Plasma-Enhanced Deposition of Silver Nanoparticles onto Polymer and Metal Surfaces for the Generation of **Antimicrobial Characteristics**

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ABSTRACT: Silver nanoparticle thin layers were deposited onto formaldehyde-radio frequency (RF)-plasma-functionalized medical- and food-grade silicone rubber, stainless steel, and paper surfaces. The silver deposition was carried out under ex situ plasma conditions using the Tollen's reaction. Results from survey and high-resolution electron spectroscopy for chemical analysis, scanning electron microscopy (SEM), atomic force microscopy (AFM), and energy dispersive X-ray spectroscopy investigations confirmed the presence of thin silver layers on the plasma-exposed and subsequently modified substrate surfaces. In addition, SEM and AFM demonstrated the nanoparticle-based morphology

INTRODUCTION

Silver is one of the strongest bactericides. It occurs under several oxidation states, including elemental silver (Ag^0) , which is the most common, monovalent silver ion (Ag^+) , and higher oxidation states (Ag^{2+}) and Ag^{3+}). The exact antimicrobial action of silver is not completely understood; several possible mechanisms have been proposed, which involve the interaction of silver with biological macromolecules, such as enzymes and DNA.^{1–5} Tetrasilver tetroxide (Ag_4O_4 ; a molecular crystal form) has been reported to be biocidal through an electron release mechanism.⁶ The effect of silver on microorganisms has been related to the inactivation of enzymes due to the formation of silver complexes with electron donors containing sulfur, oxygen, and nitrogen, such as thiols, carboxylates, amides, imidazols, indoles, and hydroxyls.^{1–5, 7}

Silver has been considered as a potential disinfectant in many investigations due to its intense antimicrobial activity and low toxicity to mammalian cells and tissues.^{8,9} It is one of the most powerful natural

of the deposited layers. Our results showed that thin macromolecular layers bearing aldehyde functionalities can be deposited onto silicone rubber, stainless steel, and paper surfaces. The bactericidal properties of the silver-coated surfaces were demonstrated by exposing them to Listeria monocytogenes. No viable bacteria were detected after 12 to 18 h on silver-coated silicone rubber surfaces. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1411-1422, 2004

Key words: antimicrobial polymer; cold plasma; functionalization of polymers; formaldehyde; Listeria monocytogenes

disinfectants known, therefore its deposition onto prosthetic device surfaces (catheters, heart valves, etc.) would be an attractive approach for preventing bacterial attachment and biofilm formation, which can lead to serious infections. Biomaterial-associated infections are common and can cause serious health problems. Another potential application could be in food processing equipment and packaging materials, where the presence of undesirable bacteria can cause food spoilage and foodborne diseases.

Colloidal silver, a dispersion of tiny silver particles in water, is the form that is commonly used for disinfectant purposes. The ultimate colloidal silver suspension would be at the molecular level. It has been suggested that, the smaller the silver particles, the more stable and effective the colloid suspension. It is also significant that bacteria exposed to colloidal silver have not been shown to develop resistance, unlike antibiotics. However, there are not many volatile and stable organometallic silver compounds; consequently, silver deposition, even using cold plasma techniques, is limited. The only published study describing deposition of silver from an organometallic derivative under cold plasma conditions was based on the use of perfluoro-1-methylpropenylsilver as a precursor.¹⁰ However, both the stability and the volatility

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of this compound are not adequate for practical applications; in addition the compound is very expensive.

In this contribution the deposition of silver nanoparticles under formaldehyde-radio frequency (RF)plasma conditions onto polydimethylsiloxane (medical- and food-grade silicone rubber), paper, and stainless steel surfaces is presented, and the antimicrobial characteristics of the silver-coated substrates are discussed.

EXPERIMENTAL

Materials

Paraformaldehyde (powder, 95% purity), silver nitrate (>99% purity, ACS reagent), sodium hydroxide, and ammonium hydroxide were purchased from Aldrich Chemical (Milwaukee, WI). Argon and oxygen used as gas media for plasma-enhanced reactor-cleaning operations were obtained from Liquid Carbonic (Brookfield, WI). Medical- and food-grade silicone rubber (SR) were obtained from McMaster-Carr Supply Company (Chicago, IL). Additive-free paper was supplied by the USDA Forest Products Laboratory (Madison, WI). Stainless steel type 304 (#4 finish) was obtained from Temperature Systems (Madison, WI). All substrates were cut into 1-cm² pieces. The stainless steel and SR chips were washed in a hot alkaline detergent (Micro; International Products, Trenton, NJ) for 30 min, rinsed five times in distilled water, and air dried before use.

Analytical methods.

The relative surface atomic concentrations and the relative ratios of carbon, oxygen, silicon, and silver atoms present in nonequivalent atomic environments of unmodified and formaldehyde-plasmamodified surfaces were analyzed by electron spectroscopy for chemical analysis (ESCA) using a Perkin–Elmer Physical Electronics 5400 Small Area Spectrometer (Mg source; 15 kV; 300 W; pass energy, 89.45 eV; angle, 45°; Perkin–Elmer, Palo Alto, CA). Carbon (C_{1s}), oxygen (O_{1s}), silicon (Si_{2p}), and silver (Ag_{3d}) atomic compositions were evaluated and the peaks corresponding to atoms located in nonequivalent positions were analyzed. To correct for surface-charge-origin binding energy shifts, calibrations were performed based on the well known C–C (C_{1s}), Si–C (Si_{2p}), and Ag_{3d3/2} and Ag_{3d5/2} peaks.

Volatile compounds resulting from the recombination of molecular fragments generated during the thermal decomposition of paraformaldehyde were identified using a MKS Instruments (Morgan Hill, CA) Spectra Products Residual Gas Analysis (RGA) LM78/ LM505 mass spectrometry system.

The morphologies of plasma-exposed polymer surfaces and the silver clusters structures, composed of nanoscale particles, present on surfaces were analyzed using atomic force microscopy (AFM) employing a Digital Instrument Nanoscope III microscope (scan rate, 1.9 Hz; sampling number, 512; Santa Barbara, CA), and scanning electron microscopy (SEM). Images of palladium/gold sputtered substrates were produced using a LEO 1530 Field Emission, Digital Scanning Electron Microscope (LEO Electron Microscopy Inc., Thornwood, NY). The presence of silver atoms on the formaldehyde-plasma-exposed substrate surfaces, which were subsequently immersed in Tollen's reagent, was also evidenced by energy dispersive X-ray spectroscopy (EDS).

Deposition of silver nanoparticles on plasmafunctionalized substrate surfaces

Thin silver layers were deposited on plasma-functionalized surfaces according to Tollen's reaction. Tollen's reagent contains diamminosilver (I) ions, $Ag(NH_3)_2^+$, and is prepared by mixing aqueous silver nitrate with aqueous ammonia. These ions will oxidize aldehydes to carboxylate ions according to the following reaction:



As it is well known, the Tollen's reagent gives a negative result with all ketones, except α -hydroxy ketones.

Tollen's reagent was prepared according to the following procedure: one drop of 10% sodium hydroxide was added to 50 mL of 1% silver nitrate solution and then 5% ammonium hydroxide was added with constant stirring until any precipitate of

silver oxide was dissolved. Silver deposition was performed by immersing the formaldehyde-plasmatreated substrates in the silver solution for 10 min at 80°C. The substrates were then removed from the solution, washed with distilled water, dried, and subjected to analytical evaluation and assessment of antibacterial activity.

Plasma functionalization of substrate surfaces

Generation of aldehyde functionalities on polymer surfaces using plasma technique, to our knowledge, has not been accomplished until now. Plasma-enhanced oxidation even of polyolefin surfaces usually results in the formation of (C=O), O-C=O, or C-O-O- functionalities. Polymers prepared by conventional reaction-mechanisms (e.g., polymerization and polycondensation) and bear multiple aldehyde functionalities on their chains are also not too numerous.

To implant aldehyde functionalities onto polymer substrate surfaces by using electrical discharges, the presence of CH=O plasma-generated species are required. These active species are difficult to synthesize owing to the fact that the C-H bond is significantly weaker (338 KJ/mol) in comparison to the C-O (594 KJ/mol) or C=O (1,076 KJ/mol) bonds and, consequently, detachment of hydrogen atoms will be the favored reaction mechanism. In addition, formaldehyde is only available in water solution (the highest concentration is close to 37%) and using it as the starting material would introduce water molecules into the discharge environment with obvious undesirable consequences. At the same time, higher aldehyde homologues are usually less volatile and readily generate hydrocarbon fragments under plasma environments.

As a consequence, in our investigations, paraformaldehyde, which is an oligomeric structure of poly-(methylene glycol), is used as the starting component for the generation in the discharge of the–CH==O functionalities. Paraformaldehyde is a solid-phase material, which decomposes at relatively elevated temperatures into formaldehyde. Accordingly, a specially designed "monomer" feeder (starting material container) has been designed and developed, which allows the controlled thermal decomposition of paraformaldehyde and the introduction of the resulting formaldehyde at selected pressures into the plasma reactor.

Implantation of aldehyde functionalities into silicone rubber and paper and deposition of thin layers containing aldehyde groups onto stainless steel substrate surfaces were carried out in a capacitively coupled (6-cm disc-shaped electrodes separated by a 10-cm gap), 40-kHz cylindrical glass plasma reactor presented in Figure 1. The reactor is composed of Pyrex-glass cylindrical walls (13) and two disc-shaped stainless steel electrodes (11 and 16). The upper electrode is connected to the monomer-feeding installation (2 and 3), vacuum system (4 and 5), and pressure gauge (10) and also includes a perforated, disc-shaped gas/vapor distribution stainless steel plate and a gas/ vapor flow-out-guiding glass tube (14). The lower electrode serves also as the substrate holder and is connected to the RF-power supply; the upper elec-



Figure 1 Scheme of dense medium plasma reactor. 1, RFpower supply; 2, digital electrical controller of "monomer"feeder; 3, "monomer"-feeder; 4, mechanical vacuum pump; 5, large cross section valve; 6, micrometric needle valve; 7 and 12, injection connection for liquid-phase materials; 8, Teflon-coated silicon rubber septum; 9 and 10, MKS baratron system; 11, stainless steel grounded upper electrode and gas-feeding and evacuation system; 13, outside glass (Pyrex) wall of the reactor; 14, inner cylindrical glass tube designated for the control of the gas/vapor supply and evacuation route; 15, substrate to be plasma treated; 16, lower stainless steel electrode connected to the RF power supply; 17, gas/vapor supply/evacuation route.

trode is grounded. The temperature of the lower electrode can be controlled (cooled or heated) by immersing its outside surface area into a controlled-temperature liquid environment (e.g., Lauda recirculator).

Formaldehyde was generated by the thermal decomposition of paraformaldehyde in a specially designed stainless steel container provided with a controlled heating unit, pressure gauge, safety valve, and a needle valve system for the connection of the container to the plasma reactor.

In a typical experiment the reactor, having a specific substrate positioned on the lower RF-connected electrode, was evacuated to base pressure. The container with the paraformaldehyde was degassed and the formaldehyde supply system (FSS) was isolated from the plasma reactor (specific valve closed). In the next step the FSS was heated to the preselected temperature, the formaldehyde working pressure was created in the reactor, and the plasma was initiated and sustained for the required treatment period. At the end of the reaction the FSS was isolated from the discharge chamber and the reactor was evacuated to base pres-



Figure 2 High-resolution (A) C_{1s} , (B) O_{1s} , and (C) Si_{2p} ESCA spectra of medical-grade silicone rubber.

sure and then repressurized using air. The plasmaexposed substrates were removed from the reactor for analytical evaluations and silver deposition reactions.

The following plasma parameters were used: base pressure in the absence of plasma, 50 mTorr; formaldehyde pressure in the absence of plasma, 150 mTorr; pressure in the presence of plasma, 250 mTorr; RF power dissipated to the electrodes, 50–150 W; reaction time, 5 s to 2 min; temperature of the FSS container, 170°C. Unless noted otherwise, results presented were generated using 50 W and 1 min.

Evaluation of bactericidal activity

The bactericidal activity of medical- and food-grade SR substrates coated with silver nanoparticles was



Figure 3 High-resolution (A) $C_{1s'}$ (B) $O_{1s'}$ and (C) Si_{2p} ESCA spectra of medical-grade silicone rubber treated with formaldehyde plasma.







Figure 5 High-resolution (A) C1s and (B) O1s ESCA spectra of additive-free paper treated with formaldehyde plasma.

evaluated. Five strains of *Listeria monocytogenes*, including human and food isolates from listeriosis outbreaks, were grown overnight in trypticase soy broth (TSB; Becton Dickinson Microbiology Systems, Cockeysville, MD) at 37°C. The strains were combined to form a five-strain cocktail and diluted with sterile distilled water to achieve a bacterial concentration of about 10^5 colony-forming units (CFU)/mL. Samples (30 μ L) of the combined culture

were inoculated onto untreated and silver-coated surfaces, which were incubated at room temperature for 0, 6, 12, 18, and 24 h. After each incubation time, two control and two silver-coated SR chips were each added to a tube containing 5 mL 10 mM phosphate-buffered saline (pH 7.2) and glass beads and were vortexed for 30 s to detach bacteria from the surfaces. The number of viable bacteria was evaluated by plating onto brain heart infusion agar



Figure 6 High-resolution (A) C_{1s} and (B) Ag_{3d} ESCA spectra of additive-free paper treated with formaldehyde plasma and Tollen's reagent.



Figure 7 High-resolution C_{1s} ESCA spectra of (A) untreated and (B) formaldehyde plasma treated stainless steel type 304.

(Difco Laboratories, Detroit, MI) plates. The plates were incubated at 30°C for 48 h, and the numbers of CFUs developed were counted and expressed as log CFU/chip.

Results and discussion

The relative surface atomic composition and the high resolution (HR) C_{1s} , O_{1s} , and Si_{2p} ESCA diagrams of medical grade SR are presented in Figure 2. It can be

observed that both the relative surface atomic composition and binding energy (BE) values of atoms present in non-equivalent linkages of virgin SR are in good agreement with the theoretical values of polydimethylsiloxane. The main C_{1s} , O_{1s} , and Si_{2p} BE peaks were assigned to the presence of: C–Si (284.4 eV), Si–O–Si (532.2 eV), and $Si_{2p3/2}$ and $Si_{2p1/2}$ (101.6 eV and 102.2 eV).

Exposure of SR to formaldehyde-plasma induced an intensive surface modification (Fig. 3). The relative



Figure 8 High-resolution (A) C_{1s} and (B) Ag_{3d} ESCA spectra of stainless steel treated with formaldehyde plasma and Tollen's reagent.



Figure 9 EDS diagram of medical-grade silicone rubber treated with formaldehyde plasma and Tollen's reagent.

surface atomic composition was altered significantly and the nature and relative ratios of surface functionalities were modified substantially. The major C_{1s} BE peaks of formaldehyde-plasma-treated SR were assigned to the presence of-C-O-(286.5 eV), H-C=O and-(CH₂-O)-(288 eV), C-C(O)-O-C-(285.7 eV), and HO-C(O)-(289.2 eV) groups. The O_{1s} diagram substantiates the conclusion that an extensive plasmainduced surface modification has taken place; the presence of BE peaks characteristic of carbon and oxygen-based structures [linear and/or cyclic-(CH2- $CH_2-O)_n$ -, -($CH_2-O-)_m$ -, -C-CO-C, and C-CO-H-: 532.8eV; -C-CO-*O-C-: 534 eV] is obvious. In addition, the Si_{2p} HR diagram indicates that the silicon atom of the modified SR is connected to more than two oxygen atoms. Demethylation reaction mechanisms are probably responsible for this structural transformation.

Chemical derivatization reactions performed on formaldehyde-plasma-exposed SR surfaces for the identification of C=O (pentafluorophenylhydrazine; PFPH) and–OH (trifluoroacetic anhydride; TFAA) functionalities¹¹ also demonstrate the presence of aldehyde (ketone) and hydroxyl functionalities. Relative surface fluorine atomic concentrations of 2 and 4%, respectively, were detected on formaldehyde-plasmamodified SR surfaces that were subsequently derivatized using PFPH and TFAA.

Plasma-treated SR substrates that underwent subsequent Tollen's reaction showed the presence of silvercoated surfaces and the removal of most of the macromolecular layers deposited during the formaldehyde-plasma surface-modification reactions (Fig. 4). The HR C_{1s} diagram indicates the existence of a major

C–Si BE peak (284.4 eV) characteristic for polydimethylsiloxane-type structures, accompanied by a small surface area oxygen- and carbon-based peak, which was assigned to the presence of C–O (286.5 eV) linkages. The absence of CO-O-C (289.2 eV) linkages on SR surfaces at the end of Tollen's reaction might be explained by their low concentration relative to the C-Si- and C-O-based remnant structures. Similarly the O_{1s} diagram shows a dominant Si–O–Si BE peak (532 eV) and a relatively large surface area SiO₂ and/or Si(O–C)₃₋₄ peak (530.5 eV) in addition to an extremely low surface area-CO-O-C peak (533.5 eV). The presence of a symmetrical Si peak [Fig. 4(C)] suggests that most of the aldehyde-origin structures, which might be attached to polydimethylsiloxane chains, were removed from the SR surface during Tollen's reaction. The relatively high silver surface atomic concentration (around 6%) and the presence of a characteristic HR silver doublet peak, Ag_{3d3/2} (347.2 eV) and $Ag_{3d5/2}$ (368.2 eV), clearly indicate that the deposition of silver onto plasma-modified SR surfaces has been accomplished successfully.

Similar survey and HR ESCA data were recorded for SR surfaces exposed to formaldehyde-plasma environments using various treatment times (5 s, 30 s, 1 min, and 2 min) (data not shown). It was found that very low formaldehyde-plasma exposure periods were sufficient for the generation of SR surfaces containing aldehyde functionalities and were capable of promoting Tollen's reaction.

Additive-free paper (PP) substrates subjected to similar surface-modification reactions also resulted in efficient silver-deposition processes. A typical C_{1s} HR ESCA diagram of a formaldehyde-discharge-treated PP surface and the $Ag_{3d3/2}$ and $Ag_{3d5/2}$ diagram of formaldehyde-plasma-treated PP, which was subsequently reacted under Tollen's reaction conditions, in comparison to the unmodified PP substrate are presented in Figures 5 and 6. The C1s HR diagram clearly indicates the plasma-enhanced formation of macromolecular layers composed of polyoximethyleneand/or polyoxyethylene-type linkages, which incorporate aldehyde and ketone functionalities. It is noteworthy that, in this case, the presence of COOH functionalities, as a result of the development of Tollen's reaction, is more evident. As with SR, the plasmadeposited macromolecular layers are mostly removed from the PP substrate surfaces during the development of Tollen's reaction.

The fact that a formaldehyde-plasma-mediated deposition process is dominant relative to a surface-functionalization reaction mechanism opened up the possibility for plasma-enhanced technologies for the deposition of thin silver layers even onto metal surfaces. Accordingly stainless steel (SS) substrates were treated under surface-modification conditions similar to those used for their polymeric counterparts. The HR



Figure 10 RGA spectra of (A) feeding gas products and (B) of outlet gas during plasma treatment (pressure inside plasma reactor: 150 mTorr; pressure inside RGA: 5.0×10^{-6} Torr).

 C_{1s} and Ag_{3d} diagrams of formaldehyde-plasmatreated SS substrates (Figs. 7 and 8) clearly indicate the presence on the substrate surfaces of oxygen- and carbon-based structures and silver as a result of Tollen's reaction, regardless of the nature of the specific SS substrate. It can be observed that detergent-cleaned SS substrates have on their surfaces a thin, oxidized hydrocarbon-type layer. Even oxygen-plasma environments cannot remove this layer entirely (data not shown). The formaldehyde-plasma treatments of SS substrates resulted in deposition of macromolecular layers with oxygen- and carbon-based functionalities identical to those characteristics for depositions on SR substrates (Fig. 7). However, the relative ratios of specific functional groups (relative ratios of peak surface areas) are significantly different, namely, the relative



Figure 11 SEM images of medical grade silicone rubber (A) untreated and (B) treated with formaldehyde plasma and Tollen's reagent.

surface areas assigned to C-*CO-O-groups are higher in the case of SS substrates. During Tollen's reaction, part of the deposited layers were removed, as in the cases of SR and PP samples (Fig. 8). The presence of strong Ag BE peaks is obvious and clearly indicates that silver was successfully deposited onto SS substrates as a result of Tollen's reaction (Fig. 8). The presence of silver on the plasma-modified substrate surfaces that underwent Tollen's reaction has also been demonstrated by SEM/EDS analysis (Fig. 9), where the existence of silver peak can be noted.

MS-electron-impact (70 eV) fragmentation [Fig. 10(A)] indicates that, even at these high electron-energy values, the main molecular ion fragments are:



Figure 12 AFM images of medical grade silicone rubber (A) untreated and (B) treated with formaldehyde plasma and Tollen's reagent.

CH= O^+ (*m*/*z* = 29) and H₂O⁺ (*m*/*z* = 18). The intensity of the molecular hydrogen signal is notably low. Electron energies are substantially lower in glow discharges than 70 eV; accordingly, a significantly less intense fragmentation process will characterize the plasma environment. It was shown previously that MS-electron-fragmentation data and especially data resulting from low electron energy (5–10 eV) fragmentation processes can help to predict the nature of species generated by plasma-electron-induced fragmentation mechanisms.^{12–14} Consequently, it can be assumed there will be sufficient CH=O charged and neutral species in formaldehyde plasma for the implantation of aldehyde functionalities onto polymer substrate surfaces. However, RGA data [Fig. 10(B)] acquired from formaldehyde-plasma environments indicate only the presence of H₂, CO, and CO₂. This might be related to the extremely high reactivity of

CH=O charged and neutral species and their very fast consumption at the surfaces that confine the discharge. The rapid recombination of CH=O species could also explain the efficient deposition of macro-molecular layers on formaldehyde-plasma-exposed surfaces.

SEM (Fig. 11) and AFM (Fig. 12) images show the existence of granular-type structures of silver-coated SR substrate surfaces. It appears that the silver layers are composed of 20 to 60-nm silver particles.

The antibacterial activity of silver-coated medicaland food-grade SR substrates are presented in Figs. 13(A and B), respectively. The number of *L. monocytogenes* on untreated SR surfaces remained essentially the same throughout the 24-h exposure period. In contrast, the bacterial numbers on silver-coated surfaces began to decline after 6 h. After 12 h, there was a reduction of over 2 log CFU/chip on the medical-



Figure 13 Bactericidal effect of silver coated (A) medicalgrade and (B) food-grade silicone rubber surfaces on *L. monocytogenes.*

grade SR, while no *L. monocytogenes* could be recovered from the food-grade SR surfaces. It is possible that a higher concentration of silver was deposited on the latter surface, thus making it slightly more effective. No viable bacteria were detected on both types of silver-coated SR after 18 and 24 h.

CONCLUSION

Silver nanoparticles were deposited onto formaldehyde-radio frequency-plasma-functionalized medicaland food-grade silicone rubber, stainless steel, and paper surfaces. No viable bacteria were detected after 12 to 18 h on silver-coated silicone rubber surfaces exposed to *L. monocytogenes*.

These results suggest that plasma-mediated silver coating of various inorganic and organic substrate surfaces might play a significant role in novel future technologies for the generation of surfaces that kill bacteria on contact.

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