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STUDY OF ELECTROSPUN NYLON-6/CHITOSAN COMPOSITE NANOFIBERS

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Abstract: Nanofibers of nylon-6/chitosan composite with weight ratio of chitosan to nylon-6 between 5 – 25 % were fabricated using electrospinning process. Nylon-6/chitosan solutions were prepared by dissolving chitosan powder (5 – 25 % weight ratio compared to nylon-6) into nylon-6 solution (20 % wt.) in formic acid. Nanofibers were electrospun at a potential of 20 kV and a distance of 20 cm from the target. Morphologies of the obtained nanofibers were investigated by scanning electron microscope. Pure nanofibers were obtained at low chitosan content (5 – 15 % weight ratio) while bead formation was found at higher chitosan content (20 - 25 % weight ratio). It was found that size of nanofibers was decreased at higher chitosan content. Water dynamic contact angle measurements revealed that increased chitosan ratio enhanced the surface hydrophilicity of the composite nanofibers.

1. Introduction

Electrospinning technique has attracted increasing attention because it is a simple and low-cost method for producing continuous ultrafine polymer fibers with diameters ranging from tens of nanometers to a few micrometers. Fiber formation by electrospinning of polymer solutions has been extensively studied in terms of applied voltage, tip to collector distance, feeding rate of polymer solutions and polymer solution properties [1-2]. These fibers with high specific surface areas and porous structure lead themselves to a wide range of applications including filtration [3-4], biological substrate [5-6], optical [7-8] and chemical sensors [9] as well as electrical conductors [10-11].

Chitosan, a (1-4)-linked 2-amino-2-deoxy-D-glucopyranose (in figure 1), is derived from chitin, one was found in sea shell such as shrimp, crab and cuttle-bone. Chitosan is biopolymer, has amino and hydroxyl functional groups along the polymer chains. It is well known for its nontoxic, biocompatible and biodegradable properties. In addition, it has several unique properties: it is antimicrobial and inhibits the growth of a wide variety of fungi, yeasts and bacteria, which can be beneficial for use the field of biomedicine [12-14]. It can also adsorb toxic metal ions, which can be beneficial for use in air cleaning and water purification applications [15-16]. These properties arise as a result of protonation of amino groups on the chitosan backbone. So far, preparations of chitosan based nanofibers fabricated by electrospinning have been reported. However, pure chitosan nanofibers were produced very difficult because the high viscosity of chitosan, which limits its spin ability and bead [17]. Recent research has focused on electrospinning blends of chitosan and other compatible polymers such as poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO), poly(ethylene terpthalate (PET), polycaprolactone (PCL), poly(lactic acid) (PLA), nylon-6 and others. These composite nanofibers are more advantageous over the electrospun nanofibers of pure chitosan, because the mechanical, biocompatible, antibacterial and other properties of the nanofibers were enhanced by the addition of these polymers [17]

Although the fabrication of composite nanofibrous membranes based on a series of nylon-6/chitosan complex with different weight ratio of nylon-6 to chitosan using a mixed solvent system have been studied previously [18]. The morphology and diameter of nanofibers were affected by the combination of the polymer blending, ranging from 0.1 to 0.9 μm and non-uniform. In this present work we studied of electrospun nanofiber with nylon-6/chitosan solutions were prepared by dissolving chitosan powder (5 – 25 % weight ratio compared to nylon-6) into nylon-6 solution (20 % wt) in formic acid solvent. The purpose of this investigation was to prepare nylon-6/chitosan blend solution that contained maximum levels of chitosan content in the blend and expect to obtain the electrospun nylon-6/chitosan composite nanofibers having more uniform structure and decreasing diameter.

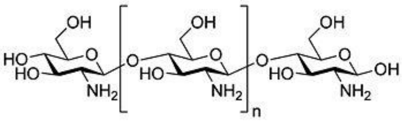


Figure 1. The molecular structure of chitosan [17]

2. Materials and Methods

2.1 Materials

Nylon-6 (AR grade) was obtained from Asia Fiber Public Co. Ltd. Chitosan (medium molecular weight with over 90 - 98 % deacetylation was purchased from Aldrich Chemistry. Formic acid (analytical reagent grade 98 %) from Fisher Scientific was used to dissolve the blends of nylon-6 and chitosan.

2.2 Solution preparation

Nylon-6 powder was dissolved in formic acid at concentration of 20 wt % (g/ml) and stirred for 3 h at room temperature. Chitosan powder amount of 1 g to 5 g was gradually added into previously nylon-6 solution and stirring until the blend polymer solution to get homogenous. This preparation obtained the blend solutions in weight ratio of chitosan to nylon-6 between 5 – 25 wt% for electrospinning process.

2.3 Electrospinning procedure

Electrospinning procedure was performed at room temperature. The polymer mixed solution was placed in a 3 ml syringe with a metal needle of 0.9 mm in diameter which was connected to the positive electrode. A power supply was used to provide a high voltage, 20 kV to the syringe needle tip (positive electrode) and metal collector (negative electrode). The electrospun fibers were collected on an aluminium foil. The distance between metal needle and collector was 20 cm with solution flow rate of 0.15 ml/min. The collection time was about 2 h per each sample.

2.4 Characterization

The morphology and diameter of the electrospun nanofibers were observed by field emission scanning electron microscope (FE-SEM; Hitachi, S-4700). The diameters of fibers were analyzed using image pro plus visualization software. The surface hydrophilicity of composite nanofibers mats was studied by measuring the water contact angle.

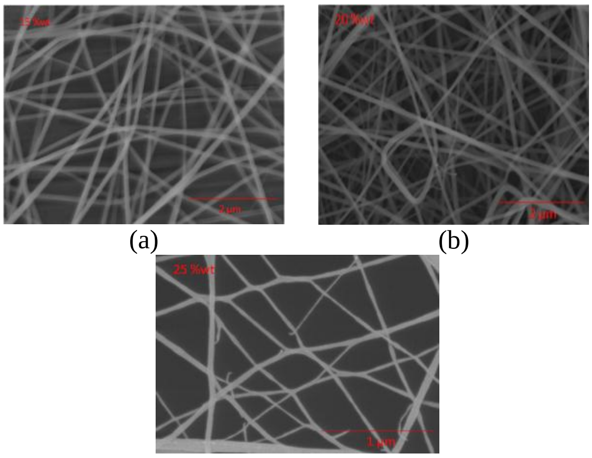
3. Results and Discussion

3.1 Characterization of nylon-6 nanofibers

Initially an attempt was made to blend chitosan onto pure nylon-6 solution in formic acid to forming a blend polymer for electrospinning process. The nylon-6 electrospun nanofibers at various concentrations were initially investigated. Figure 2 shows SEM micrographs of pure nylon-6 electrospun nanofiber using the applied voltage of 20 kV at the syringe to collector distance of 20 cm. All of the obtained nylon-6 nanofiber at 15 – 25 wt% concentrations showed cylindrical shape, with the size of 88 ± 13 nm, 86 ± 11 nm and 33 ± 14 nm, respectively. The average fiber size and size distributions of the nanofiber are shown in figure 3. It can be seen that the 15 – 20 wt% concentrations, very large amount of nanofibers web were obtained while the 25 wt% concentration, electrospun nanofibers were rather not came out due to too-low applied voltage and very more concentration also gives rise to higher solution viscosity. Therefore, the higher nylon-6 solution viscosity is a problem of solubility while adding a various chitosan fractions. In addition, the 15 - 20 wt% concentrations of nylon-6 solution were used to generating of the nylon and chitosan blended electrospun nanofibers in this work.

3.2 Characterization of complex nanofibers

SEM micrographs of the electrospun nanofibers mat that was formed using nylon-6/chitosan blend with varying weight ratios of chitosan to nylon-6 between 5 – 25 wt% (ratio of nylon-6:chitosan was 20:1 – 20:5 wt%) are shown in figure 4. Results showed that the morphology and average diameter of the nanofibers change significantly with respect to the various weight ratios between nylon-6 and chitosan. The fiber diameter decreased with increasing chitosan content. Therefore, it is shown that the morphology of the composite fibers also changed gradually from the uniform cylindrical shape (5 - 15 wt% chitosan content) onto the ribbon/bead mixed cylindrical shapes with increasing concentration (20 wt% chitosan content). At 25 wt% chitosan content, the fibers formation was nonuniform and became to branch shape. When the chitosan content above 25 wt% nanofibers spinning became impossible under the spinning condition was fixed at 20 kV applied voltage and 20 cm distance.



(a) (b)

(c)

Figure 2. SEM micrographs shown size and morphology of nylon-6 nanofibers with various concentration (a) 15 wt. %, (b) 20 wt%, (c) 25 wt%.

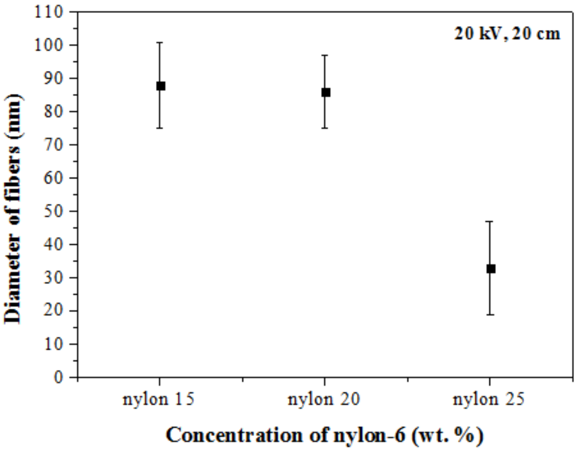
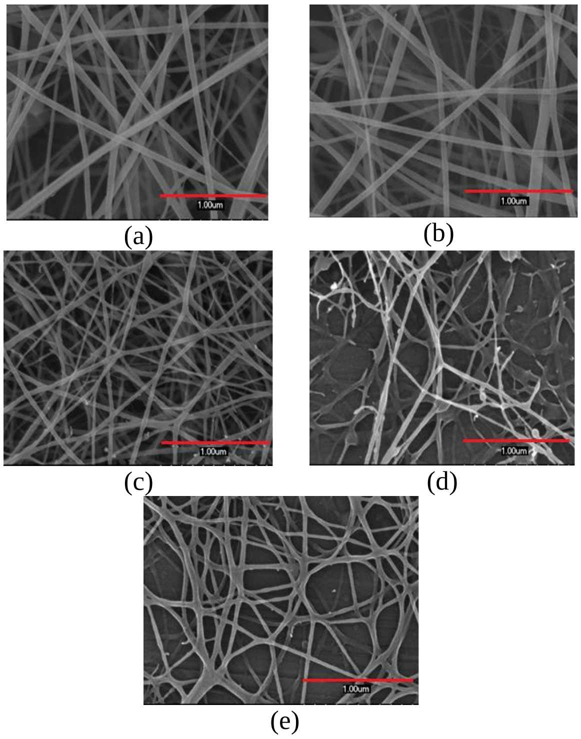


Figure 3. Average diameter and diameter distribution of nylon-6 nanofibers with difference concentration.

The average diameter and diameter distribution of composite nanofibers showed in figure 5. The smaller composite fiber diameter was obtained ranging from 30 to 50 nm. It was reported that the addition of cationic and anionic polyelectrolytes could increase the conductivity of polymer and consequently lead to thinner fibers [19]. Chitosan is a cationic polysaccharide with amino groups which had a higher charge density on the surface of ejected jet formed during electrospinning. As the charges carried by the jet increases, higher elongation forces are imposed to the jet under the electrical field. It has been known that the overall tension in the fibers depend on the self-repulsion of the excess charges on the jet. Thus, as the charge density increases the diameter of the final fibers becomes smaller [20].



(a) (b) (c) (d) (e)

Figure 4. SEM micrographs shown size and morphology of composite nanofibers with various ratio between nylon-6 and chitosan (a) 20:1 wt%, (b) 20:2 wt%, (c) 20:3 wt%, (d) 20:4 wt%, and (e) 20:5 wt%.

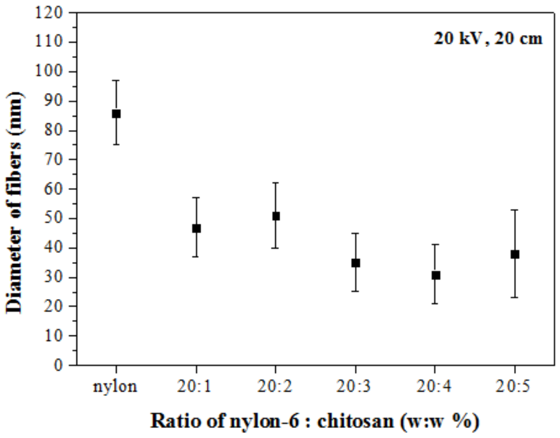


Figure 5. Average diameter and diameter distribution of composite nanofibers with difference weight ratio of nylon-6 to chitosan.

The surface hydrophilicity of electrospun nanofibers was studied by the water contact angle measurement. The dynamic water contact angle values at 0th to 350th second after the droplet contacted with nanofibers was shown in figure 4. It was found that the contact angle decreases gradually from 40° to 30° and this occurs as the content of chitosan in the copolymer increased from 5 to 15 wt% after the 60th second the droplet had contact with the electrospun mats. After about 150 - 350 s, the water droplets were placed on the nanofiber mats, the water contact angle of the pure nylon-6 nanofiber mats was about 70˚, while those of the nanofiber mats mixed 5 – 15 wt% chitosan content were closed to 0˚. The results also showed that the pure nylon-6 nanofibers had the lowest hydrophilicity (highest water contact angle), while the mat with 15wt% weight ratio of chitosan showed the highest hydrophilicity (smallest water contact angle). This results were confirmed previous speculations that chitosan, has several functional groups that are able to interact with other functionalized polymer. Due to chitosan has four hydroxyl groups, an amine group, and a minor proportion of amide group, which are in general, partially hydrolyzed. All these functional groups enhance the hydrophilic properties of chitosan and so enhance hydrophilicity when complexes with hydrophobic material such as nylon-6. Blend that includes varying amounts of chitosan will affect the degree of hydrophobicity compared to pure nylon-6 system.

Note that the nanofibers mats mixed 5 – 15 wt% chitosan content showed hydrophilicity while those with the nanofibers mats mixed 20 – 25 wt% gave a hydrophilic property. The inset in figure 6 illustrated contact angle with 20 – 25 weight ratio of chitosan to nylon-6 which contact angle were closed to 0˚ after the 3000th second. Due to the preparation procedure obtained the blend solution in weight ratio of chitosan to nylon-6 between 20 – 25 wt% for electrospinning process, the blend solutions get a more viscous and not completely dissolved. The concentration of blend solution was diluted by adding more amount of formic solvent into the previous blend solution until get homogeneous solution and could be electrospun condition. It is believed that at 20 cm distance between the end tip of the needle and grounded plate, the solvent was completely evaporated when fibers were collected on the ground plate. For this method remained the weight ratio of chitosan to nylon-6 at the same concentration and increasing solubility but higher solution viscosity was obtained. It was found that a little bit of fibers was collected onto the ground plate because of the viscous solvent was clogged at the end of needle tip. The surface properties by the water contact angle measurement of 20 – 25 wt% chitosan content electrospun nanofibers cannot mention. It is believed that most of the fibers were rather not come out during electrospun. The obtained water contact angle values after the droplet contacted showed the surface properties of aluminium foil substrate and did not exhibit nanofibers mats themselves.

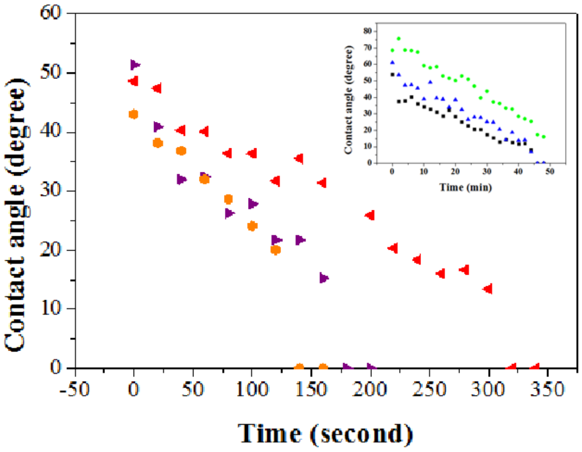


Figure 6. Water contact angle variations of electrospun nylon-6/chitosan blend nanofibers with difference weight ratio of nylon-6 to chitosan: (◄) 20:1 wt%, (▸) 20:2 wt%, (●) 20:3 wt%, (●) 20:4 wt%, (▲) 20:5 wt%, (■) pure nylon-6.

4. Conclusions

The nylon-6/chitosan composite nanofibers with varying weight ratio of nylon-6 to chitosan were successfully by electrospinning process. It was found that increasing chitosan content (5 – 15 wt %), fiber diameter was decreased (50 nm diameter size). The water contact angle was confirmed that increasing chitosan content enhanced the hydrophilic properties of nylon-6/chitosan nanofibers.

Acknowledgements

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