Anti-bacterial Property of Hydrogen-ion and Oxygen-ion Treated Polytetrafluoroethylene (PTFE) Materials*)

Hernando S. SALAPARE III, Gene Q. BLANTOCAS[1)], Windell L. RIVERA[2,3)], Vanissa A. ONG[2,3)], Ralph S. HIPOLITO[2,3)] and Henry J. RAMOS

Plasma Physics Laboratory, National Institute of Physics, College of Science, University of the Philippines, Diliman, Quezon City 1101, Philippines

[1)]*Department of Electrical Engineering, College of Engineering, Qassim University, Buraydah 51452, Kingdom of Saudi Arabia*

[2)]*Molecular Protozoology Laboratory, Natural Sciences Research Institute, College of Science, University of the Philippines, Diliman, Quezon City 1101, Philippines*

[3)]*Institute of Biology, College of Science, University of the Philippines, Diliman, Quezon City 1101, Philippines*

(Received 19 November 2010 / Accepted 15 March 2011)

The anti-bacterial property of hydrogen-ion and oxygen-ion treated polytetrafluoroethylene (PTFE) materials is determined using contact angle measurements, scanning electron microscopy (SEM), and *Escherichia coli* (*E. coli*) adhesion tests. PTFE samples are irradiated using a gas discharge ion source (GDIS). Ion energies are varied by changing the plasma discharge current (I_d). Results show that both the hydrogen and oxygen plasma treatments modify the PTFE surface in morphology. Both treatments exhibited changes in the wettability of the samples at different I_d, Hydrogen treatment shows that lower I_d improved material hydrophobicity and higher I_d resulted in enhanced hydrophilicity, while oxygen treatment shows that as the I_d increases, PTFE becomes more hydrophilic. The hydrogen and the oxygen treated PTFE exhibited a reduced *E. coli* attachment on the samples. Oxygen treatment exhibited a lower *E. coli* adhesion as compared to using hydrogen.

Keywords: polytetrafluoroethylene, gas discharge ion source, oxygen plasma, hydrogen plasma, *Escherichia coli*, bacterial adhesion

DOI: 10.1585/pfr.6.2406043

1. Introduction

Biomaterials such as polytetrafluoroethylene (PTFE) are extensively utilized in synthetic vascular surgery and medical devices because of its chemical and mechanical stability, and low flammability [1]. Some of the implanted materials experience failures due to common complications such as bacterial colonization on the surface and the subsequent device infections [2]. The most common solutions to these biomaterial-related infections often require the removal or the replacement of the implanted device as well as immediate aggressive antibiotic therapy [3]. These remedial methods dealing with biomaterial-related infections are usually expensive and increase patient's discomfort [3]. Surface modification technology is seen to alleviate the problems of implanted biomaterials [1,4]. Different techniques usually offer different results especially on their ability to reduce bacterial adherence [5]. Surface modification techniques of biomaterials using different gases could enhance or modify their desirable characteristics for better adhesion and biocompatibility [6]. In this study, PTFE materials are treated using hydrogen low-energy gas discharge and oxygen low-energy gas discharge. Characteristic changes in wettability, surface morphology and bacterial adhesion on treated samples are presented.

2. Methodology

PTFE tape of size $1 \times 2\,cm^2$ was wrapped around a $2 \times 2\,cm^2$ stainless steel plate holder. The surface of the clean samples was blow-dried to prevent the formation of moisture on the surface. PTFE was then irradiated using a low-energy hydrogen ion shower (LEHIS) from a gas discharge ion source (GDIS). Another set of PTFE samples were irradiated using oxygen low-energy gas discharge from the same source. Complete details of the facility and its operation are described in references 7 to 11. Treatment conditions are summarized in Table 1. The comparison of the bacterial adhesion performance of the samples treated using the different gases were investigated using contact angle measurements, scanning electron microscopy (SEM), and *Escherichia coli* (*E. coli*) cellular adhesion tests.

E. coli was cultured in nutrient agar (NA) plates at 37°C for 24 hours. A 35 mL suspension of *E. coli* in sterile phosphate buffered saline (PBS) solution was prepared at about 6.0×10^8 cells/mL. The untreated and treated sam-

author's e-mail: hssalapare@up.edu.ph, hsalapare@nip.upd.edu.ph

*) This article is based on the presentation at the 20th International Toki Conference (ITC20).

Table 1 Summary of experimental parameters.

Treated Group	Gas Treatment	Discharge Voltage, V_d (kV)	Discharge Current, I_d (mA)
1	Hydrogen	1.00	1.0
2	Hydrogen	1.30	2.0
3	Hydrogen	1.40	3.0
4	Oxygen	0.46	1.0
5	Oxygen	0.47	2.0
6	Oxygen	0.49	3.0

ples were exposed to the cell suspensions for 1 hour at room temperature at constant shaking. The samples were taken out and gently washed with PBS to remove the loosely adherent bacteria on the sample. *E. coli* that adhered on the PTFE surface were then scraped off using a sterile cotton swab and 10-fold serial dilutions in 0.1% peptone were inoculated onto NA plates. After the plates were incubated for 24 hours at 37°C, the cell density of *E. coli* (CFU/cm^2) was calculated manually.

3. Results and Discussion

Table 2 shows the contact angle measurements for the untreated and treated samples. Hydrogen-ion treatment of PTFE samples shows that in relation to the untreated, samples treated with higher discharge currents became hydrophilic ($\theta < 90°$) while samples treated using low discharge current showed slightly improved hydrophobicity. By convention, wettability property is established through the initial contact angle θ ($t = 0$), wetting occurs at $\theta < 90°$ and non-wetting if $\theta > 90°$ [7, 8]. The cause for the increased hydrophilicity of the samples can be attributed to the increased surface roughness [12,13] and porosity of the material.

For the oxygen-ion treated PTFE samples, the untreated and treated samples exhibited hydrophobic behaviors but there is a decrease in the initial contact angle as the discharge current increases.

Previous studies reported the morphological effects of hydrogen and oxygen ion treatment on PTFE materials [14, 15]. Figures 1 and 2 shows the SEM result for the hydrogen treated PTFE and the oxygen treated PTFE, respectively. SEM images of the untreated and hydrogen-ion treated samples shows the surface of samples from group 1 subjected to lower energy ion shower (I_d = 1 mA) that are much smoother than the rest of the specimens. Samples from groups 2 and 3 subjected to higher energy ion showers ($I_d \geq 2$ mA) show surfaces that are rough and have striations and fissures [14]. The surface deterioration of group 3 looks more pervasive than that of sample 2, possibly due

Table 2 Contact angle and bacterial adhesion results.

Sample Group	θ (°) (± 2°)	Bacterial adhesion [CFU/cm^2]
Untreated	114	7.4×10^5
H_2 : 1mA	116	4.9×10^5
H_2 : 2mA	74	9.0×10^4
H_2 : 3mA	61	2.4×10^5
O_2 : 1mA	111	6.8×10^4
O_2 : 2mA	108	2.6×10^4
O_2 : 3mA	95	≤ 250

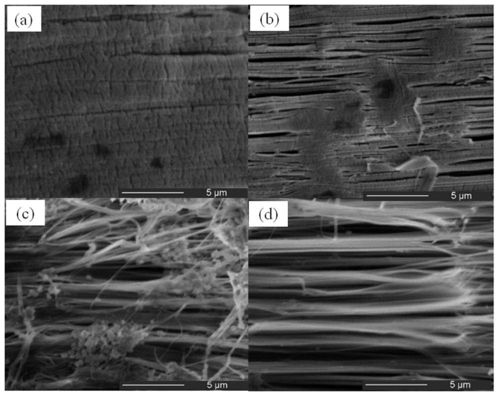

Fig. 1 SEM result of PTFE samples treated with hydrogen-ion. All SEM images were recorded at 20 k x magnification. (a) control group, (b) processed at I_d = 1.0 mA, (c) processed at I_d = 2 mA, and (d) processed at I_d = 3 mA.

higher discharge current. It becomes clear from this figure vis-à-vis wettability and porosity parameters that generally a surface becomes more wettable as it roughens. Roughening by high energy ion irradiation leads to surfaces becoming more hydrophilic and porous. Conversely, low energy ion irradiation results in relatively smooth, hydrophobic surfaces. PTFE materials become thinner when bombarded by high flux density ion showers [7]. These changes are brought about by a variety of factors such as increased polymeric cross-linking [16], carbonization [17], surface erosion forming spires and needles whose vertical dimensions may range from tenths to hundreds of microns [18] and alterations in refractive index due to structural modifications [19].

SEM results of the PTFE samples treated with oxygen-ion shows that surface of the sample subjected to higher energy ion shower (I_d = 3 mA) is smoother than the rest of the specimens [15]. The sample roughens as the discharge current decreases.

The result of the oxygen-ion treated samples is opposite to the trend exhibited by the hydrogen-ion treated samples. Chemical changes and not morphological changes in the oxygen-ion treated samples may be the main factor for the change of its wettability in relation to the discharge currents but an X-ray photoelectron spectroscopy (XPS) characterization must be performed to confirm this hypothesis.

Figure 3 and Table 2 show the result of the *E. coli* adhesion to the hydrogen low-energy gas discharge and oxygen low-energy gas discharge specifically the nutrient agar plates for the untreated and treated samples. The number of *E. coli* that adhered on the surface of the samples is lower than the untreated samples for both the hydrogen and oxygen treated samples. The lowest number of adhered cells on the surface of the PTFE was observed with the oxygen treated samples. As the discharge current increases, the number of adhered *E. coli* decreases. For the hydrophilic - hydrogen treated PTFE samples, the number of adhered *E. coli* increases as the discharge current increases, while a relatively high number of adhered *E. coli* was observed for the hydrophobic–hydrogen treated PTFE samples. The difference on the trends on the hydrophobic and hydrophilic samples maybe associated with the changes in the surface morphology of the PTFE since there were no chemical changes seen as discussed in the reference [7].

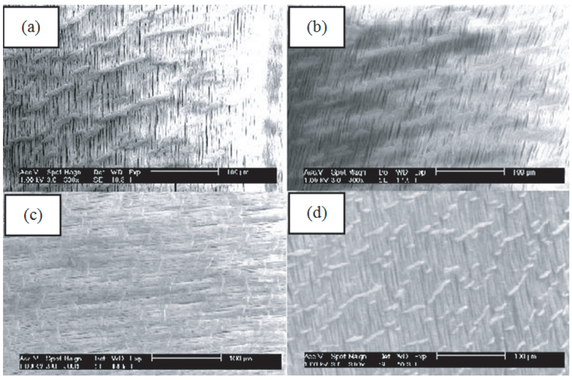

Fig. 2 SEM result of PTFE samples treated with oxygen-ion. All SEM images were recorded at 300x magnifications (a) control group, (b) processed at I_d = 1.0 mA, (c) processed at I_d = 2 mA, and (d) processed at I_d = 3 mA.

4. Conclusions and Recommendations

The cellular adhesion performance of hydrogen-ion and oxygen-ion treated PTFE materials were evaluated using contact angle, SEM, and *E. coli* adhesion tests. Both the hydrogen and oxygen plasma treatments modified the PTFE in morphology. Both treatments exhibited changes in the wettability of the samples at different I_d, hydrogen treatment shows that lower I_d improved material hydrophobicity and higher I_d resulted in enhanced hydrophilicity due to the increased surface roughness and porosity of the material, while oxygen treatment shows that as the I_d increases, PTFE becomes more hydrophilic. For oxygen treated PTFE, reduced bacterial adhesion was seen for higher discharge currents. Oxygen treatment was superior in reducing the number of adhered bacteria as com-

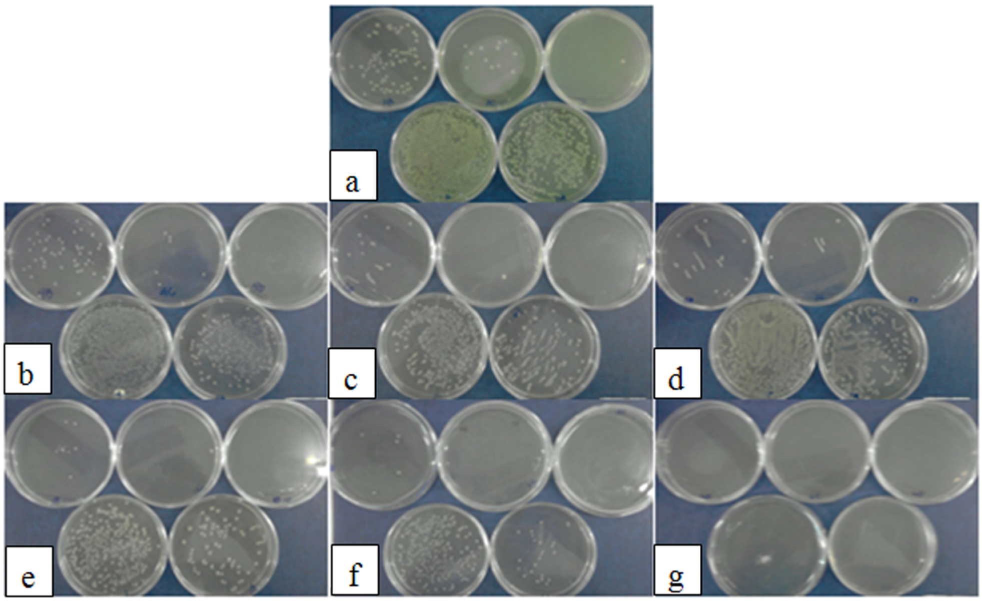

Fig. 3 Nutrient agar plates of untreated samples (a), hydrogen-ion treated samples (b-d), and oxygen-ion treated samples (e-g). A white dot in a nutrient agar plate corresponds to one colony forming unit of bacteria, bacterial adhesion is high if there are more colony forming units in the plate. The five nutrient agar plates per group shows the different concentration of exposure to bacteria since it underwent a 10-fold serial dilutions, the lower row corresponds to exposure to high concentration of bacteria while the top row corresponds to exposure to low concentration of bacteria.

pared to the hydrogen treatment. Further characterizations like XPS are necessary to better explain the phenomenon.

Acknowledgement

We would like to thank the Department of Science and Technology - Philippine Council for Industry, Energy and Emerging Technology Research and Development (DOST-PCIEERD) for the financial grant.

[1] J.H. Noh, H.K. Baik, I. Noh, J.C. Park and I.S. Lee, Surf. Coat. Technol. **201**, 5097 (2007).

[2] T. He, Z.L. Shi, N. Fang, K.G. Neoh, E.T. Wang and V. Chan, Biomaterials **30**, 317 (2009).

[3] C.I. Pereni, Q. Zhao, Y. Liu and E. Abel, Colloids Surf. B: Biointerfaces **48**, 143 (2006).

[4] K.L. Mittal (Ed.), Polymer Surface Modification: Relevance to Adhesion **4**, VSP/Brill, Leiden (2007).

[5] J.H. Loh, Med. Device Technol. **10** (1), 24 (1999).

[6] J.Z. Wu, E.T. Kang, K.G. Neoh, C.Q. Cui and T.B. Lim, Int. J. Adh. Adhesives **20**, 467 (2008).

[7] H.S. Salapare III, G.Q. Blantocas, V.R. Noguera and H.J. Ramos, Appl. Surface Sci. **255**, 2951 (2008).

[8] H.S. Salapare III, G.Q. Blantocas, V.R. Noguera and H.J. Ramos, in: Contact Angle, Wettability, and Adhesion, K.L. Mittal (Ed.), **6**, p.207, VSP/Brill, Leiden (2009).

[9] H.J. Ramos, J.L. C. Monasterial and G.Q. Blantocas, Nucl. Instrum. Meth. Phys. Res. B **242**, 41 (2006).

[10] G.Q. Blantocas, H.J. Ramos and M. Wada, Rev. Sci. Instrum. **75**, 2848 (2004).

[11] G.Q. Blantocas, H.J. Ramos and M. Wada, Jpn. J. Appl. Phys. **45**, 8525 (2006).

[12] G.S. Tzeng, H.J. Chen, Y.Y. Wang and C.C. Wan, Surface Coatings Technol. **89**, 108 (1997).

[13] G.Q. Blantocas, P.E.R. Mateum, R.W.M. Orille, R.J.U. Ramos, J.L.C. Monasterial, H.J. Ramos and L.M.T. Bo-ot, Nucl. Instrum. Meth. Phys. Res. B **259**, 875 (2007).

[14] H.S. Salapare III, G.Q. Blantocas, A. Gines, M. Poral, M.T. Agcaoili and H.J. Ramos, Proceedings of the 27th Samahang Pisika ng Pilipinas Physics Congress, ISSN 1656-2666 Vol. 4, October 2009, p.28.

[15] H.S. Salapare III, G.Q. Blantocas, E.V.B. Lagsa, V.R. Noguera and H.J. Ramos, Proceedings of the 26th Samahang Pisika ng Pilipinas Physics Congress, ISSN 1656-2666 Vol. 5, October 2008, p.13.

[16] P.G. Pape, J. Vinyl Additive Technol. **6** (1), 49 (2004).

[17] Z.A. Iskanderova, J.I. Kleiman, Y. Gudimenko, G.R. Cool and R.C. Tennyson, US Patent 5,683,757 (1997).

[18] J.M. Mirtich and J.S. Sovey, US Patent 4,199,650 (1980).

[19] C. Darraud, B. Bennamane, C. Gagnadre, J.L. Decossas and J.C. Vareille, Polymer **35** (11), 2447 (1994).