The results indicated that the nanofibers deposited with zinc films significantly improved the surface conductivity and the reactive sputter coating of zinc oxide obviously enhanced the ultra-violet absorption.

1. Introduction

Nanofibers have recently attracted a lot of attention due to the great potential for a wide range of applications. The expanding applications include tissue engineering, biomaterials, nanocomposites, filtration and drug delivery (Frenot and Chronakis, 2003).

For a variety of applications there is a great need for such polymer nanofibers with well-defined surface properties. Nanofibers with specific surface properties are also of importance in many technical applications as the surface chemistry and physics affect wettability, adsorption, biocompatibility and electro-optical properties of nanofibers. The surfaces of polymer nanofibers, however, are often not ideal for a particular application due to the inertness of polymer materials. Various techniques have been used to treat the surface of polymer nanofibers, based on changes to both the physical and chemical properties of polymer nanofibers, for example, surface grafting (Ma et al., 2005), plasma treatment (Wei et al., 2005) and self-assembly (Ding et al., 2006).

The deposition of metallic or metal oxide materials, such as zinc or zinc oxide onto polymers has attracted a lot of attention recently. The electrodeposition of zinc was made from aqueous zinc sulphate solution and the coated zinc particles improved the barrier property of polymer films (Tüken, 2006). The formation of zinc oxide by sol–gel techniques has also been investigated (Lira-Cantu and Krebs, 2006). These chemical approaches often generate chemical pollution as the reaction takes place in liquid solutions. The surface coating by physical vapor deposition provides an environmentally friendly technique to functionalize various materials (Meerkamm et al., 1999). In this study, the electrospun polyamide nanofibers were coated with zinc by a reactive sputter coating of zinc. The sputter coating was performed at room temperature. Atomic force microscopy (AFM) and environmental scanning electron microscopy (ESEM) were employed

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to study the morphology and chemistry of the nanofiber surfaces, respectively. The electrical conductivity and light transmittance of the nanofibers were also investigated.

2. Experimental

2.1. Materials preparation

2.1.1. Electrospun nanofibers

The polymer material used in this study was commercial polyamide 6 (PA6), which was supplied by BASF. The polymer material was dissolved in formic acid to form spinning solution. The concentration of the solution was adjusted to 10 wt.%. The polymer nanofibers were spun using electrospinning. For electrospinning, the prepared polymer solution was placed in a 50-ml syringe with a needle of 0.5 mm diameter. The electrospinning was performed by applying a high voltage electrostatic force of about 15 kV. The ejected solution droplets from a needle of the syringe were spun and collected. As the jets accelerated towards a grounded receiver, the solvent evaporated and the spun polymer fibers were collected on an aluminium foil. The nanofiber web was collected for 1.5 h and dried in a vacuum oven at room temperature for 24 h to remove the residual solvent.

2.1.2. Sputter coating

The deposition system used in this study was a lab radio frequency (RF) sputtering system JZCK-420B. The frequency was 13.56 MHz and the target used was zinc with a high purity of about 99.999%. The sputtering chamber was pumped to 1×10^{-5} Pa before the sputtering. After the sputtering gas was introduced into the chamber, the pressure was adjusted to 1.0 Pa. The sputtering was carried out in argon (Ar, gas flow 60 sccm) and Ar–O$_2$ (90:10) (gas flow: 54 sccm:6 sccm) gas, respectively. The gases were supplied through two gas inlets and controlled by electrical device. The power used for the sputtering was set at 100 W. The sputter coating was performed on the one side of the nanofiber substrate. The substrates were kept at room temperature using water-cooling. The thickness of the deposition layer was measured using a coating thickness detector (FTM-V) fixed in the sputtering chamber. The coating thickness was set at 20 nm and 50 nm for zinc and zinc oxide, respectively.

2.2. Surface characterisation

2.2.1. EDX analysis

The ESEM integrated with a Phoenix energy-dispersive X-ray detector adds extraordinary capabilities to the entire system. It allows analyzing of elemental compositions down to boron including the light elements such as carbon, nitrogen and oxygen. The charging artifacts can be eliminated due to the existence of gas in the ESEM chamber (Yu et al., 2005). In this study, the fiber surface was examined by the EDX at an accelerating voltage of 20 kV with accounting time of 100 s.

2.2.2. AFM characterisation

Scanning probe microscope (SPM), particularly in the form of atomic force microscopy uses a physical probe scanning across the sample using piezoelectric ceramics and the position of the probe and the feedback signal are electronically recorded to produce a three-dimensional map of the surface or other information depending on the specialty probe used (Park et al., 2007). The scanning probe microscope used in this study was a CSPM4000 atomic force microscopy made by Benyuan Co., Ltd. Scanning was carried out in contact mode atomic force microscopy and all samples were scanned at room temperature in atmosphere. The scanning was set at a size of 1000 nm × 1000 nm, and the scanning frequency was set at 1.0 Hz.

2.3. Optical properties

The optical properties of the functional nanofibers were examined based on the transmittance of Ultra-violet (UV) and visible (vis) light through a sample. The samples of the nanofiber webs were separated from the alumina foil for the UV/vis spectroscopy test. The UV/vis spectroscopy used was a PerkinElmer Lambda 900. UV/vis spectra were obtained by passing different wavelengths of light ranging from 200 nm to 600 nm through the nanofiber sample.

2.4. Electrical property

Electrical property was characterized by resistivity measurement. The resistivity of the samples was measured using a collinear four-probe array. The apparatus used was SX1934 made by Baishen Technologies. In order to minimize the deviations brought by the unevenness of nanofiber surface, the resistivity of each sample was measured three times, and the average values were used.

3. Results and discussion

3.1. EDX analysis

The formation of functional structures on the nanofibers is revealed by the EDX analysis, as presented in Fig. 1. The EDX spectrum in Fig. 1a indicates the compositions of C, N and O of the PA6 nanofibers. The composition of hydrogen (H) in the material is too light to be detected in the EDX analysis. A significant amount of Zn on the nanofiber surface after the zinc coating of 20 nm can be seen in Fig. 1b, but the amount of C, N and O is also reduced in the EDX spectrum, indicating the coverage of the surface by Zn coating. The similar phenomenon is also detected on the surface of the nanofibers with the reactive zinc coating as indicated in Fig. 1c. The compositions of O and Zn are obviously increased and C and N are significantly reduced compared to Fig. 1a. The increased amount of O and Zn reveals the formation of zinc oxide on the surface of the PA6 nanofibers after the reactive sputter coating of zinc in argon and oxygen mixed atmosphere.

3.2. Surface morphology

The electrospinning produces the fibrous structure of nanofibers as shown in Fig. 2a. The PA6 nanofibers have varying diameters with an average diameter of about 350 nm.
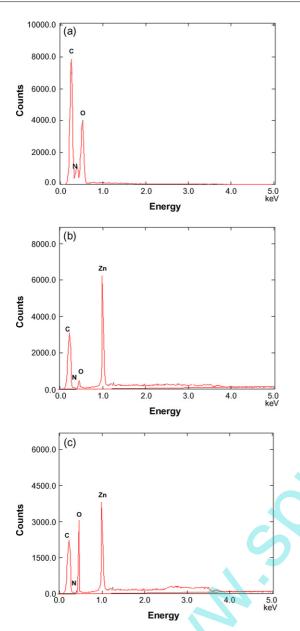
Fig. 1 – EDX spectra of the functional nanofibers: (a) uncoated; (b) zinc-coated; (c) zinc oxide-coated.

Fig. 2 – Structure and surface of PA6 nanofibers: (a) 5000 nm × 5000 nm scan; (b) 1000 nm × 1000 nm scan.

The AFM image also reveals that the nanofibers are randomly oriented in the web. The surface of the nanofiber looks quite smooth as presented in Fig. 2b. The surface has an average roughness of 5.21 nm as presented in Table 1.

The sputter coating obviously modifies the surfaces of the PA6 nanofibers, as revealed in Figs. 3 and 4. The metallic coating of zinc deposits zinc nanoparticles on the nanofiber surface, as indicated in Fig. 3a. The nanoparticles form aggregation structures on the nanofibers surface and the pores among the nanofibers are still visible as the coating thickness is 20 nm. The surface roughness is also increased to 9.56 nm. It is found that more nanoparticles are covered on the nanofiber surface as the coating thickness is increased to 50 nm. The zinc nanoparticles are also cover the pores of nanofibers as revealed in Fig. 3b. The surface roughness is further increased
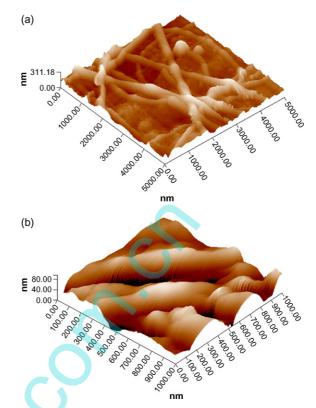
to 12.35 nm due to the growth of the sputtered particles formed on the nanofiber surface.

The similar phenomenon is also observed on the surface of the nanofibers by the reactive zinc coating. The zinc oxide clusters scatter on the nanofiber surface and the clusters are in the form of aggregation as indicated in Fig. 4a. These aggregations cause the higher surface roughness as indicated in Table 1. As the coating thickness is increased to 50 nm, the sputtered functional layer covers up the original surface structures of the nanofibers and the pores among the nanofibers, as revealed in Fig. 4b. This is attributed to the growth of the sputtered grains as the sputter coating time is extended. The surface roughness is also increased as revealed in Table 1.

3.3.   Optical properties

The optical properties of the PA6 nanofibers are shown in Fig. 5, which presents the transmittance of the UV and visi-

Table 1 – Surface roughness	
Materials	Roughness (nm)
PA6	5.21
Zn-coated	
20 nm	9.56
50 nm	12.35
ZnO-coated	
20 nm	16.79
50 nm	20.32

Fig. 3 – Structure and surface of zinc-coated PA6 nanofibers: (a) 20 nm coating; (b) 50 nm coating.
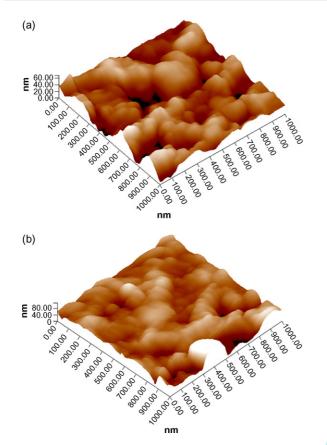

Fig. 4 – Structure and surface of zinc oxide-coated PA6 nanofibers: (a) 20 nm coating; (b) 50 nm coating.

ble light through the material. The original nanofiber material shows the transmittance of about 35% in the range from 400 nm to 600 nm, indicating a good transmittance of visible light. The transmittance drops gradually from 35% to less than 10% in the range between 400 nm and 300 nm, indicating the UV shielding effect of the nanofiber material. The Zn sputter coating significantly alters the optical properties of the PA6 nanofibers, as displayed in Fig. 5. The transmittance of UV light and visible light in the range between 300 nm and 600 nm is considerably reduced to the level below 5% as the thickness of the Zn coating is 20 nm. The increase in coating thickness leads to a little further decrease in transmittance in both UV and visible light range, as revealed in Fig. 5. The UV/vis spectra in Fig. 5 also clearly indicates that the average transmittance of the ZnO-coated samples over the wavelength range between 450 nm and 600 nm exceeds 30%, which is very close to that of the original nanofibers, revealing the transparent property of the ZnO coatings in visible light range. The absorption of ultra-violet (UV) from 300 nm to 400 nm by the ZnO-coated samples is obviously observed in Fig. 5. It is also found that the ZnO coating in a thickness of 50 nm shows a little better UV absorption than the 20 nm coating. The UV absorption of the ZnO coating is attributed to its chemical structure of the material (Shishodia et al., 2006).

The optical band gap, E_g, calculated using the relations given by Tauc et al. (1966), is about 3.29 eV, which is a little lower than the value in literature (3.4 eV) (Jagadish and
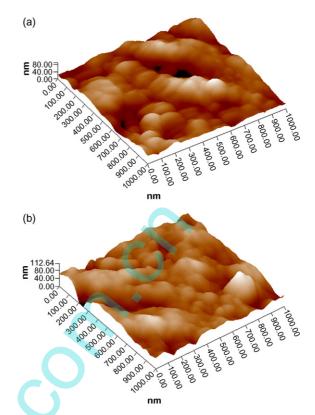
Pearton, 2006). This may be ascribed to the growth structure in the sputtered ZnO films (Hong and Jeong, 2005).

3.4. Electrical property

The electrical properties of the nanofibers before and after the sputter coatings are presented in Table 2. It clearly shows that the electrospun PA6 nanofibers have a very high surface resistivity of over $10^6 \, \Omega \, \text{cm}$ (out of the range of the test apparatus), indicating the electrical isolation behavior of the material. The Zn coatings, however, significantly reduce the surface resistance, as revealed in Table 2. The 20 nm coating of Zn on the
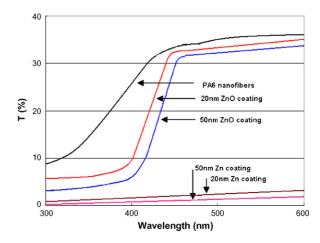

Fig. 5 – UV/vis spectra of the functional nanofibers.

Table 2 – Results of electrical conductivity tests

Coating	Average resistivity (Ω cm)
PA6 nanofibers	Over 10^{-6}
20 nm Zn coating	3.62
50 nm Zn coating	0.12
20 nm ZnO coating	Over 10^{-6}
50 nm ZnO coating	Over 10^{-6}

nanofibers lowers the surface resistivity to 3.62 Ω cm from over $10^6 \Omega$ cm, indicating a significant drop in surface resistivity. The 50 nm coating of Zn on the nanofibers further reduces the surface resistivity to 0.12 Ω cm. This is attributed to the formation of compact and improved coverage of the Zn clusters on the nanofiber surface and the pores among the nanofibers, as revealed in Fig. 3. The resistivity of the ZnO-coated nanofibers is still very high, as indicated in Table 2, but the optical properties are significantly altered as revealed in Fig. 5.

4.   Conclusions

This study has investigated the formation and properties of the functional nanostructures deposited on the PA6 nanofiber substrate by the reactive sputter coating of zinc. The surface functionalization of polymer nanofibers was made by reactive sputtering of zinc (Zn). The AFM and EDX analyses revealed the formation of the functional coatings on the nanofiber surfaces. It was found that the electrical conductivity of nanofibers was significantly improved by the sputter coating with zinc and the UV absorption of the material was considerably enhanced by the reactive sputter coating of zinc oxide. The functionalized polymer nanofibers with Zn coating have great potential for a wide range of applications in such areas as anti-static and electromagnetic shielding, while the functionalized polymer nanofibers with ZnO coating can be used for UV absorption and UV shielding.

Acknowledgements

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