



Black Rice Added Nanofiber Food Packaging Production and Marine Based Bioceramic Synthesis by Electrospinning Technique

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When the amount of free radicals in the living body is high, they damage the cells involved in the vascular structure, and also cause atherosclerosis and paralysis. The higher the amount of free radicals on the cell, the more serious the cells in the environment are damaged. The main task of antioxidants is to react with these free radicals to neutralize their activity, that is to terminate their functionality. With this study, bioceramic production from sea urchin shells and the production of polyurethane (PU) biocompatible and biodegradable nanofibers with high antioxidant content will be produced by electrospinning method and the materials to be used in the food packaging sector will be produced. Structural (X-Ray Diffractometer-XRD, Fourier Transform Infrared Spectrometer-FTIR) and morphological (Scanning Electron Microscope-SEM) characterizations are provided for these nanofiber membranes. Within the scope of these features, it is aimed to be used in health, textile, agriculture, defense, filtration applications, especially in the food sector.

Keywords: Sea urchin, bioceramic, antioxidant, biodegradable, biocompatible, electrospinning, polyurethane, black rice

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1. Introduction

Rice is consumed as the main food product in Asian countries. In addition to white rice, which has the highest

consumption rate, red and black types are also available [1]. Due to the antioxidant properties of colored rice products, their use in various food production has been supported.

Therefore, red rice is widely consumed in Japan due to its high polyphenol and anthocyanin content. While the full benefits of the health benefits of colored rice are not known, consuming black rice organic food colorants will begin to be in demand and therefore the consumption rate of black rice has increased [2]. Black rice, which has high added value in terms of economy, takes its name from the rich natural anthocyanin compounds cyanidin 3-glycoside and peonidin 3-glycoside. Black rice has many advantages over other rice colors in terms of nutritional content. It is rich in protein, vitamins and minerals compared to black rice white [3].

Polyurethane (PU) are copolymers containing urethane groups in their structure [4]. Its physical and mechanical properties and good biocompatibility have enabled it to be used in a wide variety of uses [5]. With these features, it is also used as a wound dressing material. The wound dressing facilitates epidermal cell migration by preventing the risk of water loss on the wound surface [6]. The linear PU structure is seen in Figure 1.1.

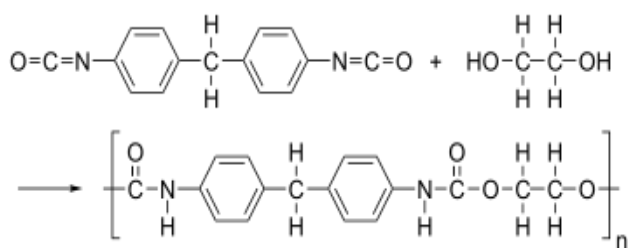


Figure 1.1. PU chemical structure [7]

Sea urchin is the name of the spiny sea creatures within the Echinoidea class. Sea urchins have spherical shells covered with thorns. Shell size is usually in the range of 3-10 cm in adult structures [8]. The basic ingredients of spiny sea creatures are composed of magnesium calcium carbonate (MgCO_3) compound [9]. Figure 1.2. shows the native sea urchin.



Figure 1.2. Native sea urchin [8]

Electrospinning method is defined as the production of nanometer scale fibers from charged polymer solutions as a result of electric field strength [10]. In this method, the production of solid form yarns from polymer solutions does not involve coagulation chemistry and high temperature conditions. This is a state of the manufacturing process involving large-scale production and the use of complex molecules. In this method, while the solvent dissolves the polymer, it evaporates away from the system while the system is operating.

In this study, bioceramic synthesis by chemical precipitation method from sea urchin shells, and the production of antioxidant-containing black rice-added polyurethane biocompatible and biodegradable nanofibers by electrospinning method, to develop materials to be used mainly in the food packaging industry. The material properties will be determined by characterizing the materials obtained.

2. Experimental Studies

2.1. Materials

Sea urchin sea shells required for the synthesis of bioceramics were obtained from a seafood market. Black rice was purchased from a market that sells organic products in package form. Orthophosphoric acid (H_3PO_4) (85% reagent purity) was purchased from Merck. Thermoplastic polyurethane (PU) was supplied from BASF. molecular weight for solving polymer 73.29 g / mol dimethylformamide (DMF) (Sigma-Aldrich / Turkey) and molecular weight of 88.11 g / mol ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$) (Sigma-Aldrich / Turkey) organic solvents used.

2.2. Bioceramic production in sea urchins

Sea urchin shells were turned into thin shells by pounding in a ceramic mortar with a ceramic mallet. It was sieved through a 100 mesh stainless steel sieve to bring it to standard powder size and 2 g of the accumulated powders were weighed. 50 ml of pure water was added to a 100 ml beaker and the mixture was started by putting it in a magnetic stirrer. During the mixing, 2 grams of sea urchin powders below 100 microns were added and the mixture was achieved at 80 °C for 2 hours. Orthophosphoric acid was added to this homogeneous solution in an amount calculated according to the rate determined by the sea urchin thermogravimetric analysis (TGA) graph, and the mixture was provided at 80 °C for 8 hours. By drying the liquid part at room temperature in the oven for 24 hours, the settled part of the beaker was removed and sintered at 450 °C and 850 °C.

2.3. Production of black brass reinforced polyurethane nanofibers by electrospinning method

14% PU and 1%, 5%, 8% black brass added PU nanofibers were dissolved in DMF / Ethyl acetate (80/20% mixture) solvent solution at 50 °C for 8 hours, and the production of nanofibers with a viscosity suitable for nanofiber production process was ensured by electrospinning method. Nanofiber production process was achieved by spinning 1%, 5%, 8% black brass samples added to 14% PU and 14% PU matrix for 2 hours at 30 °C. In the production process, the parameter values in Table 2.1. were taken as basis. Table 2.1. contains the parameter values applied to the electrospinning solutions. Figure 2.1. shows the production stages of biocomposite products.

Table 2.1. Parameters applied to electrospinning solutions

Compound		Parameter		
PU (wt.%)	Black Rice (wt.%)	Working Distance (cm)	Voltage (kV)	Flow Rate (ml/hr)
14	-	17	24	0.9
14	1	17	24	0.9
14	5	17	24	0.9
14	8	17	24	0.9

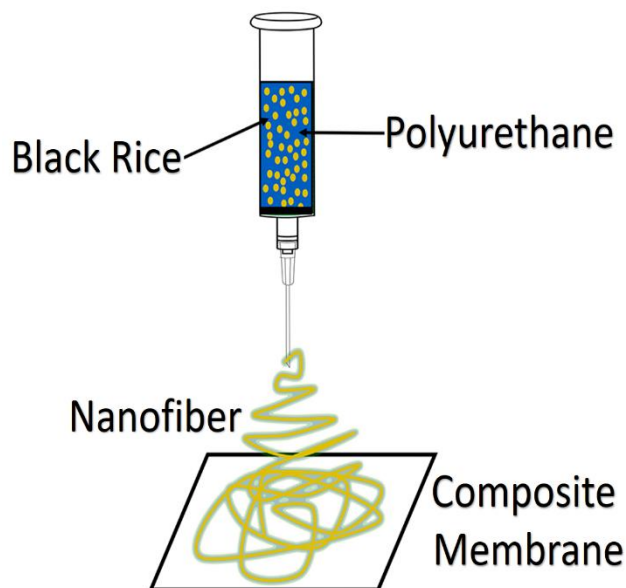


Figure 2.1. Biocomposite production stages

2.4. Characterization studies

XRD structural analysis of HA powder was determined using the Panalytical X'Pert-Pro diffractometer. FTIR structural analysis was determined using Jasco 6600, America, generated as a graph obtained over the 400-4400 cm^{-1} region. Morphological properties of bioceramic and

biocomposite materials were evaluated with FEGSEM Quanta FEG 250. The size of the particles and fibers is the average of the measurements taken from forty regions.

3. Result and Discussion

3.1. XRD analysis

Different crystal structure, formula concentrations, calcium phosphate compounds have been found, such as monoteite, whisker, calcium pyrophosphate, tetracalcium diphosphate monoxide, fluorapatite and hydroxyapatite.

3.2. FTIR analysis

Calcium pyrophosphate crystal phases give three different wavelengths. There are PO_3 and $\text{O} - \text{PO}_3$ bands in the wavelength range of 400-630 cm^{-1} , P-O-P bands in the wavelength range of 630-980 cm^{-1} , and PO_3 bands in the wavelength range 980-1270 cm^{-1} [11,12]. There are P-OH band in the wavelength range of 820-1100 cm^{-1} , asymmetric strain band in the wavelength range of 1030-1090 cm^{-1} , bending stress in the wavelength range of 560-600 cm^{-1} and symmetrical strain bands in the wavelength range of 962 cm^{-1} . 566.1, 602.2, 1049.7, 1092.0 cm^{-1} wavelengths are the peaks of HA crystal phase [13]. Peaks in the wavelength range of 500-1500 cm^{-1} belong to the PO_4 bands. Along with the new peaks between different temperatures, the structures of the existing peaks also changed. When the spectrum of PU structure was evaluated, it was determined that there were CH_2 strain bands at 2956 cm^{-1} wavelengths, and $-\text{C} = \text{O}$ absorption bands at 1727 cm^{-1} and 1701 cm^{-1} wave numbers. The peaks at wavelengths of 1597 cm^{-1} and 1464 cm^{-1} correspond to the C-C stretch bands in the benzene ring; The bands belonging to the N-H and C-N bonds in the amide group at a wave number of 1527 cm^{-1} belong to the bands between 1100 cm^{-1} and 916 cm^{-1} to the C-O-C stretch bands [14]. Depending on the vibration characteristics of the O-H bond, black rice reveals the presence of water. Although it is observed that there is not much change on the PU structure of black brass materials at the rates of 1%, 5% and 8% due to the low contribution, they are located in significant peaks.

3.3. SEM analysis

When the structure of sea urchin powders was examined, besides the crystal structures in thin plate form, needle-like whisker crystal structures were determined. Grain sizes are between 1-20 μm . The foggy regions in the FEGSEM images were determined as the density of the nanoparticles in that region. Sea urchin has a finer structural form in terms of particles in its morphology at a temperature of 450 °C and a temperature of 850°C It is seen that the needle-like

structures with the increase in the temperature value, the sharp types take an oval shape, and their needle-like structures deteriorate and transform into different types of crystal structures. When the PU nanofiber structure was examined, nanofiber formation was observed, but it was observed that the nanofiber structures were not in the form of thin fibers. By adding 1% black rice powder to a 14% PU solution, a composite structure was formed by spinning, and as can be seen from its morphology, it was observed that black rice grains were not homogeneously distributed, they were not in thin fiber form, and they had agglomerate structures. When 5% black rice was added, the fiber structures became homogeneous, when the concentration amount was brought to 8%, it was observed that the fiber dimensions of the PU nanofibers with black rice were homogeneous, as well as finer dimensions. When the fiber sizes were taken averages, it was seen that it was 30-350 nm. Figure 3.1. shows the bioceramic morphology of sea urchin and 14%PU-14% PU/ 1,5,8 % Black brass biocomposite materials.

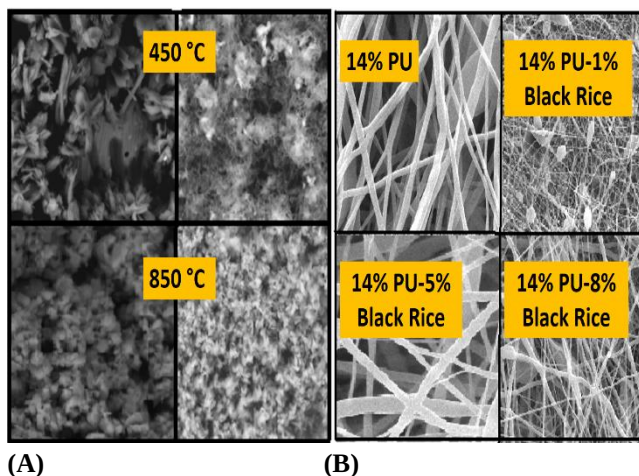


Figure 3.1. (A) Sea urchin bioceramic morphology, (B) 14% PU - 14% PU / 1,5,8% black rice biocomposite morphology

4. Conclusion

When the results of the study were evaluated, bioceramic powders were obtained from sea urchins by chemical precipitation method. High amount of hydroxyapatite (HA) structure was determined by XRD analysis. The HA structure was supported by the presence of functional peaks by FTIR analysis. Biocompatible and biodegradable food packaging product has been successfully produced from black rice reinforced polyurethane matrix material. It was determined that black brass and polyurethane composites were produced with functional groups determined by FTIR analysis. Fiber dimensions of PU and PU / Black brass nanofibers were found to be 30-350 nm by FEGSEM analysis. It is concluded that these fine fibers are not broken,

and the risk of bacterial adhesion decreases with the increase in the amount of black rice, as the black rice particles are bonded straight to the PU fibers, and it is used as a biodegradable and biodegradable container material to be used in the ideal food packaging industry.

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