Fabrication of nanofiber mats from electrospinning of functionalized polymers

Burcu Oktay¹, Nilhan Kayaman-Apohan¹, Serap Erdem-Kuruca²

¹ Marmara University, Department of Chemistry, 34722 Göztepe-Istanbul, Turkey
² Istanbul University, Istanbul Medical Faculty, Department of Physiology, 34390 Çapa-Istanbul, Turkey
burcu_chemist@hotmail.com

Abstract. Electrospinning technique enabled us to prepare nanofibers from synthetic and natural polymers. In this study, it was aimed to fabricate electrospun poly(vinyl alcohol) (PVA) based nanofibers by reactive electrospinning process. To improve endurance of fiber toward to many solvents, PVA was functionalized with photo-crosslinkable groups before spinning. Afterward PVA was crosslinked by UV radiation during electrospinning process. The nanofiber mats were characterized by scanning electron microscopy (SEM). The results showed that homogenous, uniform and crosslinked PVA nanofibers in diameters of about 200 nm were obtained. Thermal stability of the nanofiber mat was investigated with thermal gravimetric analysis (TGA). Also the potential use of this nanofiber mats for tissue engineering was examined. Osteosarcoma (Saos) cells were cultured on the nanofiber mats.

1. Introduction

Electrospinning is a versatile and easy technique for preparation of nanofiber network structure. In the electrospinning setup consist of three main equipment; a syringe pump, a high voltage source and a ground collector. Basically, a polymer solution (or melt) is loaded into the syringe. The polymer solution pushes out of the syringe with constantly rate via the pump. Simultaneously, an electrical field is applied by the high voltage source [1]. The stable electrospinning jet composes of four region; the base, the jet, the splay and the collection. The shape of the base depends on the surface tension of liquid. The charging of the jet occur the base. The shape is called as the Taylor cone. With increasing electrical field, charging the pendant drop of the polymer liquid takes on a conical shape. Additionally, begin to evaporate and diameter of the jet decrease. In the next region, the jet forms to the splay into many small fibers [2]. Fiber diameters are affected by various parameters; flow rate, applied voltage, tip to collector ratio, molecular weight, viscosity, surface tension, solution conductivity and ambient parameters [3].

Nanofibers have exciting a new class of material which used for a wide range of applications from medical to consumer products such as, filtration, wound dressing, adsorbent, energy storage, protein separation, immobilization, drug delivery and composites. The main features of nanofibers are large surface area–to-volume ratio, good mechanical, strength, excellent flexibility, and high porosity. These properties make them suitable for many applications. [4,5]

Crosslinked nanofiber mats have been prepared with many processes. One of the processes is a reactive electrospinning. In this process, the photo-crosslinkable polymers are in-situ crosslinked with UV radiation during electrospinning process [6]. As it is known, poly(vinyl alcohol) nanofibers dissolve in many solvent due to its hydroxyl groups in structure. Our aim is to prepare insoluble PVA nanofiber mats. For this purpose, PVA was modified by methacrylate groups and then crosslinking of PVA was conducted by UV light attached electrospinning setup. The thermal properties, the morphological properties and the cell adhesive properties of the resultant nanofiber mats were characterized.
2. Experimental Details

2.1. Materials
Poly(vinyl alcohol) (Molecular weight 146000-186000, degree 99+% hydrolyzed), glycidyl methacrylate (97%) were purchased from Sigma Chem. Co. Freshly double distilled water was used throughout the experimental work.

2.2. Characterization
The surface morphology of the nanofibers was examined with scanning electron microscopy (SEM) on Philips XL30 ESEM-FEG/EDAX. Thermal degradation of the nanofiber mat was investigated using a Perkin–Elmer Thermogravimetric analyzer Pyris 1 TGA model.

2.3. Electrospinning process
PVA was functionalized by glycidyl methacrylate according to literature [7]. The methacrylated PVA solution was prepared by dissolving in distilled water at a concentration of % 10. The methacrylated PVA solution was electrostatically spun with in situ UV cured electrospinning. A nanofiber web was formed under following conditions: flow rate 3 mL/h, tip to collector distance 15 cm, voltage 25 kV. The reaction scheme was shown in Figure 1.

Figure 1: Preparation scheme of PVA based on nanofibers

3. Results and Discussions
The chemical structure of methacrylate modified PVA was confirmed with FT-IR. The new band observed at 1650 and 1715 cm$^{-1}$ relating to methacrylate groups of PVA Also the characteristic band of PVA were occurred at 2090 and 1020 cm$^{-1}$ due to C–H stretching and C–O stretching, respectively (figure not shown) [8].
The morphology of both the crosslinked and the cell seeded nanofiber mats were investigated by SEM. Morphological results show that, homogenous network of the crosslinked nanofiber with diameters in the range of 150-200 nm was obtained (Figure 2). In figure 3 it can be seen, the linear PVA fibers were covalently crosslinked with each other.

![Figure 2: SEM micrograph of nanofiber mat at 1000 magnification](image1)

![Figure 3: SEM micrograph of crosslinked nanofiber mat at 5000 magnification](image2)
The nanofibers were cultured with Saos (Osteosarcoma) cells during 24 hours in DMEM (Dulbecco’s modified Eagle’s medium). The cells adhered and spread on the nanofiber. The results showed that the nanofibers have the cellular compatibility for Saos cells (Figure 4).

![Figure 4: Saos cell culture of nanofiber mat examination](image)

Thermal stability of crosslinked PVA nanofiber was investigated by TGA. As shown in Figure 5, TGA thermogram displayed two main decompositions. First weight loss was observed at around 280 °C due to decomposition of side chain of PVA. Second weight loss was monitored around 550 °C due to decomposition of main chain of PVA.

![Figure 5: TGA curve of functionalized PVA at air atmosphere](image)
Conclusion
In this study, we crosslinked nanofiber mats were prepared by electrospinning. The nanofibers became enduring toward to many solvents with UV radiation along electrospinning. Also, Osteosarcoma cells were cultured on the crosslinked nanofiber mats. The mats were characterized by SEM, TGA and FT-IR spectra. The results showed that, the crosslinked nanofiber mats could be used as a biomaterial a wide range.

Acknowledgements:
This work was supported by Marmara University, Commission of Scientific Research Project (M.U.BAPKO) under grant FEN-C-DRP-150513-0179

REFERENCES
[1] Baştürk E, Demir S, Danış Ö and Kahraman MV 2012 J Apply Polym Sci 127 349.
[2] Pham QP, Sharma U and Mikos AG 2006 Tissue Eng 12 1197.
[3] Jayesh Doshi J and Reneker DH J of Electrostat 1995 35 151.
[4] Oktay B, Baştürk E, Apohan NK, Kahraman MV Polym Com 2013 34 1321
[5] Wnek G, Marcus M, Simpson D and Bowlin G 2003 NanoLetters, 3 213.
[6] Yuan J, Mo H, Wang M, Li L, Zhang J and Shen J 2012 J Apply Polym Sci 124 1067
[7] Cavalieri F, Miano F, D’Antona P, and Paradossi G 2004 Biomacromolecules 5 2439.
[8] Bastürk E, Kahraman MV 2012 Poly Composite 33 829.