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A Study on Chitosan Modification of Polyester Fabrics by Atmospheric Pressure Plasma and Its Antibacterial Effects

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Abstract: Chitosan is a natural nontoxic biopolymer used widely in various fields due to the antimicrobial activities. In this study, the properties of polyester fabrics grafted with chitosan oligomers/polymers after being activated by atmospheric pressure plasmas were evaluated. The antibacterial effect was most evident when the surface of fabrics was activated by atmospheric pressure plasma for 60 to 120 seconds and grafted with chitosan oligomers. The modified fabrics also exhibited good biocompatibility. This process can be applied to a large area and used to produce antibacterial polymer fibers.

Keywords: Polyester fabrics, Air plasma, Chitosan, Chitosan oligomer, Antibacterial

Introduction

In recent years, much attention has been paid to creating more comfortable living conditions, especially for health and hygiene. For example, fabrics treated with antimicrobial agents are used to suppress bacteria, molds, algae, and microorganisms that cause some health concerned problems such as corruption, spots, and odor. Normally, antimicrobial agents exert their functions in two ways. Since traditional antimicrobial agents react with microorganism after being released from the textile, the efficacy time and the dosage are less predictable. Unconventional antimicrobial agents combine with the textile at the molecular level to destroy contacted microorganism by means of physical puncture through cell membrane or biochemical reaction of the cell membrane which was a new subject of study recently. One example is to treat the fabrics with plasma, UV light or radioactive rays, *etc*., to modify the surface of textile material. After the treatment, special functional groups are generated on the surface and can be further grafted with other molecules that possess antimicrobial activities [1].

In 2001, Huh *et al.* [2] grafted nonwoven PET (poly(ethylene terephthalate)) fabrics with acrylic acid by RF-powered low piezoelectricity plasma and utilized 1-ethyl-3-(3'-dimethyl-aminopropyl) carbodiimide to activate the carboxyl groups of the acrylic acid (O=C-OH). Then chitosan was fixed by the amide groups (O=C-NH) formed via covalent bonding between activated carboxyl groups and biological primary amino groups (-NH_2). The modified PET fabrics showed antimicrobial performance in following tests [2]. In 2002, Yang *et al.* [3] utilized UV light and RF-powered low piezoelectricity plasma to graft the surface of nonwoven PET fabrics with silver nitrate, vinyl quaternary ammonium salt (VQAS), and chitosan. All the modified fabrics were more hydrophilic and antimicrobial. The VQAS grafted on PET fabrics was most durable against the flushing water. The more chitosan were grafted on the fabrics, the better rinse-resistance was obtained [3].

The properties of chitosan, including antimicrobial effects, biocompatibility, biodegradability, biological functionality, non-toxicity, anallergicity, high humidity absorption, hemostasis, and promoting tissue regeneration, etc., make it an excellent polymer for biomaterial use [4-6]. This research presents results from polyester fabrics grafted with chitosan oligomers/polymers after being activated by atmospheric pressure plasmas, which is one of the environmentally friendly ways to make fabrics antimicrobial.

Materials and Methods

Materials and Equipments

Uncolored PET woven fabric with an area density of 14.8 mg/cm^2 was provided by the Far Eastern Textile, LTD (Chungli, Taiwan). To assure the same clean condition before plasma treatment, the fabric was heated to 70 ^{o}C in water for 1 hour and completely dried in an oven at 65 ^{o}C for 30 min. Chitosan polymers (P, M_w=360,000) and chitosan oligomers (O, M_n=12,000, M_w=60,000) were purchased from Charming Beauty Co., Ltd. (Taipei, Taiwan). The degree of deacetylation for the oligomer and polymer was both greater than 90 %. For grafting experiment, the chitosan polymer was dissolved in the deionized water containing 1 % acetic acid. The final concentration of the chitosan polymer solution was 2 %. The chitosan oligomer was dissolved in deionized water and the final concentration was 3 %.

The atmospheric pressure plasma reactor used in this study was a laboratory-fabricated parallel-plate plasma system as shown in Figure 1, which was designed and built by the Institute of Nuclear Energy Research, Taiwan. The plasma reactor consisted of a pair of parallel aluminum-electrodes adhered to two pieces of borosilicate glasses as dielectric barriers. The pair of the electrodes have a surface area of

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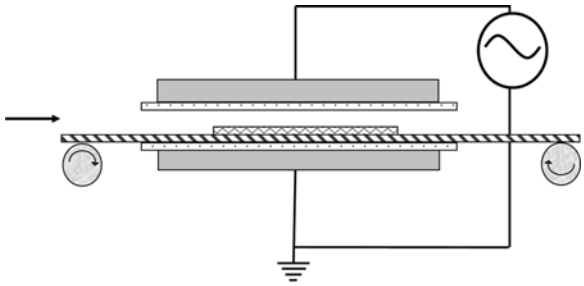

Figure 1. Atmospheric pressure discharge plasma system by Institute of Nuclear Energy Research; ( ) electrode, ( ) conveyor, ( ) dielectric barrier, ( ) power supply, ( ) gas direction, ( ) sample.

15×15 cm^2 each and the gap distance was ~5 mm. The thickness of the dielectric barriers was 1.75 mm. The top electrode was connected to a pulsed high voltage power supply and the bottom electrode was grounded. The frequency of the pulsed high voltage power supply was 3 kHz and the power was 100-150 W. The working gas used was an industrial grade of argon (99.99 %) mixed with a few percent (3-10 %) of oxygen (99.8 %) to optimize the plasma treatment. The plasma system was operated in glow discharge mode to ensure good uniformity in plasma distribution.

Plasma Treatment and Chitosan Grafting

Different conditions were set for three groups of cleaned PET fabrics as listed in Tables 1-3. In Groups 1 and 3, PET fabrics were plasma-treated with 3 % oxygen while Group 2 PET fabrics were with 10 % oxygen. Except for Fabrics 4-7 in Group 1, all other fabrics were plasma-treated for one side only. Activation for two sides meant that after activation of the first side of fabrics was finished, the activated side was placed down and back into the reactor chamber within 30 seconds. Power levels were 100 W for Group 1 fabrics and 150 W for the other two groups. After the plasma treatment was completed, fabrics were exposed to the laboratory atmosphere for oxidization. Oxidized fabrics were immersed in chitosan polymer (2 % aqueous solution with 1 % acetic acid) or chitosan oligomer (3 % aqueous solution) at room temperature and then baked at 95 °C for 8 min except that Fabric 10 of Group 2 was baked for 4 min. Grafted fabrics were then immersed in deionized water at room temperature for 5 hours and ultrasonic bathed for 20 min. All fabrics were dried at 65 °C for 20 min.

Surface Element Analysis

XPS analysis was performed using PHI QUANTUM 2000 (USA) operated at a pressure of 1×10^{-9} Torr. Aluminum target was used for the X-ray source at a power of 25 W at a take-off angle of 45 °. High resolution scans for the C1s (258-298 eV), N1s (379-419 eV), and O1s (505-545 eV) were operated separately with an energy resolution of 0.2 eV and repeated for 10 times to improve the counting statistics of the various atomic peaks.

Biocompatibility Analysis

A fibroblast cell line, L929 cells, were cultured onto the modified and sterilized PET fabrics. The viability was then assayed at 12, 24, 48, 96 hours by MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) cell proliferation assay. The optical density (O. D.) was measured by an ELISA reader (GDV DV 990 BV5, Italy). L929 cells were cultured onto tissue culture polystyrene (TCPS) as control.

Table 1. Experimental parameters for Group 1 PET fabrics (oxidization for 6 min and grafting polymerization for 6 min)

Fabric number	1	2	3	4	5	6	7
Grafted material	none	P	P	P	P	O	O
Activation method	none	one	one	two	two	two	two
Activation time (s)	0	120	80	120	80	120	60

Note: P: materials grafted with chitosan polymer, O: materials grafted with chitosan oligomer, one: fabrics activated for one side, two: fabrics activated for both sides.

Table 2. Experimental parameters for Group 2 PET fabrics

Fabric number	1	2	3	4	5	6	7	8	9	10
Activation time (s)	0	120	60	45	30	15	10	60	60	60
Oxidization time (min)	6	6	6	6	6	6	6	1.5	6	6
Grafting time (min)	5	5	5	5	5	5	5	5	1	5

Tabe 3. Experimental parameters for Group 3 PET fabrics (oxidization for 6 min, and grafting polymerization for 5 min, except that Fabric 2 was not grafted)

Fabric number	1	2	3	4	5	6	7	8	9	10
Activation time (s)	0	60	120	120	60	60	30	30	15	15

Assay for Antibacterial Activities

The width of antibacterial zone was measured according to American Association of Textile Chemists and Colorists (AATCC 90 1982). The number of bacterial colony was counted according to Japanese Industrial Standard (JIS Z 2801: 2000). Then the antibacterial activity was determined by the following two equations:

The width of antibacterial zone=
(diameter of the restraining zone−sample diameter)/2 (1)

Antibacterial ratio (R)=[(number of bacterial colony from culture with untreated fabrics−number of bacterial colony from culture with treated fabrics)/number of bacterial colony from culture with untreated fabrics]×100 (2)

Hydrophilic Property Analysis

Following grafting polymerization, the hydrophilic properties of modified PET fabrics were measured with an optical contact angle analyzer (Ten Angstrom Company, Model FTA-125). The initial contact angles and the dynamic contact angles of water droplets on the fabric surface were measured. The dynamic contact angles were used to calculate the wicking time of water droplet on the fabric surface. The wicking time is an index showing the combined effects of wicking and absorbing properties of the fabrics. Thus the shorter the wicking time, the better the hydrophilicity or the drying property of the PET fabrics was.

Statistical Analysis

All experiments were carried out in triplicate. Mean values with standard deviations were reported. Variations within groups were analyzed using the One-way ANOVA. Mean separation and significance between treated and control groups were analyzed using Unpaired Student's t-test. Mean values marked with different superscripts were significantly different (p<0.05).

Results and Discussion

Surface Element Analysis

The surface chemical compositions of PET fabrics were characterized by XPS (Table 4). Treated PET fabrics had higher O/C ratios than untreated samples due to oxygen gas introduced during plasma activation. The surface nitrogen contents showed increases of more than 20 folds in PET fabrics grafted with chitosan oligomer, while those in plasma-activated PET fabrics only raised slightly. The remarkable increases in nitrogen contents on the surface of modified PET fabrics were attributed to the amine groups from grafted chitosan, which was in accordance with the previous findings [2].

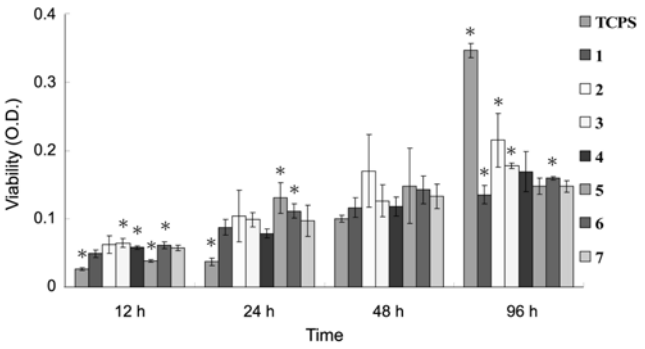

Figure 2. The viability of L929 fibroblasts cells grown on Group 1 PET fabrics. *Means with superscripts indicate significant difference from Fabric 1 (p<0.05).

Biocompatibility

Group 1 fabrics (Table 1) were used for biocompatibility analysis. The viabilities of L929 fibroblasts cells grown on modified fabrics were in general better than on untreated plasma fabrics at all time (Figure 2). The biocompatibilities of modified fabrics were better than tissue culture polystyrene (TCPS) within 48 hours. Chitosan was proven to be highly biocompatible [4-6]. Our results showed that by means of plasma activation, chitosan could be grafted onto PET fabrics and therefore made PET more biocompatible.

Antibacterial Activities of Chitosan Polymers and Chitosans Oligomers

Group 1 PET fabrics and *Bacillus subtilis* were used for antibacterial experiments following the method of AATCC 90 1982. As shown in Figure 3, the growth of *Bacillus subtilis* was inhibited by Group 1 fabrics grafted with chitosan (Table 1). The inhibitory effects were stronger when fabrics were grafted with chitosan oligomer than polymer. No *et al.* [7]

Table 4. XPS results for PET fabrics treated with Ar-O_2 plasma

Activation time (s)	C1s C, %	O1s O, %	N1s N, %	O/C	N/C	(O+N)/C
Untreated	71.9	28.1	< 0.1	0.391	0.000	0.391
60A	69.1	30.7	0.2	0.444	0.003	0.447
60G	66.8	30.7	2.5	0.460	0.037	0.497
120A	68.8	30.6	0.6	0.445	0.009	0.454
120G	66.4	31.6	2.0	0.476	0.030	0.506

Note: A: fabrics activated by Ar-O_2 plasma treatment (150 W) only, G: fabrics grafted with chitosan oligomer following plasma activation.

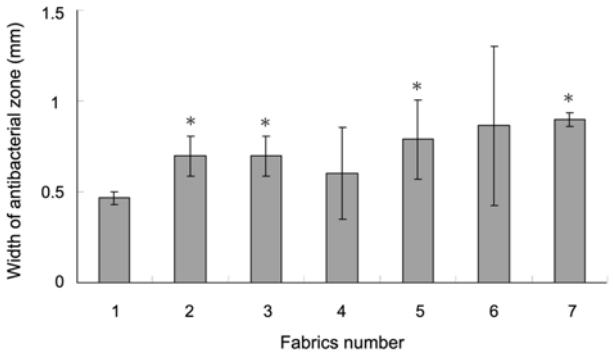

Figure 3. Antibacterial activities of Group 1 PET fabrics. *Means with superscripts indicate significant difference from Fabric 1 ($p<0.05$).

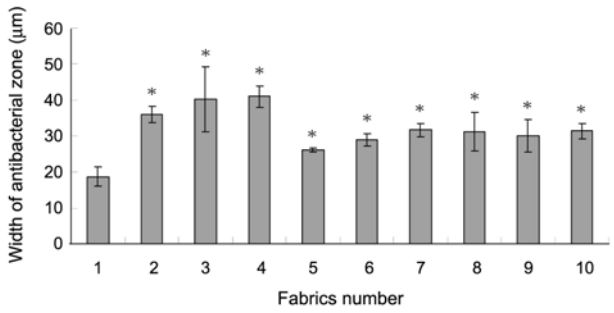

Figure 4. Antibacterial activities of Group 2 PET fabrics. *Means with superscripts indicate significant difference from Fabric 1 ($p<0.05$).

examined antibacterial activities of six chitosan oligomers and six chitosan polymers with different molecular weights. Chitosan oligomers showed higher antibacterial activities than chitosan polymers and markedly inhibited the growth of most bacteria tested. Chitosan grafted onto PET fabrics remained to be antibacterial in our study. The hydrophilicity of chitosan oligomer assured it to be released from the fabric more easily, thus it could react with bacteria more effectively and showed stronger antibacterial effects than chitosan polymer. As a result, Group 2 and 3 PET fabrics were all grafted with chitosan oligomers.

Antibacterial Properties of Fabrics Activated on One Side or Two Sides

When PET fabrics were activated by plasma for 120 seconds, fabrics activated for one side (Fabric 2) showed better antibacterial effects (in Figure 3) than for two sides (Fabric 4). While the activation time was 80 seconds, the antibacterial effects of fabrics (in Figure 3) activated for both sides (Fabric 5) were better than for one side only (Fabric 3). Excessive activation time of plasma treatment might result in surface crosslinking or increased grafting of chitosan. The structure of PET fabrics might be destroyed due to over-treatment of plasma and bonded to chitosan less efficiently. Alternatively, increased reaction of chitosan might leave less amino groups ($-NH_2$) on chitosan to be exposed. In either case, the antibacterial effectiveness was affected [8]. Our results revealed fabrics activated for 80 seconds with both sides (Fabric 5) might have reached saturation of treatment and showed the best antibacterial effects. Prolonging activation time to 120 seconds was disadvantageous for antibacterial activities in fabrics activated on two sides.

Antibacterial Properties for Other Grafting Parameters

Group 2 PET fabrics (Table 2) and *Staphylococcus aureaus* were also used for antibacterial experiments following the method of AATCC 90 1982. As shown in Figure 4, Shortening the times for oxidization, grafting polymerization, and baking had adverse effects on antibacterial activities of Group 2 fabrics. It was well known that after plasma treatment the fabric surface was activated. The active surface was then subject to reacting with oxygen to form peroxide when exposed to the air. Therefore the longer the oxidization time produced more peroxides, the more chitosan was grafted. Prolonged grafting polymerization time meant a longer reaction time for chitosan to be fixed onto the fabric surface. These were how different grafting degrees of chitosan influenced the antibacterial effects. Final baking process determined the dryness of fabrics with grafted chitosan. Our results showed the antibacterial effects were affected when the baking time was shortened to 4 min. 4 min might not be enough time for the fabric to be dry. Part of the grafted chitosan may have been hydrolyzed due to moisture and lost the antibacterial function.

Antibacterial Properties for Different Plasma Activating Time

Group 3 PET fabrics (Table 3) and *Staphylococcus aureaus* were used for antibacterial experiments following the method

Table 5. Antibacterial ratios of Group 3 PET fabrics. Initial bacterial concentration=3.2×10^5 CFU/fabric (CFU=colony forming units)

Fabric number	Culturing time (h)	CFU/m*l* ($\times10^4$)	R (%)
1	0	28.99±0.57	–
1	48	2.15±0.16	–
2	48	0.51±0.08*	76.28±3.88
3	48	0.25±0.04*	88.60±1.76
4	48	0.29±0.03*	86.74±1.40
5	48	0.23±0.05*	89.30±2.24
6	48	0.24±0.03*	88.84±1.21
7	48	0.69±0.12*	67.91±5.45
8	48	0.58±0.06*	73.26±2.64
9	48	0.72±0.16*	66.51±7.38
10	48	0.77±0.11*	64.42±5.27

*Means with superscripts indicate significant difference from Fabric 1 ($p<0.05$).

Table 6. Hydrophilic properties of Group 2 PET fabrics

Fabric number	Activation time (s)	Initial contact angle of water droplet (°)	Wicking time (s)
1	0	110	>2000
2	120	30±9	0.135±0.085
3	60	49±10	0.172±0.103
4	45	46±9	0.160±0.092
5	30	60±13	0.390±0.294
6	15	61±12	1.040±0.812
7	10	78±15	4.370±2.941
8	60	23±3	0.068±0.039
9	60	27±8	0.107±0.134
10	60	27±6	0.114±0.071

of JIS Z 2801:2000. As listed in Table 5, the antibacterial ratios (approaching 90 %) were the highest when activation times were 60 (Fabrics 5-6) or 120 (Fabrics 3-4) seconds. The ratio of Fabric 2 that was plasma-activated but not grafted was 75 %. Shortening the activation times to 30 and 15 seconds (Fabrics 7-10) remarkably decreased the ratios to 60 to 70 %. According to the results presented, the major factor to determine antibacterial effects of the modified fabrics appeared to be the activation time.

Hydrophilic Properties of Modified PET Fabrics

Group 2 PET fabrics (Table 2) were used to evaluate the hydrophilicity of modified fabrics. As listed in Table 6, the wicking time was shorter for fabrics with the longer activation times, which indicated that the fabrics activated by plasma for longer time was more hydrophilic (Fabrics 2-7). Treatments with shorter oxidization times (comparing Fabrics 3 & 8), grafting times (comparing Fabrics 3 & 9), and baking times (comparing Fabric 3 for 8 min & Fabric 10 for 4 min) also had advantageous effects on hydrophilicity. It had been well documented that the surface hydrophilicity of material could be enhanced by plasma treatment. Chen and Wakida [9] treated poly(tetrafluoroethylene) (PTFE) film with low temperature plasma in O_2, Ar, He, H_2, NH_3, and CH_4. The surface free energy and surface wettability of PTFE treated with Ar, He, H_2, NH_3, and CH_4 increased remarkably. Decrease of fluorine and the increase of oxygen or nitrogen polar functional groups, including -CO-, -CN-, -COO-, and -CON-, on the surfaces contributed to an increase of surface free energy and wettability of the PTFE film. Paynter [10] treated polystyrene (PS) and PET with plasma in He, He-O_2, and N_2-H_2 and found that the oxygen and nitrogen introduced by the plasma treatments tended to bind to the same carbon atoms to form amide groups. Treated samples with higher concentrations of nitrogen in the surfaces were more wettable and showed less contact-angle hysteresis. Our observations were consistent with the previous findings. The hydrophilicity of our modified fabrics increased with prolonged plasma activation time probably because more peroxides or polar functional groups formed on the fabric surfaces. With a shorter oxidization time, grafting time or baking time, the modified fabric surfaces were grafted by less chitosan and therefore relatively more polar functional groups were exposed. As a result, the hydrophilicity of modified fabrics under these conditions increased.

Conclusion

The current investigation discusses various plasma treatment and grafting conditions on antibacterial effects of chitosan grafted PET fabrics. Chitosan grafted on PET fabrics surfaces was identified by XPS. PET fabrics plasma-activated for 60 and 120 seconds and grafted with chitosan oligomers showed the best antibacterial activities. Treatment with longer activation time increased the hydrophilicity of PET fabrics. The biocompatibility of modified PET fabrics was better than that of the untreated fabrics. Therefore, PET fabrics modified with atmospheric pressure plasma and chitosan at these conditions are antibacterial and safe for human skin from allergies induced by fabrics treated with metal antibacterial agents.

Acknowledgements

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