Surface Characterization of PET Nonwoven Fabric Treated by He/O_2 Atmospheric Pressure Plasma

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ABSTRACT: The surface of polyethyleneterephthalate (PET) nonwoven fabric was modified by He/O_2 atmospheric pressure plasma treatment, varying plasma exposure time. The plasma treated PET surfaces have been analyzed to investigate the chemical nature and morphology of surface by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively. The change of wettability was measured depending on plasma exposure time. XPS results indicated the presence of oxygen-based functional groups on the PET nonwoven fabric surface after plasma treatment and oxygen content increased as exposure time increased. The mean roughness increased after 30 s exposure and further increase in exposure to 60 s led to decrease of the roughness and then again increase. The root mean square roughness followed the similar trend to mean roughness. The average difference in height, Rz, increased after plasma exposure for 30 s, while it slightly decreased after 60 s exposure. Despite of redeposition, the Rz of 90 s exposed sample increased more than two times compared with those of 30 and 60 s exposed. Wettability increased progressively up to 10 times after 90 s exposure compared with the untreated. It is attributed to the increases of hydrophilicity and surface roughness. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 785–790, 2008

Key words: surface modification; atmospheric pressure plasma; XPS; AFM; wettability

INTRODUCTION

Poly(ethyleneterephthalate) (PET) is a preferred material in many applications of nonwoven because of its use of ease, excellent mechanical strength, and good stability. However, its poor surface wettability has prevented end use versatility. Surface wettability of polymer materials is closely related to many fields, such as in printing, spray, adhesion, dyeing, and functional finishing.[1] Plasma treatment is widely employed to modify surface properties of polymers, such as adhesion, friction, penetrability, wettability, dyeability, and biocompatibility, to adapt them to specific application.[2] The surface modification of polymers has been carried out under low-pressure RF plasma environments. It requires complex and expensive vacuum systems associated with quick decay of modification effects and low productivity batch-type processes. To overcome these drawbacks, atmospheric pressure plasma system was introduced as an alternative.[3] The system makes possible to perform an atmospheric treatment at low temperature and at relatively high speeds ($\sim$ 900 m/min), which is favorable to the cost of products. In addition, plasma technologies can advantageously replace some wet chemical application with ecofriendly green process.

Functionalization of PET nonwoven fabrics would increase their versatility and market penetration in cosmetics, bedding, automotive interior, footwear, apparel lining, air filter, wipers, medical and hygienic products, biomedical applications, and so on. However, most researches use RF plasma and focus on the treatment of PET films instead of fabrics because of the relatively easy X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) measurements due to the flat surface of the polymer film. Few works have been done about the surface modification of PET nonwoven by He/O_2 atmospheric pressure plasma treatment.[4,5] Surface modification of PET film (strip) and PET woven and knitted fabrics was investigated using He/O_2 mixtures.[6–9]

In this study, the surface of PET nonwoven fabric was modified by He/O_2 atmospheric pressure plasma treatment. Surface changes of the plasma treated PET nonwoven fabric in chemical composition and morphology depending on plasma exposure time were investigated by XPS and AFM, respectively. The change of wettability was measured depending on plasma exposure time and compared the results, taking into account the surface changes.

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EXPERIMENTAL

Materials and equipment

PET nonwoven fabric (spunbond, 50 g/m^2) used in this study was manufactured by the Nonwoven Technical Research Center, North Carolina State University.

The schematic illustration of plasma reactor used has been described elsewhere.[4] The reactor used has an inner plasma chamber installed inside of an outer chamber. The device is capable of batch process using a test cell, as well as continuous process using a fabric rolling system. The working gas is fed into the chamber through gas flow controllers. The PET nonwoven in this study were exposed to oxygenated-helium plasma using the test cell.[4] Samples are placed on a suspended grid within the test cell. He (99%)/O_2 (1%) mixture was used and flow rates of He and O_2 were held at 10.09 L/min and 0.13 L/min, respectively. RF frequency was fixed at 5.0 KHz and exposure times were varied in the range of 0–90 s.

Characterization

XPS was carried out using ESCA-2000 spectrometer (VG microtech, East Grinstead, UK) equipped with hemispherical analyzer and X-ray source (Al Kα, 1286.6 eV) under UHV condition of 1.0×10^{-9} mbar and the anode of 200 W power. The surface topography was studied by a tapping mode AFM using a Nanoscope IV (Digital Instruments, CA). The AFM analysis program allowed computation of various statistics related to surface roughness on a predetermind scanned areas. The evaluation of roughness parameters of each sample was based on various scan area. Wettability (AATCC 39-1980) was assessed by measuring absorption time to absorb 10 μL of distilled water completely.

RESULTS AND DISCUSSION

Surface chemical analysis

In the XPS, X-rays hit the sample and produce photoelectrons whose energy is measured. The energy is specific to each element and can be used to identify all the elements except hydrogen and helium present in the outer 10 nm of the surface.[10] As shown in Figure 1, O_{1s}/C_{1s} ratio increases progressively from 0.37 for the control sample to 0.46 for the 90 s exposed sample. This result indicates the increase of oxygen-based functional groups on the surface. The O_{1s} spectrum consists of oxygen atoms singly bonded to carbon (O—C) and oxygen atoms doubly bonded to carbon (O=C).

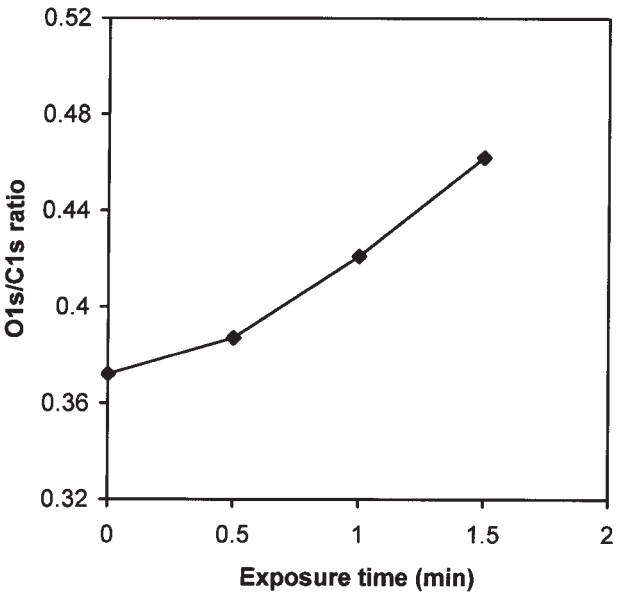

Figure 1 O_{1s}/C_{1s} ratio depending on exposure time.

Figure 2 shows C_{1s} signals of the control and plasma exposed samples. They contain three well separated peaks at 285.0, 286.7, and 288.8 eV, corresponding to the three carbon environments in PET, namely; carbon atoms bound only to carbon or hydrogen in the benzene ring (C—C group), to methylene carbons singly bound to oxygen (C—O group), and to ester carbon atoms (O=C—O group), respectively. C—C peaks is decreased, while C—O and O=C—O peaks slightly increased. Ton-That et al. reported that a low intensity shoulder appeared at higher binding energy, around 292 eV, due to a π–π* transition caused by the aromatic structure in PET.[11] But its presence was not observed in this study. The peak is very weak and negligible. Other researches also did not verified it.[12,13]

In this study, the changes of relative intensities of three peaks in PET nonwoven fabric depending on plasma exposure time are presented in Table I. The C—C component decreases slowly up to 60 s exposure and then decreases sharply at 90 s exposure, in total 5.9% decrease of the component when compared with the untreated. The C—O component shows initial decrease up to 30 s and then increases with further increase in the exposure time. After plasma treatment for 90 s, the decrease of C—C peak due to benzene ring carbon atoms reaches to 5.9%, while C—O peaks increases up to 1.9%. Some of C—O bonds may undergo fragmentation during plasma treatment and contribute to the formation of —OH, such as alcohol and phenol groups, and —OOH groups.[9,12,14] The intensity of O=C—O peak significantly increases up to 30 s exposure and then slightly decreases at 60 s exposure, and shows the

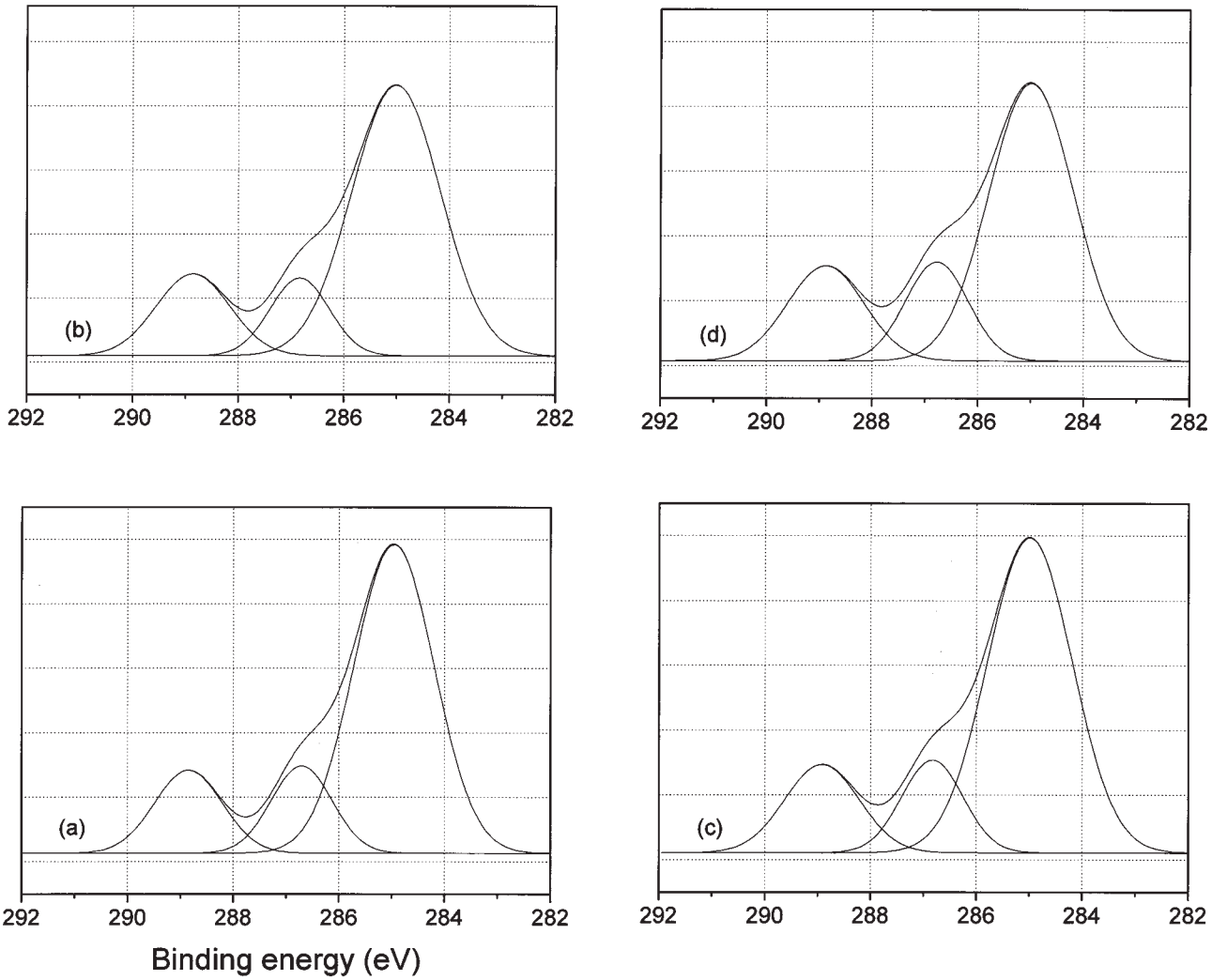

Figure 2 Deconvolution of XPS core level C_{1s} spectra of PET nonwoven fabric: (a) 0 s, (b) 30 s, (c) 60 s, and (d) 90 s exposure.

highest intensity at 90 s exposure, which is 4% higher compared with the untreated sample. An increase of O=C—O peak indicates the introduction of acidic groups.[14]

With He/O_2 mixture plasma, oxygen induces reactions such as chain breaking and surface oxygenation. The oxidative functionalization is introduced at the surface being etched by the action of oxygen species. This has been confirmed by weight loss measurements, as presented in Figure 3. On the other hand, cross-linking occurs by the combination of two aryl radicals formed by hydrogen abstraction from the benzene ring as a result of an He gas discharge action.[7] Helium is the most efficient of the inert gases for the cross-linking of the uppermost few monolayers of a polymer.[14] This is probably due to the large amount of energy available to transfer to the polymer surface via ion neutralization. The competitive action of these two reactions will depend on the composition ratio of He/O_2 mixture. It was reported that surface cross-linking takes place simultaneously with the surface functionalization and small amount of oxygen less than 5% resulted in a strong hydrophilic effect, and a more cross-linked surface in textiles.[7,8] It is speculated that plasma treatment with He (99%)/O_2 (1%) mixture used in this study induces a surface oxidation and simultaneous cross-linking reaction in one-step process.

TABLE I
Chemical Composition (%) from XPS Data

Exposure time (s)	Atomic ratio (%)		
	C—C	C—O	O=C—O
0	69.5	14.8	15.7
30	69.3	13.3	17.4
60	68.6	14.5	16.8
90	63.6	16.7	19.7

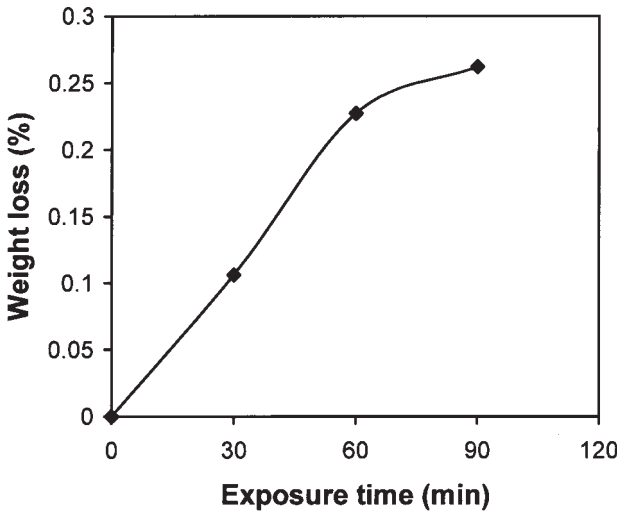

Figure 3 Weight loss depending on exposure time.

These two mechanisms makes possible to obtain a reactive surface with good stability to aging time on PET nonwoven.

Surface morphology

AFM is a newly developed high resolution technique to study the surface morphology of nonconducting materials. It has been used to obtain directly three-dimensional topographic images of the surface up to atomic level resolution in air or in liquid by scanning a sharp tip, situated at the end of a microscopic cantilever, over a surface. Its main advantage over electron microscopy techniques is that previous preparation such as heavy metal coating in SEM and TEM is not needed. In addition, the AFM software program allows computation of various statistics related to the surface roughness by use of the images in conjunction with digitally stored line profiles.

Figure 4 shows 3D views of AFM images of the untreated and plasma treated PET with the light regions being the highest points and the dark regions, the depressions (pores). The surfaces of all nonwoven are not smooth and show bright peaks and dark valleys. Three-dimensional image of the untreated PET spunbond nonwoven sample looks more like that of PET film rather than that of PET

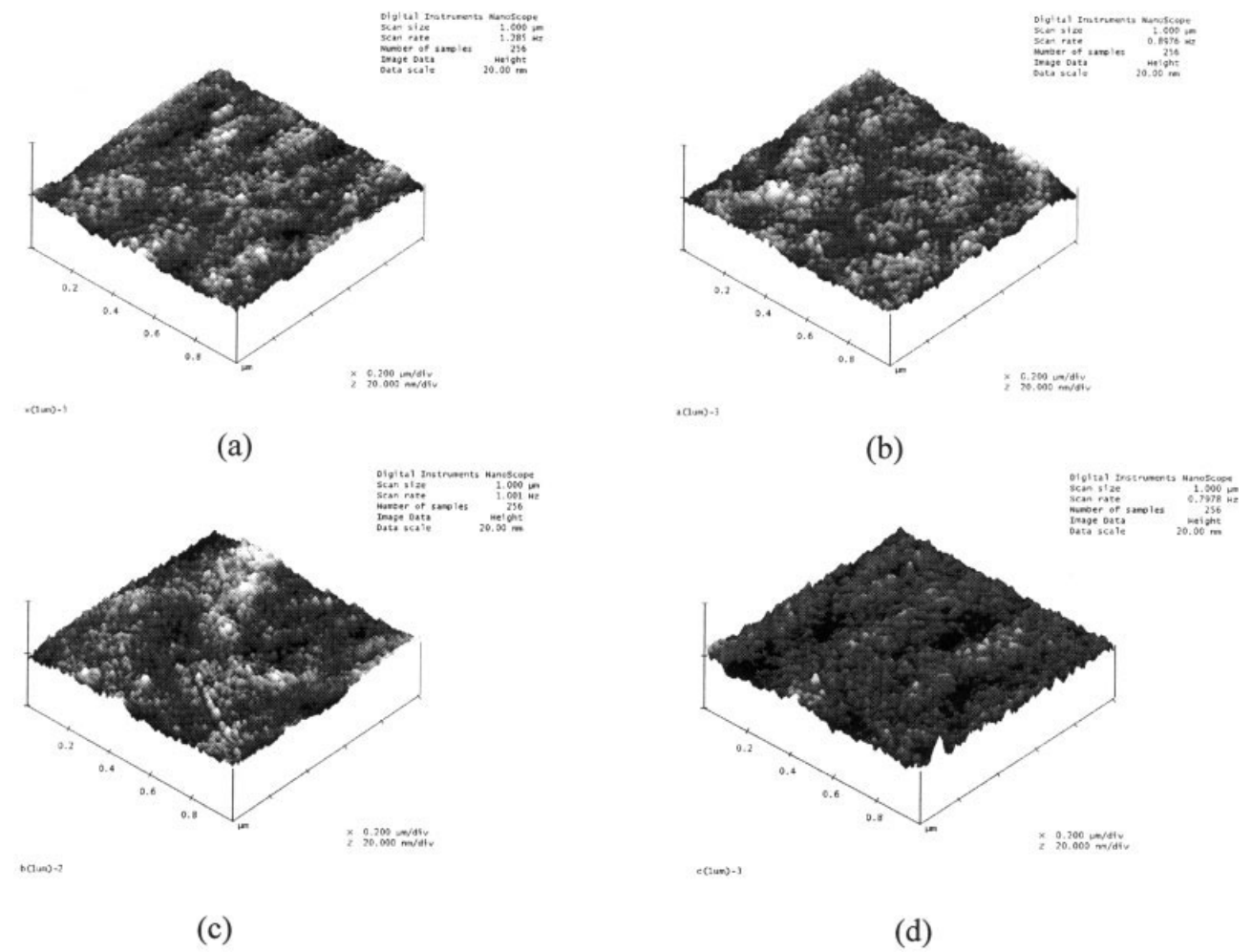

Figure 4 Three dimension views of AFM images of PET nonwoven fabric: (a) 0 s, (b) 30 s, (c) 60 s, and (d) 90 s exposure.

TABLE II
Surface Parameters Obtained from AFM Analysis

Exposure time (s)	Ra (nm)	Rms (nm)	Rz (nm)
0	0.805	1.015	7.829
30	1.218	1.529	11.151
60	0.900	1.162	10.973
90	1.364	1.675	23.907

woven sample.[11,14] During manufacturing process of PET spunbond nonwoven fabric, melted PET polymers are extruded through a spinneret and laid to form a continuous web, and the fibers seal together as the web cools completely. The fibers, composing spunbond nonwoven fabric, do not go through the drawing step as the fibers for woven fabrics. Thus the AFM image of spunbond nonwoven fabric resembles with that of PET films. In previous study,[4] we reported that crystallinity of the PET nonwoven is 31.50%.

Surface roughness parameters obtained from the AFM images of different locations from each samples and the average values are presented in Table II. The mean roughness (Ra) represents the mean value of the surface relative to the center plane for which the volumes enclosed by the images above and below this plane are equal. The root mean square roughness (Rms) is the standard deviation of the height values within the specific area and determined from several 1 μm^2 AFM images. The average difference in height (Rz) between the five highest peaks and the five lowest valleys is calculated relative to the mean plane, which is a plane about which the image data has a minimum variance.

As shown in Table II, the Ra increases after 30 s exposures and further increase in exposure to 60 s leads to decrease of the roughness and then again increases. The Rms follows the similar trend to Ra. During plasma treatment, etching, redeposition, and cross-linking occurs concurrently and these would affect surface morphology. Etching in plasma is a physical removing process of material on the surface of the substrate, which occurs in amorphous regions selectively. This etching effect derives micro-roughness, thereby surface morphology change. On the other hand, the particles etched would be redeposited on the substrate surface. At 30 s exposure, etching occurs mainly and creates pits and micro pores on the surface, which appears dark regions in AFM images, to increase surface roughness. In contrast, light regions (nodules) represent the crystalline zones little degraded of the surface.[15]

The roughness, Rms, is decreased at 60 s exposure when compared with that at 30 s exposure. It is considered the reason of this result in two aspects. Etching would be occurred overall area at longer exposure, leading to more uniform surface relative to the surface exposed for shorter time, 30 s. And also, further exposure induces to occur the redeposition of particles etched, resulting in the decrease of roughness at 60 s exposure. Consequently, the roughness of PET nonwoven fabric increases initially during etching then decreases due to deposition. The redeposition could induce coating and deposited materials on the surface of the PET reduce roughness.[16] In the previous study,[4] redeposited particles were shown in AFM images of 30 and 60 s exposed samples, appearing white spots. The Rz increases after plasma exposure for 30 s and decreases slightly after 60 s exposure. This result also verifies the effect of redeposition. On the other hand, despite of redeposition, Rz value after 90 s exposure increases more than two times compared with those after 30 and 60 s exposures. This indicates that etching seems to occur more dominantly than deposition at the prolonged exposure of 90 s. In overall, plasma treatment produces rougher surface and both of the etching and redeposition take important roles in surface roughness. From the results, it was confirmed that exposure time affected surface roughness. For better understanding the results, other characteristics such as peak to valley distance and surface area might be evaluated.[17] In addition to the plasma exposure time, gas pressure also influences surface roughness and surface area. Poletti et. al. found that surface roughness and surface area of PET fabrics increase with increasing the pressure of air cold plasma.[17]

Wettability

The wettability of treated samples was assessed by measuring water droplet absorption time, which yields much more reliable results than water advancing contact angle in the case of fibers.[14] Contact angle measurement is complex because of the rough surface of fiber. There is a change from one point to another along the contact line, inducing errors and lower reliability of measurement.[18] He/O_2 plasma treatment significantly affects the behavior of PET surface towards water, increasing the surface tension and resulting in faster water spreading over the treated fabric.[19]

As shown in Figure 5, the wettability of PET nonwoven fabric increases as exposure time increases. Control sample takes more than 1 h to absorb 10 μL of water, while the sample exposed by He/O_2 plasmas for 90 s takes 6 min. These results indicate that the surface of the PET nonwoven fabric is considerably changed chemically and morphologically after plasma treatment because that the wettability is mostly affected by the surface polarity and morphology. The decrease in water droplet absorption time is an indicative of the chemical changes taking place

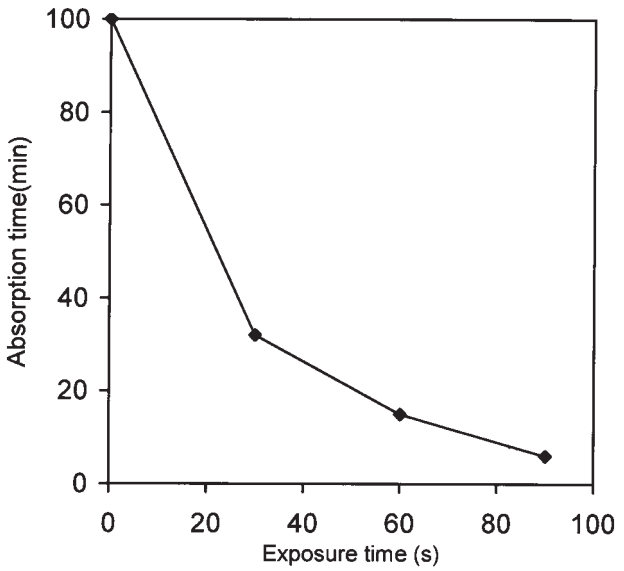

Figure 5 Wettability change with exposure time.

at the surface of PET nonwoven fabric, implying more hydrophilic relative to the untreated surface.

The wettability results are agreed with the XPS results, showing O_{1s}/C_{1s} ratio increases as plasma exposure time increases. The formation of oxygen-based functional groups by plasma treatment, as in the former XPS results, increases surface tension making the fiber surface more hydrophilic, thereby more wettable. Hirose et al.[20] found that an increase in surface roughness determined by AFM resulted in a higher water permeation flux. In addition, the morphology of the surface may take an important part in the transportation of water. Morphological changes are verified by AFM analysis. However, it is difficult to quantify the independent contributions of hydrophilicity and surface roughness to wettability.[11] Nevertheless, the presence of polar functional groups on surface relates more closely to wettability than surface roughness.[1]

CONCLUSIONS

XPS results indicated the presence of oxygen-based functional groups on the PET nonwoven fabric surface after plasma treatment and surface oxygen composition increased as exposure time increased. The Ra increased after 30 s exposure and further increase in exposure to 60 s led to decrease of the roughness and then again increase. The Rms followed the similar trend to Ra. The Rz increased after plasma exposure for 30 s, while it slightly decreased after 60 s exposure. Despite of redeposition, the Rz of 90 s exposed sample increased more than two times compared with those of 30 and 60 s exposed. Wettability increased progressively up to 10 times after 90 s exposure compared with the untreated. The increase of wettability is contributed by hydrophilic and rougher surface after plasma treatment.

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