Functional Finishing of Nonwoven Fabrics. I. Accessibility of Surface Modified PET Spunbond by Atmospheric Pressure He/O_2 Plasma Treatment

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ABSTRACT: The surface of a polyethylene terephthalate (PET) spunbond nonwoven was modified by using atmospheric pressure He/O_2 plasma treatment. Accessibility of the modified PET nonwoven has been investigated in terms of crystallinity, surface chemical composition, hydrophilicity, and dye uptake. Differential scanning calorimetry (DSC) for crystallinity measurement and X-ray photoelectron spectroscopy (XPS) for chemical composition measurement were used. Surface morphology was studied by using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Percentage crystallinity increased due to the depletion of amorphous region by plasma etching. Redeposition of etched particles was observed. Oxygen-based functional groups on the surface of PET increase from 27 to about 32% after 90 s exposure. Wettability increases by more than 10 times and moisture regain increases by three times, compared with the untreated sample. Dye uptake was not changed significantly. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4306–4310, 2006

Key words: nonwoven; plasma; accessibility; crystallinity; hydrophilicity

INTRODUCTION

Nonwoven continues to penetrate world markets with increased versatility, flexibility, and efficiency. In 2003, global production of nonwovens increased by 7% to 4.5 million tons. Spunbonds account for a 24% share in the nonwoven technologies. The growth rate of polyester spunbonds leads this field with a 75% share. Polyethylene terephthalate (PET) is a preferred textile fiber in many durable applications of nonwoven for its ease of use and compatibility with other fibers when blended.[1] Although PET has excellent mechanical strength and good stability, end-use capacity is limited because it is difficult to do functional finishing due to lack of polar groups on the surface and poor wettability. Development of PET spunbond products with functional properties such as absorption, bioactivity, and antimicrobial activity would expand end-use capability in cosmetics, bedding, footwear, automotive interior, and air filter, as well as medical and hygienic products.

Plasma treatments are widely employed to modify surface properties of polymers to adapt them for specific application while it modifies the fiber surface without affecting bulk properties.[2] Plasma modification of PET has been studied in terms of changes in surface morphology and chemical composition.[3–8] Up to now, most of the works reported deals mainly with PET films (strips) using low pressure plasma treatments, which have disadvantages such as quick decay of modification effects, high cost, and low productivity. Recently developed atmospheric plasma technology makes it possible to modify polymer surface at atmospheric pressure and low temperature with relatively high speeds (~900 m/min). However, there have been few reports on PET spunbond using atmospheric pressure plasma technology.

In this study, surface of a PET spunbond was modified by using atmospheric pressure He/O_2 plasma treatment and accessibility of the modified fibers was investigated in terms of changes of crystallinity, morphology, chemical composition, hydrophilicity, and dye uptake.

EXPERIMENTAL

Materials

PET spunbond nonwoven (50 g/m^2) was manufactured and provided by the Nonwoven Technical Research Center, North Carolina State University.

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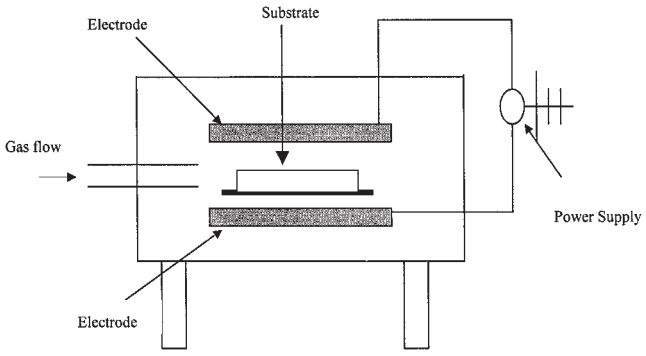


Figure 1 Schematic view of the atmospheric pressure plasma system (closed ventilation).

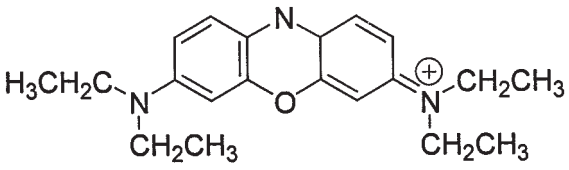
Plasma treatment

The atmospheric pressure plasma device is shown in Figure 1. The reactor used for plasma treatment has been described in detail elsewhere.[9] Treatment was carried out with He (99%)/O_2 (1%) plasma. Flow rates of He and O_2 were 10.09 and 0.13 L/min, respectively. Operating frequency was fixed at 5.0 kHz and the supplied power was 4.8 kW. After plasma treatment, the nonwoven samples were stored in a freezer.

Characterization

Thermal analysis of the samples was carried out using a PerkinElmer 7 Differential Scanning Calorimeter. The DSC trace was recorded through a preset temperature from 25 to 300°C at a rate of 20°C/min. Surface of the plasma-treated samples was observed with SEM (JSM-5400, JEOL, Tokyo, Japan) and AFM (Nanoscope IV, Digital Instruments, CA). AFM images were taken by a tapping mode. 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 $\times$ 10^{-9} mbar and the anode of 200 W power.

Wettability (AATCC 39–1980) was assessed by measuring absorption time to absorb 10 μL of distilled water completely. Moisture regain (ASTM Test Method D2654–76) was measured by following the standard procedure. A basic dye (Maxilon Blue 5G, Ciba-Geigy) was used for dyeability experiment. Chemical structure of the dye is shown in Scheme 1. Dyeing conditions were 3% (owf) dyestuff, 0.1% (owb) sodium acetate, 0.1% (owb) acetic acid, 100°C, 60 min. Dyeability was determined by measuring K/S value with a Macbeth Coloreye 3000 (Datacolor, NY).



Scheme 1 Maxilon Blue 5G (C.I. Basic Blue 3).

TABLE I
Crystallinity Change Depending on Exposure Time

Exposure time (s)	Onset temperature (°C)	ΔH_f (J/g)	Crystallinity (%)
0	242.67	42.782	31.50
30	244.65	46.902	34.54
60	241.03	44.890	33.06
90	241.01	43.798	32.25

RESULTS AND DISCUSSION

Crystallinity

DSC was carried out to correlate plasma exposure time with crystallinity change. Melting enthalpy (ΔH_f) was obtained from area under a peak of DSC thermogram, and crystallinity was calculated from ΔH_f of 100% crystalline PET, 135.8 J/g.[10] The results are summarized in Table I. Percentage crystallinity increases noticeably at 30 s exposure. This indicates that amorphous regions are etched selectively, resulting in the increase of crystallinity. After reaching a maximum at 30 s exposure, percentage crystallinity decreases continuously with further exposure. After all, plasma treatment decreases the accessibility of PET nonwoven by depleting amorphous region. Redeposition seems to prevail over etching between 30 and 60 s exposures, considering less percentage crystallinity after 60 s exposure.

Melt onset temperature of the sample exposed for 30 s increases by 2°C because of the increase of crystallinity. The samples exposed for 60 and 90 s show lower melt onset temperature than the untreated sample, even though the percentage crystallinity of both samples is higher than that of the untreated. This seems to be due to the decrease of molecular weight resulted from polymer chain scission by prolonged plasma exposure.

Surface morphology

Figure 2 shows the SEM pictures of untreated and plasma-treated samples. The untreated PET nonwoven sample shows very smooth surface. Grainy surface, due to redeposited particles, is observed with the 30 s exposed sample. Interestingly, lumps appear on the surface with further exposure. And, ripples and layers are observed with the sample exposed for 90 s. White spots on the AFM images of Figure 3(c) and 3(d) seem to be redeposited particles. More redeposition is observed in the sample with longer plasma exposure.

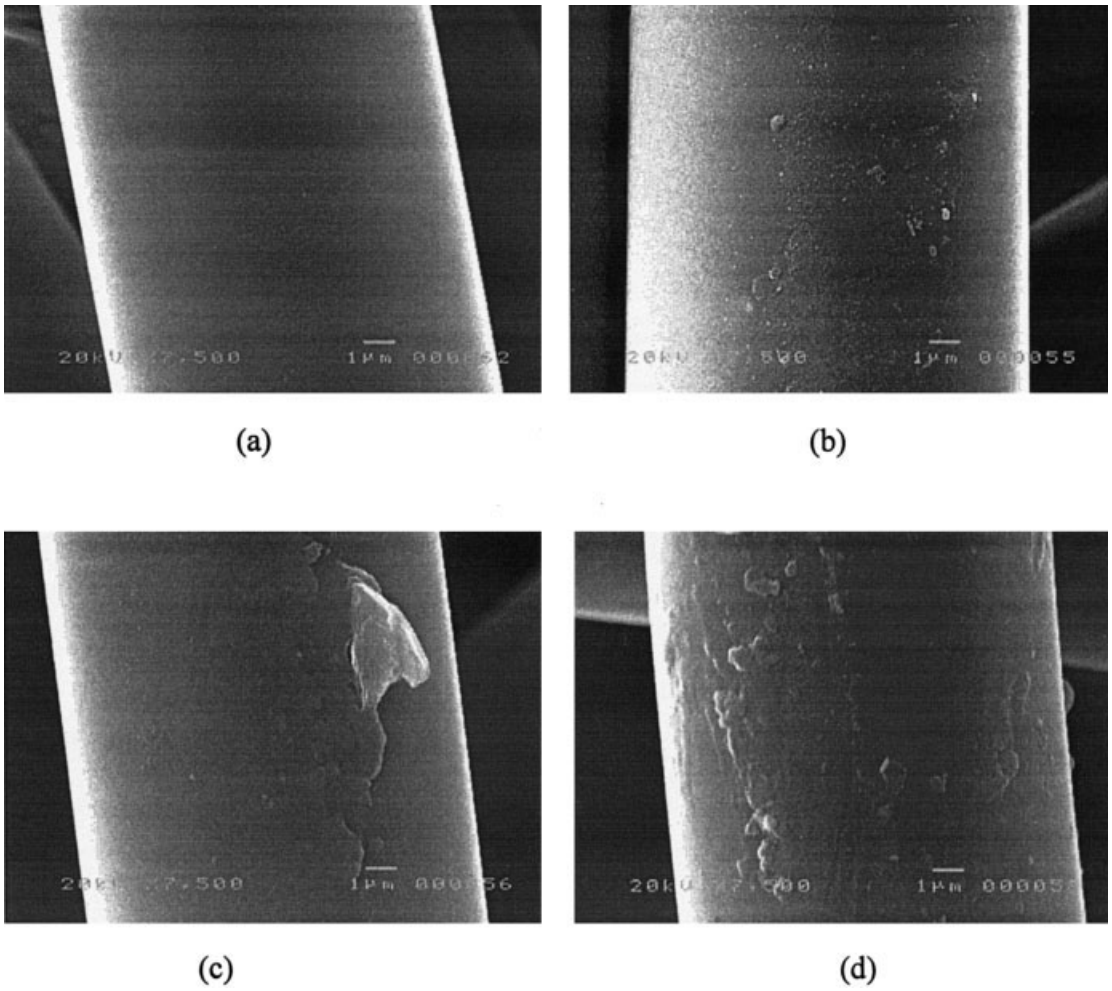


Figure 2 SEM pictures of plasma-treated samples: (a) untreated; (b) 30 s; (c) 60 s; and (d) 90 s exposure.

Surface chemical composition

Table II shows chemical composition of the untreated and plasma-treated samples. Surface oxygen composition increases progressively from 27.1 (untreated) to 31.6% for 90 s exposed sample. O_{1s}/C_{1s} ratio increases from 0.37 in the untreated sample to 0.46 in the sample exposed for 90 s, indicating a higher level of oxygen-based functional groups, such as hydroxyl and carboxylic, on the surface after plasma treatment.

Hydrophilicity

Table III shows the effect of exposure time on wettability, moisture regain. Wettability is mostly affected by surface morphology and hydrophilicity at the surface of polymer. Moisture regain is related to the amount of hydrophilic groups accessible in amorphous region.

The wettability of the treated samples was assessed by measuring water droplet absorption time, which is known to be more reliable than contact angle in the case of fibers.[3] As shown in Table III, the untreated PET nonwoven sample takes more than 1 h to absorb 10 μL of distilled water, while the sample exposed by He/O_2 plasmas for 90 s takes 6 min. The decrease in water droplet absorption time results from the increase of hydrophilicity at the surface of PET nonwoven relative to the untreated surface. The wettability results agree with the XPS results. Plasma treatment increases the surface tension of the fabric, resulting in faster water spreading over the treated fabric.[11] The plasma-treated samples were stored at –20°C in a freezer for more than 1 week after plasma treatment. Even so, wettability of the sample exposed for 90 s is more than 10 times higher than the untreated. Gupta et al. found that the surface hydrophilicity can be maintained to a greater extent by keeping the PET films at a lower temperature.[4]

Moisture regain increases significantly after 30 s exposure exhibiting two times higher than that of the untreated sample. But, it shows little change for further exposure up to 60 s. At 90 s exposure, moisture regain increases about three times higher than that of the untreated sample. This is contributed by the in-

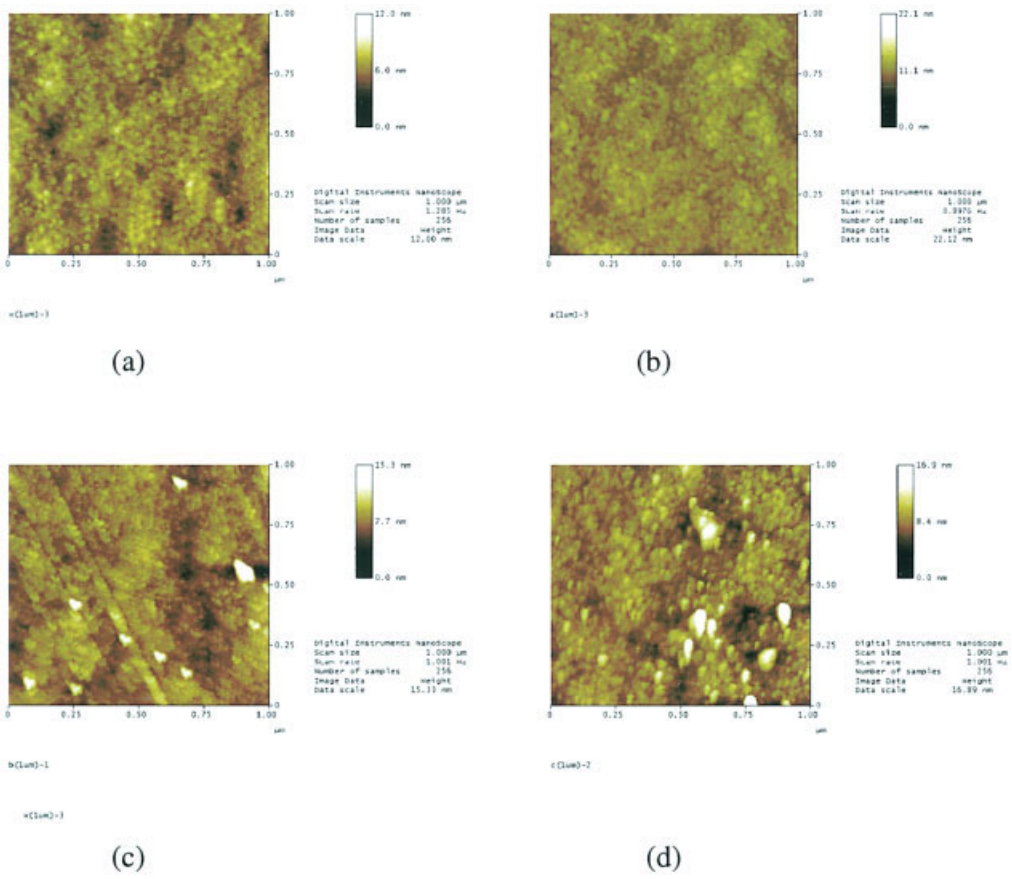


Figure 3 AFM images of the PET spunbond(scan area 1 μm^2): (a) untreated; (b) 30 s; (c) 60 s; and (d) 90 s exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

creases in polar functionality, reflected by the increase of O_{1s}/C_{1s} ratio, as in Table II. In addition, plasma etching opens up newly accessible surface to moisture, even though it depletes amorphous region. The redeposited particles may provide accessible sites for water molecules, affecting moisture regain.

Dye uptake

The change of dye uptake (K/S) is not significant as shown in Table III. Dye uptake is affected by the amount of accessible dyeing sites in amorphous region. The basic dye used in this study is capable of binding with carboxyl groups of the plasma treated PET. Therefore, dye uptake results indicate the amount of carboxyl groups accessible to dye molecules. Considering the increase of crystallinity, the dye uptake of plasma-treated samples is expected to decrease. On the other hand, plasma etching opens up newly accessible sites. This would lead to increase dye uptake. Dye molecules need larger pores for reaching accessible sites due to much larger size than moisture. So, dye uptake is limited, even though accessibility on the surface of PET nonwoven increases. Okuno et al.[12] have reported that the dyeability of PET fibers treated by air plasma significantly decreased, because the dye-

TABLE II
Chemical Composition (%) Obtained by XPS

Exposure time (s)	Surface composition (%)		Ratio O_{1s}/C_{1s}
	C	O	
0	72.9	27.1	0.37
30	72.1	27.9	0.38
60	70.4	29.6	0.42
90	68.4	31.6	0.46

TABLE III
Effects of Plasma Exposure Time on Hydrophilicity and Dye Uptake of PET Spunbond Nonwoven

Exposure time (s)	Absorption time (min)	Moisture regain (%)	Dye uptake (K/S)
0	100	0.22	0.259
30	32	0.44	0.261
60	15	0.45	0.253
90	6	0.65	0.273

able noncrystalline region reduced due to etching of polymers. Some part of the redeposited particles and polymer chains with low-molecular weight would wash away during dyeing process at 100°C. This also depletes amorphous region. After all, plasma treatment does not affect the dye uptake significantly.

CONCLUSIONS

Percentage crystallinity decreases after reaching a maximum at 30 s exposure. The plasma-treated samples show higher percentage crystallinity than the untreated. Surface oxygen composition increases from 27.1% for the untreated to 31.6% for the 90 s exposed sample. O_{1s}/C_{1s} ratio increases with the increase of exposure, indicating a higher level of oxygen-based functional groups on the surface. Wettability improves remarkably by 10 times, compared with the untreated sample. At 90 s exposure time, moisture regain increases up to three times compared to the untreated sample. Although plasma treatment increases the accessibility of PET nonwoven, dye uptake change is marginal.

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