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RESEARCH PAPER

Nano-Structure Roughening on Poly(Lactic Acid)PLA Substrates: Scanning Electron Microscopy (SEM) Surface Morphology Characterization

Farnaz Fattahi [1], Akbar Khoddami [1], and Ozan Avinc [2]*

[1] *Department of Textile Engineering, Isfahan University of Technology, Isfahan, Iran.*

[2] *Textile Engineering Department, Engineering Faculty, Pamukkale University, Denizli, 20160, Turkey*

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ABSTRACT

Scanningelectron microscopy (SEM) has been utilized to examine the morphology and topography alterations in the surface of Poly(Lactic Acid)(PLA) fabrics due to UV/Ozoneirradiation. In the past decade, a growing attention in the usage of "Green Techniques" in industrial applications has been observed owing to many benefits such as low impurities and their relatively low cost to substitute the conventional processes.The effects of UV/Ozone irradiation along with the pretreatments with distilled water, hydrogen peroxide, and hydrogen peroxide/sodium silicate solutions on the surface morphology of the PLA fibers by means of SEM were investigated and the images were compared with that of virgin untreated samples. The observations presented dramatically increase in insurface roughness andsurface area of the samples after the treatment. Nano-size roughening (827 nm) has been clearly observed on the samples. The changes in morphology mainly surface roughness and surface area, on the PLA fabrics surface due to UV/Ozone irradiation seem to be due mainly to the intensified etching effect of the UV/Ozone process and these alterations maximized by the pretreatment of the fabrics with the hydrogen peroxide/sodium silicate solution.

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INTRODUCTION

Surface modification of the fibers with various approaches, such as Plasma technique, alkaline hydrolysis and enzyme treatment are an active capacity of the research in the textile knowledge. One of the operative and efficient systems for surface modification of natural and synthetic fibers including wool, cotton, silk, Poly-Propylene (PP), and Poly (Ethylene Terephthalate) (PET), is Ultraviolet/Ozone (UV/O_3) irradiation. Excitation and dissociation of the molecules occur throughout exposing the surface to the UV/O_3 irradiation, which is recognized as a Photo-Sensitized oxidation method [1-5]. Polymers derived from renewable resources like corn, wheat, rice and sweet potato are now labeled as Bio-Polymers and are capable substitutes to old-style (petro) polymers because they achieve present environmental concerns in positions of environmental pollution, green-house gas emissions and the reduction of fossil resources (Fig. 1)[6-8]. Poly (Lactic Acid) (PLA) $[(C_3H_4O_2)_n]$ has been the favorite among these bio-polymers because of its proper mechanical characteristics, renew-ability, bio-degradability and comparatively low-cost[9-13].

PLA is a sustain-able, renew-able, Bio-Based, Bio-Degradable, Bio-Absorbable, Bio-Compatible linear aliphatic thermoplastic Poly-Ester (Fig. 2)

* *Corresponding Author Email: fattahi_farnaz@yahoo.com*

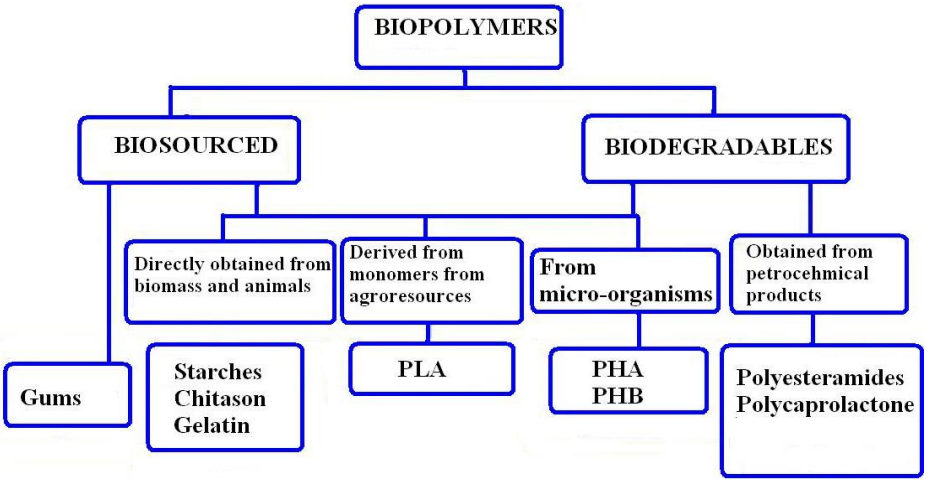

Fig. 1. Catalog of the various kinds of Bio-Polymers.

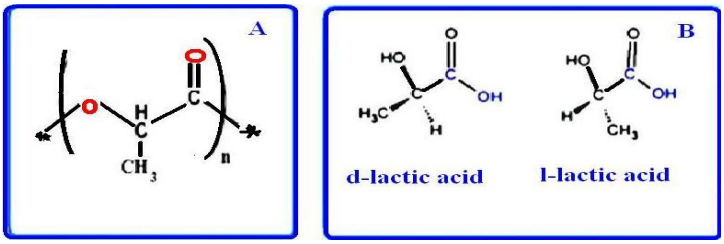

Fig. 2. A) Chemical structure of PLA, B) Stereoisomers of PLA[21].

[14-16]. The first effort for manufacturing PLA was attributed to Pelouze in 1845 with condensing L-Lactic acid and removing water constantly, resulting to low molecular-weight PLA. Besides its bio-degradability and renew-ability, PLA shows a Young-Modulus of about 3 GPa, a Tensile-Strength among 50 to 70 MPa, Elongation-At Break of 4%, and an Impact-Strength nearly to 2.5 kJ/m2. With comparison to product polymers like PE, PP, PS and PET, the Mechanical-Properties of semi crystalline PLLA are good, mainly its Young's-Modulus, making it as an outstanding alternative for usual polymers [17-20].

PLA associates ecological benefits and brilliant performance in textiles (High mechanical strength, compost-ability, bio-compatibility), Also PLA displays good moisture-management and comfort-characteristic, in addition has benefits with respect to smoke-generation and flammability (Table 1) [22-24].

Some positive points of PLA fibers are briefly reported [25-27]: sustain-ability, renew-ability,

Table 1. Characteristics of PLA fibers[25].

Fiber Characteristics	
Specific gravity	1.25
T_m (˚C)	130-175
Tenacity (g/d)	6.0
Elastic recovery (5% strain)	93
Moisture content (%)	0.4-0.6
Flammability	Continues to burn for 2 min after flame removed
Smoke generation	63 m^2/kg
Limiting oxygen index (%)	26
Refractive index	1.35-1.45

Table 2. Specifications of the PLA fabrics.

Yarn Linear Density	Fabric structure	Thickness(mm)	Weight(g/m^2)
150/144 dtex/filament	Pique	0.781	18.45

bio-degradability, excellent wicking and moisture management, excellent handle and drape, low flammability and low smoke emission, could be utilized either alone or in blends with cotton, wool, and other fibers.

This investigation was started in a work to explore the changes in the surface morphology and topography of PLA fibers after UV/O_3 irradiation in various settings (Wet, Dry) by means of the sample's SEM images. Also, on this aspect, to the best knowledge of the authors, papers on the influence of the pre-treatment of the UV/O_3 irradiated fabrics with distilled water, Hydrogen peroxide and hydrogen peroxide plus sodium silicate solutions on the surface morphology could not be found in the literature. Consequently, part of this exploration was devoted to consider the effectiveness of these pre-treatment methods.

MATERIALS AND METHODS

This effort employed identically-constructed piqué type of knitted fabrics produced by Nature Works LLC, USA and derivative from 150/144 dtex/filament PLA (IngeoTM fibre). These types of crops are usually utilized for outerwear garments such as socks, sportswear, active wear, women's dress, fashion wear and childrens' wear. "Ingeo™ fibre" is the trademark of NatureWorks LLC's Poly (lactic acid) polymer created from corn starch. The characteristics of the greige PLA fabrics are presented in Table 2.

The PLA fabrics were scoured to eliminate any probable impurities which could possibly affect the subsequent surface treatment. Unprocessed PLA fabrics were pre-scoured in a bath having 1 g/l Kieralon Jet B conc. (non-ionic surfactant, BASF) and 1 g/l sodium carbonate at 60˚C for 15 min, using a liquor ratio of 40: 1. Then PLA fabrics were rinsed with cold water for 10 min and flat dried at room temperature without any tension. The clean fabric samples were conditioned according to ASTM D1776 at the relative humidity of 65 ± 2% and 21 ± 1 ˚C for at least 24 h prior to all experiments.

In order to introduce new chemical groups on the fiber surfaces, UV/OZONE procedure is used.

UV/OZONE Exposure Reactor

The interior of the reactor (A cubic box with side length 60 cm) was equipped with 6 low-pressure lamps without outer envelope (11mW/cm^2 intensity, made in Poland). Strips of PLA fabrics (2×2 cm) were exposed on both sides with a suitable distance (~1 cm) between sample and lamp. The lamps were able to transmit the two strong lines at 184.9 and 253.7 nm. For UV irradiation in the presence of ozone gas (UV/O_3), extra-dry air was introduced into an ozone generator (COG-2A Model, ARDA/France). The ozone produced was fed into the UV reactor at 10 gr/h (Fig. 3).

This method was used in 2 techniques on the PLA fabrics: Dry method and Wet method.

Dry Method

First, PLA fabrics were irradiated by UV/OZONE

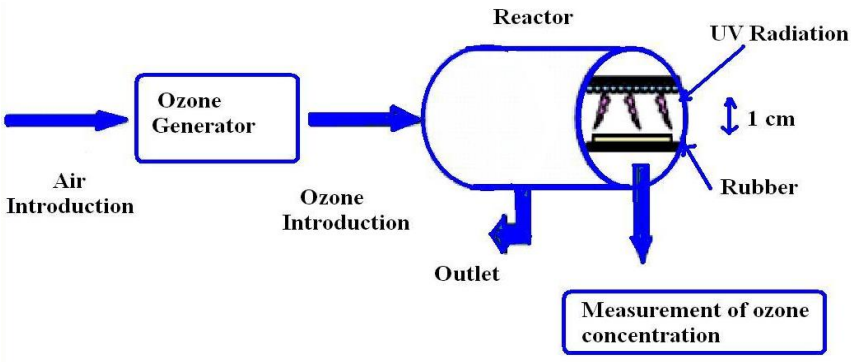

Fig. 3. Scheme of the UV reactor provided with an external supplemental ozone generator.

for different period times of 5, 10, 20 and 40 min at both sides. Finally the fabrics were rinsed with running water and dried in air.

Wet Method

In order to optimize the synergistic effect between the UV/ozone exposure and chemical solution pad–batch system, the effect of solution formulation (varying chemicals: Distilled water, Hydrogen Peroxide, Hydrogen Peroxide plus Sodium Silicate) was examined in 3 styles.

Synergistic effect between the UV/ozone exposure and Distilled water pad–batch system

PLA fabrics were padded (two dips, two nips) to 70% wet pick-up, 2 m/min speed and 1.1 bar pressure with a liquor containing Distilled water (pH ~ 7), immediately irradiated with UV/OZONE for 40 min.

Synergistic effect between the UV/ozone exposure and Hydrogen Peroxide pad–batch system

PLA fabrics were padded (two dips, two nips) to 70% wet pick-up, 2 m/min speed and 1.1 bar pressure with a liquor containing 4ml/l Hydrogen Peroxide (35%) solution, immediately irradiated with UV/OZONE for 40 min.

Synergistic effect between the UV/ozone exposure and Hydrogen Peroxide plus Sodium Silicate pad–batch system

PLA fabrics were padded (two dips, two nips) to 70% wet pick-up, 2 m/min speed and 1.1 bar pressure with a liquor containing 4ml/l Hydrogen Peroxide (35%) plus 7 g/l Sodium Silicate (72˚TW) solution, immediately irradiated with UV/OZONE for 40 min.

After exposure time, the fabrics were carefully washed for 15 min in 60˚ C and then kept in a 1% aqueous solution of Acetic Acid for 3 min. Finally, the samples was rinsed with running water and dried in air. The morphological modifications produced on the treated PLA fabric surfaces were analyzed in a Phillips XL 30 SEM system at 15–20 kV. The PLA fabrics were gold coated to prevent charging prior to analysis and a SCDOOS Sputter gold coater was used. A Bomem-MB 100 FTIR spectrometer was used to analyze the chemical modifications produced in the top 0.5–1 mm of the treated PLA fabric surfaces. IR spectra between 4000 and 400 cm^{-1} were acquired by transmission FTIR. 20 scans were obtained and averaged with a resolution of 4 cm^{-1}. The anti-static property of the PLA fabric substrates was determined via a STATIC voltmeter R-1020 (Rotchschild, Swiss) by means of resistance measurement. The fabric substrates were first charged-up and then the elapsing time was measured. The elapsing time, stated as “half-life decay time”, is the time needed for discharging half of the charge present in the fabric substrates as accrued throughout the charging-up procedure. The shorter the half-life decay time, the improved the anti-static property is going to be . The moisture content of the fabric substrates were obtained in accordance with ASTM D2654. Labeling of PLA fibers that exposure with UV/Ozone in various conditions is briefed in table 3.

RESULTS AND DISCUSSION

Structural properties

UV/Ozone exposure is efficient technique for oxidizing organic materials, so that it might be expected to result in oxidation on the surface of the fiber and cause the chemical modification on the fiber. IR spectra show typical absorption bands of PLA (Fig. 4).

The FTIR spectrum of PLA-treated with UV/Ozone shows increasing in intensity of peaks at 1763 cm^{-1} (C=O stretching vibrations in carboxylic acid), 1216 cm^{-1} (stretching vibrations) and 1080 cm^{-1} (-C-O- stretching vibrations) (Fig. 5), indicating

Table 3. Labeling of samples and methods.

Fabric Condition	Exposure Time of UV/Ozone (Min)	Samples Label	Techniques Label
Dry	0	Untreated	-
Dry	5	UV/O_3:5 min	Dry-UV/O_3
Dry	10	UV/O_3:10 min	Dry-UV/O_3
Dry	20	UV/O_3:20 min	Dry-UV/O_3
Dry	40	UV/O_3:40 min	Dry-UV/O_3
Padded in distilled water	40	H_20-UV/O_3: 40 min	Wet-UV/O_3
Padded in Hydrogen Peroxide aquase	40	H_2O_2-UV/O_3: 40 min	Wet-UV/O_3
Padded in Hydrogen Peroxide plus Sodium Silicate	40	H_2O_2-Na_2siO_3-UV/O3: 40 min	Wet-UV/O_3

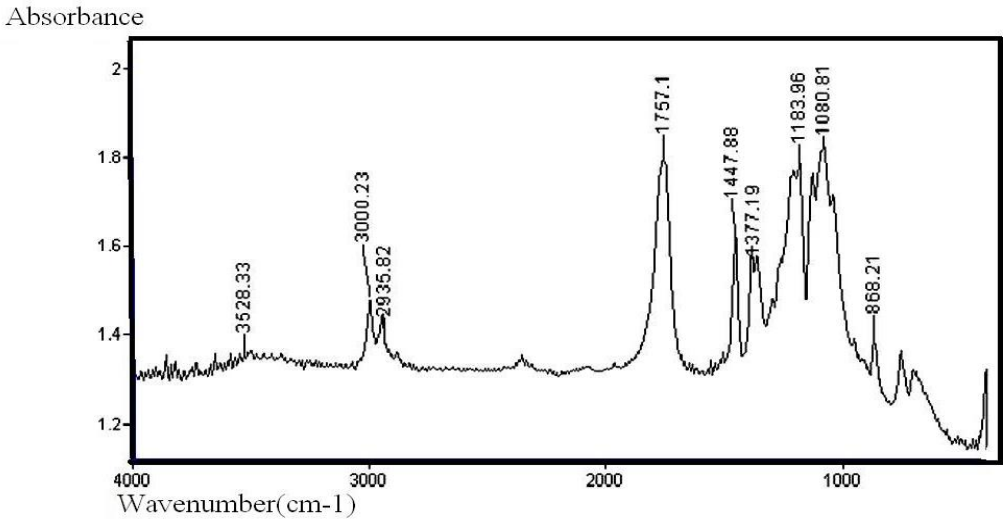

Fig. 4. FTIR spectra of untreated PLA.

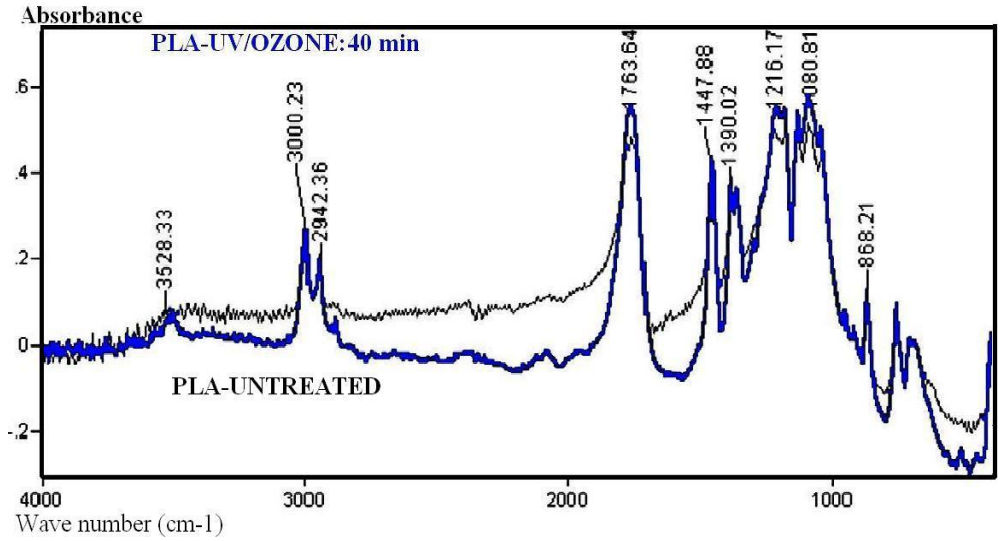

Fig. 5. FTIR spectra of untreated PLA and UV/O3:40 min PLA fibers.

an introduction of new chemical groups onto the fiber surface after UV/Ozone exposure.

The FTIR results shown in Fig. 5 confirmed that there is the probability of introducing oxygen-comprising polar groups (such as C=O) on the PLA fiber surface afterward the UV/Ozone treatment.

Morphology analysis

We studied the surface topography of PLA fibers before and after UV/O_3 irradiation by means of SEM observation (Fig. 6).

There is apparent difference between the surface morphology of the virgin PLA fibers and UV/O_3 treated samples. After UV/O_3 radiation, PLA surfaces display a remarkable change in topography from the original surface, as small hills form on the fibers. The virgin sample exhibited markedly smooth surface, but the UV/O_3-treated samples show breakages on the out-most layer of the fiber surface. Ruptures formed on the surface of PLA fibers. In addition, some characteristically snaps shaped, also few cracks and holes observed in fissures of treated fibers. A higher-resolution image (Fig. 7) further emphasized the distinctive features between the untreated and UV/O_3-treated fibers. It is very interesting that the

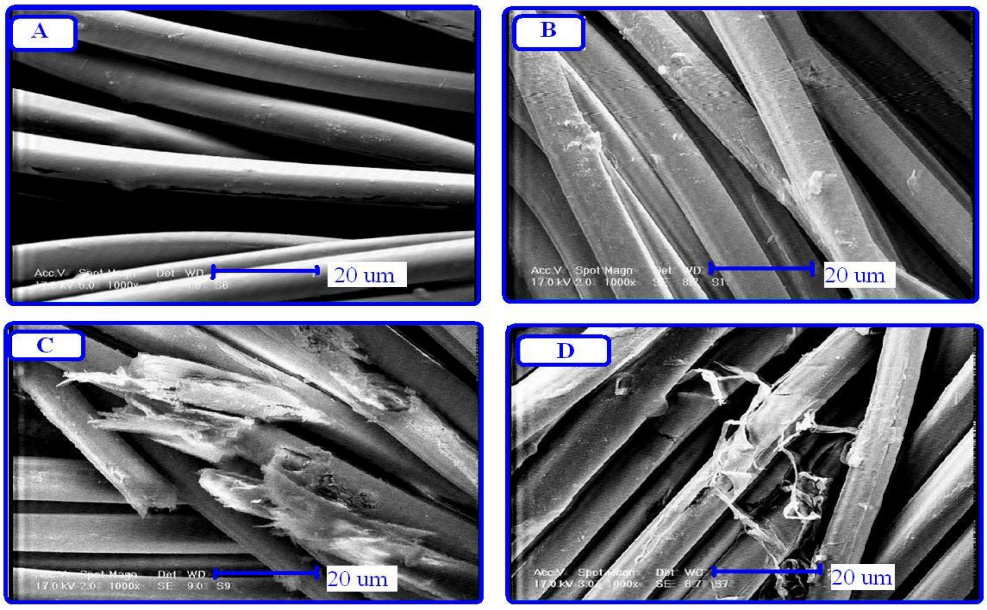

Fig. 6. A) Untreated, B) H_2O_2-Na_2SiO_3-UV/O_3: 40 min, C) H_2O_2-UV/O_3: 40 min, D) UV/O_3:40 min PLA fibers. (x:1000).

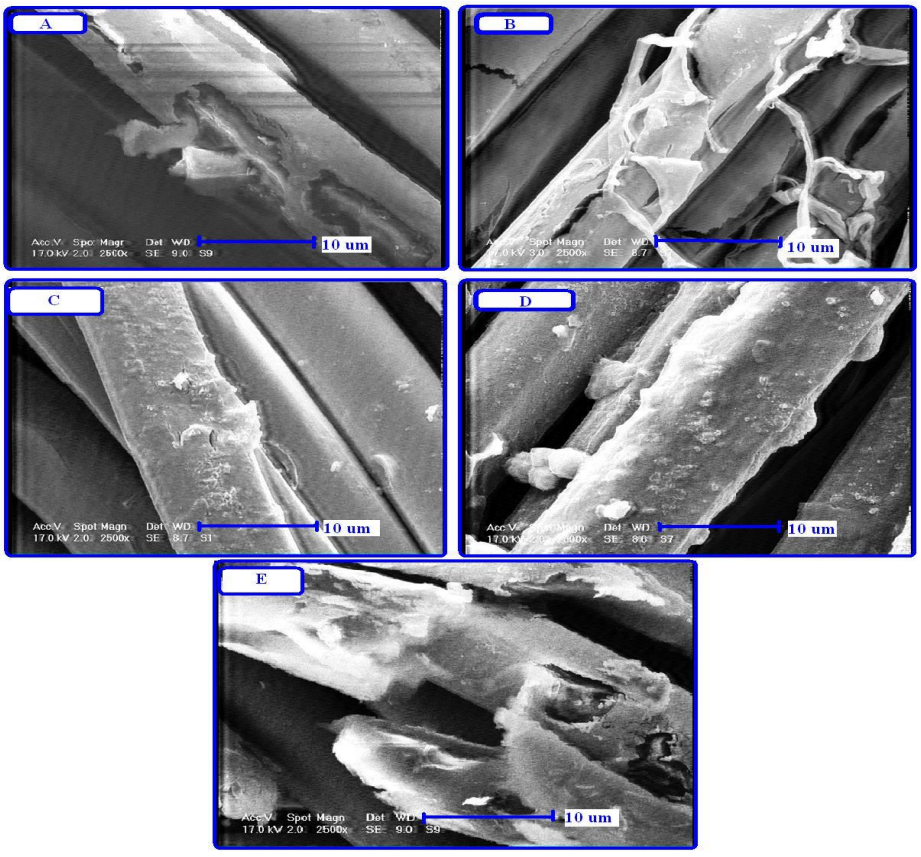

Fig. 7. A) H20-UV/O_3: 40 min, B) UV/O_3:40 min, C) H_2O_2-Na_2SiO_3-UV/O_3: 40 min, D) UV/O_3:40 min, E) H_2O_2-UV/O3: 40 min PLA fibers (x:2500).

degraded surface layers have cracks that spread on the fiber moderately.

The SEM images in Fig. 7 (A,B,C, D, E) demonstrate that after UV/O_3-Exposure on both wet and dry samples, physical breaks occurred and were spread through a large proportion of fiber area.

As revealed clearly in Fig. 8A and B the significant roughness occur on the outside layer of PLA fibers because of its large surface curving. The

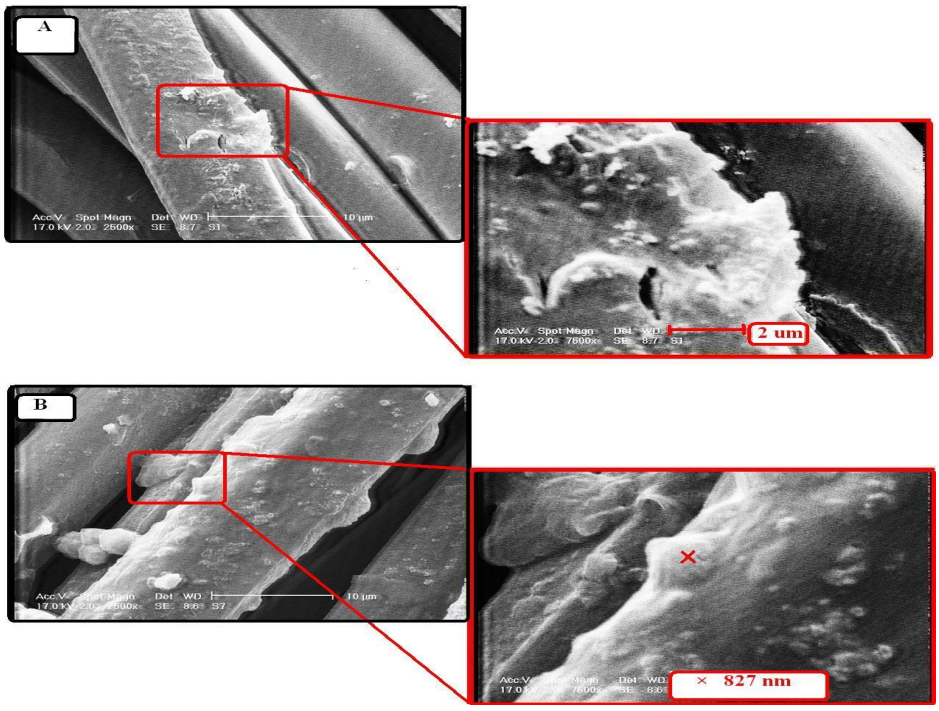

Fig. 8. A) H_2O_2-Na_2SiO_3-UV/O_3: 40 min, B) UV/O_3:40 min PLA fibers (x:7500).

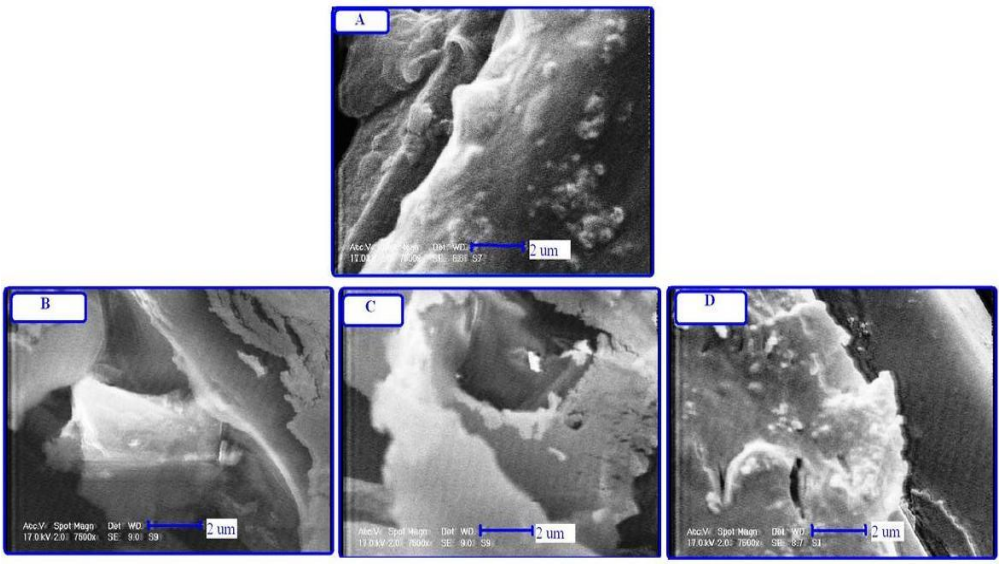

Fig. 9. Dry-UV/O_3 : A- (UV/O_3:40 min), Wet-UV/O_3 : (B- H_2O-UV/O3: 40 min , C- H_2O-UV/O_3: 40 min, D- H_2O_2-Na_2SiO_3-UV/O3 PLA fibers.) (X: 7500).

physical roughs were seen to form at PLA surfaces in a Nano-Meter scale (827 nm) that is signed with red color (×) icon on the picture. The Nano-size roughs were in shapes of either closely packed irregularities or homogeneous form, presumably due to etching effect of UV/O_3 irradiation.

It is obviously shown in Fig. 9B, 9C and 9D that the Dry-UV/O_3 modifies the PLA fiber surfaces to a less degree than does the Wet-UV/O_3. It is clear that, after Wet-UV/O_3 the PLA fiber surface had much more topography variations with various peak to valley distances, volumes and the surface areas, though it was apparent that PLA fibers in Wet-UV/O_3 condition were carved and scraped more than Dry-UV/O_3 condition. In contrast Dry-UV/O_3 treatment caused a less pitted surface on the PLA fibers. It is possible that the Wet-UV/O_3 exposure have a more etching effect on PLA surface structure.

Moisture Content Properties

Table 4 shows the variation of the Moisture Contents as the UV/Ozone treatment is changed. The Moisture Content for untreated PLA fabric was found to be approximately 0.4%. After UV/Ozone exposure for 40 min, the Moisture Content increases sharply to 0.59%.

Static properties

Table 5 shows half-life decay times of PLA fabrics.

The of PLA fabrics was calculated from equation (1) as fallowing[28]:

$$half - life\ decay\ time\ \ (seconds) \times 10^{11} = R\ (ohm)$$

Table 6 demonstrates Average Values of R (ohm) of PLA fabrics.

Fig. 10 displays the association between the half-life decay time and moisture content.

The similar phenomenon was also experienced study of C. W. Kan and C. W. M. Yuen for the application of low temperature plasma treatment

Table 4. Average Values of Moisture Content (%) of PLA Fabrics after UV/Ozone Treatment.

PLA Fabric	Moisture Content (%)
Untreated	0.4
UV/O: 5 min	0.41
UV/O: 10 min	0.43
UV/O: 20 min	0.43
UV/O: 40 min	0.59
H_2O-UV/O : 40 min	0.43
H_2O_2-UV/O : 40 min	0.43
H_2O_2-Na_2SiO_3- UV/O : 40 min	0.49

Table 5. Half-life decay times of PLA fabrics.

PLA Fabric	half-life decay time (seconds
Untreated	5.2
UV/O: 5 min	4.6
UV/O: 10 min	3.8
UV/O: 20 min	3.7
UV/O: 40 min	2.5
H_2O-UV/O : 40 min	2.9
H_2O_2-UV/O : 40 min	4
H_2O_2-Na_2SiO_3- UV/O : 40 min	2.7

Table 6. Average Values of R (ohm) of PLA Fabrics after UV/ Ozone Treatment.

PLA Fabric	*R(ohm)*
Untreated	5.2E+11
UV/O: 5 min	4.6E+11
UV/O: 10 min	3.8E+11
UV/O: 20 min	3.7E+11
UV/O: 40 min	2.5E+11
H_2O-UV/O : 40 min	2.9E+11
H_2O_2-UV/O : 40 min	4E+11
H_2O_2-Na_2SiO_3- UV/O : 40 min	2.7E+11

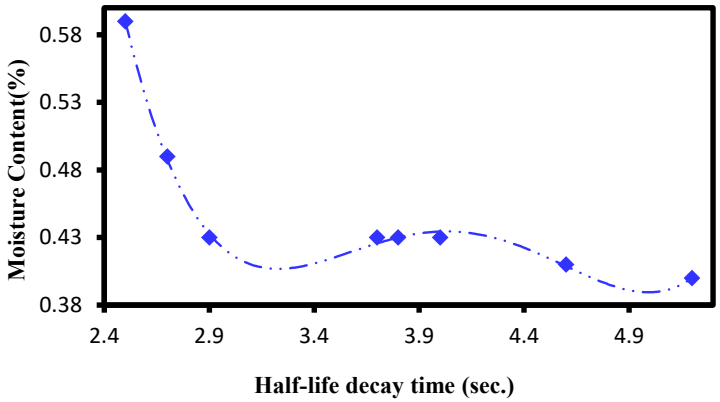

Fig. 10. Relationship between half-life decay time and moisture content.

to improve the anti-static property of polyester fabric [28]. The realized mechanism was very well explained in their study for low temperature plasma treated polyester fabric [28].

The increment in moisture content of PLA fabrics may decrease the half-life decay time, i.e. the anti-static property of PLA fabric was improved. As also experienced in polyester [28], as moisture comprising water is polar in nature, hence the conductivity of the PLA fabric (as an aliphatic polyester fiber) with higher moisture content can be better. Consequently, the localized static charge present on the PLA fabric surface would be dissipated more easily [28]. Besides, as also observed in the case of polyester fabric [28], the moisture film generated on the PLA fabric surface may evaporate in air and instantaneously carry away sufficient amount of static charges from the PLA fabric surface into air, thus decreasing the amount of static charges present on the PLA fabric.

Anti-static mechanism

The SEM images shown in Fig. 5-8 UV/ Ozone treatment cause the increment of surface roughness. According to Wenzel-Equation ($\cos\theta^{rough} = r\cos\theta_0$), the roughness of the surfaces affects the contact angle. θ^{rough} is the Contact-Angle on a surface of studied sample, θ_0 is the Contact-Angle on the smooth surface and r is the roughness (ratio of the actual area of the interface to the geometric surface area) [28]. When the surface possesses a contact angle smaller than 90˚, the incremental surface roughness may possibly decrease the contact angle and contribute to the improved surface wettability [28]. As water is a electricity conductor, hence, the improved surface-wettability reduce the accumulation of electrostatic charges [28]. The increment of surface-roughness also induces the rise in the specific surface-area. The enhanced specific surface area may result in a more Moisture—Rich surface, that increases the conductivity of the fibers [28]. Also Fig. 11 shows the relationship

between the R(ohm) and moisture content.

The Surface Resistance of PLA fabrics were calculated from equation (2) as fallowing:

$$\log \rho s = \log \left(R \times {}^{W}/_{L}\right) \quad (2)$$

Where: ρ_s : Surface Resistance; R : Calculated Resistance by Instrument ; W: Sample`s Width;

L : Sample`s Length(28).

Relationship between Surface Resistance and half-life decay time

Fig. 12 displays the association between and half-life decay time, and outstanding statistical relationship of $R^2 = 1$ was achieved.

The improved in half-life decay time of PLA fabrics would increase the Surface resistance.

CONCLUSION

Scanning Electron Microscopy (SEM) images of treated Poly(lactic acid) (PLA) fabrics showed that the UV/O_3 exposure creates pits and pores with different depth and size on PLA fiber surface. In addition, it can be clearly observed that UV/O_3 irradiation promote Nano-meter surface roughness, and Wet- UV/O_3 method had more effects on increasing surface cracks, crashes and breaks with different surface area on PLA fibers. It can be suggested that alterations on surface topography of PLA fibers can be achieved mainly due to an etching process of UV/O_3 irradiation.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

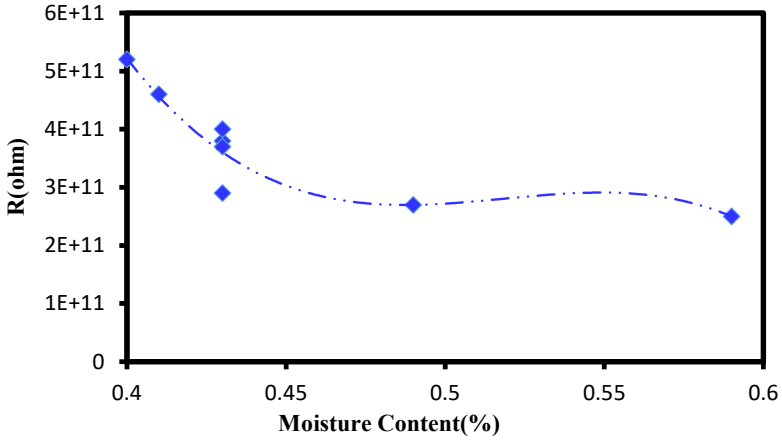

Fig. 11. Relationship between R(ohm) and moisture content (%).

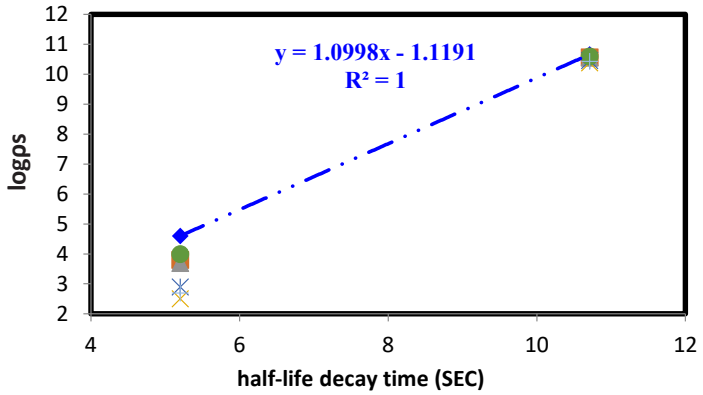

Fig. 12. Relationship between logps and half-life decay time.

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