RESEARCH PAPER

A New Approach toward Ultraviolet/O_3-Assisted Nano-etching of Ingeo™ Surface

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ABSTRACT

Nano-etching of materials offers the possibility of driving significant surface properties such as wettability and anti-reflectivity. Remarkably, plasma and laser processes can lead to favorite nano-features through a one-step procedure based on etching. The literature will be reviewed regarding such micro- and nano-etching for different materials, such as natural and synthetic polymers, and various methods such as argon plasma. In this work, the nano-etched surface of the novel synthetic fibers (Ingeo™) was obtained by using Ultraviolet/O_3 irradiation for 80 minutes on the mats which were pre-impregnated in a distilled water solution with a wet pick-up of 70 %, pressure of 1.1 bar, and speed of 2 m/min (Ultraviolet/O_3/H_2O system). Ingeo™ is the world's first and only human-made fiber produced from 100% annually renewable resources such as corn, not oil. After the Ultraviolet/O_3/H_2O procedure, a textured layer containing fractures with nanoscale sizes are created on the Ingeo™ fiber surface owing to the ion bombardment in the radiation space. The nano-etching process results in increasing the surface roughing which is responsible for the growth in the specific surface area. This procedure can improve wetting properties; thus, after the Ultraviolet/O_3/H_2O nano-etching of Ingeo™ surface, the moisture-regain of fibers increases from 0.417 to 0.452%.

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INTRODUCTION

Patterned surfaces are usually used for various applications like biomedical uses[1]. The response of tissues to an implant mainly depends on the physico-chemical properties of its surface [2]. Surface properties such as topography (or texture) determine the interaction of implants with the biological environment [3, 4]; therefore, the nano-engineering of material surfaces is of great importance for researchers.

Scientists have reported several investigations about micro- and nano-etching of material surfaces such as the nanotexturing of fluorinated ethylene propylene surfaces with plasma [5], nanotexturing of polyaniline thin films using argon plasma [6], micro texturing of polymer surfaces using lasers [7], nanofabrication of polymer surfaces [8], nano-etching of alumina surface via plasma [9], nano-texturing of polystyrene nanoparticles [10], nano-fibrillar patterning of PET films by plasma etching [11], surface nano-texturing of stainless steel by femtosecond laser [12], nano-structuring of polystyrene thin film surface by UV Femtosecond Laser Beam [13], nano-scale patterning of polymer films using UV irradiation [14], periodic surface texturing of amorphous-Si thin film irradiated by UV nanosecond laser [15], laser-induced periodic surface structures on bismuth thin films with ns laser pulses below ablation threshold [16], hierarchical patterning of indium tin oxide thin films with laser [17], femtosecond laser-induced

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Table 1. Properties of the greige fabrics.

Type of Physical characteristics	
Fiber type	Ingeo^{TM}
Whiteness index (%)	71
Tint factor	-0.2
Thickness(mm)	0.781
Purity (%)	100
Weft density (cm^{-1})	25
Wrap density (cm^{-1})	23
Weight(g/m^2)	18.45

periodic surface structures formation on bismuth thin films upon irradiation in ambient air [18], and nano-dimension pore formation on PET knitted fabrics throughout UV/O_3 radiation [19].

Nano-etching of Ingeo surface leads to the increase of fiber roughing. As stated by the *Wenzel equation*, the roughing of the surfaces affects the contact angle. When the surface owns a contact angle of less than 90, the significant surface unevenness might decrease the contact angle. In addition, the increase of surface roughing results in growing the specific surface-area, which, in turn, might lead to a more moisture-rich surface, enhanced wetting properties, and increased electrical conductivity [20].

Hence, the aim of this work is to design nano-etched surface on novel Ingeo™ fibers via an environmentally friendly method which can improve the “green technology” in the textile industry.

EXPERIMENTAL METHOD

Materials

This investigation employed a set of identically constructed ‘piqué’ type of knitted fabric provided by Nature Works LLC, USA and derived from 150/144 tex/filament (Ingeo^{TM} fibre) yarns, respectively. Ingeo™ is the world’s first and only human-made fiber produced by NatureWorks LLC, from 100% annually renewable resources such as corn – not oil[21]. Being warm, cozy, and comfortable, its properties are well-suited for bedding products including comforters, pillows, blankets, mattress pads, and so on. The properties of the greige fabric are shown in Table 1.

The greige fabrics were scoured with 2 g/L anionic/non+ionic detergent, 1 g/L Kieralon Jet B conc. (non+ionic surfactant, BASF) and 1 g/L sodium carbonate (‘soda ash’) at 60 ºC for 15 min at a liquor ratio of 10: 1, washed thoroughly. After scouring, the fabrics were rinsed with cold water for 10 min and dried in ambient conditions to remove mill dirt and lubricants.

Ultraviolet/O_3/H_2O Technique

A piece of the knitted fabric (around 5 g) was immersed in the distilled water (1 L) solution and padded twice through a laboratory padder with a wet pick-up of 70 %, pressure of 1.1 bar, and speed of 2 m/min. After the pre-impregnation process, the poly (lactic acid) fabrics were radiated in an Ultraviolet/O_3 irradiation cabinet for 80 min (40 min face-up and 40 min face-down, respectively). The Ultraviolet/O_3/H_2O system is shown in Fig. 1.

Ultraviolet/O_3 irradiation cabinet: 11 mW/cm^2 intensity UV lamps without outer envelope (6 Lamps, made in Poland) were placed in a cubic box with the side length of 60 cm. The strips of the samples were placed around the source at a suitable distance (~2 cm). Atomic oxygen is generated both when molecular oxygen is subjected to the 184.9 nm radiation and when ozone is irradiated at 253.7

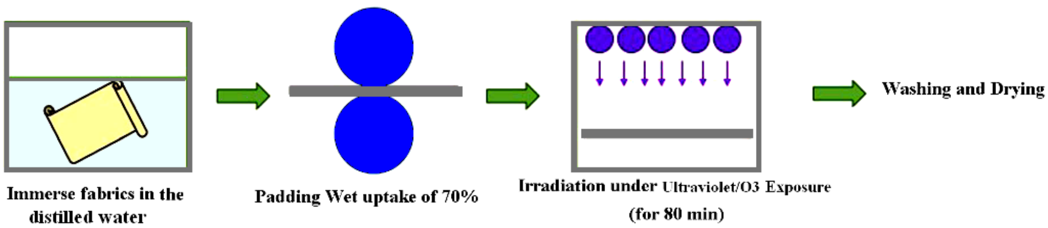

Fig. 1. Scheme of the Ultraviolet/O_3/H_2O process.

Fig. 2. Ultraviolet/O_3 irradiation cabinet.

nm. The radiation at 253.7 nm is absorbed by most hydrocarbons as well as by ozone (Fig. 2).

After-treatments of samples

When the irradiation was completed, the sample was rinsed adequately with cold water (30+40 ºC) at room temperature for 10 min in a liquor to goods ratio of 20:1, and then the oven was dried at 60 ºC for 30 min.

Scanning Electron Microscopy

A scanning electron microscopy examination of the fibers was carried out to assess whether the various treatments had caused any visible degradation to the fiber surfaces. A XL30 MODEL/ PHYLIPS Company/Netherland instrument was used for this purpose.

Gold sputter coating: In order to avoid problems due to charge build-up, the poly (lactic acid) fabrics were previously sputter coated with gold palladium for two minutes in a SCDOOS MODEL/Bal-Tech Company/Switzerland sputter coating unit. The images were captured with the magnifications of 2500, 7500, 15000 and 30000.

Wetting properties

The moisture regain of the Ingeo™ fibers was attained according to ASTM D1909-04 (Equation 1).

$$R(\%) = {}^{W}\!/_{D} \times 100 \qquad (1)$$

Where W is the weight of water (gr) in the fibers, and D is the weight of oven-dry fibers (gr).

RESULTS AND DISCUSSION

Topography Analysis by Scanning Electron Microscopy Micrographs

Scanning electron microscopy was applied to observe the morphology and topography changes in the surface of Ingeo™ fibers. The clarity of Ingeo™ surface before radiation process was observed with scanning electronic microscope (SEM), as shown in Fig. 3. The images were taken at different spots of the Ingeo™ sample.

Micro-morphology of Etched Ingeo™ Surface

The detailed SEM analysis of the surface of Ingeo™ fibers after Ultraviolet/O_3/H_2O process is shown in Fig. 4, and the surface morphologies of the Ingeo™ fibers are compared.

As seen in Fig. 4, after the Ultraviolet/O_3/

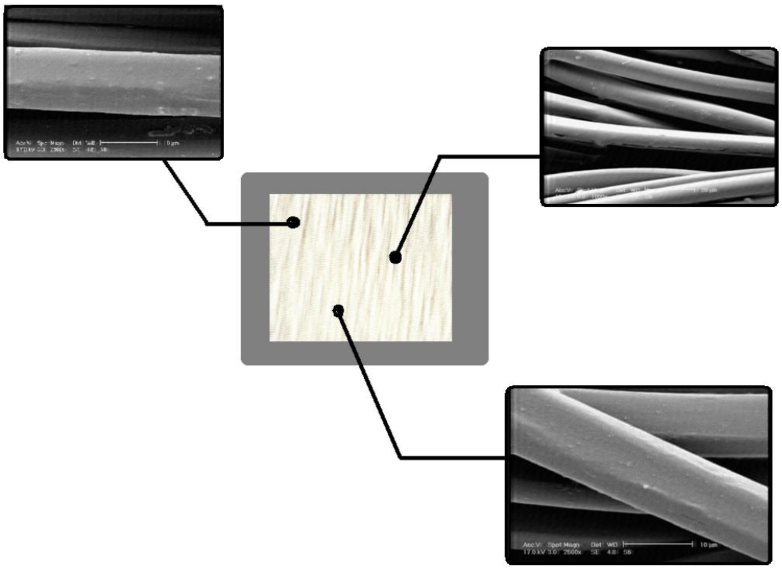

Fig. 3. Photographic and SEM visualized surface morphology of virgin Ingeo™ fibers (1000x and 2500x).

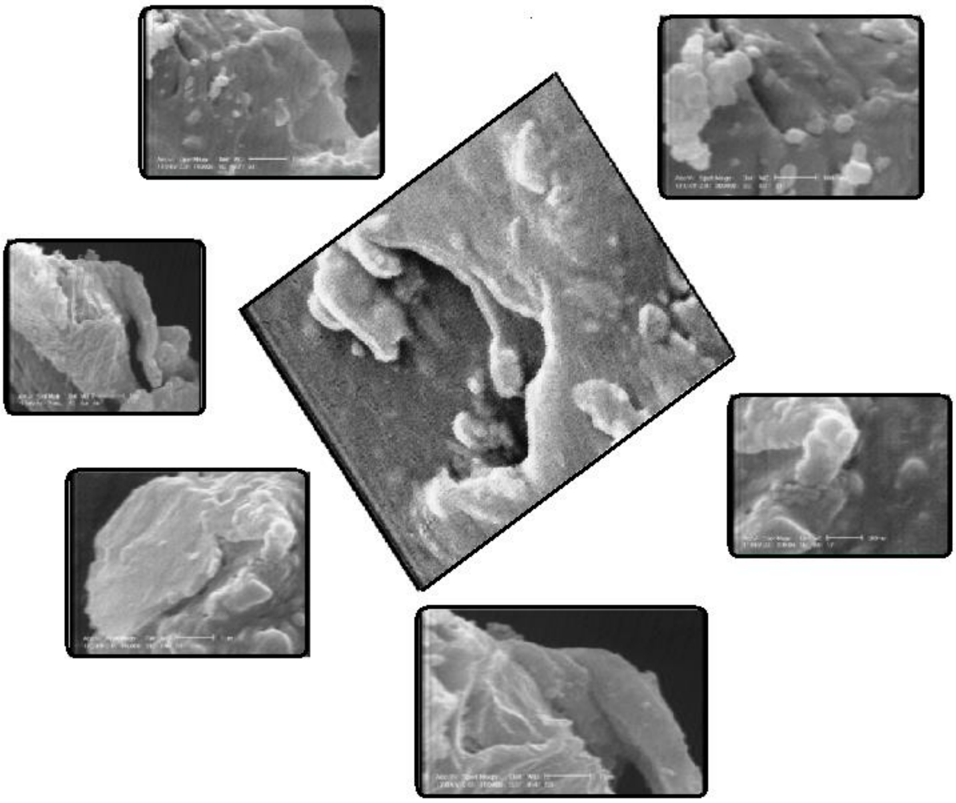

Fig. 4. Morphology of nano-etched Ingeo™ surface: 2D topography obtained by SEM (7500x, 15000 x and 30000 x).

H_2O process, a textured layer including fractures with nanoscale sizes are produced on the fiber surface. These alterations in the topography of the fibers are due to the physical etching influence of Ultraviolet/O_3 irradiation. The formation of surface unevenness, due to the physical etching properties, is an important factor in the surface engineering of polymeric fibers and films via Ultraviolet/O_3 irradiation[22, 23].

It seems that the morphology of the fibers radiated with Ultraviolet/O_3/H_2O process display a major modification in the fiber surface. In fact, the fiber surface is destroyed. Grooves, cavities, and ruggedness are formed on the surface. This surface ruggedness is caused by the influence of physical deterioration produced by the bombardment of the ions inside the chamber. The kinds of physical variations on the fiber surface are unlike those under various processing conditions. This is due to the changes in ions which create various erosion influences. These physical alterations are regularly in the shape of cavities and pores. In some cases, the surface layer of fibers is broken up heterogeneously, generating peaks and valleys. In some other cases, the surface changes of the fibers result from creating horizontal channels which have a diameter of nanometers and are consistently spread on the surface [3, 24-26].

Wetting Properties

The Moisture-regain for virgin Ingeo™ fibers was found to be about 0.417%. After the Ultraviolet/O_3/H_2O nano-etching of Ingeo™ surface, the Moisture-regain increases to 0.452%. The SEM images revealed in that Ultraviolet/O_3/H_2O nano-etching cause the increase of surface roughing (Fig. 4). Increasing the surface roughing raises the available surface area of water molecules, thus the hydrophilic properties will be improved.

CONCLUTIONS

In recent years, the industries have focused on the use of new pollution-free and environmentally friendly equipment called "green technology". Ultraviolet/O_3 radiation is one of the top ecofriendly approaches for these purposes. In this effort, a new approach known as the Ultraviolet/O_3/H_2O procedure is applied for nano-etching of

Ingeo™ surface under mild conditions. The chief consequences are as follows: The Ultraviolet/O_3/H_2O process is defined for the Ultraviolet/O_3 irradiation (80 minutes) on the Ingeo™ fibers which pre-impregnated in a distilled water solution, After the Ultraviolet/O_3/H_2O process, a textured layer including fractures with nanoscale sizes are produced on the surface of Ingeo™ fibers due to the ion bombardment in the radiation chamber, After the Ultraviolet/O_3/H_2O nano-etching of Ingeo™ surface, the Moisture-regain of fibers increases from 0.417% to 0.452%.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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