The Production of Hollow Nanofibers from PBS / TPU Blends by Coaxial Electrospinning Method

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Abstract
In this study, the production of hollow Polybutylene Succinate (PBS)/Thermoplastic Polyurethane (TPU) nanofibers as biodegradable nanomaterials with improved mechanical properties were carried out by coaxial electrospinning method. The polymer solutions of pure PBS, pure TPU, and PBS/TPU blends (60/40, 40/60, 20/80 w/w) (as the shell) versus pure Polyvinylpyrrolidone (PVP) (as core) were put together for bi-component nanofibers production. The core structure of nanofibers was dissolved in distilled water. Thus, hollow nanofibers were obtained with the removal of PVP from the structure. Characterization studies (SEM, FTIR, and Tensile tests) of hollow nanofibers were performed. The morphological properties of PBS/TPU blends in ratios of 60/40 and 20/80 were observed as homogeneous and non-adhered fiber structures. It was determined that the hollow PBS/TPU (60/40) mat has the thinnest nanofibers. New bond formations within the interactions of substances as studied in the chemistry of blended electrospun webs were examined with FTIR analysis. Therewithal, this test showed the removal of PVP in the core of all nanofibers. It was observed that the adhered fibers increased the tensile stress and decreased the tensile strain at mechanical test results that were verified also by SEM views. It is suggested that the hollow nanofibers produced by this study can be used in the biomedical field as a biodegradable and breathable wound dressing.

1. INTRODUCTION
Nowadays, hollow nanofibers are attractive in wide research areas due to their great length-to-diameter proportions, tiny diameters, hydrophilic structures, and large uppermost layer-to-unit mass advantages. Those exceptional features make them suitable for producing desired end products with special properties. In parallel, biodegradable polymers have gained great importance with the discovery of their usability in biomedical implementations like wound dressing, drug delivery, suture thread, and scaffolding due to their mechanical strength, biodegradation, and biocompatibility properties. Coaxial electrospinning is the most effective method to form excellent hollow core-shell electrospun webs of polymers [1-5] exclusively for biomedical applications. In this production method, two or more different polymers (dissolved) through a spinneret form bi-component fiber spun in a Core/Shell (C/S) structure [6]. X. Zhang et al. [7] reviewed the recent advances in the design of electrospun nanofibers produced by coaxial electrospinning technology mainly in air purification applications in terms of nanofibers’ diameter, porosity, high specific surface area, and hollow-structured nanofibers types.

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Polybutylene succinate (PBS) is aliphatic thermoplastic polyester obtained by condensation polymers reaction of butanediol and biobased succinic acid, biodegradable, having non-toxic degradation products, easily processable, thermal, and structural properties, and advanced mechanical properties [8, 9]. In Cooper et al. [10] studies, the effects of different solvents on the structure of BioPBS nanofibers were evaluated and less bead formation was observed when CF/DMSO solvent system was used. Besides, the highly porous BioPBS micro and nanofibers have been shown to result in a graduated structure with adequate tensile properties for possible practices in the curing of injuries and biomedical soft tissue structure designs. Thermoplastic polyurethane (TPU) is a superior material combining the elasticity of rubber with the hardness and strength of metals, whose use for biomedical purposes is increasing day by day. The hydrophobic polyurethane/polyactic acid (PU/PLA) blend solid [11, 12] and hollow [13, 14] nanofibers by the coaxial electrospinning method were presented with characterization test results in our previous studies. Meanwhile, the biocompatible solid ones were recommended for dry wounds and the hollow ones for use on exuding (wet) wounds with also quick drying capability to support patient comfort. Although the polymers were hydrophobic, the hollow tubular cross sections provided the super wettability property to the nanofibers mats with 756% liquid absorption capacity. Najafi et al. [15] produced hollow TPU nanofibers yarn by electrospinning process. Hollow electrospun nanofibers are generated by running PVA fibers inside the structure and then taking the PVA core out from the fiber in warm distilled water. Great strength and excellent flexibility have been evaluated as the unique properties of TPU electrospinning yarn. This study showed the possible practices as artificial vessels in hollow electrospun nanofibers structures and artificial tandems in pure form. Polymethylpyrrolidone (PVP) polymer, which is soluble in water and many organic solvents [16], provided many advantages in our study, as it was preferred in the coaxial electrosprining production method in the internal structure.

In this study, due to the author’s knowledge, for the first time, PBS/TPU blended hollow nanofibers have been successfully obtained with the coaxial electrospinning method, and the effects of pure PBS, pure TPU, PBS/TPU blended hollow nanofibers were investigated morphologically by Scanning Electron Microscopy (SEM), mechanically by tensile test, and chemically by Fourier Transform Infrared Spectroscopy (FTIR). Biodegradable PBS and biocompatible TPU polymers with hydrophobic character can be converted into the hydrophilic structure to be used in medical implementations for example tissue scaffolding and wound dressing in the future.

2. MATERIALS AND METHODS

BioPBS FZ71PM as poly(butylene succinate) (PBS) (Mw: 104,000 g/mol) from PTT MCC Biochem CO. Ltd. (Thailand), Ravamec 240 A85® as thermoplastic polyurethane (TPU) (Mw: 120,156 g/mol) from Ravago (Türkiye) and PVP 40 as polyvinylpyrrolidone (PVP) from Sigma-Aldrich (Germany) were purchased. As solvents: the chloroform (CF), the dimethylformamide (DMF) from Merck Company, the dimethyl sulfoxide (DMSO) from Carlo Erba, and the ethanol from Tekkim Kimya were supplied.

Hollow nanofibers production consists of 3 parts. Firstly, the polymer solutions were prepared with determined conditions. Secondly, the obtained solutions were directed to the co-axial electrospinning process for nanofibers production. Thirdly, the core structure of nanofibers was dissolved in distilled water. Thus, hollow nanofibers were obtained with the removal of PVP from the structure. In the first part, the 12 wt% pure PBS, the 7 wt% pure TPU, and the 20 wt% pure PVP solutions were prepared in CF/DMF/DMSO (8.5/1/0.5, v/v/v) solvent systems. The PBS/TPU solutions were also prepared with 8 wt% concentration. All were stirred with a magnetic mixer at 60°C for 3.0 hours and then at 80°C for another 0.5 hours, only the PVP solution was dissolved at 60°C for 2 hours in total. In the second part, all the prepared solutions were subjected to the co-axial electrosprining process without waiting. The compositions of the studied polymer solutions are given in Table 1. The obtained hollow nanofibers codes are the same as the name of the polymer solutions. In the third part, to obtain hollow nanofibers, the produced mats from electrospinning processes were washed with distilled water to dissolve the PVP core polymer. In this way, the removal of dissolved PVP from the fiber structures was achieved. The nanofibers mats productions have been carried out with the co-axial electrospinning method in which a needle with 0.64 mm (22G) diameter is located within a nozzle with 1.6 mm (14G) diameter. The process conditions were performed as 20 cm distance, 1.50 mL/h feeding rate, and 16 kV applied voltage. The process durations of all productions were two hours.
Table 1. Compositions of the polymer solutions

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>PBS/TPU/PVP (wt/wt/wt)</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure PBS</td>
<td>100/0/0</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Pure TPU</td>
<td>0/100/0</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>Pure PVP</td>
<td>0/0/100</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>60-PBS/40-TPU</td>
<td>60/40/0</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>40-PBS/60-TPU</td>
<td>40/60/0</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>20-PBS/80-TPU</td>
<td>20/80/0</td>
<td>8</td>
</tr>
</tbody>
</table>

The surface morphologies of the electrospun webs were investigated by QUANTA 400F Field Emission branded scanning electron microscopy (SEM) analysis. The chemical structures of nanofibers were investigated with a Perkin Elmer spectrum 100 branded Fourier-transform infrared spectroscopy (FTIR) analysis with wavelengths between 4000 - 650 cm\(^{-1}\). The mechanical properties of hollow nanofibers were tested with Lloyd Instruments LRX Plus considering ASTM D882 conditions.

3. THE RESEARCH FINDINGS AND DISCUSSION

SEM images of electrospun nanofibers are presented at 10000x magnification with 10µm scale bar in Figures 1, 2, 3, 4. Due to SEM images, the morphological properties of PBS/TPU blends in ratios of 60/40 and 20/80 were observed as smooth, homogeneous, and non-adhered fiber structures. However, the beaded structure was observed in pure PBS nanofibers (Figure 1). Also, the 40-PBS/60-TPU blend hollow nanofibers showed irregular and adhered fiber structures after distilled water treatment. When the nanofibers were compared, it was determined that the hollow 60-PBS/40-TPU mat has the thinnest nanofibers (Figure 3). The hollow nanofibers of the 60-PBS/40-TPU blend presented the best result among other blended hollow nanofibers (Figure 4).

![Figure 1](image1.png)
**Figure 1.** SEM views of nanofibers, a) process of electrospinning of pure PBS from one syringe feeding, b) process of coaxial electrospinning of “pure PBS + PVP” (S/C) from two syringes into one spinneret, c) hollow nanofibers of pure PBS with removed PVP core after the distilled water treatment

![Figure 2](image2.png)
**Figure 2.** SEM views of nanofibers, d) process of electrospinning of pure TPU from one syringe feeding, e) process of coaxial electrospinning of “pure TPU + PVP” (S/C) from two syringes into one spinneret, f) hollow nanofibers of pure TPU with removed PVP core after the distilled water treatment
The primary goal of the electrospun webs manufacturing technique is to develop beadless fibers of uniform thickness. In electrospinning, the liquid jet has to be kept constant to create smooth nanofibers of the same kind and to achieve a balance between surface tension, viscoelastic forces, and electrostatic impulse. Moreover, the stability of process repeatability is another considerable requirement of electrospinning. The conditions stated are pertinent to the density of the polymer. In previous works, the density of the polymer was found to be the most prevailing factor to have homogeneous diameters of nanofiber webs [12, 17]. The polymer’s molecular weight has also a significant effect on the nanofiber morphology. In general, when the polymer’s molecular weight is decreased, possibly a beaded structure is created while the concentration is kept constant. As the molecular weight increases, smoother fibers are formed [11, 12, 18]. The pure TPU nanofibers’ diameters were thick (Figure 2). In this condition, it can be interpreted that the molecular weight of the pure TPU polymer is higher than the molecular weight of the pure PBS polymer. With this result, it is also confirmed that the molecular weight of the pure TPU polymer is higher than the molecular weight of the pure PBS polymer. As the PBS ratio in the blends increased, it was expected that finer fibers would form. Such that, it was predicted that there is a fiber diameter balance in the form of 60-PBS/40-TPU < 40-PBS/60-TPU < 20-PBS/80-TPU. Due to its high molecular weight, it is expected that the fibers will thicken as the TPU ratio in the structure increases. However, in this study, it can be emphasized that the effect of molecular weight was not revealed according to the SEM images of hollow nanofibers, since the cohesive-appearing fibers changed the nanofiber structure after distilled water process.

The FTIR-ATR spectra of the nanowebs are presented in Figures 5, 6, and 7. The peaks of pure TPU nanofibers were observed for aromatic C=O group vibrations at 1600 cm⁻¹, N–H group oscillations at 3318 cm⁻¹, for CH₂ at 2855 cm⁻¹, for C=O group oscillations at 1709 cm⁻¹ and oscillations of (N–H) + (C–N) + (C–H) at 1311 cm⁻¹ [11, 19]. The characteristic peaks of PBS (2945, 1722, 1158, 1044 and 802 cm⁻¹) [20, 21] in Figure 5 and the characteristic peaks of TPU (3306-3501, 2938-2848, 2700-2250, 1698, 1592-1525, 1442, 1381, 1305, 1080 cm⁻¹) [22, 23] in Figure 6 are presented. The characteristic peaks of PVP were determined as (3454, 2968-2900, 1658, 1495, 1288 cm⁻¹) [24] in Figure 5 (b), 6 and 7 are presented.

The electrospinning method is based on the evaporation of solvents, so no peaks belonging to CF, DMF, or DMSO solvents were observed in the FTIR analysis performed after these preliminary trials [25-27].
**Figure 5.** FTIR spectra of nanofibers, a) pure PBS and electrospun of pure PBS, b) hollow nanofibers of pure PBS, electrospun of pure PVP and electrospun of pure PBS
The presence of hollow nanofibers was supported by FTIR analysis. As can be seen from the FTIR results, there are no characteristic peaks of PVP in “pure PBS”, “pure TPU” and “60-PBS/40-TPU” hollow nanofibers. The peaks of the hollow nanofibers match exactly with the peaks of the non-hollow nanofibers. Thus, it is proved that the fibers are hollow.

The tensile properties of the hollow electrospun mats of “pure PBS”, “pure TPU” and “PBS/TPU blends” are presented in Figures 8 and 9 as tensile strength and elongation at break.
Figure 8. Tensile strength of the hollow electrospun mats

Figure 9. Elongation of break of the hollow electrospun mats

All hollow nanofibers showed high tensile strength and high elongation behavior compared to pure PBS. The hard parts of TPU increase the tensile strength, while the flabby parts of TPU improve the elasticity feature [11]. When the tensile strength of the “20-PBS/80-TPU” hollow nanofibers is evaluated, it is higher than the elongation and tensile strength of the “pure PBS” hollow nanofibers and lower than the elongation and tensile strength of the “pure TPU” hollow nanofibers. An in-between value was observed as expected. According to these results, the use of PBS and TPU polymers together, it is possible to enhance their tensile properties. It can be interpreted that better elongation and tensile strength values can be observed in other nanofibers to be studied if the brittleness of pure PBS nanofibers is reduced by using TPU. Because the electrospun webs do not present a yielding attitude, the tensile strain values at break are almost the same and these graphs can be evaluated together. Once the fiber fractures, its strength commences falling, and entire fibrous materials within a web can keep going to break and bend individually. Therewithal, the evaluations of the percent of elongation at break keep going till the final holding thread breaks. Also, it can
be mentioned that it is not significant for nanofibers or fibrous webs whether the elongation at break data is greater than the elongation percent [11, 13, 14].

4. RESULTS

In this study, pure PBS, pure TPU, and PBS/TPU blended hollow nanofibers were first time produced with coaxial electrospinning method with PBS/TPU polymers mixing. The production of hollow nanofibers was improved with bi-component fiber production techniques by combining the different properties of two different polymers. Some of the surfaces of produced hollow nanofibers were observed to be beaded and adhered when distilled water was used as a solvent to remove the PVP core structure. Significant improvements in the mechanical properties of hollow nanofibers were observed by PBS/TPU mixing. It has been added to the literature that a new structure that can absorb liquid was reported when nanofibers having hydrophobic character were produced as hollow. It is suggested that hollow PBS and TPU nanofibers that can absorb liquid can be used as wound dressings for exuding wounds in medical applications in the future.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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REFERENCES


