Available online at www.sciencedirect.com
ScienceDirect
Polymer 47 (2006) 7441–7445
polymer
www.elsevier.com/locate/polymer

# Antimicrobial properties of copper plasma-modified polyethylene

Wei Zhang [a,b,d], Yi-He Zhang [c], Jun-Hui Ji [b], Jun Zhao [a], Qing Yan [b], Paul K. Chu [a,*]

[a] Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
[b] Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China
[c] School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China
[d] Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Received 10 May 2006; received in revised form 22 July 2006; accepted 23 August 2006
Available online 8 September 2006

**Abstract**

Copper plasma immersion ion implantation is utilized to produce an antibacterial surface on polyethylene. XPS analysis of the plasma-treated materials reveals that a relatively large amount of copper, about 11% relative to carbon, is implanted into the near surface region. At the same time, about 3% copper is found to be also deposited on the surface. The implanted copper is observed to have the zero valence state indicating that the implanted Cu does not bind chemically with the atoms in the polymer. On the other hand, the copper atoms close to the surface are found to have the divalent state due to surface oxidation. Formation of C=C bonds is also observed due to dehydrogenation following copper plasma implantation. Based on the results of atomic force microscopy and contact angle measurements, the surface hydrophilicity and roughness are not significantly altered. Our antibacterial experiments indicate that the copper implanted polyethylene exhibits excellent antibacterial effects against *Escherichia coli* and *Staphylococcus aureus*, and the effectiveness is 96.2% and 86.1%, respectively.


*PACS:* 82.35.-x Polymers: properties, reactions, polymerization; 52.25.-b Plasma properties; 87.15.-v Biomolecules: structure and physical properties

*Keywords:* Plasma immersion ion implantation; Polyethylene; Antibacterial

## 1. Introduction

Medical polymers are used widely in nosocomial therapy such as artificial heart valves and artificial blood vessels because of their excellent mechanical properties and moderate biocompatibility [1–3]. However, infection of medical devices is a life threatening complication and can lead to significant morbidity and mortality. Therefore, it is of importance to improve the antibacterial properties of polymers [2–6]. It has been reported that the antimicrobial properties of medical polymers can be enhanced by the incorporation of biocide into bulk polymers or by the application of surface coatings comprising antimicrobial agents [7–10]. The main drawback of these two approaches is that the antimicrobial properties are typically unstable and short-lived. Medical devices such as artificial heart valves and vascular grafts are now designed for a life time and so better techniques are needed to improve the antimicrobial properties of medical polymers.

Plasma immersion ion implantation (PIII) has evolved to be a useful surface treatment technique in many applications in microelectronics, nanotechnology, and biomedical engineering [11,12]. Its advantages include hardware simplicity, high efficiency, and conformal treatment of large and irregular-shaped objects. However, the use of PIII in surface modification of polymers is relatively scarce, particularly that pertaining to surface antimicrobial properties. In the work described here, we use PIII to introduce an inorganic antibacterial element, Cu, into a medical polyethylene (PE). Our results show that low-energy (several keV) plasma implantation can introduce a large amount of Cu into the near surface region to achieve excellent and long lasting antibacterial properties while

* Corresponding author. Tel.: +852 27887724; fax: +852 27889549.
*E-mail address:* paul.chu@cityu.edu.hk (P.K. Chu).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.08.057

plasma and ion beam induced substrate damage can be kept to a minimum [13–17].

## 2. Experimental details

Medical-grade polyethylene (PE) samples (LDPE, 51215B Beijing Huaer Co., Ltd.) with dimensions of 2 cm × 2 cm × 0.2 cm were laid on stainless steel substrates and inserted into the plasma immersion ion implanter equipped with a copper cathodic arc plasma source [11–13,18]. The arc was ignited using a pulse duration of 300 μs, repetition rate of 30 Hz, and arc current of 1 A. The copper plasma was guided into the vacuum chamber by an electromagnetic field via a curved magnetic filter to eliminate deleterious macro-particles. Cu plasma implantation was conducted by applying an in-phase bias voltage of −5 kV with a repetition rate of 30 Hz and pulse width of 300 μs to the PE samples. The working pressure in the vacuum chamber was $1-2\times10^{-4}$ torr and the implantation time was 10 min [11,12].

The elemental depth profiles and chemical states were determined by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5802 [14,19]. A monochromatic aluminum X-ray source was employed and the elemental depth distributions were determined using argon ion sputtering. The sputtering rate of 1 nm/min was approximated based on the sputtering rate derived from silicon oxide under similar conditions. Static contact angles using distilled water or glycerin as the medium were measured by the sessile drop method on a Ramé-Hart (USA) instrument at ambient humidity and temperature. All the contact angles reported here are the mean values of six measurements on different parts of the surface [14]. Contact mode atomic force microscopy (AFM) was conducted on a Park Scientific Instrument (PSI) Autoprobe Research System to evaluate the surface morphology and the scanned area was 15 μm × 15 μm.

The antibacterial performances against *Staphylococcus aureus* ATCC6538 (*S. aureus*, Gram-positive) and *Escherichia coli* ATCC10536 (*E. coli*, Gram-negative) were determined by the method of plate-counting [13,20,21]. Ethanol (70%) was first employed to sterilize the samples and then a 0.04 ml solution of bacteria ($1-2\times10^6$ CFU/ml) was added onto the modified surface and covered by a polyethylene (PE) film (15 mm × 15 mm). At a relative humidity (RH) of higher than 90% and temperature of 37 ± 1 °C, the bacteria on the samples were incubated for 24 h. Afterwards, they were thoroughly washed with 10 ml of 0.87% NaCl solution that contained Tween 80 with a pH of 7.0 ± 2. To observe the living bacteria, 0.2 or 0.02 ml of the washing solution was added into the different dishes containing the nutrient agar. After 24 h of incubation under similar conditions, the active bacteria was counted and the antibacterial effect was quantitatively determined using the following relationship:

$$R(\%) = ((B - C)/B)100,$$

where $R$ is the antibacterial effect (%), $B$ is the mean number of bacteria on the control samples (CFU/sample), and $C$ is the mean number of bacteria on the modified samples (CFU/sample).

## 3. Results and discussion

### 3.1. Chemistry of the modified surfaces

XPS was employed to determine the in-depth copper distribution in the PE substrate [19]. Fig. 1 shows that Cu plasma implantation is successful and the implanted copper is located in the near surface region due to the low implantation energy. The amount of implanted copper at the peak is about 11% relative to C (that is, by comparing the ratio of copper to carbon). In spite of the in-phase operation between the cathodic arc and sample bias, some surface deposition occurs and the surface Cu concentration is about 3%. The presence of surface Cu is helpful in killing bacteria that are in direct contact with the materials surface [4,22]. Based on the metal ion antimicrobial mechanism, Cu ions are consumed during the antibacterial reaction. Hence, in principle, the higher the amount of surface Cu, the better is the antibacterial efficacy. However, a high amount of Cu ion deposited on the surface will also produce side effects because they also affect cells that are in contact with the materials surface [23]. Therefore, the best scenario is to have some surface Cu for immediate antibacterial effects in conjunction with stored or embedded Cu that constantly diffuses out to replenish surface Cu to prolong the antibacterial action. This can be achieved by our plasma immersion ion implantation process.

In order to investigate the Cu chemistry and chemical state, the Cu2p and C1s peaks are acquired by high resolution XPS spectra at different sputtered depths (series) and the corresponding composite profiles are presented in Figs. 2 and 3 [19]. The montages illustrate the change in the XPS peak shape and position at different stages of the depth profiling analysis (larger series number representing longer sputtering time or larger depth). The series 1 and 2 curves in Fig. 2

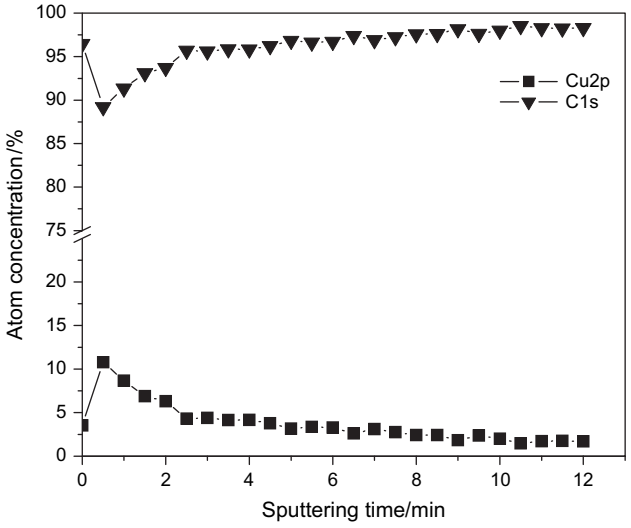


Fig. 1. Elemental depth profiles acquired by XPS from the Cu PIII PE.

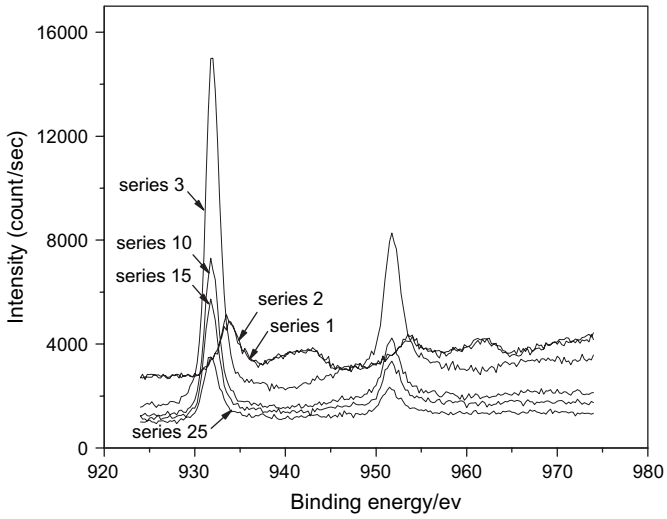


Fig. 2. Cu2p XPS spectra as a function of sputtered depths obtained from the Cu PIII PE.

show that Cu on the surface is in the divalence state, while the series 3–25 curves imply that the embedded or implanted Cu atoms are in the zero valence state, that is, forming no chemical bond with other elements in the polymer. This observation further corroborates that implantation does not modify the chemical state of Cu. The surface Cu atoms appear to be in the oxidized state due to exposure to air after plasma implantation.

As shown in Fig. 3, the difference between series 1 and 2 and series 10–25 also illustrates that the chemical state of C1s close to the surface is very different from that at a larger depth. To further analyze the situation, the spectra of series 1 and 15 are fitted by XPS software and the results are shown in Fig. 4A and B [19,24]. The presence of C=C bond in Fig. 4B implies that Cu PIII into polyethylene leads to dehydrogenation. On the contrary, C=C bond is not observed in series 1. C=O, C–O, and O–C=O bonds are observed close to the surface. This may be because after Cu plasma implantation, the carbon chain in the PE undergoes dehydrogenation forming active radical groups that further undergo oxygenation when the sample surface is exposed to air. The C results are in general consistent with the Cu XPS results.

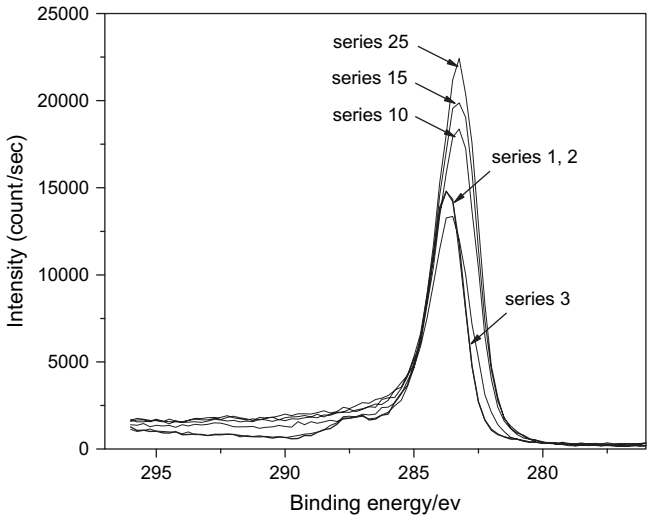


Fig. 3. C1s XPS spectra as a function of sputtered depths obtained from the Cu PIII PE.

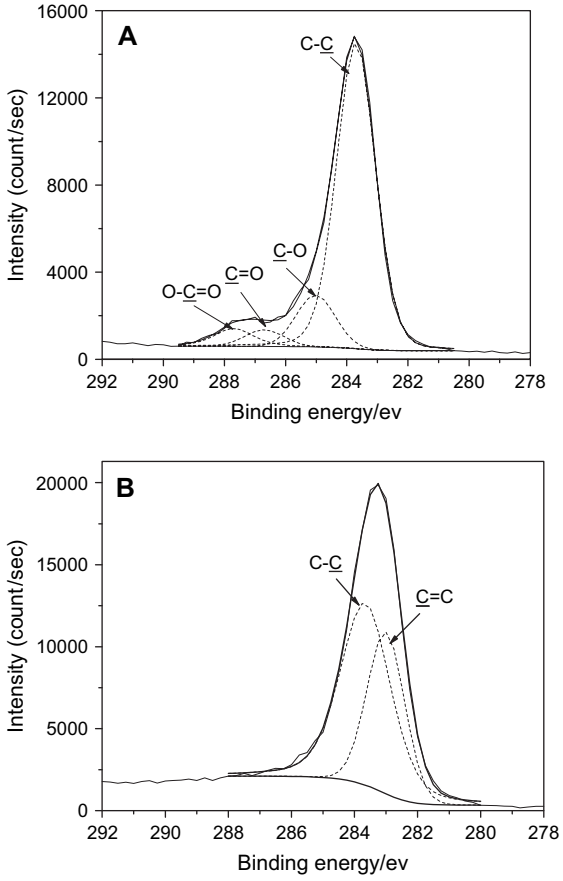


Fig. 4. Binding energies of the C1s peak at different sputtering time for the Cu PIII PE (A: series 1; B: series 15).

### 3.2. Effects of Cu PIII on surface properties of polyethylene

According to previous results [25,26], the antibacterial properties are greatly influenced by surface characteristics such as surface hydrophilicity, surface roughness, and configuration in addition to the chemical composition. This is because depending on the hydrophobicity of both the bacteria and surfaces, bacteria adhere differently onto the materials. In general, hydrophilic materials are more resistant to bacterial adhesion than hydrophobic materials. On the other hand, a rough surface has a greater surface area and the depressions or troughs may provide more favorable sites for colonization [25]. Therefore, we investigate the effects of surface hydrophilicity and topography in our experiments.

Table 1 displays the water contact angle of the Cu PIII PE. The water contact angle decreases from 87.7° to 47.2°. Moreover, the surface has a more polar chemical composition with the surface energy increasing to 55.17 nJ/cm$^2$ [26,27]. The

Table 1
Contact angle and surface energy calculated from Cu PIII PE and control PE

| Samples | Contact angle/° | | Dispersion ($\gamma_s^d$, nJ/cm$^2$) | Polar ($\gamma_s^p$, nJ/cm$^2$) | Surface energy ($\gamma_s$, nJ/cm$^2$) |
|---|---|---|---|---|---|
| | Distilled water | Glycerin | | | |
| Control | 87.7 | 74.7 | 22.16 | 4.95 | 27.11 |
| Cu PIII PE | 47.2 | 54.3 | 5.20 | 49.97 | 55.17 |

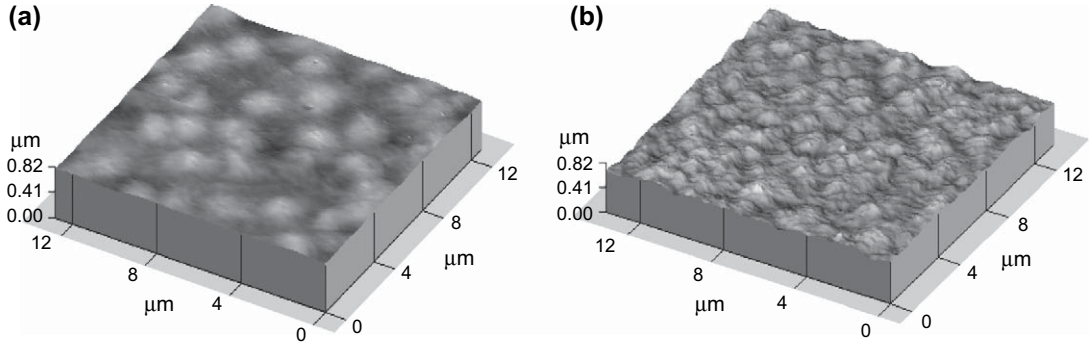


Fig. 5. AFM images acquired from (a) control PE and (b) Cu PIII PE.

results imply that the PIII surface is more hydrophilic than the unimplanted PE. High surface energy is advantageous to the inhibition of bacterial adhesion and colonization. Consequently, the plasma implanted surface possesses enhanced antibacterial effects. On the other hand, the AFM images acquired from the Cu PIII PE and control PE in Fig. 5 show that Cu PIII changes the surface roughness of polyethylene [28,29]. The root-mean-square (RMS) surface roughness over an area of $2 \times 2$ μm$^2$ changes from 15.9 nm to 27.4 nm after Cu PIII. Our experiments show that the role played by surface energy appears to be larger than that of surface roughness.

### 3.3. Antibacterial properties of Cu PIII sample

*S. aureus* and *E. coli* are the two main sources of nosocomial infection [4–6], and thus they are used in our experiments to assess the antimicrobial properties of the Cu PIII PE [13,26]. When the bacteria concentration is $1-2 \times 10^6$ CFU/ml, the antibacterial effect of Cu PIII PE against *E. coli* and *S. aureus* are 96.2% and 86.1%, respectively. It demonstrates that Cu PIII can enhance the antimicrobial properties of PE. We also monitor the surface antibacterial properties with time. After the samples are left at room temperature conditions for six weeks, their antimicrobial properties are not evidently changed. This demonstrates the long-term effects of Cu PIII. It may be due to continuous leaching of Cu from the underlying region. More work is being conducted to study the mechanism in details and we will report our findings in due course.

## 4. Conclusion

The surface antibacterial properties of polyethylene are improved by Cu plasma immersion ion implantation. At moderately low implantation energy of 5 keV, a relatively large amount of copper of about 11% relative to C is implanted into the near surface region. The surface Cu concentration is about 3%, which provides immediate antibacterial effects. After Cu plasma implantation, the carbon chain in the polymer undergoes dehydrogenation and the implanted Cu does not form chemical bonds with atoms in the PE substrate, however, oxidation is observed on the surface. Using atomic force microscopy and contact angle measurements, Cu PIII is found to render the surface more hydrophilic and rougher. The copper implanted polyethylene possesses excellent antibacterial properties. The antibacterial effects against *E. coli* and *S. aureus* are at high levels of 96.2% and 86.1%, respectively, and more importantly, the antibacterial effects do not degrade after six weeks. Our results show that metal plasma immersion ion implantation (PIII) is an effective approach to enhance the long-term antimicrobial properties of medical polyethylene.

## Acknowledgement

This research was supported by Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grant (CERG) No. CityU 112306.

## References

[1] Kennedy FJ, Thorley M. Carbohydr Polymer 2001;44:175.
[2] Ward LJ, Badyal JPS, Goodwin AJ, Merlin PJ. Polymer 2005;46:3986.
[3] Akovali G, Torun TT, Bayramli E, Erinc KN. Polymer 1998;39:1363.
[4] Vuong C, Otto M. Microbes infect 2002;4:481.
[5] Nichols LR, Raad II. Diagn microbiol infect dis 1999;33:121.
[6] Threlkeld GM, Cobbs GC, Mandell LG, Douglas RG, Bennett J. Principles and practice of infectious disease. New York: Churchill Livingstone; 1995. p. 783.

[7] Jones DS, Djokic J, Gorman SP. Biomaterials 2005;26(14):2013.
[8] Chen KS, Ku YA, Lee CH, Lin HR, Lin FH, Chen TM. Mater Sci Eng C Bio S 2005;26(2):1.
[9] Kalyon BD, Olgun U. Am J Infect Control 2001;29(2):124.
[10] Yuan YL, Ai F, Zang XP. Colloid Surface B 2004;35(1):1.
[11] Chu PK, Chen YJ, Wang LP, Huang N. Mater Sci Eng R 2002; 36:143.
[12] Chu PK. J Vac Sci Technol B 2004;22:289.
[13] Zhang W, Chu PK, Ji JH, Zhang YH, Liu XY, Fu RKY, et al. Biomaterials 2006;27:44.
[14] Zhang W, Chu PK, Ji JH, Zhang YH. Appl Surf Sci, in press.
[15] Ueda M, Tan IH, Dallaqua RS, Rossi JO, Barroso JJ, Tabacniks MH. Nucl Instrum Methods Phys Res B 2003;206:760.
[16] Boldyryeva H, Umeda N, Plaksin OA, Takeda Y, Kishimoto N. Surf Coat Technol 2005;196:373.
[17] Boldyryeva H, Kishimoto N, Umeda N, Kono K, Plaksin OA, Takeda Y. Nucl Instrum Methods Phys Res B 2004;219–220:953.
[18] Fu RKY, Cheung ITL, Mei YF, Shek CH, Siu GG, Chu PK, et al. Nucl Instrum Methods Phys Res B 2005;237:417.
[19] Beamson G, Briggs D. High resolution XPS of organic polymers – the scienta ESCA300 database. John Wiley & Sons Ltd; 1992.
[20] Zhang W, Chu PK, Ji JH, Zhang YH, Fu RKY, Yan Q. Polymer 2006;47:931.
[21] Wang J, Huang N, Yang P, Leng XY. Biomaterials 2004;25:3163.
[22] Poon RWY, Ho JPY, Liu XY, Chung CY, Chu PK, Yeung KWK, et al. Thin Solid Films 2005;488:20.
[23] Seth R, Yang S, Choi S, Sabean M, Roberts EA. Toxicol in Vitro 2004; 18:501.
[24] Kostov KG, Ueda M, Tan IH, Leite NF, Beloto AF, Gomes GF. Surf Coat Technol 2004;186:287.
[25] An YH, Friedman RJ. J Biomed Mater Res Appl Biomater 1998;43(1):338.
[26] Zhang W, Chu PK, Ji JH, Zhang YH, Yan Q. Biopolymers, in press.
[27] Fu RKY, Mei YF, Wan GJ, Siu GG, Chu PK, Huang YX, et al. Surf Sci 2004;573:426.
[28] Fu RKY, Mei YF, Shen LR, Siu GG, Chu PK, Cheung WY, et al. Surf Coat Technol 2004;186:112.
[29] Mattozzi A, Neway B, Hedenqvist MS, Gedde UW. Polymer 2005; 46:929.