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Plasma surface modification of poly vinyl chloride for improvement of antibacterial properties

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Abstract

Plasma immersion ion implantation (PIII) was used to modify medical-grade PVC coated by triclosan and bronopol to enhance the antibacterial properties. The surface was first activated by O_2 plasma to produce more hydrophilic groups so that triclosan and bronopol could be coated more effectively on the surface. Subsequently, an argon plasma treatment was conducted under optimal conditions to improve the antibacterial properties of the triclosan and bronopol-coated PVC samples. The modified surfaces were characterized by XPS, ATR-FTIR, SEM, and contact angle measurements. The antibacterial properties were evaluated utilizing the method of plate-counting of *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative). Our experimental results show that the plasma-modified PVC with bronopol exhibits good antibacterial properties while the favorable bulk properties of PVC are retained. The plasma-modified PVC with triclosan has better antibacterial performance against *E. coli* than bronopol. The change in the antibacterial effect on the modified PVC with time was also investigated and the antibacterial effect was observed to decrease with time.

Keywords: Plasma immersion ion implantation; Antibacterial; Medical poly vinyl chloride; Triclosan; Bronopol

1. Introduction

Medical polymers are important in the treatment of diseases and have a direct consequence on patient's health [1–4]. When medical polymers are implanted inside humans, they can become places for bacteria to adhere and breed [2,5]. Infection frequently results and is by far one of the major clinical complications. Prevention of device-related infection remains a major challenge to deliver quality medical care and the problem is causing a high rate of mortality and morbidity thereby significantly increasing health care costs [6–9]. As a result, there is an increasing interest in the development of anti-infective medical polymers in the biomedical industry. To obtain anti-infective properties, medical polymers are usually impregnated or compounded with some antibacterial or antimicrobial reagents [9–10]. These technologies require large quantities of the antimicrobial reagents, typically on the order of a few g/m^2 and the reagents are not immobilized on the surface. As a result, they are gradually released when these anti-infective polymers are embedded inside humans. They therefore pose great health hazards and it is necessary to develop alternative medical polymers or antibacterial surface treatments.

One of the ways to tackle this problem is to control the physicochemical interactions between the bacteria and medical polymer surface [11]. Surface modification of medical polymers or devices is a relatively simple and effective strategy to create a desirable surface and a number of surface modification techniques have been

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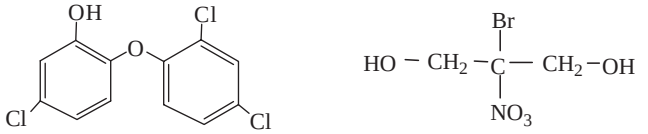

Triclosan Bronopol

Fig. 1. Chemical structures of triclosan and bronopol.

proposed to produce devices with antibacterial surfaces. Silver coatings, surface-immobilized polyethylene (PE) oxide, surface thiocyanation, and surface modification by various gas plasmas (such as oxygen and argon) have been suggested [12–17]. We propose here to use plasma immersion ion implantation (PIII) to conduct surface modification. In PIII, the specimens are surrounded by plasma and pulse-biased to a high negative potential relative to the chamber wall. Most biomedical devices have sophisticated shapes and irregular surfaces, and PIII is thus an excellent technique yielding good surface conformity and uniformity due to its non-line-of-sight characteristic [15–20]. Poly vinyl chloride (PVC) is one of the common medical polymers [4,21,22]. Triclosan (2, 4, 4P-trichloro-2P-hydroxydiphenylether) and bronopol (2-bromo-2-nitropropane-1,3-diol) shown in Fig. 1 are two types of compounds that exhibit immediate, persistent, broad-spectrum antimicrobial effectiveness as well as little toxicity in clinical use. They also deliver excellent biochemical and physical performances after plasma surface modification [23–25]. Therefore in this work, we determine the appropriate PIII treatment conditions to yield superior surface antibacterial properties and decrease the degree of bacteria adhesion on medical-grade PVC.

2. Materials and methods

2.1. Materials

Medical-grade PVC was obtained from Beijing Huaer Co., Ltd. Triclosan and bronopol were purchased from Tian Jing Well-Real Chemical Technology, Co., Ltd. The antibacterial test apparatus and reagents were obtained from Oxoid Ltd., UK.

2.2. Plasma modification

The PVC samples with dimensions of 5 cm × 5 cm × 0.2 cm were made by injection molding machine (Sound Plastics Machinery Co., Ltd., China). The samples were laid on stainless-steel substrates and inserted into the plasma immersion ion implanter [18,19]. The O_2 plasma treatment was performed at the optimal conditions based on many trial experiments: bias voltage = −12 kV, voltage pulse width = 20 μs, pulsing frequency = 30 Hz, gas flow = 35 sccm, RF power = 1000 W and treatment time = 30 min. Under these conditions, sample charging was not serious and no arcing was observed during the experiments. After the initial plasma treatment, the samples were uniformly coated with the antibacterial reagent triclosan or bronopol in 20% alcohol. After the alcohol had volatilized, the samples were reloaded into the implanter and then underwent argon plasma ion bombardment to ensure that antibacterial reagent combined well with the PVC surface. The processing parameters were: bias voltage = −4 kV, RF power = 1000 W, treatment time-30 min and gas flow = 35 sccm [20]. Again, these treatment conditions were based on trial experiments. Finally, the samples were washed three times using 70% ethanol to scour off loose triclosan or bronopol on the surface. The samples were treated using different types of processes to compare the antibacterial effectiveness. Sample 1 was the untreated control. Sample 2 underwent oxygen plasma treatment only. Sample 3 was treated with an oxygen plasma, coated with triclosan, and then treated with an argon plasma. Sample 4 was processed similar to sample 3 except that the reagent used was bronopol instead of triclosan.

2.3. Surface characterization

The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were acquired using a Perkin Elmer16 PC. The sampling depth is approximately 1 μm by ATR-FTIR and it is larger than the thickness of the modified layer on the PVC. In order to reduce errors, the method of subtraction between two spectra is adopted in this work using the following relationship [26,27]:

$$A_S = A_i - fA_0, \quad (1)$$

where A_S is the degree of absorption on modified layer, A_i and A_0 are degrees of absorption before and after modification, and f is the coefficient related to the wavelength. To further evaluate samples 3 and 4, we use the native PVC (sample 1) as background and compare the ATR-FTIR spectra obtained from sample 3 and 4 to that of sample 2.

The surface chemical states were determined by X-ray photoelectron spectroscopy (XPS, PHI 5802) employing a monochromatic Al Kα radiation operated at 14 kV and 350 W. Scanning electron microscopy (SEM) was used to study the surface of the samples. The surface hydrophilicity using distilled water as the medium was determined by contact angle measurements using an instrument made by Tantec (USA).

2.4. Anti-bacterial determination

The antibacterial performance against *Staphylococcus aureus* ATCC6538 (*S. aureus*, gram positive) and *Escherichia coli* ATCC10536 (*E. coli*, gram negative) was determined by the method of plate-counting [28,29]. The samples were first washed with 70% ethanol to kill any bacteria on the surface. After drying, a 0.2 ml solution of bacteria $2.0\sim5.0 \times 10^5$ CFU/ml was added and the surface was covered by a PE film (4 cm × 4 cm). At a relative humidity (RH) of higher than 90% and temperature of 37 ± 1 °C, the samples were incubated for 24 h. Afterwards, they were thoroughly washed with 20 ml of a 0.87% NaCl solution containing Tween 80 with a pH of

7.0±2. For observation, 0.2 or 0.02 ml of the washing solution was added onto different dishes containing the nutrient agar. After 24 h of incubation under similar conditions, the active bacteria were counted and the antibacterial effect was calculated using the following relationship:

$$R(\%) = \left((B - C)/B\right) \times 100, \quad (2)$$

where R is 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).

2.5. Bacteria adhesion

All four kinds of samples were sterilized by 70% ethanol and cut into 16 pieces of approximately 2.0 cm^2. They were put in four different flasks containing a cell suspension ($2–5 \times 10^6$ CFU/ml). A control flask containing the cell suspension without the sample was also evaluated as the control. After they were kept for 20 h at room temperature, the samples were taken out and rinsed with a 0.87% NaCl solution containing Tween 80 with pH of 7.0±2 thrice. Thereafter, the adherent bacteria were detached from the samples in 10 ml of the same NaCl solution ultrasonically. The solution containing the bacteria was used to determine the viable counts [20,28–30].

3. Results and discussion

3.1. Effects of modification on surface hydrophilic properties

The surface of most medical-grade PVC is hydrophobic. On the other hand, triclosan and bronopol are hydrophilic and easily crystallized. In order to coat the PVC samples with these two antibacterial materials, the PVC surface must be modified. In this work, we first treated the PVC surface using oxygen plasma. The contact angles of distilled water in contact with the PVC surface before and after oxygen plasma modification (namely, samples 1 and 2) were about 96° and 20°, respectively. The results indicate that the O_2-PIII PVC surfaces are quite hydrophilic and the modified PVC can be coated effectively with the antibacterial reagents. The change in the surface hydrophicity is because the C–C or C–H group on the surface of PVC is changed to C–O or C=O group by oxygen plasma [18,19,31–33].

3.2. Chemistry of the modified surfaces

XPS was used to determine the elemental composition of the modified PVC surface. Table 1 shows the atomic percentages and elemental ratios determined from sample 2, 3 and 4 [33,34]. The Cl/C ratio of the surface of sample 2 is approximately 0.043 that is indicative of dechlorination of PVC by O_2 plasma treatment. The O/C ratio increases from 0 to 0.314%, illustrating that the oxygen-containing groups increase significantly on the surface of sample 2. It should be stated that the O/C ratio was optimized based on our and others' experiments [33]. When the bias voltage was higher than 12 kV, the PVC surface was so heavily oxidized and altered (thermally and radiation-induced) that the surface turned yellow. As shown in Table 1, the quantity of Cl increases from 3.15% to 5.48% on the surface of sample 3. Generally, the amount of Cl on the surface decreases as the treatment time increases, suggesting that triclosan combines with PVC during the argon plasma treatment. We further identify the oxygen-containing groups by quantifying the C1s XPS peaks and the results are displayed in Table 2. On the surface of sample 2, C–O is the main oxygen-containing functional group. A small quantity of N can also be detected on the surface and it may be due to atmospheric N_2 reacting with the active surface functional groups.

The quantity of Cl decreases from 3.15% to 2.33% on the surface of sample 4, and it is consistent with the above analysis. It is because dechlorination of PVC increases as the treatment time increases. There is also 2.33% bromine on the surface, which further shows that bronopol combines with PVC during the argon plasma treatment. Because bronopol contains N and O, the amount of N is also larger than that on the surface of samples 2 and 3. This suggests that some bronopol reacts with the surface of PVC. It is also noticed that the amount of O is larger than that on the surface of sample 3. This is because bronopol contains more oxygen than triclosan. Our results suggest that when bronopol combines with PVC, the whole molecule may not break completely. In order to further evaluate the changes following the O_2 plasma treatment and triclosan/bronopol modification, the C1s high-resolution scans are fitted and evaluated. Fig. 2 depicts the typical C1s high-resolution spectra used to identify the chemical states on the modified PVC [32]. The peak fitting

Table 1
Atomic percentages and elemental ratios determined from samples 2, 3 and 4

	C1s (%)	N 1s (%)	O 1s (%)	Cl 2p (%)	Br 3d (%)	N/C	O/C	Cl /C	Br /C
Sample 2	72.79	1.19	22.87	3.15	—	0.016	0.314	0.043	—
Sample 3	70.36	4.2	19.96	5.48	—	0.060	0.284	0.078	—
Sample 4	69	6.76	21.36	2.33	0.56	0.098	0.310	0.034	0.0081

parameters as well as the relative abundances of the fitted carbon are summarized in Table 2. After argon plasma modification, the fitted peaks for samples 3 and 4 at the binding energy of 285.5 eV increase by 4.83% and 7.85%, respectively, because of the binding energy for C═O, C–(Br)C(NO_3)–C and C on benzene at the same energy. The amount of C–Cl on sample 3 is larger than that on sample 2, as inferred from the peak at the binding energy of 284.3 eV. However, the quantity of C–Cl on sample 4 is less than that on sample 2. Our results indicate that some of the antibacterial reagents combine with the surface.

Samples 3 and 4 were further evaluated by the ATR-FTIR spectra (Figs. 3a and b). A large peak at about

Table 2
Peak fitting parameters and percent peak areas for the C1 s high-resolution peaks for samples 2, 3 and 4

Peak	Binding energy (ev)	FWHM(ev)	Sample 2 (%) area	Sample 3 (%) area	Sample 4 (%) area
C–C/C–H	282.55	1.1±0.05	52.89	45.59	50.84
C–O	283.60	1.1±0.05	18.19	22.17	21.86
C–Cl	284.30	1.1±0.05	16.40	20.36	10.88
C═O/C–(Br)C(NO_3)–C or C on benzene	285.50	1.1±0.05	2.83	4.83	7.85
O–C═O	286.70	1.1±0.05	9.70	6.77	8.57

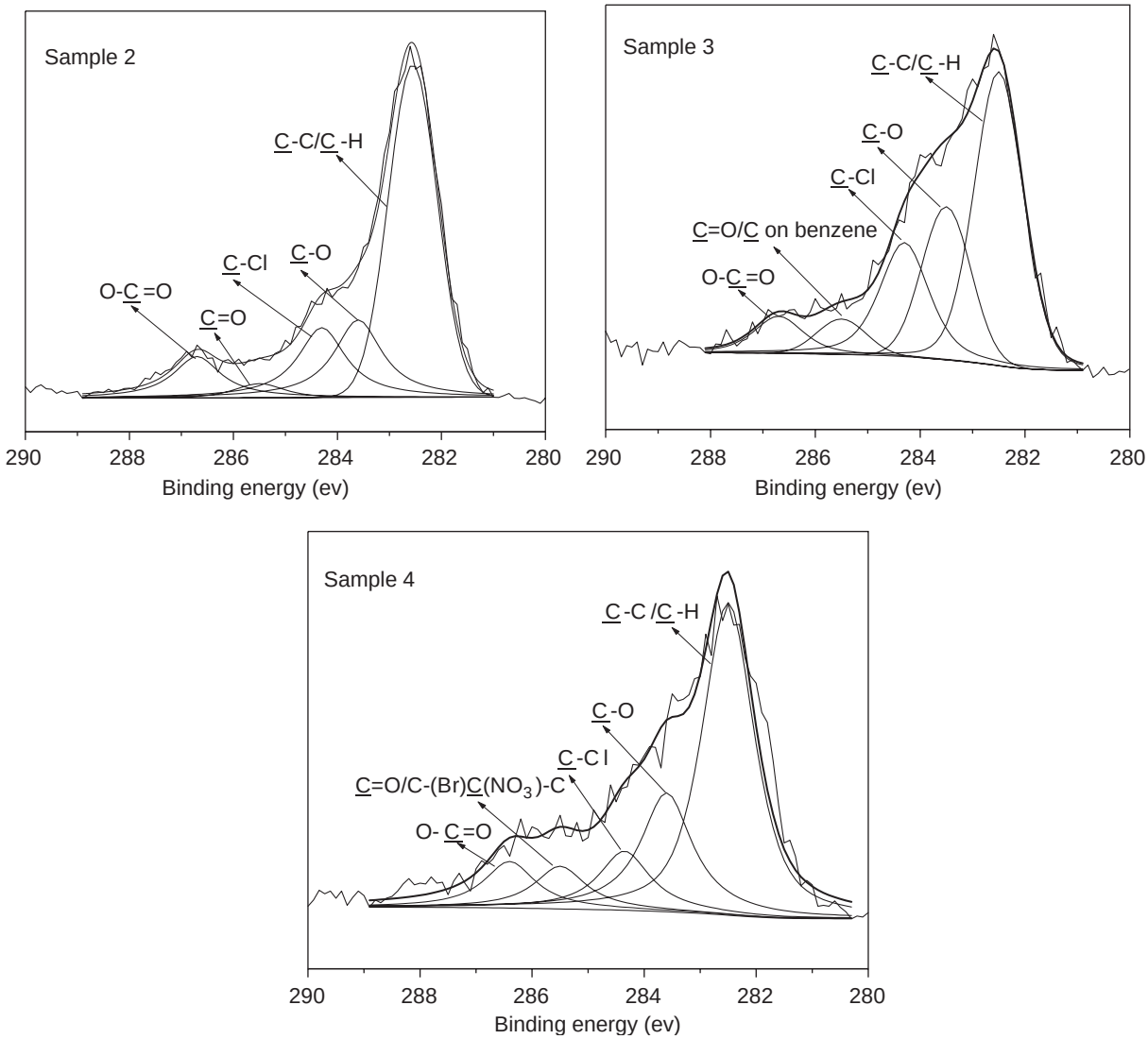

Fig. 2. Fitted C1s high-resolution scan of samples 2–4.

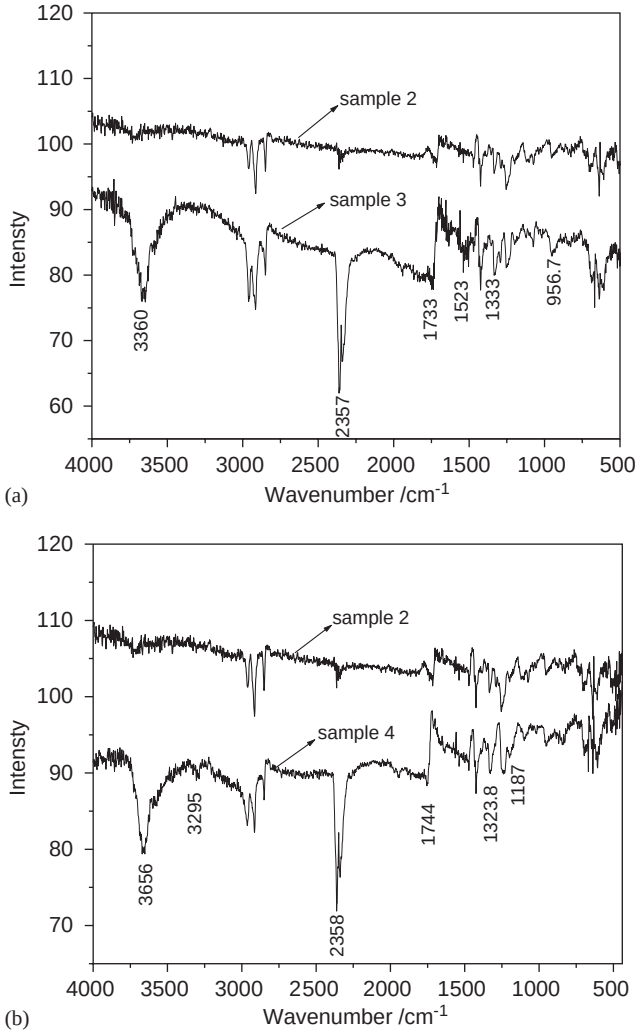

Fig. 3. Comparison of ATR-FTIR spectra acquired from: (a) samples 2 and 3 and (b) samples 2 and 4.

1740 cm^{-1} for samples 3 and 4 is the stretching vibration of C═O and the peak intensity is higher than that of sample 2. Hence, the quantity of C═O increases as the treatment time increases. This is also consistent with the XPS analysis of the modified PVC shown in Table 2. The large and broad peaks at about 3660 cm^{-1} are due to O–H bond stretching in CH_3CH_2OH and it is a consequence of incomplete drying after washing in ethanol. The three peaks between 2970 and 2846 cm^{-1} are the C–H sp3 vibration. In addition, a large peak at about 2358 cm^{-1} observed from samples 3 and 4 emerges and the magnitude is larger than that of sample 2. It is believed to be a result of the stretching vibration of C≡N or C═NH^+ or C═NH^+ and the appearance of C≡N or C═NH^+ bond arises from the incorporation of N_2 during plasma treatment. This is also illustrated in the XPS analysis shown in Table 2.

In the spectra of sample 3, the peaks at about 1523 and 1333 cm^{-1} can be assigned to the ═C–H and C–Cl stretching modes of benzene, respectively. The results indicate that the benzene structure is not fully destroyed during the treatment by argon plasma. In Fig. 3b, the peak at 1323.8 cm^{-1} is assigned to the C–N stretching mode of NO_2, and the 1187 cm^{-1} peak that is assigned to the tertiary C–OH stretching mode is stronger than that of sample 2s and 3. This may suggest that the carbon atom in the HO–CH_2- functional group in bronopol, in which the H atom is easily lost in the argon plasma action, reacts with PVC and makes C tertiary. The peak at 3295 cm^{-1} is O–H stretching in R(Br)–OH. This further illustrates that bronopol reacts with PVC and more work is being conducted in our laboratory to further fathom the mechanism of the reaction between the antibacterial reagents and PVC.

3.3. Effects of modification on appearance of PVC

Fig. 4 shows the SEM micrographs obtained from samples 1–4. There are no noticeable differences between the surfaces of sample 2 and 3 and samples 1, as shown in Fig. 4. On the other hand, the surface of sample 3 is quite different. Because triclosan can easily crystallize, some residues of the crystals remain on the surface.

3.4. Antibacterial properties of modified samples

The antibacterial properties of samples 3 and 4 are evaluated by plate counting of *S. aureus* and *E. coli* which are the most representative bacteria and the results are shown in Table 3 and Fig. 5. The antibacterial effect of sample 3 against *S. aureus* and *E. coli* are 82.2% and 79.5%, respectively. This illustrates that after combining with the PVC surface, triclosan still possesses antibacterial properties. This phenomenon should be interpreted from the antibacterial mechanism of triclosan. Based on results reported recently [23–25], triclosan acts as a non-specific biocide by affecting the membrane structure and function of the bacteria. When it reacts with bacteria, triclosan forms a stable ternary complex by interacting with amino-acid residues of the enzyme active site. If the C–Cl bond was not destroyed during modification, it would still have antibacterial effects. However, when the molecule is fixed on PVC and its environment changes, its antibacterial effect degrades. From Table 3 and Fig. 5, the antibacterial performance of sample 4 on *S. aureus* and *E. coli* are 98.0% and 77.3%, respectively. Sample 4 exhibits better antibacterial performance against *S. aureus*, but the antibacterial performance against *E. coli* is not as good. Sample 3 has better antibacterial performance against *E. coli* than sample 4. However, there have been few

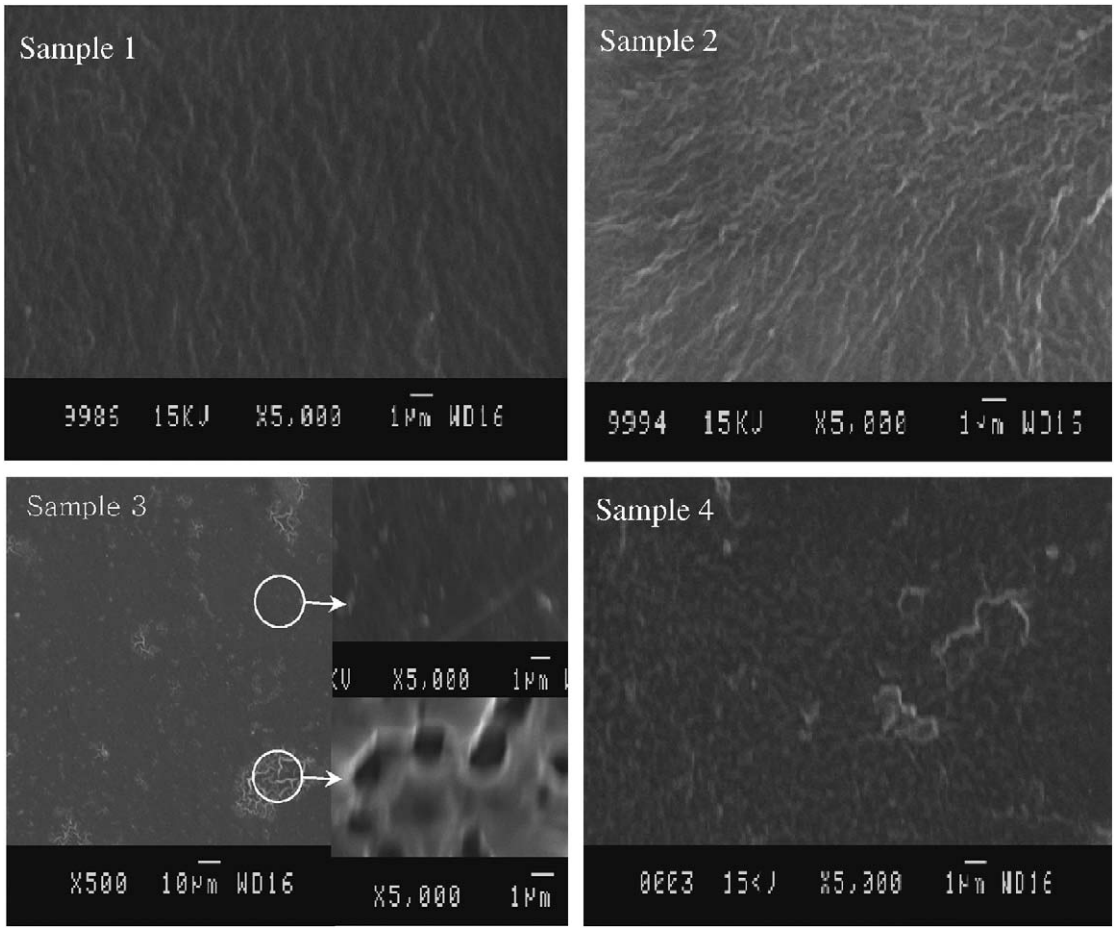

Fig. 4. SEM micrographs of samples 1–4.

Table 3
Antibacterial effects of modified PVC at the beginning and after ten days

Modified conditions		Sample 3		Sample 4	
		0 day	10 days	0 day	10 days
Antibacterial effect (modified/native) /%	*S. aureus*	82.2	73.3	98.0	86.7
	E. coli	79.6	70.1	77.3	69.3

reports about the antibacterial mechanism of bronopol, and the antibacterial activity of bronopol has not been reported in details.

Since plasma-treated surfaces tend to undergo changes with time, we have also investigated their antibacterial properties after the modified samples were left under room temperature conditions for 10 days. The results shown in Table 3 indeed indicate that the antibacterial properties of them against *S. aureus* and *E. coli* degrade after 10 days. More work is being conducted to comprehend the degradation mechanism and means to mitigate it.

3.5. Bacterial adhesions on modified PVC

As shown in Fig. 6, the amount of *S. aureus* on all the samples is higher than that of *E. coli*. This is mainly due to the difference between the physicochemical characteristics of bacteria and materials such as bacterial hydrophobicity, bacterial surface charge, material surface chemical composition, and surface hydrophobicity. Nonetheless, the two kinds of bacteria exhibit a smaller degree of adherence onto samples 3 and 4 than samples 1 and 2. In particular, a small amount of *E. coli* can be observed on sample 3 and 4. In our antibacterial

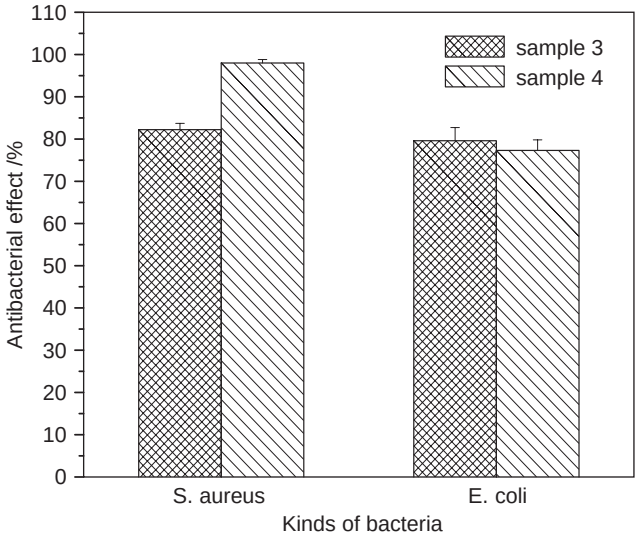

Fig. 5. Antibacterial effects of samples 3 and 4 against *S. aureus* and *E. coli*.

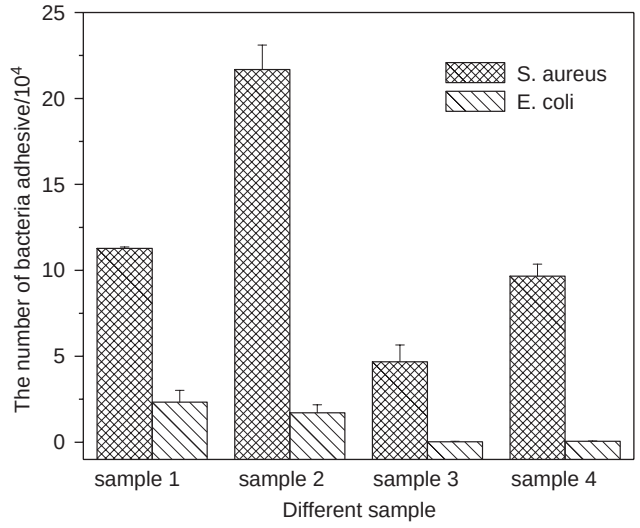

Fig. 6. Number of bacteria (*S. aureus* and *E. coli*) adherent onto samples 1–4.

experiments by plate counting, the modified samples exhibit higher antibacterial effects on *S. aureus* than *E. coli*. This may be due to the bacterial adhesion ability and antibacterial effect that are common on the modified samples.

4. Conclusion

Plasma immersion ion implantation (PIII) is demonstrated to be a viable method to modify the surface of medical poly vinyl chloride (PVC) to improve its antibacterial performance. Using an O_2 plasma treatment process at a relatively high voltage compared to traditional plasma treatment, a good hydrophilic surface can be formed enabling effective coating of antibacterial reagents of triclosan and bronopol. Our surface characterization results show that triclosan and bronopol combine well with the surface of PVC after the plasma treatment and most importantly, the antibacterial characteristics of triclosan and bronopol are retained. The modified samples with triclosan and bronopol show good performance with regard to the killing and adhesion of bacteria. Similar to many other surface plasma treatment processes, the surface properties deteriorate after 10 days and more work is being done to fathom the degradation mechanism and means to mitigate it.

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