Preparation of Poly(vinyl alcohol)/TiO_2 Nanofibers by Electrospinning

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Abstract

Nanofibers prepared by electrospinning have several advantages, such as large surface area to volume ratio, high specific surface area and small pore size, superior mechanical properties and flexibility in surface functionalities. The principle of electrospinning is to apply high voltage on syringe needle, which is connected to a polymer solution container. When polymer solution flows out from needle, the polymer is pulled onto collector by strong electric field and forms nanofibrous structure. In this paper, we prepared poly(vinyl alcohol)/TiO_2 nanofibers by electrospinning and investigated several process parameters such as concentration of polymer solution, molecular weight of polymer, applied voltage and the effect of TiO_2 nanoparticles on nanofibers of poly(vinyl alcohol). The results show that (1) the lower the concentration of poly(vinyl alcohol), the smaller the diameter of nanofiber is, (2) increasing voltage of electrospinning leads to a smaller diameter of nanofiber, (3) introducing TiO_2 nanoparticles into polymer solution changes morphology of nanofiber, (4) Increasing molecular weight of polymer increases the diameter of nanofiber.

Introduction

Nanofibers prepared by electrospinning have several advantages, such as large surface area to volume ratio, high specific surface area and small pore size, superior mechanical properties and flexibility in surface functionalities. The principle of electrospinning is to apply high voltage on syringe needle, which is connected to a syringe, which contains polymer solution. When polymer solution flows out from needle, the polymer is pulled onto a collector by strong electric field and forms nanofibrous structure. Many process parameters affect final structures of nanofibers, such as (1) viscosity and conductivity of polymer solution, (2) applied voltage at the syringe needle, (3) the gap between the needle and the collector, (3) solution temperature, humidity, and air velocity in the electrospinning environment [Doshi, 1995] (4) concentration of polymer solution [Huang, 2003], (5) molecular weight of polymer [Koski, 2004]. Zong et al. (2002) investigated the relationship between structure and process of electrospun poly(D, L-lactic Acid) (PDLA) and poly(L-lactic acid) (PLLA) nanofiber non-woven membranes for biomedical applications. Ding et al. (2002) prepared nanofiber of poly(vinyl alcohol) (PVA) by electrospinning. They observed that increasing the gap between the tip and the collector at constant applied voltage in electrospinning, the diameter of PVA nanofiber increases. While applied voltage increases, the diameter of PVA nanofiber decreases. The higher the concentration of PVA solution, the larger the diameter of PVA nanofiber is.

Several applications of nanofibers were reported. Li et al. (2002) demonstrated that electrospun fibers of synthetic polymers poly(D, L-Lactide-co-glycolide) (PLGA) is capable to be used as tissue engineering scaffold. Elias et al. (2002) concluded that carbon nanofibers improve osseointegrative properties. Kenawy et al. (2002) use electrospun poly(ethylene-co-vinylacetate) (PEVA) and poly(lactic acid) (PLA) for the application of drug delivery. Fong (2004) used electrospun nylon 6 nanofiber to reinforce dental restorative composite resins. We have proposed antibacterial nanofibrous filters by electrospinning in 2004 [Nien, 2004]. They can be used as air filters in hospitals, cars, rooms, or used for the treatment of wasted water or

drinking water. Based on our pending patent, we built our own setup of electrospinning and prepared poly(vinyl alcohol)/TiO_2 nanofibers by electrospinning and investigated several process parameters such as concentration, molecular weight, applied voltage and the effect of TiO_2 nanoparticles on nanofibers of poly(vinyl alcohol). TiO_2 nanoparticles are known for photocatalyst to decompose harmful organic compounds. For example, Kim et al. (2002) fabricated photocatalytic thin films consisting of ionic polymers and positively charged TiO_2 nanoparticles by the layer-by-layer self-assembling method to immobilize photocatalytic TiO_2 nanoparticles in thin films for the application of oxidation of iodide and decomposition of methyl orange. In this paper, PVA/TiO_2 nanofibers have been fabricated by electrospinning and characterized using scanning electron microscopy (SEM) and atomic force microcopy (AFM).

Experimental

Poly(vinyl alcohol) with Mw = 50000-85000 and Mw = 124000-186000 was purchased from Aldrich Chemical, WI. USA. Poly(vinyl alcohol) with degree of polymerization = 2000 was purchased from Showa Chemical Co. LTD., Tokyo, Japan. Photocatalyst TiO_2 nanoparticle solution (F4-APS) was purchased from Titanex Corp., Taiwan. The information of photocatalyst TiO_2 nanoparticle solution is provided by supplier as shown in Table 1. PVA solutions were prepared by dissolving PVA into distilled water at 80 °C. PVA/TiO_2 nanoparticle solutions were prepared by adding 0.025g, 0.05g and 0.1g of TiO_2 nanoparticle solution into 100 ml of PVA solution, respectively, and well mixed at room temperature. These samples of the nanofibers with the detailed fabrication are listed in Table 2.

Table 1. The information of photocatalyst TiO_2 nanoparticle solution

Product	Type	BET (m^2/g)	Particle size	pH
FA-APS	Solution	35~60	About 30 nm	8~8.5

Table 2. The samples of nanofibers made by various process parameters

	Molecular weight	PVA concentration (%)	Amount of TiO_2 solution per 100ml of PVA solution (g)	Voltage (V)
Sample #1	50000-85000	8	0	20000
Sample #2	124000-186000	8	0	20000
Sample #3	88000*	4	0	20000
Sample #4	88000*	8	0	20000
Sample #5	88000*	12	0	20000
Sample #6	50000-85000	8	0	10000
Sample #7	50000-85000	8	0	25000
Sample #8	88000*	8	0.05	20000
Sample #9	88000*	8	0.1	20000
Sample #10	88000*	8	0.1	15000
Sample #11	88000*	8	0.1	25000
Sample #12	88000*	8	0.025	20000

* Molecular weight is calculated by Poly(vinyl alcohol) with degree of polymerization = 2000.

Electrospinning apparatus used in this study consists of a programmable syringe pump, high voltage power supply (purchased from Glassman, NJ. USA), syringe, syringe needle and collecting plate (collector). The distance between syringe needle and collecting plate is adjustable. The programmable pump can control the flow rate of polymer solution by pushing the syringe. The collecting plate is connected to ground. The syringe needle is connected to high voltage power supply. When polymer solution is pushed out of the needle, the polymer solution can be pulled by strong electric field toward colleting plate and solidified on the plate to form nanofibrous structure.

The solution prepared above was put into syringe for electrospinning at room temperature. In this paper, we only changed the applied voltage range from 10000 V to 25000 V. We kept several parameters constant as follows: (1) 5 cm for the distance between syringe needle and collecting plate, (2) 0.001 ml/min for the flow rate of polymer solution controlled by the programmable pump. The various nanofibers made from various solutions were fabricated under different levels of voltage. Table 2 is the detailed process parameters of nanofibers and their notation. Scanning electron microscopy (SEM, JEOL JSM-5610) and atomic force microscopy (AFM, Seiko HV–300) were used to observe the morphology of nanofibrous structure of nanofibers.

Results and discussion

The diameter of the Sample #1 is about 193 nm and that of the Sample #2 is about 451 nm. The entanglement of polymer chains increases as molecular weight of polymer increases. The entanglement of polymer chains may lead to the increase of diameter of nanofiber, because nanofiber is formed with polymer chains. The nanofibers of the Sample #3 and #5 have diameters about 275 nm and 444 nm, respectively. The higher the concentration of polymer solution, the larger the viscosity of polymer solution is. The entanglement of polymer chains is one of the factors, which contributed to viscosity. Therefore, The higher concentration of polymer solution tends to increase the diameter of nanofiber. On the other hand, if the concentration of polymer solution is very low, the polymer chains may not aggregate enough to construct stable nanofiber. The diameter of the Sample #6 is about 250 nm and that of the Sample #7 is about 190 nm. Increasing voltage of electrospinning leads to small diameter of nanofibers. It may be the reason of higher drawing effect when electric field becomes stronger. The increase of amount of TiO_2 tends to particles aggregate together. However, TiO_2 nanoparticles show well distribution in PVA nanofibrous matrix. The reasons of TiO_2 nanoparticles without coagulation in the matrix may be (1) interaction between PVA and TiO_2 nanoparticles and (2) strong electric field during electrospinning. The interaction caused by hydrogen bonding between hydroxide groups in PVA and oxygen in TiO_2 may avoid TiO_2 nanoparticles aggregation. Nanoparticles pulled by strong electric field can be sprayed evenly on collecting plate, because of strong shear stress. The diameters of nanofibers prepared by 25000 V (Sample #11) and 15000 V (Sample #10) are about 250nm to 300 nm. Interestingly, in this study, the effect of the applied voltage range on the diameter of nanofiber is not significant. It may be caused by TiO_2 addition, which enhances the conductivity of polymer solution. We also measured single nanofiber by AFM. All of them were electrospun at applied voltage of 20000 V. The dimensions of these nanofibers are listed in Table 3. These dada show the shapes of nanofibers are oval. It may result from the impact of nanofiber on the collector to deform during electrospinning.

Table 3. The dimensions of nanofibers made of different solutions

Sample	Sample #4	Sample #12	Sample #8
Diameter (nm)	266	369	271
Height (nm)	135	175	60

Conclusions

PVA/TiO_2 nanofibers have been prepared and characterized. Several process parameters have been investigated as follows: (1) the lower the concentration of poly(vinyl alcohol), the smaller the diameter of nanofibers is, (2) increasing voltage of electrospinning leads to small diameter of nanofibers, but it is not obvious for nanofibers of PVA/TiO_2, (3) introducing TiO2 nanoparticles changes morphology of nanofibers and TiO_2 nanoparticles is able to well distribute in nanofibrous matrix, (4) the higher molecular weight of PVA increases the diameter of nanofibers.

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