Materials Science and Engineering C 43 (2014) 50–57

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Antibacterial continuous nanofibrous hybrid yarn through in situ synthesis of silver nanoparticles: Preparation and characterization

Hossein Barani *

Department of Carpet, Faculty of Art, University of Birjand, 17 Shahrivar Street, Birjand, Iran

ARTICLE INFO

Article history:
Received 6 February 2014
Received in revised form 31 May 2014
Accepted 1 July 2014
Available online 9 July 2014

Keywords:
Electrospinning
Hybrid yarn
Nanofiber
Silver nanoparticles
Antibacterial

ABSTRACT

Nanofibrous hybrid yarns of polyvinyl alcohol (PVA) and poly-L-lactide acid (PLLA) with the antibacterial activity were prepared that contains 0, 5, 10, 20, and 30 wt.% of silver nanoparticles according to the PVA polymer content. This was performed by electrospinning using distilled water and 2, 2, 2-trifluoroethanol as a solvent for PVA and PLLA respectively, and sodium borohydride was used as a reducing agent. The scanning electron microscope observation confirmed the formation of AgNPs into the PVA nanofiber structure, and they were uniform, bead free, cylindrical and smooth. The diameter of hybrid yarns and their nanofiber component was decreased as the silver nitrate concentration in electrospinning solutions was increased. The differential scanning calorimetry results indicated that the silver nanoparticles can form interactions with polymer chains and decrease the melting enthalpy. The mechanical analysis showed a lower stress and strain at break of the AgNP-loaded nanofibrous hybrid yarns than the unloaded hybrid yarn. However, there wasn't a statistically significant difference between the strain at break of electrospun nanofibrous hybrid yarns. Moreover, the bactericidal efficiency of all loaded samples was over 99.99%.

1. Introduction

The use of textiles, yarns, and fibers is known from thousands of years and is a feature of most human societies. The applications of textile materials were limited to some specific fields for several years and only produced by traditional methods. However, the production technologies of textile materials as well as their applications in various fields have experienced a remarkable progress during the past 50 years. Apart from the traditional application of textile materials in clothes and fabrics, recently they have been used widely in high-demand applications such as composites, filtration media, gas separation, sensors, and biomedical engineering. In addition, some new methods are introduced for production of fibers, yarns, fabrics, and textile materials. On the other hand, nanotechnology as a revolutionary science has been extensively progressed, and it is being applied to various industries as well as textile industry [1].

Presentation of electrospinning is one of the impressive outcomes in this field that can prepare nanofiber structures. Nanofibers present enhanced properties such as high surface area to volume ratio, flexibility in surface functionality, and mechanical properties. Nanofibers have been used in many new applications such as in medicine [2,3] (artificial organ components, tissue engineering, implant material, drug delivery, and wound dressing), filtration [4,5], and nanofiber composite construction [6]. Electrospinning method is developed during the past 10 years extensively and provides a straight-forward electro hydrodynamic mechanism to produce fibers with diameters less than 100 nm, even 5 nm [2] up to several micrometers. The resultant nanofibers can be assembled into random nonwoven layers or an ordered state like yarn. However, twisted nanofiber yarn, has been a challenging and good potential to expand the applications of nanofibers [7]. Up to now, several methods have been proposed to obtain aligned electrospun nanofiber structures and yarns. The yarns are twisting during the electrospinning process, in order to improve the mechanical properties of yarns with high interconnections between the nanofibers [8].

In recent years, there has been an increasing interest in antimicrobial consumer products in many application areas [9,10]. It's known that silver and silver compounds exhibit excellent antimicrobial efficiency against a broad spectrum of organisms such as bacteria, fungi and viruses [11,12]. Therefore, the utilization of electrospun polymer nanofibers embedded with silver nanoparticles has received much attention, mainly due to their antimicrobial properties and their ability to release Ag ions to a pathogenic environment. Electrospun Ag-containing polymer nanofiber mats have been intensively investigated for potential biomedical applications. The preparation of the antibacterial polyamide 6 nanofibers containing silver nanoparticles which the silver ions were reduced at spinning solution, is reported [13]. The electrospinning solvent is employed as a reducing agent for in situ conversion of $AgNO_3$ into silver nanoparticles during the solution preparation [14]. Kleyi et al. studied the antimicrobial properties of the electrospun nylon 6 nanofibers incorporated with 2-substituted N-alkylimidazoles and their silver(I) complexes [15]. The method for surface-confined

* Tel.: +98 561 2502050; fax: +98 561 2227225.
E-mail address: barani@birjand.ac.ir.

http://dx.doi.org/10.1016/j.msec.2014.07.004
0928-4931/

synthesis of silver nanoparticle composite coatings on electrospun polyimide nanofibers was presented [16]. Yu et al. produced the PAN nanofibers with AgNPs distributed on their surface by using a modified coaxial electrospinning process, which involved using only $AgNO_3$ solution as the sheath fluid to facilitate the electrospinning process and render the new functions of the nanofibers. The nanofibers exhibited better quality than those obtained from the single fluid electrospinning in terms of nanofiber diameter, diameter distribution, and surface morphology [17]. Polyvinyl alcohol (PVA)/regenerated silk fibroin (SF)/$AgNO_3$ composite nanofibers were prepared by electrospinning [18]. Lee and Lyoo electrospun PVA/silver composite nanofibers containing silver nanoparticles from a PVA solution with small amounts of water based silver colloidal solution. Water-based colloidal silver in a PVA solution was directly mixed without any chemical or structural modifications into PVA polymer fibers to form organic–inorganic composite nanofibers [19]. Dong et al. prepared poly (vinyl alcohol) (PVA) and poly (vinyl pyrrolidone) (PVP) nanofibers embedding Ag nanoparticles (5–18 nm) by electrospinning at room temperature. Poly (vinyl alcohol) and PVP have been found to be as a good stabilizing and reducing agent for the preparation of noble metal nanoparticles [20]. Hong et al. prepared polyvinyl alcohol (PVA) nanofibers containing Ag nanoparticles by electrospinning PVA/silver nitrate ($AgNO_3$) aqueous solutions, followed by short heat treatment, and their antimicrobial activity was investigated for wound dressing applications [21]. Liu et al., directly incorporated silver nanoparticles into spin dopes and then electrospun into biodegradable PLLA fibers. They were reported that the silver nanoparticles could be incorporated into the PLLA fibrous membrane without significantly influencing the physical and chemical properties of the PLLA fibrous membrane [22]. Penchev et al. prepared hybrid nanofibrous materials with antibacterial activity consisting of yarns from N-carboxyethylchitosan and poly (ethylene oxide) that contain silver nanoparticles (AgNPs). The concentrated formic acid as polymer solvent is a mild reducing agent for silver ions to elemental silver [23]. Employed nanoparticles in the general electrospinning of polymer solution can block the electrospinning needle by generated precipitated particles [19].

In this study, an electrospinning setup was used to produce continuous twisted hybrid yarns of PVA/PLLA containing silver nanoparticles (AgNPs). Therefore, silver nitrate was added to electrospinning polymer solution and silver nanoparticles were synthesized as in situ method into the hybrid yarn structure. The influence of silver nitrate concentration in the polymer solution on the morphology and mechanical properties of the electrospun hybrid yarns was investigated. The yarns were characterized by scanning electron microscopy (SEM), and thermal analysis (differential scanning calorimetry) was used to study their thermal properties and crystallinity. The mechanical and antibacterial properties of the resulting PVA/PLLA yarns were investigated.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA) (Mw 195,000, degree of polymerization of 4300, and degree of hydrolysis of 98.0–98.8 mol%) was purchased from Merck. Poly (L-lactide) (PLLA) with a molecular weight of 300,000 was purchased from Purac Biomaterials, Netherlands. The 2, 2, 2-trifluoroethanol (TFE), was used as solvent and was obtained from Merck Co. and used without further purification. Silver nitrate ($AgNO_3$ extra pure, >99.8%) and sodium borohydride ($NaBH_4$, 99.9%), were purchased from Merck Co. (Germany).

2.2. Preparation of electrospinning solution

PVA/$AgNO_3$ polymer solutions were prepared by dissolving weighted amounts of PVA and different amounts of AgNO3, which were 0, 5, 10, 20, and 30 wt.% of the PVA polymer content. A weighed amount of PVA was dissolved in distilled water to afford 7 wt.% solutions. The solution was stirred (approximately 750 rpm) on a hotplate stirrer for at least 3 h at 50 °C. After that, the weighted $AgNO_3$ was added to the homogeneous cooled PVA solution and stirred for 30 min at room temperature. The 7 wt.% PLLA/TFE solution (without $AgNO_3$) was prepared as a described procedure for PVA solution.

2.3. Preparation of hybrid nanofiber yarn

The electrospinning setup to produce twisted hybrid nanofiber yarn is presented in Fig. 1. The set up includes a high-voltage source, two syringe pumps, a neutral cylinder surface, and a take-up-twister unit. The applied voltage is an important parameter that should be considered for producing a continuous nanofiber yarn. A Dc high-voltage power supply was used to generate voltages up to 25 kV. The two syringe pumps (TOP-5300, Japan) were used to provide a constant feed rate (0.3 mL/h) of the polymer solution. They were controlled digitally and installed horizontally in the opposite direction. The two syringe nozzles equipped with flat-tipped needles (22-gauge, inner diameter = 0.4 mm, outer diameter = 0.7 mm) were placed at a distance of D = 30 cm. Each needle was charged with a same voltage value, but in opposite polarization (±13.5 kV). One of these syringes contained PLLA polymer solution and the other contained PVA/$AgNO_3$ solution. The neutral cylinder (6 cm diameter × 30 cm length) was vertically placed, at the middle distance of two syringe nozzles. The take-up-twister unit includes a rotating plate that can be rotated from 1 to 440 rpm and a take up roller that was controlled by a stepper motor. The linear take up speed was adjusted according to the solution feed rate. The distances between needles and from their tips to the axis of the take-up-twister unit both were 30 cm.

In order to produce hybrid nanofiber yarns, electrospinning was started from the two nozzles. Then, a piece of yarn was placed at the convergence point to collect the nanofibers, and its other end was pulled toward the take up roller. The roller take-up speed was adjusted at 0.04 m/min. Finally, nanofibers were twisted (twist rate = 240 rpm) through rotating the yarn around its axis by the take-up twister unit. All hybrid nanofiber yarns were electrospun at environmental conditions. The amount of PLLA and PVA contents in the obtained hybrid yarns was determined by dissolving the PVA component in distilled water with slight stirring at 50 °C. Then, the residual yarn (PLLA component) was rinsed with distilled water and dried in vacuum oven at 25 °C. The electrospun hybrid yarns contained 89.11 wt.% of PLLA and

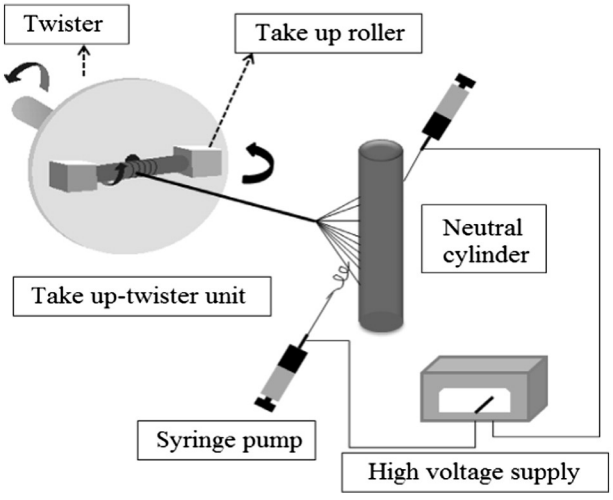

Fig. 1. Schematic setup of electrospinning.