

The Effect of Etching on Low-stress Mechanical Properties of Polypropylene Fabrics under Helium/Oxygen Atmospheric Pressure Plasma

Yoon J. Hwang¹, Jae Sang An², Marian G. McCord¹, Shin Woong Park, and Bok Choon Kang*

Department of Textile Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Korea

¹*Department of Textile Engineering, Chemistry and Science, College of Textiles, North Carolina State University, Raleigh, North Carolina 27695, USA*

²*Apparel & Sweater Technical Service Center, Korea Institute of Industrial Technology, 40-3, Euljiro-5ga, Jung-gu, Seoul 100-195, Korea*

(Received July 25, 2003; Revised October 8, 2003; Accepted October 14, 2003)

Abstract: Polypropylene nonwoven fabrics were exposed to He/O₂ atmospheric pressure glow discharge plasma. Surface chemical analysis and contact angle measurement revealed the surface oxidation by formation of new functional groups after plasma treatment. Weight loss (%) measurement and scanning electron microscopy analysis showed a significant plasma etching effect. It was investigated in low-stress mechanical properties of the fabrics using Kawabata Evaluation System (KES-FB). The surface morphology change by plasma treatment increased surface friction due to an enhancement of fiber-to-fiber friction, resulting in change of other low-stress mechanical properties of fabric.

Keywords: Atmospheric pressure plasma, KES-FB, XPS, SEM, Polypropylene

Introduction

It is well known that plasma treatment can modify polymer surface easily without using wet-chemicals. Plasma surface modification is involved in surface properties from plasma-substrate interactions; functionalization, etching, chain scission and cross-linking. Functionalization can change surface chemical properties to be hydrophilicity or hydrophobicity. Etching is closely related to physical property such as surface morphology and friction properties. It has been reported that atmospheric pressure plasma treatment did not deteriorate bulk properties of substrate [1], while tensile strength of fibers and fabrics were reduced in the intensive low-pressure plasma conditions [2,3].

Stone and Barrett [4] found that breaking strength of cotton yarns increased significantly after low-pressure plasma treatment. The reason was not explained clearly why. However, it was reported that etching effect on the surface of polymer increased the surface roughness, resulting in an increase of fiber-to-fiber friction and thus fabric tensile strength enhancement [3]. Despite the effectiveness of etching on tensile strength, the intensive plasma treatment can impart a reduction of fiber strength as a result of degradation by etching effect, corresponding to a decrease of weight loss (%) of fiber. Even in the absence of an apparent etching effect, low-pressure plasma treated single fibers showed a decrease of tensile strength, suspecting stress-concentration effect due to micro-crack by plasma [5]. For fabrics treated by low-pressure plasma, the intensive plasma treatments (with longer exposure time or higher power) could depreciate a tensile strength of

fabric due to higher degradation of bulk molecular structure. However, fiber surface roughness by etching effect could induce an increase of fabric strength at a relative short exposure time [3]. Under relative mild plasma conditions, it has been reported that the surface roughness altered low-stress mechanical properties of low-pressure plasma treated fabrics, suggesting a change of the handle properties [6-8].

Unlike low-pressure plasma treatments, atmospheric pressure glow discharge plasma treatments showed that tensile strength of filament and fabrics treated increased at some conditions with no surface morphology change [1,9-11]. Moreover, the tensile strength of high molecular weight polyethylene (HMWPE) fiber increased with a significant surface morphology change by etching effect [10,11]. The potential cross-linking on the filament would be responsible for the increase of tensile strength, expecting that helium gas used in atmospheric pressure plasma would have influence on cross-linking formation dominantly over degradation on polymer [12,13].

While the effects of low-pressure plasma treatment on fabric properties are well documented, there have been few studies of plasma-physical property relation under atmospheric pressure plasma. In this study, we examine the low-stress mechanical properties of polypropylene nonwoven fabrics treated by atmospheric pressure helium plasma using Kawabata Evaluation System (KES-FB).

Experimental

Materials

The unfinished polypropylene SMS (spunbond-meltblown-spunbond) nonwoven fabrics were used through all plasma

*Corresponding author: bckang@inha.ac.kr

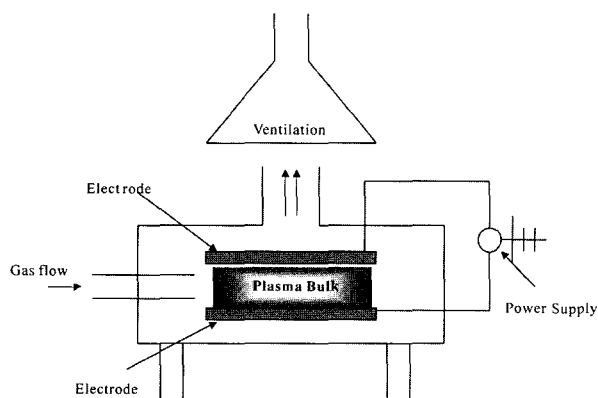


Figure 1. Schematic diagram of atmospheric pressure plasma system.

treatments (Fetisa Inc., Brazil). The fabric surface is extremely hydrophobic and unwettable and its basis weight was approximately 75 g/m^2 . All samples were cut to a size of $25 \times 25 \text{ cm}$.

Plasma Treatment

Atmospheric pressure glow discharge system was designed and developed for industrial applications for continuous process by College of Textiles and Nuclear Engineering Department at North Carolina State University [13]. This plasma system is capacitively-coupled, consisting of two parallel electrodes as shown in Figure 1. The stable and uniform plasma can be achieved in low (audible) frequency, 5.0 kHz during the operation. The voltage across the plates can be up to $7.5 \text{ kV}_{\text{rms}}$. The fabric treatments were conducted in the middle of two parallel electrodes with the voltage across the electrodes, $7.5 \text{ kV}_{\text{rms}}$. The gas used for plasma generation was helium/oxygen mixture with constant flow rates (He flow rate = 13 lpm (liter per minute) and O_2 flow rate = 0.2 lpm), and the exposure time was varied between 0 and 2 minutes at 30 seconds intervals.

Characterizations and Measurements

The weight loss (%) of polypropylene fabrics was measured right after plasma treatments as following equation:

$$\text{Weight Loss (\%)} = \frac{(W_0 - W_i)}{W_0} \times 100 \quad (1)$$

where W_0 is the initial weight of the fabric and W_i is the weight of the fabric after plasma treatment.

Hitachi model S-3200 scanning electron microscopy (SEM) was used to analyze the surface morphology change of plasma treated polypropylene fabrics at a magnification of $6000\times$ at 5.0 kV.

Surface wettability tests of plasma treated fabrics were conducted by contact angle measurements using a goniometer (Model A-100 by Ramé-Hart, Inc.) with the sessile drop technique. The contact angle of a $1 \mu\text{l}$ distilled water droplet

on the fabric was observed through the telescope in 5 different places on the fabric surface.

X-ray photoelectron spectroscopy (XPS) analyses were conducted using Perkin Elmer PHI 5400 XPS photospectrometer to examine surface chemical change of the polypropylene fabric. The x-ray source was Mg_{α} (1253.6 eV) with the take-off angle, 45° . The references of XPS spectra were used with respect of 285 eV for C_{1s} [9]. The relative atomic ratios (O/C, N/C, and (O+N)/C) were estimated as results of the relative intensities of the O_{1s} , N_{1s} , and C_{1s} core levels. The carbon related functional groups were estimated by C_{1s} deconvolution analyses on the fabric surfaces after plasma treatments.

The tensile strength test was conducted according to ASTM method D-5035 using universal instron tester (Model 3366, Instron Co.) with 5 kN load cell at a constant rate of 100 mm/min. The samples were cut to $10 \times 15 \text{ mm}$., and 6 specimens were tested for each plasma condition. Breaking strength and Young's modulus in machine direction for all plasma treated fabrics were measured to evaluate the change of bulk properties. The Kawabata evaluation system (KES-FB) was used to test the low-stress mechanical properties of plasma treated polypropylene fabrics. For conditioning of test fabrics, the fabrics were left under standard conditions, $20 \pm 2^\circ \text{C}$ and $65 \pm 2\% \text{ RH}$ for 1 day before testing. The mechanical properties (tensile, shearing, bending, surface and compression) were measured for each sample.

Statistical analyses were performed according to one-way analysis of variance (ANOVA) and Turkey pair-wise multiple comparison to compare the contact angle and the tensile strengths of the polypropylene fabrics among different treatment groups [14]. A P-value, 0.05 was adopted to test the statistical significance.

Results and Discussion

Surface Wettability

The effects of He/ O_2 atmospheric pressure plasma on surface wettability were determined by contact angle measurement with water. The dynamic contact angle

Table 1. Surface wettability on He/ O_2 atmospheric pressure plasma treated polypropylene nonwoven fabric with different exposure time

Treatment	Contact angle, degree	
	Mean	Standard deviation
Control	104.6 ^{a)}	1.5
He/ O_2 30 sec.	55.8 ^{b)}	2.5
He/ O_2 60 sec.	52.8 ^{b,c)}	1.9
He/ O_2 90 sec.	49.4 ^{c)}	4.5
He/ O_2 120 sec.	42.4 ^{c)}	1.9

^{a,b,c)}Means with different letter are statistically significant different at $p < 0.05$.

decreased with an increase of exposure time as shown in Table 1. Contact angles decreased rapidly after 30 sec. exposure time, and then became stable thereafter. This result indicates that short plasma treatment can introduce enough hydrophilicity onto surface of polypropylene fabric. The fabrics treated for longer exposure time had a higher wettability than the shorter treated. The longer duration of plasma exposure can induce more hydrophilic functional groups on the fabric surface due to higher surface oxidation from chemical interaction between plasma and polypropylene.

Surface Elemental Composition Analysis (XPS)

Figure 2 shows O_{1s} spectra of untreated and plasma treated polypropylene fabrics, indicating an apparent alteration of chemical composition after plasma treatment. The oxygen peak of He/O₂ 120 sec. plasma treatment proved that there was surface oxidation due to chemical reactions during the plasma treatment. The results of surface elemental analyses of polypropylene fabrics showed that. Carbon content (C_{1s}) decreased with an increase of plasma exposure time (Table 2). However, oxygen and nitrogen contents (O_{1s} and N_{1s}) increased as well as O/C and (O+N)/C ratios with an increase

of exposure time. The nitrogen content (N_{1s}) increment showed that nitrogen in air was involved in chemical reactions in atmospheric pressure plasma. C_{1s} deconvolution analysis shows the formation of new functional groups, which are hydrophilic groups (Table 3). The intensity of C-C bond (285.0 eV) decreased with an increase of exposure time while those of C-O (286.3 eV) and COO- (289.1 eV) groups increased, corresponding to surface wettability enhancement.

Surface Morphology Change by Etching Effect

Figure 3 shows the weights of plasma treated polypropylene

Table 2. Relative chemical composition and atomic ratios determined by XPS for polypropylene fabrics untreated and treated by He/O₂ atmospheric pressure plasmas

Treatment	Chemical composition, %			Atomic ratio, %		
	C _{1s}	N _{1s}	O _{1s}	O/C	N/C	(O+N)/C
Control	99.3	0	0.7	0.01	0.00	0.01
He/O ₂ 30 sec.	96.4	0.5	3.1	0.03	0.01	0.04
He/O ₂ 60 sec.	91.3	1.2	7.5	0.08	0.01	0.09
He/O ₂ 90 sec.	84.3	1.7	14.0	0.17	0.02	0.19
He/O ₂ 120 sec.	79.1	2.3	18.6	0.24	0.03	0.27

Table 3. Results of deconvolution of C_{1s} peaks for polypropylene fabrics untreated and treated with He/O₂ atmospheric pressure plasmas

Treatment	Relative area corresponding to different chemical bonds, %		
	C-C	C-O	COO
Control	96.2	3.8	0
He/O ₂ 30 sec.	84.0	12.7	3.3
He/O ₂ 60 sec.	80.8	15.6	3.6
He/O ₂ 90 sec.	75.2	19.3	5.5
He/O ₂ 120 sec.	71.7	22.2	6.1

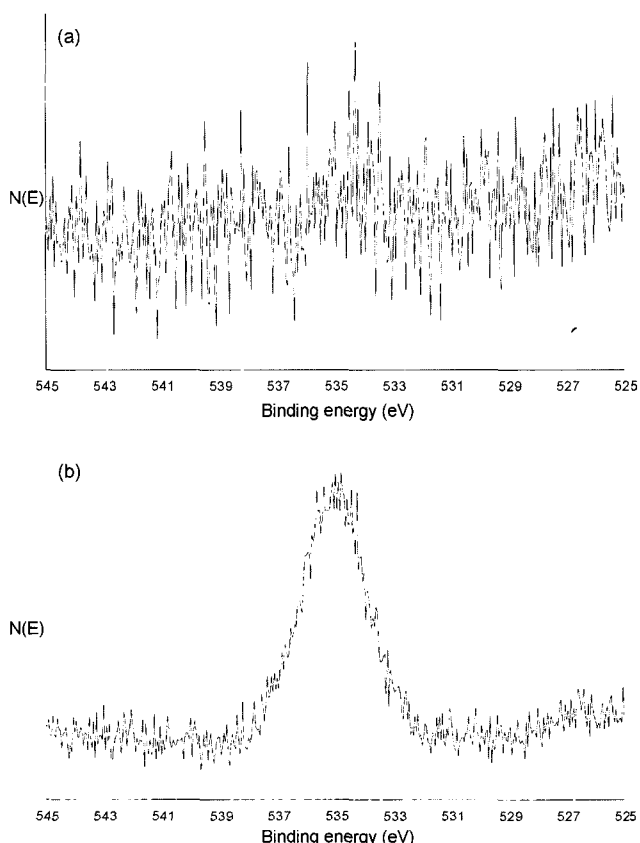


Figure 2. O_{1s} spectra of He/O₂ atmospheric pressure plasma treated polypropylene nonwoven fabrics: (a) untreated and (b) 120 sec. treated.

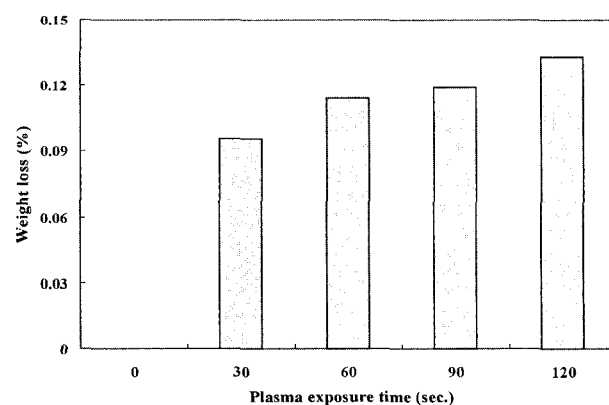


Figure 3. Weight loss (%) of polypropylene fabrics after He/O₂ atmospheric pressure plasma treatments.

fabrics as function of plasma exposure time. The weight loss (%) of plasma treated fabric increases with an increase of exposure time. Longer plasma treatment leads to higher weight loss (%) than shorter treatment because higher etching effect is involved in longer exposure time.

The morphology change by plasma treatment appears significant as shown in Figure 4. Untreated fibers had a relatively smooth surface, while He/O₂ plasma treatments resulted in an increase in waviness with an increase of

exposure time. The significant surface morphology changes can be derived from the etching effect of plasma active species bombardment into polypropylene surface. The waviness on polypropylene fiber surface appears slightly at 30 sec. exposure times in plasma treatments. However, the surface of polypropylene filament changed more dramatically at longer plasma treatment because longer duration of plasma-substrate interaction can lead to higher etching effect. Our results correspond to previous studies [1,15].

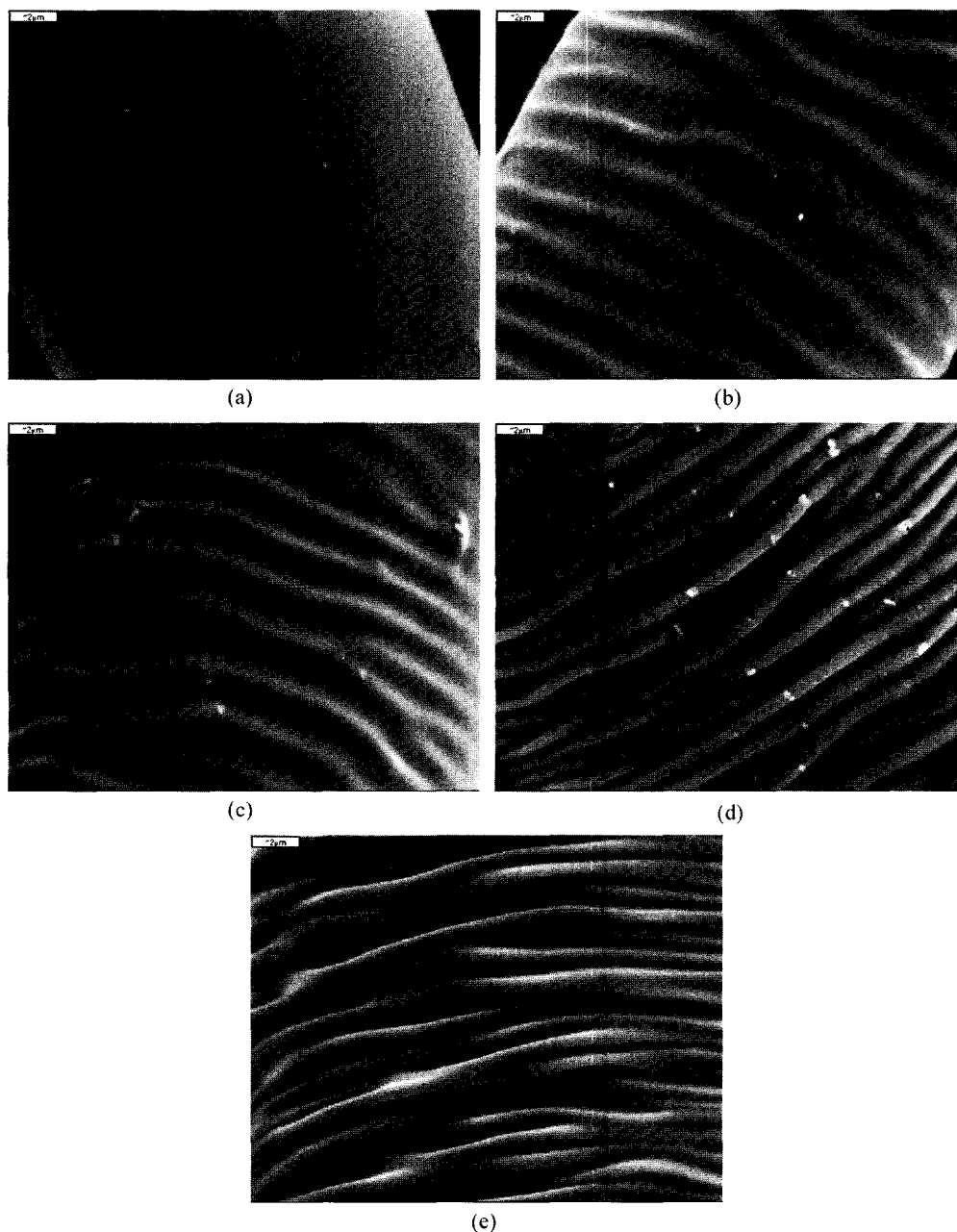


Figure 4. SEM photographs of He/O₂ atmospheric pressure plasma treated polypropylene nonwoven fabrics: (a) untreated; (b) 30 sec.; (c) 60 sec.; (d) 90 sec.; (e) 120 sec.

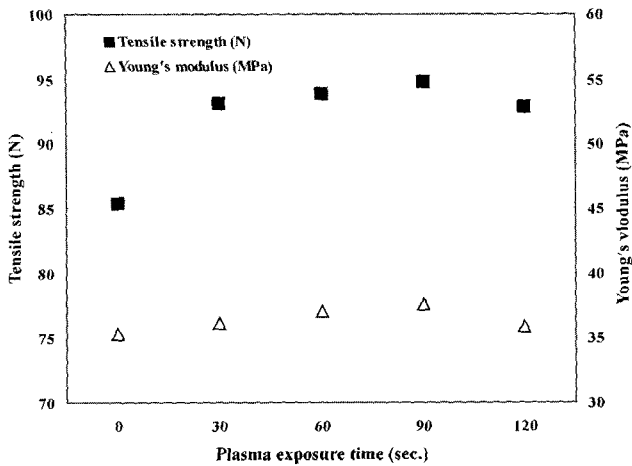


Figure 5. Tensile strength results of He/O₂ atmospheric pressure plasma treated polypropylene fabrics (Means are different significantly at $p < 0.05$).

Mechanical Properties of Treated Polypropylene Nonwoven Fabrics

Figure 5 shows the results of tensile properties of plasma treated polypropylene fabrics. Tensile strength and Young's modulus increased up to 90-second exposure time, and then decreased thereafter. The increment of fiber-to-fiber friction by etching might result in the enhancement of tensile strength and Young's modulus. However, the extensive plasma treatment would impart the degradation of polypropylene fibers at 120-second exposure time, leading to the reduction of tensile properties. It was expected that the degradation of the fibers might result in initiation of fracture by stress-concentration effect.

Low-stress Mechanical Properties Treated Polypropylene Nonwoven Fabrics

Surface roughness of fibers treated by plasma plays an important role in changing mechanical properties of fabrics [6-8]. Figures 6-9 show the low-stress mechanical properties of plasma treated polypropylene fabrics by KES-FB system. Friction coefficient (MIU) and surface roughness (SMD) increased with an increase of exposure time as shown in Figure 6. It is noticeable that an increase of surface roughness (SMD) corresponds to an increase of coefficient (MIU). The significant morphology change (Figure 4) on polypropylene fibers is closely related to the change of fabric surface properties.

The change of surface properties by plasma treatment affects other mechanical properties (bending, shearing and tensile). Figure 7 shows that bending rigidity (B) and bending hysteresis (2HB) increased up to 60-second exposure time, and then decreased. The increase of surface friction results in the increase of bending properties due to fiber-to-fiber friction, which can resist bending deformation

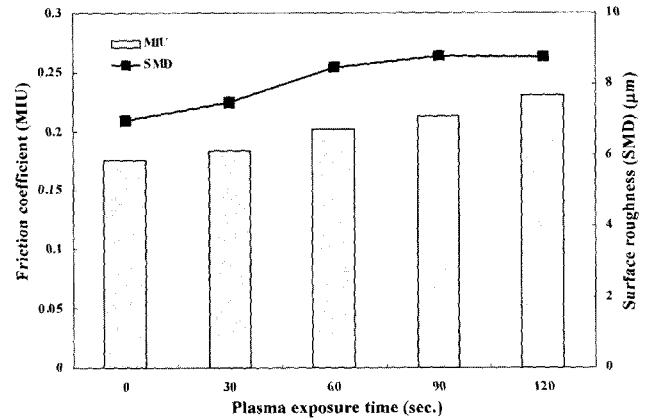


Figure 6. Friction coefficient (MIU) and surface roughness (SMD) of He/O₂ atmospheric pressure plasma treated polypropylene fabrics.

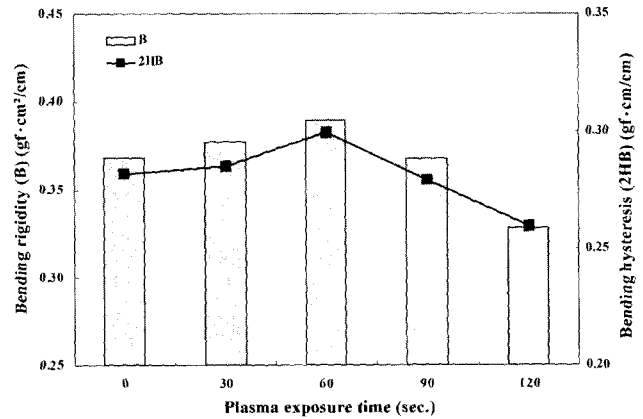


Figure 7. Bending rigidity (B) and bending hysteresis (2HB) of He/O₂ atmospheric pressure plasma treated polypropylene fabrics.

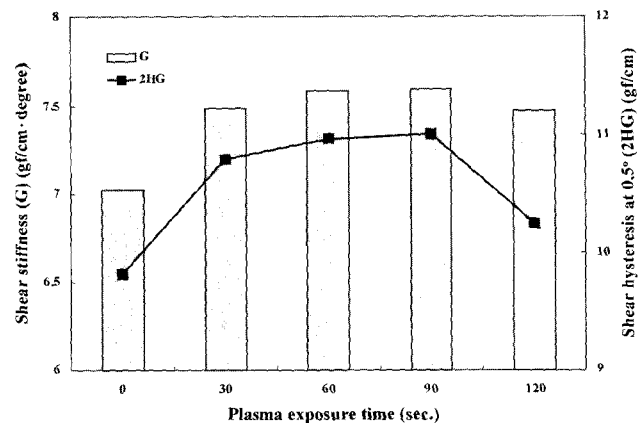


Figure 8. Shear stiffness (G) and shear hysteresis (2HG) of He/O₂ atmospheric pressure plasma treated polypropylene fabrics.

and recovery. However, the reduction of bending properties at further exposure time might result from the degradation of

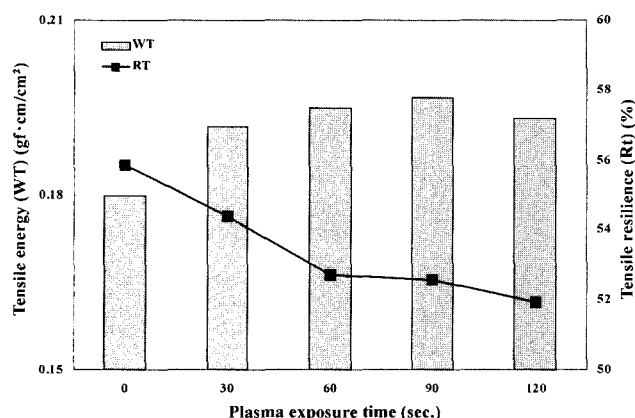


Figure 9. Tensile energy (WT) and tensile resilience (RT) of He/O₂ atmospheric pressure plasma treated polypropylene fabrics.

fiber surface, corresponding to the results of tensile properties in Figure 5.

Shear stiffness (G) and shear hysteresis (2HG) also increased up to 90-second exposure time as a result of fiber surface roughness, and then decreased as a result of fiber degradation as shown in Figure 8. The result of tensile energy (WT) shows the same trend along plasma exposure time (Figure 9). Generally, the fiber-to-fiber contact point could increase as fiber surface roughness increased, leading to fiber-to-fiber friction enhancement. A reduction of tensile resilience (RT) can show that the recovery of fabric deformation might be delayed by cohesiveness between fibers due to surface roughness when the stress is removed.

Conclusions

It was found that the physical properties of polypropylene fabrics were changed as well as surface chemical properties after He/O₂ atmospheric pressure plasma treatment. XPS analyses showed the surface oxidation on polypropylene fabric after plasma treatment, resulting in surface wettability enhancement. Surface microscopy analysis revealed an apparent surface morphology change on polypropylene fibers after plasma treatment. The increase of weight loss (%) was closely related to etching effect of plasma treatment, observed from SEM.

He/O₂ plasma treatments did not depreciate tensile properties of polypropylene fabric. The tensile strength increased by 11.0 % ($p < 0.05$), and Young's modulus increased up to 6.8 % ($p < 0.05$) by plasma treatment (Figure 5). Generally, fiber tensile strength is reduced due to ablation or etching effect of plasma treatments, however the fiber-to-fiber friction as a result of surface roughness enhanced fabric

tensile properties. The extensive plasma treatment (120-second exposure time) imparted the reduction of tensile properties due to surface degradation. The etching effect on fiber surface appeared intensely in low-stress mechanical measurement. Surface properties (MIU and SMD) increased with an increase of exposure time. It is suggested that an increase of fiber-to-fiber friction is closely related to the change of shear, bending, and tensile properties. Our results correspond to the previous works conducted under low-pressure plasma [6,15].

Acknowledgement

This work was supported by Inha University Research Grant (INHA-30283).

References

1. M. McCord, Y. Hwang, P. Hauser, Y. Qiu, J. Cuomo, O. Hankins, M. Bourham, and L. Canup, *Textile Res. J.*, **72**, 491 (2002).
2. T. Yasuda, M. Gazicki, and H. Yasuda, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **38**, 201 (1984).
3. K. Wong, X. Tao, C. Yuen, and K. Yeung, *Textile Res. J.*, **69**, 846 (1999).
4. R. Stone and J. Barrett Jr., *Textile Bulletin*, **1**, 65 (1962).
5. D. Ferrante, S. Iannace, and T. Monetta, *J. Mater. Sci.*, **34**, 175 (1999).
6. J. Yip, K. Chan, K. Sin, and K. Lau, *J. Mater. Process. Tech.*, **123**, 5 (2002).
7. I. Negulescu, S. Despa, J. Chen, and B. Collier, *Textile Res. J.*, **70**, 1 (2000).
8. M. Kim and T. Kang, *Textile Res. J.*, **72**, 113 (2002).
9. Y. Hwang, Y. Qiu, C. Zhang, B. Jarrard, R. Stedeford, J. Tsai, Y. Park, and M. McCord, *J. Adhesion Sci. Technol.*, **17**, 847 (2003).
10. Y. Qiu, Y. Hwang, C. Zhang, and M. McCord, *J. Adhesion Sci. Technol.*, **16**, 449 (2002).
11. Y. Qiu, C. Zhang, Y. Hwang, B. Bures, and M. McCord, *J. Adhesion Sci. Technol.*, **16**, 99 (2002).
12. G. Placinta, F. Arefi-khonsari, M. Gheorghiu, J. Amouroux, and G. Popa, *J. Appl. Poly. Sci.*, **66**, 1367 (1997).
13. Y. Hwang, S. Matthews, Y. Park, M. McCord, and M. Bourham, *202nd The Electrochemical Society Meeting*, Salt Lake City, Utah, USA, October, 2002.
14. G. Snedecor and W. Cochran, "Statistical Methods", 8th ed., Iowa State University, Ames, Iowa, 1989.
15. P. Tasi, L. Wadsworth, and R. Roth, *Textile Res. J.*, **67**, 359 (1997).