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Electrospun Nanocomposite Materials, A Novel Synergy of Polyurethane and Bovine Derived Hydroxyapatite

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Abstract. Polyurethane (PU) is a synthetic polymer that is used for construction of scaffold in tissue engineering applications in order to obtain desirable mechanical, physical and chemical properties like elasticity and durability. Bovine derived hydroxyapatite (BHAp) is a ceramic based natural polymer that is used as the most preferred implant material in orthopedics and dentistry due to their chemically and biologically similarity to the mineral phase found in the human bone structure. PU and bovine derived hydroxyapatite (BHAp) solutions with different concentrations were prepared with dissolving polyurethane and BHAp in Dimethylformamide (DMF) and Tetrahydrofuran (THF) solutions. Blended PU-BHAp solutions in different concentrations were used for electrospinning technique to create nanofiber scaffolds and new biocomposite material together. SEM, FTIR and physical analysis such as viscosity, electrical conductivity, density measurement and tensile strength measurement tests were carried out after production process.

1. Introduction

Tissue engineering deals with the creation of tissue scaffolds in the laboratory conditions for implanting organs and tissues [1]. Tissue engineering, physical and chemical aspects of bone extracellular matrix



(ECM) that may mimic (biomimicry) biomaterial (tissue scaffold), aims to repair or regenerate the damaged tissue or not functional ones in any part of human body, using the bone formation components of stimulating molecules and the cells with the potential to create under appropriate conditions [2].

Tissue engineering methods can be generally described as cell adhesion and preserving the functionality of a tissue support that supports a rich source of cells selected according to the target tissue and include growth factors that control the behavior of these cells [3].

The materials used in tissue scaffolds should be biocompatible and not to lead undesirable tissue response also it should have a surface chemistry increasing the cell adhesion and function. Tissue scaffolds fabricated from biodegradable material which has degradation ability in the body [4]. In addition to these features, biomaterials should be processable for the production of damage-specific structure; it can be recycled to the physical integrity of the bone if tissue scaffold is expected to have the desired mechanical strength. Providing these features depends on selected tissue scaffold production method and used biomaterials. Tissue scaffold should be possessed specific feature that can be listed as follows: Biocompatibility, biodegradability, mechanical properties, scaffold architecture and manufacturing technology [5].

Hydroxyapatite (HA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is a ceramic based polymer that is used as the most preferred implant material in orthopedics and dentistry due to the chemically and biologically similarity to the mineral phase found in the human bone structure. BHAp which is possessed of rhombic hexagonal lattice structure, plays an active role ensuring the bone mineral balance and maintaining the mechanical strength but it is brittle failure for that reason bovine derived BHAp is combined with PU in this way mechanical properties of resulting composite can be improved while establishing interfacial bond strength between the ceramic phase and the polymer matrix [6,7].

Polyurethanes are synthetic polymers, used for construction of scaffold due to their flexibility and versatile chemistry [8]. Biocompatible and biodegradable polyurethanes are used as suitable scaffold for tissue engineering in order to obtain desirable mechanical, physical and chemical properties like elasticity and durability [9]. Polyurethane is one of the most widely used polymers that are used in biomedical applications that contacts with blood. As a result of this, it can be easily synthesized in different forms and surfaces as compared to other polymers would not coagulated. Current applications of polyurethanes are catheters, blood bags and artificial heart systems etc.

Electrospinning technique is an efficient and relatively easy polymer fabrication technique that is allowed to produce wide range of nanofibers from various polymers by using voltage to create an electric field [10].

Previous research has been investigated for electrospun polyurethane/hydroxyapatite scaffolds [11], development and characterization of Polyurethane-Hydroxyapatite bio nanocomposites [12], Polyurethane/fluorhydroxyapatite nanocomposite scaffolds [13], investigation of PU and HA [14].

Aim of this study is to improve the bioactive properties of BHAp and PU nanofibers compared to only-polymer scaffolds while establishing interfacial bond between each other so that preferable mechanical properties of nanofibers were acquired with using that biomaterials together. We also investigated the mechanical properties of BHAp particles and PU nanofibers with different tests respectively; electrical conductivity, density, viscosity, tensile measurement, scanning electron microscopy (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR).

2. Experimental process

2.1. Materials and chemicals

Solvents named Tetrahydrofuran (THF), Dimethylformamide (DMF) were supplied from Sigma - Aldrich (St. Louis, MO, USA) and PU were purchased from TERMOSAN (Istanbul, Turkey) used without distillation or pre-treatment. BHAp were prepared in the nano sized diameters, derived from bovine bone.

2.2. Methods

2.2.1. Solution preparing and electrospinning process. PU was dissolved in different concentrations with THF/DMF (70:30 wt. %) solvents. Magnetic stirrer (WiseStir®, MSH-20A, Deutschland) were used to speed up the dissolving process. BHAp were added to the selected solutions and magnetic stirring process were repeated for 8 hours at 50 °C. Pure PU and PU-BHAp blend solutions were prepared in twelve different concentrations with the purpose of determining the best composite components to obtain novel and enhanced features. Contents of the samples were shown together with electrospinning parameters in Table 1.

Table 1. Nomenclature for the samples used with their contents and parameters.

Abbreviation of the samples prepared	Content		Parameters	
	PU (wt. %)	BHAp (wt. %)	Voltage (kV)	Flow rate (ml/hr)
s1	3	0	27	1
s2	5	3	21.5	1.1
s3	7	3	32.4	1.3
s4	14	3	21	1.5
s5	3	3	26.4	0.3
s6	5	3	27.4	0.7
s7	7	3	23.6	0.6
s8	14	3	18.6	0.4
s9	3	5	23	0.6
s10	5	5	18	0.3
s11	7	5	26.2	0.7
s12	14	5	24	0.9

2.3. Characterization

Characterization properties of Pure PU and PU-BHAp blend solutions and nanofibers were described and tests were done in order to get appropriate scaffolds.

2.3.1. Viscosity electrical conductivity and density of the solutions. Viscosity measurement of prepared Pure PU and PU – BHAp blend solutions were processed with Rheometer Device (Manufacturer- M/s Malvern Instruments Ltd., U.K., Model: Bohlin Gemini Rheometer) at room temperature, range between 1-200 Pa.s. Electrical conductivity tests were carried out with (WTW, Cond 3110 SET1, Germany) related device at room temperature. Density measurements were carried out with pycnometer at room temperature and all results were shown in Table 2.

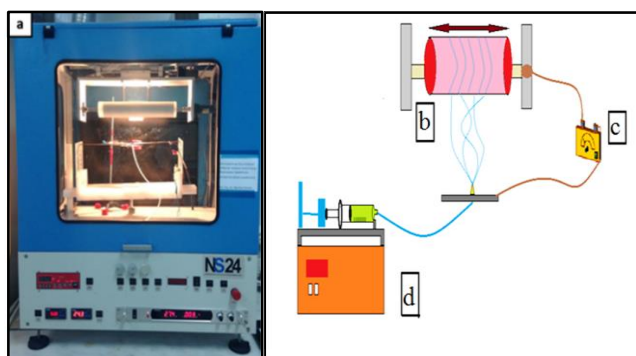


Figure 1. Camera image of the electrospinning device (a) and its schematic design with rotating collector (b), regulated power supply (c), digital syringe pump (d).

2.3.2. Mechanical properties of nanofibers. Mechanical characteristics of the nanofibers obtained were tested by the tensile strength measurement device (INSTRON 4411, Massachusetts, USA) at room temperature (23 °C) adjusted speed were set to 10 mm/min. Thicknesses of the fibers produced were analyzed with digital micrometer (795.1 MEXFL-25, Starrett, USA).

Table 2. Physical test results of the samples such as density, viscosity, electrical conductivity and tensile strength measurement tests.

Concentration of the solutions	Tensile Strength Measurement (MPa)	Electrical Conductivity ($\mu\text{S/m}$)	Viscosity (Pa.s)	Density (kg/m^3)
3 wt. % PU (s1)	0.93	1.4	6.403	0.926
5 wt. % PU (s2)	1.11	0.9	4.632	0.927
7 wt. % PU (s3)	1.15	0.8	3.059	0.929
14 wt. % PU (s4)	1.64	0.8	0.520	0.950
3 wt. % PU, 3 wt. % BHAp (s5)	0.22	9.4	4.240	0.935
3 wt. % PU, 5 wt. % BHAp (s6)	0.19	10.2	5.318	0.936
5 wt. % PU, 3 wt. % BHAp (s7)	0.69	8.1	7.241	0.939
5 wt. % PU, 5 wt. % BHAp (s8)	0.57	9.1	6.148	0.941
7 wt. % PU, 3 wt. % BHAp (s9)	0.47	9.7	3.067	0.958
7 wt. % PU, 5 wt. % BHAp (s10)	0.58	13	2.616	0.960
14 wt. % PU, 3 wt. % BHAp (s11)	0.11	8.5	0.423	0.971
14 wt. % PU, 5 wt. % BHAp (s12)	0.09	10.5	0.312	0.975

2.3.3. Scanning electron microscopy. Morphological and topographical details of prepared Pure PU and PU-BHAp electrospun fibers were analyzed with scanning electron microscopy (Zeiss Evo LS10, Germany) and tests were carried out at Yildiz Technical University. Prior to imaging, samples were coated with gold powder at 60 seconds. Coated samples were analyzed at 5 kV, a spot size of 7 and a magnification of 10000 times.

2.3.4. Fourier transform infrared spectroscopy. Content of the Pu-BHAp nanocomposite fibers were analyzed with Fourier-Transform Infrared Spectroscopy (GC-IR Interface for Nicolet™ FT-IR Spectrometers, USA). Spectroscopy was performed to determine the chemical components of the nanofibers produced between the ranges from 525 to 4000 cm^{-1} .

3. Results and Discussions

Table 1 shows the contents and concentrations of the materials used with two major parameters of the electrospinning process which are flow rate and voltage used to produce nanofibers. In Figure 1, (a) camera image of the electrospinning device can be seen in schematic design of the electrospinning device and its components such as (b) rotating collector, which increases the surface area in order to collect polymers solution on it and causes liquid to evaporate, (c) regulated power supply, which provides power to the systems (d) digital syringe pump to adjust flow rate of polymer solutions into electrical field.

On the SEM images nanofiber formations were observed and shown in Figure 2 as (a) low magnification and (b) high magnification images of the 's5'.

At %14 PU concentration nanofiber scaffolds were observed with the bead like structures which is generated by the presence of BHAp. Due to results of blending process, fiber structures and bead-like

structures were seen together as one fine scaffold. Diameters of the nanofibers were observed from 126.7 nm to 175.1 nm for 's8' and from 131.2 to 154.2 nm for 's12'.

As seen on the (c) low magnification and (d) high magnification images of 's8' and (e) low magnification and (f) high magnification images of 's12' respectively at Figure 2.

When the concentration of the BHAp increased, the presence and sizes of the bead like structures and inner diameters of the fiber scaffolds were also slightly increased. Viscosity of our solutions between 7.2 and 0.3, when the concentration of PU and BHAp were increased, viscosity of solutions was decreased as shown in Table 2. Densities of solutions are between 0.92 and 0.97 kg/m³. Electrical measurement of our solutions is between 0.8 and 13 μs/m, when the concentration of PU was increased, dielectric constants of solutions were decreased as shown in Table 2.

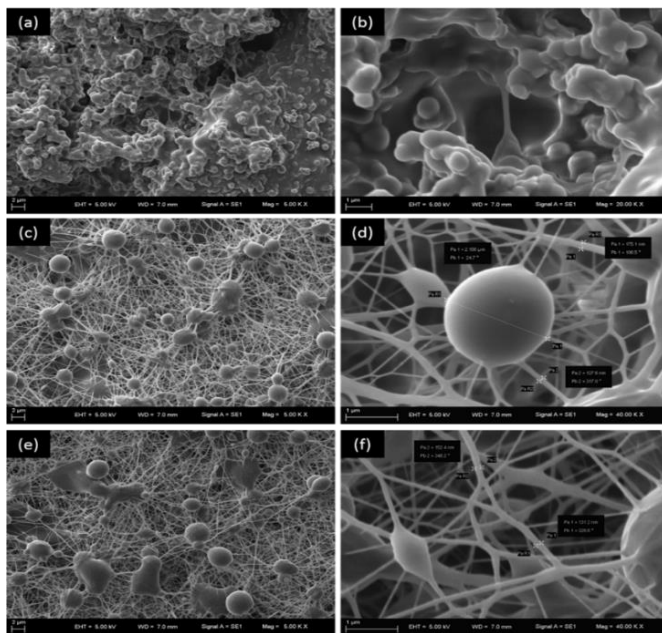


Figure 2. SEM images of the s5, s8, s12 respectively, (a,c,e) low and (b,d,f) high magnification.

FTIR spectra patterns of different concentration of PU and PU-BHAp composites nanofibers were shown in Figure 3. The peak at 3325 cm⁻¹ represents N-H bonds which is characteristic for PU. The peak at 3550 cm⁻¹ is related to OH bending which is characteristic for HA. The peak at 3000 cm⁻¹ describes CH₂ (Methylene) which is characteristic for HA. The peak at 1510-1700 cm⁻¹ regions were assign -C=O groups which is characteristic for PU. The peak at 3000 cm⁻¹ represents CH₂ (Methylene) which is characteristic for HA. The peak at 1510-1700 cm⁻¹ regions were assign -C=O groups which is characteristic for PU. The peak at 1500 cm⁻¹ region was assigned CO groups. The peaks between 1000-1200 cm⁻¹ region denote the (PO₄)⁻³ group which is characteristic for HA. The bands in the 570 and 1000 cm⁻¹ specify the P-O bonds of PU and 630 cm⁻¹ indicates the O-H, 600 and 560 indicates the P-O bonds of HA [16-19].

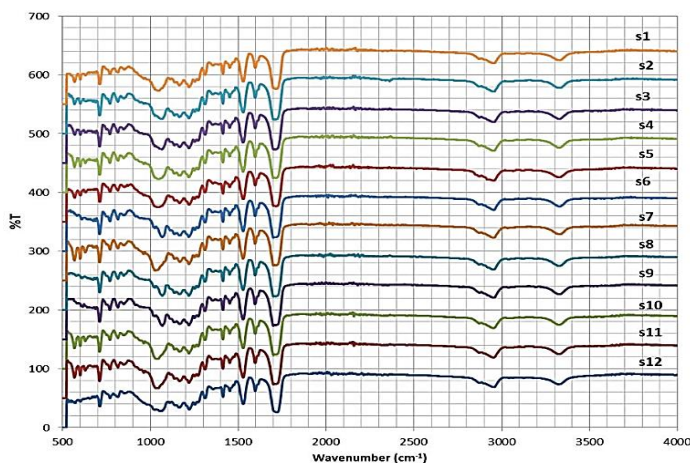


Figure 3. FTIR spectra of the obtained nanofibers.

4. Conclusions

Using the BHAp with PU was very important for ensuring biocompatibility, biodegradability, and mechanical strength of the fibrous materials. PU scaffolds were fabricated from DMF and THF solutions with THF/DMF (70:30 wt. %), which has been found to be most suitable solvent combination. Results are found to be promising for bone tissue engineering applications due to the

characteristics of the PU-BHAp composite nanofiber materials.

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References

- [1] Atala A 2011 Tissue engineering of human bladder *Ox. J. Med. Health Brit. Med. Bull.* **97** 1:81-104
- [2] Perez R et al 2015 Therapeutically relevant aspects in bone repair and regeneration *Mat. Today* **18(10)** 573-589.
- [3] Chan B P and Leong K W 2008 Scaffolding in tissue engineering: general approaches and tissue-specific considerations *Eur Spine J* **17** 467-479.
- [4] Dhandayuthapani B et al 2011 Polymeric scaffolds in tissue engineering application: A Review *Int. J. Poly. Sci.* **2011** 1-19.
- [5] O'brien, F J 2011 Biomaterials and Scaffolds for Tissue Engineering *Mat. Today* **14**, 88-95.
- [6] Polo-Corrales L et al 2014 Scaffold Design for Bone Regeneration *J. Nanosci. Nanotechn.* **14(1)** 15-56.
- [7] Martinez Valencia A et al 2011 Production of polyurethane/nanohydroxyapatite hybrid materials and microstructural characterisation. *Int. J. Phys. Sci.* **6** 2731-2743.
- [8] Guelcher S A 2008 Biodegradable polyurethanes: synthesis and applications in regenerative medicine. *Tissue Eng. Part B: Rev.* **14** 3-17.
- [9] Zdrahala R J and Zdrahala I J 1991 Biomaterial application of polyurethanes: review of past promises, present realities and a vibrant future *J. Biomater. Appl* **14** 67-90.
- [10] Demir M M et al 2002 Electrospinning of polyurethane fibres. *Polymer* **24** 3303-3309.
- [11] Tetteh G et al 2014 Electrospun polyurethane/hydroxyapatite scaffolds for bone tissue engineering: The role of solvent and hydroxyapatite particles, Elsevier, *J. Mech. Beh. Biomed. Mat.* **39** 95-110.
- [12] Díez Pascual A et al 2014 Development and characterization of novel poly(ether ether ketone)/ZnO bionanocomposites. *J. Mat. Chem. B* **2(20)** 3065.
- [13] Asefnejad A et al 2011 Polyurethane/fluor-hydroxyapatite nanocomposite scaffolds for bone tissue engineering. Part I: morphological, physical, and mechanical characterization, *Int. J. Nanomedicine* **6** 93-100.
- [14] Gorna K and Gogolewski S 2003 Biodegradable porous polyurethane scaffolds for tissue repair and regeneration. *J. Biomed. Mater. Res.* **79A** 128-138.
- [15] Tsui Y K and Gogolewski 2009 Microporous biodegradable polyurethane membranes for tissue engineering. *J. Mater. Sci. Mater. Med.* **20(8)** 1729-1741
- [16] Bil M et al 2007 Bioactivity of polyurethane-based scaffolds coated with Bioglass *Biomed. Mater.* **2** (2) 93-101.
- [17] McCarthy S et al 1997 In-vivo degradation of polyurethanes: transmission-FTIR microscopic characterization of polyurethanes sectioned by cryomicrotomy. *Biomater.* **18** 1387-1409.
- [18] Gorna K et al 2002. Synthesis and characterization of biodegradable poly (ϵ -caprolactone urethane) I. Effect of the polyol molecular weight, catalyst, and chain extender on the molecular and physical characteristics. *J. Polym. Sci. A Polym. Chem.* **40** 156-170.
- [19] Bakan F et al. A novel low temperature Sol-gel synthesis process for thermally stable nano crystalline hydroxyapatite. *Powder Technol* 233:295-302.