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Design of Modified Electro-Spun Poly Urethane Nanofiber Film using Chemical Method

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ABSTRACT

Background

Tissue engineering is defined as the designing and engineering of structures to rebuild and repair a body damaged tissue. Scaffolding Poly urethane (PU) has shown good biocompatibility and biodegradable properties. Nanofibers have improved the performance of biomaterials, and could be considered effective. One of the important methods for designing nanofiber scaffold is the electrospinnig method. In this study, PU nanofibers were well designed; then, modified with the immobilized gelatin via the chemically method. The samples were evaluated by ATR-FTIR, SEM, contact angle.

Results

ATR-FTIR structural analysis showed the presence of gelatin on the nanofiber surfaces. The SEM images showed the size average of nanofibers as to be about 300 nm; that increased with a gelatin coating up to 500 nm. Contact angle analysis showed 63 degree for uncoated nanofibers and 41 degree for coated nanofibers.

Conclusions

In this work, the PU nanofibers with a size average about 300 nm were designed. Nanofibers were successfully coated with gelatin via the chemically methods. These gelatin-coated nanofibers could be used well for tissue engineering.

Key words: PU, Surface modification, Nanofiber, Gelatin Coating.

INTRODUCTION

Polyurethanes are inherently resistant to cell growth and adhesion. When blood cells do not adhere, they do not accumulate and cause undesired thrombus formation, consequently this makes them hemocompatible .[1] Another application of PU is wound healing.[2] In order to modify the surface chemistry of Polyurethane and promote rapid tissue repair, various methods such as plasma

surface treatment have been developed .[3] Electro-spinning has been rapidly developed into a technique to prepare nanofibers with the diameter ranging from tens of nanometers to several microns[4-6].The electro-spun fibrous mats also show extremely high surface area and large porosity. Besides, the fibrous structure of the electro-spun mats may mimic the extracellular matrix. It is well-known that the gelatin is a natural extracellular matrix derived from the collagen inside animals skin and bones[6].Therefore; during the last few years, many works considering the tissue engineering of electro-spun nanofibers have been reported. Most recently, electro-spun nanofibers were prepared by Yang *et al.* and were applied in neural tissue engineering[7]. Although the presented nanofibers may mimic the morphologies of extracellular matrix to some extent, some modifications are still required to create a friendly environment for the cells attachment, proliferation, and functions such as communications. Some natural materials such as collagen, fibronectin and some peptides have been reported as scaffold modifiers[8,9]. Controlling surface properties is very important for the high performance of adhesion. Biomaterials wettability is an important factor in the surface modification of materials . Surface modification of hydrophobic polymer surfaces can be achieved by wet (acid, alkali), dry (plasma) and radiation treatments (ultraviolet radiation and laser)[10-13].

In this study, the coated gelatin PU nanofibers were obtained through the chemical method. The samples were evaluated by ATR-FTIR, SEM and the contact angle .

MATERIALS AND METHODS

Nanofiber Preparation

For preparation of PU film, 250 ml solution of dimethylformamide (Sigma Co.) poured in 50 ml tube then 2.5 g polyurethane (Bayer Co.) added to the solution and was well stirred for 12 h in order to obtained homogeneous solution. The solution poured in Petri dish and kept at 25°C for a few days to remove the solvent.

For design of PU nanofibers , polyurethane (Bayer Co.) (10%W) added to the solvents of DMF and DMF/THF (1:1) separately and were well stirred for 12 h in order to obtained homogeneous solution. An electro-spinning apparatus used in this study was prepared from the Asia Nanomeghyas Company (Iran). The PU solutions were dissolved at determined concentration in solvents. The PU solutions (10%w) in a glass syringe was controlled by the syringe pump. A positive high voltage source through a wire was applied at the tip of the syringe needle. In this situation, a strong electric field was generated between the PU solution and a collector. When the electric field reached a critical value with increasing voltage, the mutual charge repulsion overcame the surface tension of the polymer solution and the electrically charged jet was ejected from the tip of a conical shape as the Taylor cone. fibers were formed by the narrowing of the ejected jet fluid as it underwent increasing surface charge density due to the evaporation of the solvent.The electro-spun PU mat was carefully detached from the collector and was dried in vacuo for 2 days at room temperature to remove solvent molecules completely. The used parameters for this nanofibers preparation can be seen in Table1.

Gelatin Immobilization

Gelatin (purchased from Sigma) was immobilized onto the nanofiber surface based on the following protocol. A weighted amount of the nanofibrous mat was rinsed into the gelatin solution (15 mg/mL in aqueous solution) and was shaken gently for 2 h at 50 °C. The samples were exposured to glutaraldehyde 12% in hot water bath (80 °C). The obtained samples were placed inside a vacuum oven so that they would fully lose humidity.

ATR - FTIR Analysis

For surface identification of modified samples, the samples were studied before and after surface modification by an infrared spectrometer device (Thermo Nicolet Nexus. 870. USA). For this study, the samples must be cleaned before being used in the study.

Scanning electron microscopy

The surface characteristics of various modified and unmodified films were studied by scanning electron microscopy (SEM; Cambridge Stereo-scan, model S-360; Cambridge Instruments, Wetzlar, Germany) to analyze the changes in the

surface morphology. The films were first coated with a gold layer (Joel fine coat, ion sputter for 2 hours) to provide surface conduction before their scanning.

Contact angle analysis

The sample surfaces static contact angles were investigated by a contact-angle-measuring device (Krüss G10; Krüss, Matthews,NC) following the sessile drop method.

RESULTS

ATR-FTIR Analysis

ATR-FTIR spectra results of normal and modified polyurethane samples are shown in Figure 1 .ATR-FTIR Spectra of normal polyurethane is shown in Figure 1A. The spectra was observed in 1750 cm^{-1} that could be related to C=O group . The tension peak was in 1000-1310 cm^{-1} that could be related to C-O group and peak of 3000 cm^{-1} that could be related to CH_3 group. The tension peak observed in 3300 cm^{-1} could be related to NH group of PU.

ATR-FTIR Spectra of gelatin coated polyurethane is shown in Figure 1B. There was no significant difference between normal (A) and coated samples. However, a significant difference was observed in 3400-3700 cm^{-1} that could be related to OH and COOH groups and it is because of surface treatment with gelatin

SEM Investigations

The figures 2 - 4 show the Electron Microscopy Images of the uncoated and the coated nanofibers with gelatin in different magnifications. Figure 2 shows lock of PU nanofiber prepared to the electro-spinning method only to DMF solvent.

Figures 3 and 4 show the normal and coated-nanofiber mat prepared to the electro-spinning method with DMF/THF (1:1) solvent in different magnifications

Image analysis of the electrospun normal nanofibers fabricated from PU- DMF/THF solution and coated – nanofiber revealed an unimodal distribution of fiber diameters with an observed average diameter of 300 nm and 500 nm respectively (Figure 5).

Contact Angle Results

Table 2 shows the contact angle obtained for the uncoated and the coated nanofibers. The contact angles of 79° , 63° and 41° were obtained for the normal film and uncoated and the coated nanofibers, respectively. The 16-38° difference in the contact angle, obtained between samples, shows a better hydrophilicity of the coated nanofibers than the uncoated nanofibers and PU film.

Table 1: Used parameters for nano fibers preparation

Time (h)	Temperature (°C)	Voltage (kv)	Syringe tip distance to deram (mm)	Injected speed (mL/min)	Dram speed (rpm) (mm)	Syringe Diameter
7	30	20	75	2	1000	17

Table 2: Contact angle for normal film , uncoated and coated gelatin nanofibers

PU nanofiber (coated) (degθ)	PU nanofiber (uncoated) (degθ)	PU film (normal) (degθ)	T(°C)
41± 2.1°	63± 2.6°	79± 1.1°	25

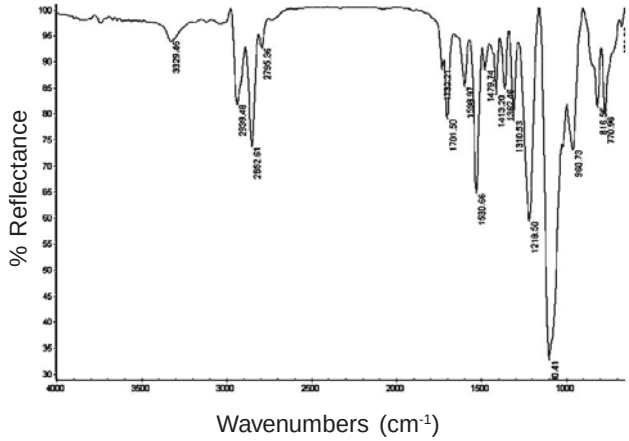

Fig.1(a): ATR-FTIR analysis of uncoated nanofiber film

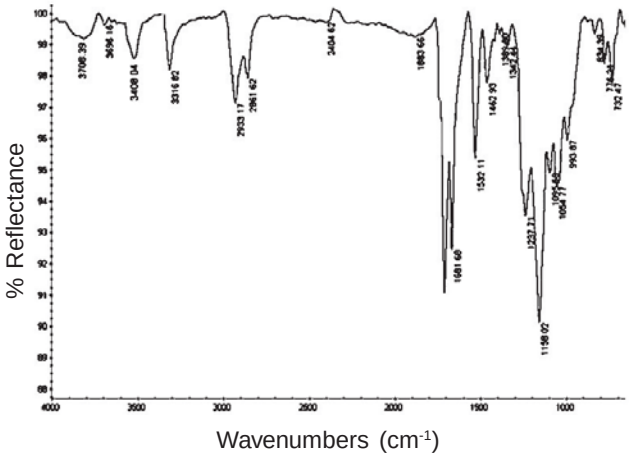

Fig.1(b): FTIR analysis of coated nanofiber film

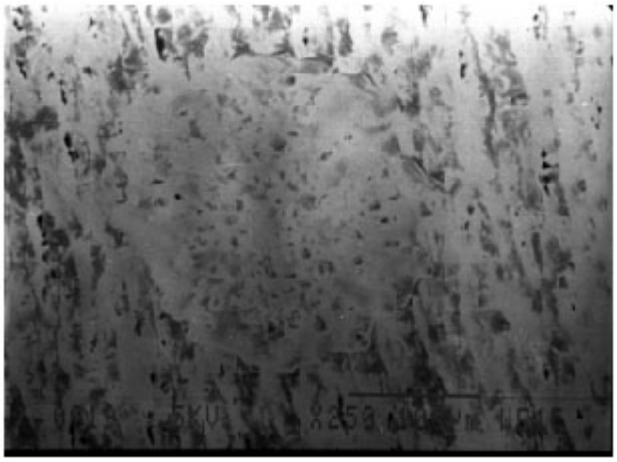

Fig. 2: SEM images of lock of PU nanofibers with DMF solvent

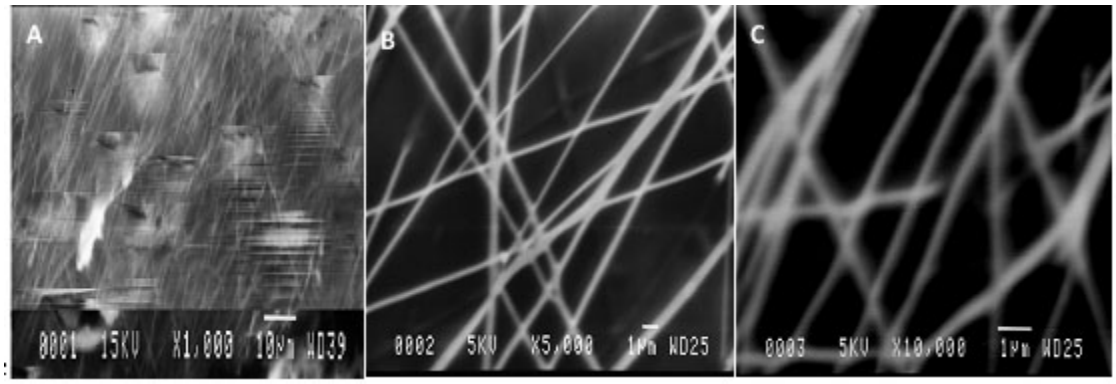

Fig. 3: SEM images of PU nanofibers in different magnifications (3a ; 1000x - 3b;5000x - 3c; 10000x)

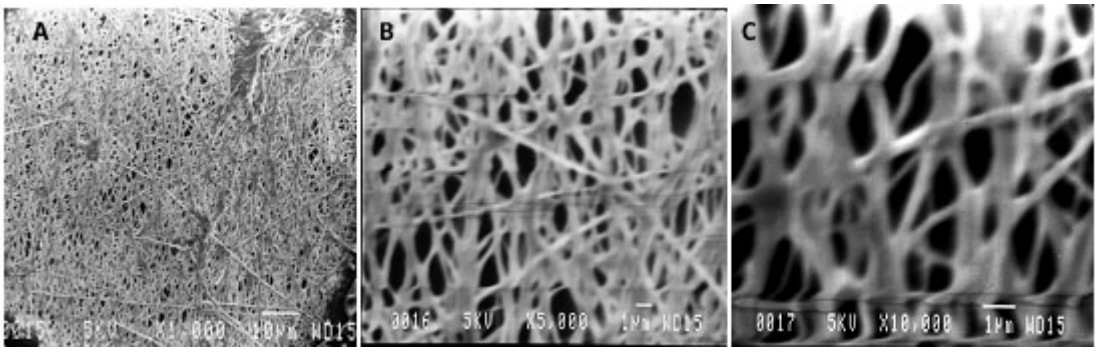

Fig. 4: SEM images of coated gelatin PU nanofibers in different magnifications (4a; 1000x - 4b; 5000x - 6c; 10000x)

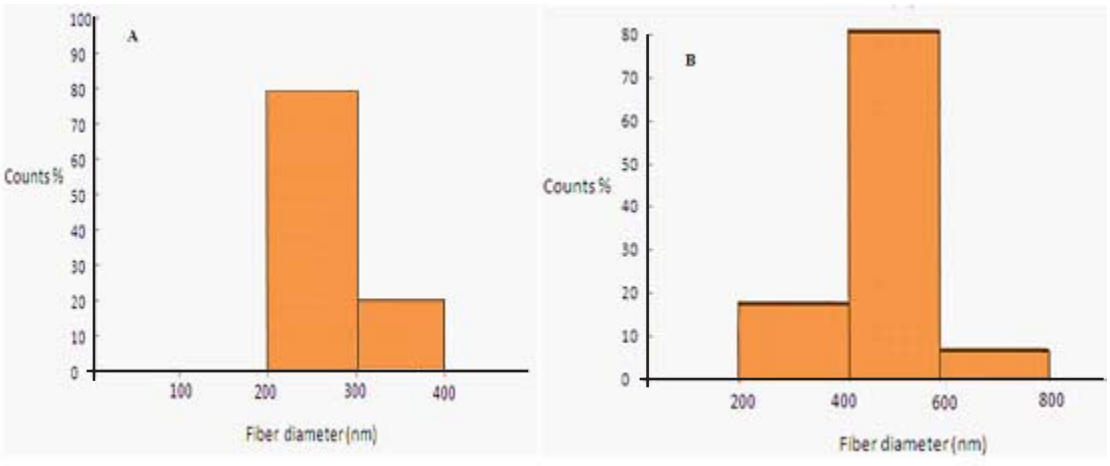

Fig. 5: Fiber diameter analysis of normal and coated PU nanofibers. The average fiber diameter were about 300 and 500 nm for normal (A) and coated (B) PU nanofibers respectively

DISCUSSION

In this study, the PU nanofibers with a size average about 300 nm were designed. Nanofibers were successfully coated with gelatin via the chemical methods shown in the analysis The smooth and homology modified nanofibers have been clearly shown in the figures. The size average was obtained for the modified nanofibers to be about 500 nm, whose increasing is due to gelatin coated on the PU surfaces. The 20°of difference in the contact angle, obtained for the samples (normal and Coated nanofibers), shows a better hydrophilicity of the coated nanofibers than the uncoated nanofibers. These coated nanofibers could well be used for tissue engineering.

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