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Development of electrospun nanofibers having novel morphologies via corona plasma treatment

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ABSTRACT

Purpose: Traditional nanofibers are weak in mechanical strength and also they lack in functional capacity to some extent for some of high performance applications. In this paper, in the light of these facts, development of plasma treated nanofibers having novel morphologies was reported. In other words, the surface of the nanofibers was treated using corona plasma instrument to differentiate fiber morphology so that they gain potential functional capabilities. To answer the question whether dramatic changes into nanofibrous architecture could be possibly obtained, the experiments were designed and carried out at different plasma and electrospinning process parameters such as different concentration of polymers solutions and bombardment of different power range and density to assess their consequences. SEM investigations and camera shots revealed that plasma treatment have provided unique structural changes even at low frequencies due to large surface area to volume ratio of nanofibers. The effect of plasma treatment on nanofibers alignment and morphology resulted in formation of duple and triple agglomerated nanofibers and a dramatic decrease in fiber diameters. Treated nanofibers might have switchable liquid absorption properties as well as specific air permeability that could be potentially used for functional applications.

Findings: The experimental design and findings are unique in nanofibers literature in terms of application of standard plasma process and carbonization trials together as well as suggestion and introduction of a novel idea into development of a new apparatus in order to produce plasma treated nanofibers simultaneously.

Practical implications: Practically, experimental results have also shown that, apart from application of plasma over nanofibers after electrospinning, it is expected that integration of electrospinning process and plasma process together will likely have better and longer lasting effects on fiber morphology. To this aim, a novel joint electrospinning/plasma apparatus could be designed with combination of a plasma box right after electrospinning area.

Keywords: Plasma finishing; Nanofibers; New morphologies; SEM investigation

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MANUFACTURING AND PROCESSING

1. Introduction

Nanofibers are engineering materials having extra-ordinary features such as enormous surface area and interconnected pore structure making them an ideal candidate for aerospace, medicine, filtration, mobile and electronics applications [1]. However, traditional nanofibers are not able to meet some requirements of high performance applications due to their low strength, unordered alignment and low elasticity [2,3]. In order to improve functional capabilities, nanofibers should be modified and/or treated with specific treatment techniques such as corona plasma [4,5].

Corona plasma is a plasma type generated through air under atmospheric pressure. Plasma; are generated through ionization of air around high voltage areas such as thin wires, sharp edges or end points. Coronal discharges occur when the voltage value reached to required voltage value for ionization of used gas (air) [6-8].

Plasma technology is becoming common in textile industry and scientific research for surface functionalization day by day. Recent years, although plasma is amongst finishing processes of nanofibers, it hasn't been industrialized yet enough.

Park et al. [9] treated PLGA nanofibers with plasma in existence of oxygen or ammonium gas having an average diameter of 340 nm that were produced via electrospinning. Contact angle measurements and X-Ray Photoelectron Spectroscopy (XPS) analysis have shown that plasma processing increased the number of polar groups in the surface of nanofibers and therefore a remarkable increase in hydrophilicity of nanofibers have been detected by researchers.

Jeong et al. [10] treated electrospun silk fibroin nanofibers with plasma in the existence of oxygen or methane gas and characterized surface properties via XPS and contact angle measurements while they characterized cell development properties via cell culture tests. Besides plasma treatment has increased surface hydrophilicity, especially nanofibers treated with plasma containing oxygen have shown higher cellular activity and this was attributed to the increase of surface hydrophilicity by researchers.

Apart from other studies, Shi et al. [11] treated $AgNO_3$/PAN polymer solution with atmospheric plasma at 4.8 kW and 1-20 kHz sound frequency power supply just before electrospinning and later on they have produced nanofibers from this solution. According to SEM, EDX and TEM analysis, it has been found that manufactured nanofibers have shown high degree of anti-bacterial activity and high durability against Gram-positive and Gram-negative bacteria.

In case of this study, as a different perspective from available literature, plasma treatment and carbonization trials have been applied respectively for the nanofibers having the same production parameters. Biodegradable PEO nanofibers electrospun and then treated with plasma at two different process parameters for normal plasma application and carbonization trial. Camera images and SEM images were co-ordinately taken in order to one-to-one comparison to reveal the effect of plasma on morphological structure.

2. Material and method

In this paper, PEO polymer nanofibers produced via electrospinning was plasma treated with corona plasma equipment.

2.1. Material

In order to develop plasma finished polyethylene oxide (PEO) nanofibers with novel morphologies, PEO polymer having a molecular weight of 1000.000 (PEO 1000.000 Mw) was purchased from Sigma-Aldrich Company. Then, 3% wt PEO solution was prepared by dissolving 3 g PEO of 1000.000 mw in 100 ml distilled water and mixing the solution for 6 hours.

2.2. Method

In the first part of study, PEO nanofibers were electrospun using basic electrospinning setup. In the second part, surface of PEO nanofibers were treated using corona plasma instrument. Finally, plasma treated nanofibers were characterized using Scanning Electron Microscopy (SEM).

<u>Electrospinning</u>

Electrospinning was carried out using basic electrospinning setup (Fig. 1) at 0.9 kV power, 1 mL/h feeding rate, 16 cm grounded collector to needle tip distance and 5 h duration.

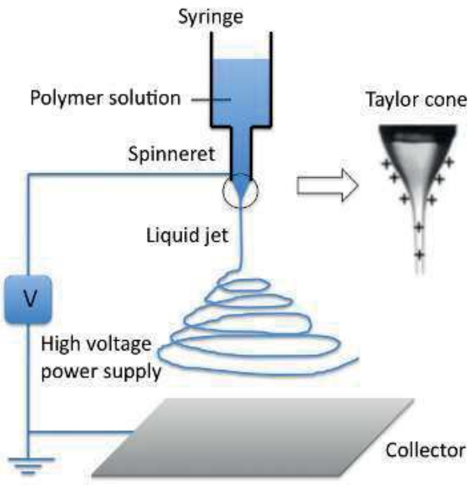


Fig. 1. Electrospinning setup

Corona plasma treatment

Corona plasma instrument (Electro Tech Industries 125 15 BH Model) was used for surface functionalization of nanofibers (Figure 2.). Experiments were carried out using PEO nanofibers of 3%wt and corona plasma discharge. Plasma conditions were applied as 0.05 kWatt for normal plasma and applied as 2 kWatt for carbonization trial. Each sample was treated by passing nanofiber layers over cylinder of the corona plasma instrument 10 times at 2 m/min process speed.

Fig. 2. Corona plasma instrument

SEM characterization

The morphology of plasma treated nanofibers was characterized using SEM instrument (LEO 440, Technical Sales Solutions, Beaverton, OR, USA).

3. Results and discussion

In order to investigate whether the plasma finishing have a significant effect on nanofibers' morphology, PEO nanofibers were treated using corona plasma discharge and the surface morphology was observed using a camera and SEM instrument.

3.1. Camera images

Figure 3 and Figure 4 has shown that plasma treatment changed the surface morphology of PEO nanofibers in that nanofibers had a laminar and/or crack alike structure.

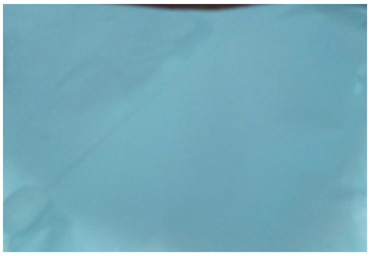


Fig. 3. PEO nanofibers (untreated)

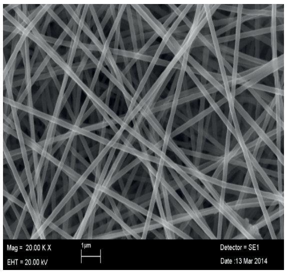
Fig. 4. Plasma treated PEO nanofibers under 0.05 kWatt power

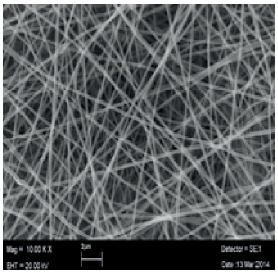
Figure 5 has shown that applying 2 kWatt plasma power, carbonized the PEO nanofibers and turned their colours from white to black.

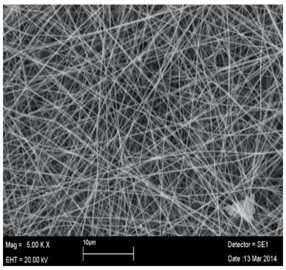
Fig. 5. PEO nanofibers (untreated)

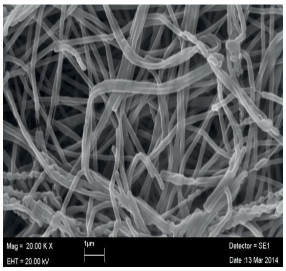
3.2. SEM images

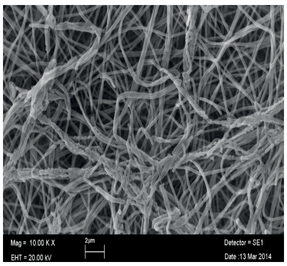
Figure 6 represents SEM images in different magnifications (20 kX, 10 kX and 5 kX) belonging untreated PEO nanofibers (1, 2 and 3) and plasma treated nanofibers (4, 5 and 6) under 0.05 kWatt plasma power and 2 m/min process speed. SEM images revealed that untreated nanofibers have exhibited a normal alignment while plasma treated nanofibers had an alignment style where two-three nanofibers adhered together and space/pores decreased within structure. This result is promising in terms of future applications such as protective textiles, electronic textiles/devices and medical textiles where a higher mechanical strength and protection needed. Before plasma processing, the average diameters of nanofibers were approximately 285 nm, while the diameters have been measured as approximately 400 nm after plasma treatment.


1-20 kX


2-10 kX


3-5 kX


4-20 kX


5-10 kX

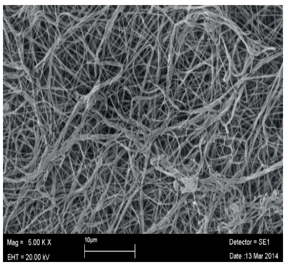

6-5 kX

Fig. 6. (1), (2) and (3) – respectively, untreated nanofibers. (4), (5) and (6) – r espectively, plasma treated nanofibers under 0.05 kWatt plasma power

As it can be clearly seen from the Fig. 7, increasing plasma power from 0.05 kWatt to 1 kWatt and 2 kWatt, led formation of ash instead of morphological change.

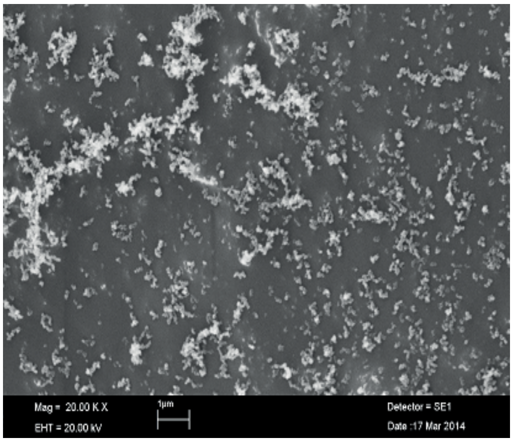


Fig. 7. Carbonization trial of PEO nanofibers under 1 kWatt (once) to 2 kWatt (4 times) plasma power and 2 m/min process speed

4. Conclusions

In conclusion, camera images and SEM analysis have provided a clear understanding regarding the effect of plasma at different process parameters on morphological change of PEO nanofibers that were electrospun via electrospinning. Application of plasma treatment onto nanofibers had a remarkable effect on morphologies. During plasma process, increasing plasma power from 0.05 kWatt to 1 kWatt and then to 2 kWatt had a dramatic effect on nanofibers' morphology in that nanofibers transformed into the ash form from fibrous state.

In future work, hydrophilicity analysis will be carried out for the plasma treated PEO nanofibers and then best treatment process parameters will be defined for an ideal hydrophilicity. Later on, designing a new electrospinning setup assembling a small-size plasma treatment apparatus will be carried out and it will be placed at the end of nanofiber formation area in order to simultaneously assess the effect of plasma over nanofiber morphology.

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