Polyamide-6 surface cracked forms nanofibers: A novel way for increasing the surface roughness, and porosity

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Research Article

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Abstract
Here away used to reduce the porosity of the nanofibers, which is removing PVA nanofibers from PVA/PA6 nanofibers by water treatment. Measuring the porosity of the electrospun web before and after treatment by the BET method proved this. The specific surface area of the web was 60% reduced after water treatment. Surface roughness and pore volume have reduced after water treatment. Also, I introduced BET as the method for measuring the diameters of mesopores (or lower than 100nm). I used BET to prove that the cracks can make mesopores on the nanofibers.

Highlights
Electrospinning of PVA/PA co-solution used to prepare nanowebs.

The tension applied to the jet was high and resulted in higher surface roughness.

I used etching PVA with water treating to reduce the porosity of the nanofibers.

Introduction
There are many methods for forming porous nanofibers, which are presented in Table 1[1]. Here, I used two methods: 1) high tension applied to the jet which could not tolerate it, and cracks made on the nanofibers, and 2) removing one part. Reducing porosity by solving PVA or PEO [2-4] is used to reduce the porosity of the PVA/non-hydrophobic nanoweb, but here reducing the porosity for a web of PVA/hydrophilic nanofibers happened differently. It happened due to the different hydrophilicity of the first part of the web. This product can use for applications in which we need lower porosity than usual [5]. The porosity measurements did by BET (measuring surface area and pore sizes). Cracks reduced a lot after water treatment. Also, using a hydrophilic polymer as the first part gave the same results compared to previous works [4]. Both reducing cracks and removing the PVA resulted in porosity reduction.

Table 1. Pore formation methods in/on nanofibers [1].
<table>
<thead>
<tr>
<th>Method explanation</th>
<th>Porosity formation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>jet partially fast freezing by fast evaporating of very volatile solvent or collecting nanofibers in the liquid bath</td>
<td>Phase separation between polymer and solvent</td>
</tr>
<tr>
<td>Vapor phase separation (usually, with electrospinning in high humidity, the water molecules in the air works as nonsolvent) and liquid phase separation</td>
<td>Phase separation between polymer and nonsolvent</td>
</tr>
<tr>
<td>Jet with triple-phase separation due to difference between volatility of solvent and nonsolvent (by changing ratios of this system) and pores form by changing relative rates of solvent/nonsolvent, controlling phase separation dynamic</td>
<td>Phase separation of the liquid section in polymer, nonsolvent, and solvent system</td>
</tr>
<tr>
<td>Phase separation between polymer and nonsolvent due to residual solvent in nanofiber by receiving nanofibers to nonsolvent bath and pore formation due to miscibility between solvent and nonsolvent</td>
<td>Collecting the nanofibers in a nonsolvent bath</td>
</tr>
<tr>
<td>Washing small molecules (like salt), block copolymers, polymers from nanofibers, or calcinating (the best way because pores formation by solvent evaporating is time-consuming and sometimes is impossible to remove one phase)</td>
<td>Selective removal of one phase of nanofiber</td>
</tr>
<tr>
<td>Controlling porosity by adjusting the ratio of two phases in nanofibers</td>
<td>Thermal degradation of one phase</td>
</tr>
</tbody>
</table>

Materials

PVA pellets (molecular weight = 78000g/mol) were purchased from Merck Company, and PA6 pellets (molecular weight of 35000g/mol) were purchased from Sigma Aldrich Company. Formic acid with analytical grade prepared from Merck Company.

Instruments and sample preparation

One nozzle horizontal electrospinning (digital pump from DAWHA company with MS-2211 model, drum collector, voltage supply with a voltage range of 1-22kV) used to prepare PVA/PA6 nanofiber web. The electrospinning condition was 15wt%(50/50wt), 9cm, 0.5ml/h, and 20kV. Electrospinning continued for two hours. Samples were cut from the resultant web, and then the samples were sent for solving PVA and floated in 70°C distilled water for two hours.

Samples characterizing

FESEM images of the nanofibers prepared from Seron Technology (South Korea, AIS2100 model) microscope. Nanofiber's diameter was measured by Image J software. An average of 100 nanofiber diameters was used. Thickness and weight of the web measured by Insize digital microscope micrometer and digital balance with 0.0001 g accuracy. All the histograms are drawn with Minitab 19 software.

Morphology of the nanofibers
There is a bit difference between average diameters before and after the water etching (according to table 1) [6]. With higher resolution, the pores on the nanofibers were seen. In the electrospinning process because of applying, high tension to nanofibers [7-8], the cracks made on the nanofibers are like mesopores but after water treatment, they are reduced. So, cracks are the new way of making mesopores. From the FESEM results, it is clear that the porosity and the pore size have reduced after removing the PVA [4]. Unfortunately, the nanofibers did not get more porous after removing PVA.

Porosity and pore size measurement

The porosity of the web was measured by BET [5, 9], and results showed that the porosity was reduced by solving one part (according to table 2). Image processing shows the surface porosity, and BET shows the total porosity (only for mesopores which are not made usually in nanofibers webs). BET adsorption and desorption curves showed that the pores of the nanowebs are slit-like (table 3). BET showed that the nanoweb is not porous because it is for mesopores. The cracks increased the surface roughness of the nanoweb compared to my previous work [4] so, it is a new way for increasing the surface roughness. After water treatment, the cracks changed, and the removal of PVA resulted in lower porosity. Overall, the porosity reduced after water treatment. So, this work gave a new way for making higher surface roughness on the nanofibers and showed that compared to previous works using a hydrophilic polymer for hybrid nano webs or co-solution results in lower porosity. Comparing to my previous article, the specific surface area is lower, and it is for higher nanofibers diameters of this work. In p/p0 >0.6, the curves of adsorption and desorption are almost on each other, so the pores are open, but in my previous article was vice versa, and that means that the pores are near to micropores (<2nm) [4].

Measuring surface roughness and pore volume by Matlab

By using Matlab, surface roughness [10], and pore volume were measured. They decreased according to the results (Table 5). As you see in table 5, the threshold images show that the roughness of the nanofibers decreased after water treatment. Reduction in the surface roughness is for reducing the cracks.

Measuring the orientation of the nanofiber web

By using Matlab the orientation of the nanowebs measured, which the results are reported below (table 6). Water treatment had not any special effect on orientation degree, but same in other works, it has been more isotropy than before etching [6]. It happened because water replaces the nanofibers.

Results

From the results, electrospinning of this co-solution and solving PVA in water resulted in lower porosity. The application of this nanoweb is in applications that need lower porosity than usual. This method increased the porosity and pore size without changing the average nanofiber diameter [3]. Surface roughness and pore volume reduced too. Overall, BET measures specific surface area, and pore size
diameters and gives the average diameter of the pores, which are the most, but it is not the real average, but it is only for mesopores. FESEM images are appropriate for measuring surface porosity and pore sizes. The density method is an appropriate method for investigating the overall porosity of the nanowebs, but it does not give any information about pore sizes. It was proved that using a hydrophilic polymer cannot result in increasing the porosity. My previous suggestion for reducing the porosity was 10% more successful than this work. Here cracked nanofibers are interesting.

Declarations
The author declares no competing interests.

References


Tables

Due to technical limitations, the tables are only available as downloads in the supplementary files section.

Supplementary Files

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- tables.docx