Antibacterial activity on Polyamide and Natural fabrics using Low Temperature Plasma

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ABSTRACT

Low-temperature plasma is generated when a gas at low pressure and near ambient temperature is exposed to an electric field and contains radicals, ions, electrons, photons and other excited species. These species can interact either physically or chemically with the substrate surface to a depth of a few tenths of nanometers, due to their high reactivity. The advantages of plasma technology for making suitable implants or medical devices are both technological and administrative. The techniques are easy to implement, reproducible, clean and can be set up in any type of clean room. The techniques are non pollutant, there are no organic residuals. Plasma treatment can be used to create a functionalized surface through attachment of new chemical groups. In the present paper, we have investigated the possibility of obtaining antibacterial fabric with views on their application on dressings by using a single process, plasmas sputtering. Also the other modification investigated consisted of an Oxygen glow discharge pre-functionalization, followed by a one-step wet-treatment in silver nitrate. The surface was first activated by O2 plasma to produce more hydrophilic groups so that silver could be coated more effectively on the surface. Different fabrics such as cotton and polyamide have been treated; their surface properties have been studied by different techniques, and correlated to their antibacterial action.

Keywords: Fabric, Antibacterial, Cotton, Polyamide, Low Temperature Plasma

1 INTRODUCTION

In recent years, the demand for antibacterial fabrics in domestic and abroad markets has grown significantly because of more awareness of the potential threat of spreading diseases. Bio-protective fabrics such as medical clothes, protective garments, and hygienic textiles are the main application of the antibacterial fibers [1].

Natural textiles such as those made from cellulose and protein fibers are often considered to be more vulnerable to microbe attack than man-made fibers because of their hydrophilic porous structure and moisture transport characteristics. Thus, the use of antibacterial agents to prevent or retard the growth of bacteria is becoming a standard finishing for textile goods. There is, however, an increasing public concern over the possible effects of antibacterial finishing on environmental and biological systems since many antibacterial agents are toxic chemicals. They are also lack of efficiency and durability. Thus, an ideal textile antibacterial finishing should be safe and environmentally benign besides killing undesirable micro-organisms [2].

Also Polyamide (PA) synthetic textiles are among the most used fibers in the biomedical textile field [3].

The formation of nano-structured surfaces gained high interest due to their large surface area which might yield a highly functional surface. The main approach is the incorporation of nano particles into wet-chemical coatings or compounds. However, some difficulties during the handling of nano particles (agglomeration, nano toxicology) and concerning the distribution of nano particles at the surface as well as mechanical durability occur. Nanoporous structures, on the other hand, which can be obtained by plasma polymerization/etching processes might avoid these issues and yield an even higher surface area. Furthermore, nano particles with homogeneous size and spatial distribution can also be embedded in situ by a plasma polymerization/co-sputtering process. Products made with the help of textiles and fibers become more and more sophisticated and "multifunctional". Tailored surface modifications are required to meet customer needs and to assure a share in the market. However, conventional finishing techniques applied to textiles (dyeing, stain repellence, flame retardance, antibacterial treatments) generally use wet-chemical process steps and produce a lot of wastewater. Plasma treatment, on the other hand, as a dry and eco-friendly technology, is offering an attractive alternative to add new functionalities such as water repellence, long-term hydrophilicity, mechanical, electrical and antibacterial properties as well as biocompatibility due to the nano-scaled modification on textiles and fiber. At the same time, the bulk properties as well as the touch of the textiles remain unaffected [4-11] In the present paper, we have investigated the possibility of obtaining antibacterial fabric with views on their application on dressings by using a single process, plasmas sputtering. Also the other modification investigated consisted of an Oxygen glow discharge pre-functionalization, followed by a one-step wet-treatment in silver nitrate. The surface was first activated by O2 plasma to produce more hydrophilic groups so that silver could be coated more effectively on the surface. Different fabrics such as cotton and polyamide have been treated; their surface properties have been studied by different techniques, and correlated to their antibacterial action.

2 EXPERIMENTAL PART

2.1 Materials

Woven Cotton and Polyamide fabrics were kindly supplied by the Baft Azadi Co (Tehran, Iran). Before LTP treatment, fabrics were washed with 1 g. lit $^{-1}$ nonionic detergent and the washed samples were dried in a laboratory oven.

2.2 Sputtering Plasma Process

Deposition of copper on the surface of samples was performed in DC magnetron sputtering, made by Plasma Physics Research Center (Tehran, Iran), by using the setup schematically presented in Figure 1. Copper post cathode was used; also as it can be seen samples were placed on the anode, and exposed to argon plasma in a cylindrical glass tube. The chamber was evacuated to a pressure of 2×10^{5} torr, using rotary and diffusion pumps, and then argon gas was introduced into the chamber up to a pressure of 2×10^{2} torr. Voltage was kept at 1500V and the discharge current was about 220 mA. The duration of deposition was up to15 min. By this treatment, samples were coated with copper.

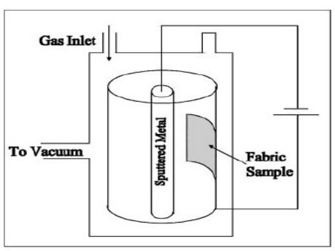

Figure 1: The schematic view of Plasma System.

2.3 Oxygen Plasma Treatment

The DC magnetron-sputtering device also was used for Low Temperature Plasma (LTP) Treatment. Oxygen gas has been used as working gases. And Al post cathode was used. First of all chamber was pumped down to 2×10^{3} torr using a rotary pump, and then O_2 was admitted up to a pressure of 5×10^{-2} torr and flowed for 7minutes. After plasma treatment the chamber was re-evacuated to 5×10^{3} torr to remove any by-products of the plasma processing. The samples were subsequently removed and those reserved for $AgNO_3$ modification were directly placed in the $AgNo_3$ solutions (described below).

2.4 $AgNO_3$ Incubation Technique

Silver nitrate was purchased from Merck. First, the native and RF-oxygen-modified substrates were incubated for 72 hours at room temperature in a 0.1 M solution of AgNO3, protected from light. After this period expired the samples were rinsed 3 times with deionized water, subsequently analyzed by the various surface characterization techniques, or submitted to bacterial activity test. Immediately before surface analysis the samples were dried in the laboratory oven.

2.5 FTIR

Fourier Transform Infrared spectroscopy (FTIR) was used for the investigation of the chemical structure of the Fabrics. Infrared spectra have been measured with a Perkin-Elmer, FTIR spectrometer.

2.6 Morphological Study

The morphology of the fabrics was observed using a scanning electron microscope (SEM; LEO 440I, made in England). All of the samples were gold coated before conducting the SEM examination. The EDX unit connected to the SEM microscope was used to determine the percentage of atomic contents of elements present in the treated fabrics.

2.7 Testing of Antibacterial activity

The agar test (Halo method) is a well-established method to provide a semi-quantitative analysis. A Swatch of fabric was placed on a bacteria culture spreading on a medium.
Staphylococcus aureus were selected for testing. The dish was then incubated at 37^{o} C for 24 h. The medium was Mc-Conkey from Merck (Germany), and contained the peptone mixture: 1.5, Neutral Red: 0.03, Crystal Violet: 0.001, Agar–agar: 13.5.
After incubating under controlled conditions, the area surrounding the sample (the Halo) showing where the growth of bacteria was inhibited demonstrates the efficiency of the antibacterial sample.
For Bacteria counting test, Luria Bertani media (LB) broth was used as growing medium for Staphylococcus aureus. Bacteria were dripped in 10 mL of LB broth to reach a cell concentration of 1×10^{8} (CFU)/mL. Then it was diluted to a cell concentration of 1×10^{6} (CFU)/mL. 1cm×1cm size fabric sample was cut and put into 1mL Bacteria suspension. All samples were incubated for 24 h at 37^{o} C. From each incubated sample, 100 µL of solution was taken and distributed onto an agar plate. All plates were incubated for 24 h and colonies formed were counted. The percentage reduction was determined as follows:

$$Reduction\ (\%) = (C-A)/C \tag{1}$$

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Where C and A are the colonies counted from the plate of the control and treated sample, respectively.

3 RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FTIR) was used to examine the functional groups of the untreated and Oxygen plasma treated samples. The results are shown in Figure 2-3. As shown, slight increase in absorbance at 1720 cm^{-1} (C=O) band and 3400 cm^{-1} (O-H) band and 1080-1300 cm^{-1} (C-O) after Oxygen plasma treatment can be noticed [12-16]. These functional Groups were produced on the fabric through the reaction between the active species induced by the plasma in the gas phase and the C-surface atoms.

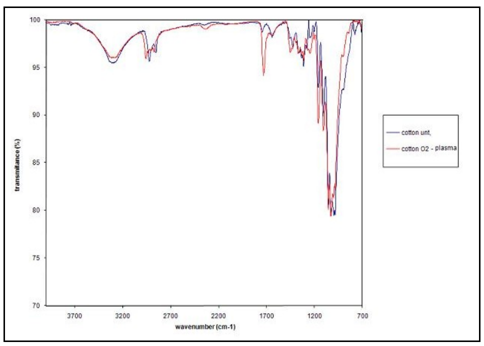


Figure 2: FTIR Results of Untreated (a) and O2 plasma Treated Cotton

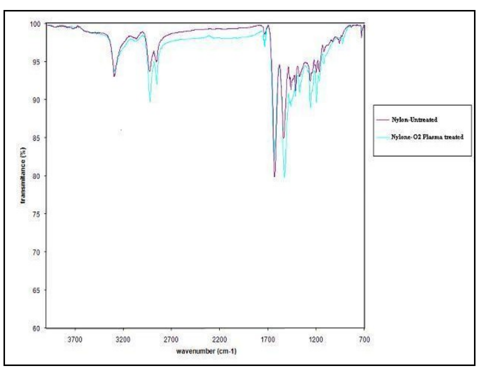


Figure 3: FTIR Results of Untreated (a) and O2 plasma treated Nylon.

The activation of the surfaces can help to absorb more amounts of silver particles. The SEM micrographs of untreated and O_2 plasma treated fabrics show that, after LTP treatment ripple like patterns oriented in a fiber axis are developed(see Figure 4{a, b} and Figure 5{a, b}).
As it is shown in SEM images, more silver particles have been attached to the surface of pre-functionalized samples and the size of particles is reduced from 800 nm for untreated cotton sample to 250 nm after plasma treatment (Figure 4-5).

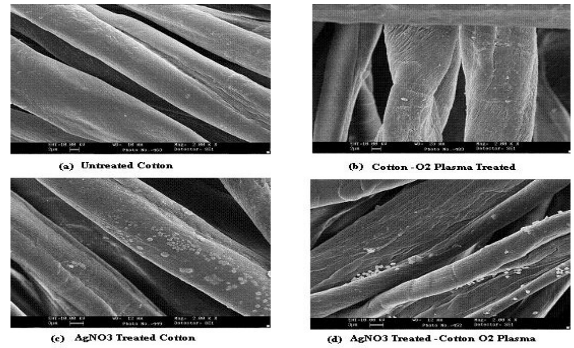


Figure 4:SEM images of Cotton Untreated (a) and Treated (b)-(d).

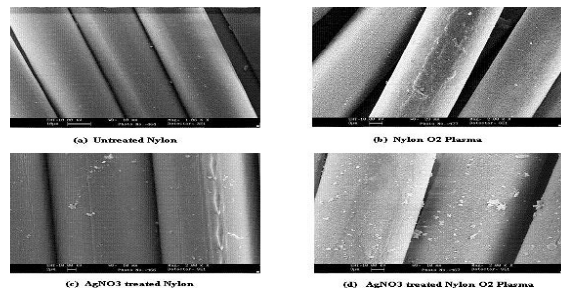


Figure 5:SEM images of Nylon Untreated (a) and Treated (b)-(d).

The physical and chemical modification using LTP treatment causes, this reduction of particle size.
Also the results show that, the silver particle size appeared on the surface of Nylon fibers is about 70 nm and smaller than those existed on the cotton samples. And the EDX results in Figure 6 show the amount of Ag on Nylon samples is more.

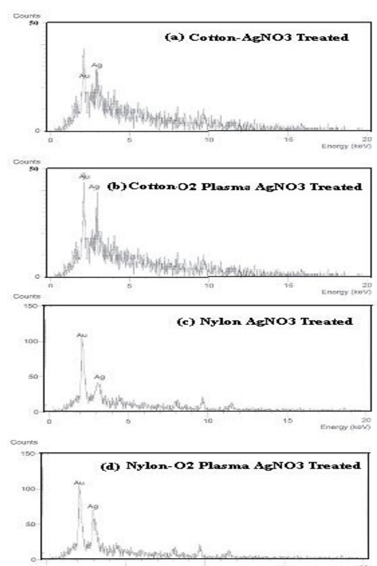
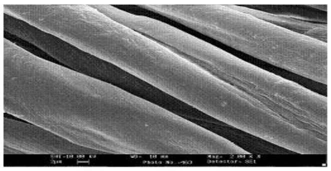


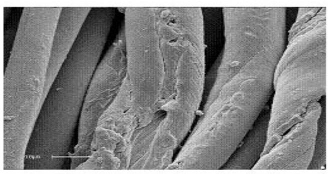
Figure 6: EDX results of $AgNO_3$ Treated samples

SEM is the best known and most widely used tool for surface morphological analyses. SEM micrographs of untreated cotton fabric and Cu-coated samples are shown in Figure 7. The scale, magnification and voltage of the beam are 3 μm, 2000 and 10 kV, respectively.

As shown, a very thin layer of copper has covered the surface of treated cotton fibers that did not exist on the surface of untreated cotton fibers



(a) Cotton Untreated



(b) CU Coated Cotton

Figure 7: SEM images of Cotton Untreated (a) CU coated cotton

After investigating about Physical and chemical modifications of fabrics using Low Temperature Plasma (LTP) treatment, the antibacterial activity of samples were tested. The tests done to evaluate antibacterial textiles were divided into two types, agar based zone of inhibition tests and bacteria counting tests.

The agar culture medium is transparent, when the bacterium is inhibited from growth, a transparent area in the form of a halo around the fabric will be observed.

There is no halo observed for untreated cotton and nylon fabrics. This control test shows that the original fabric does not have any antibacterial properties, But the $AgNO_3$ treated and Cu-Coated samples showed very good antibacterial activity. The interaction between silver and copper ions with bacteria can change the metabolic activity of bacteria and eventually cause the death.

Figure 8 just illustrate the test results for the cotton- CU coated fabric. The diameter of the halo is shown in Table 1. As it is shown, coating of samples with Copper has the best antibacterial activity.

Figure 8: Antibacterial activity of cotton-coated fabrics with S. aureus Halo method.

Samples	Diameter of Inhibition (mm)
Untreated cotton	--------
Cu-Coated cotton	19
$AgNO_3$ treated cotton	12
$AgNO_3$ treated o2 plasma cotton	12.3
Untreated Nylon	--------
Cu-Coated Nylon	19
$AgNO_3$ treated Nylon	13
$AgNO_3$ treated O2 plasma Nylon	13

Table 1: The result of zone of inhibition tests.

The pre-plasma modification didn't have any significant affect on inhibition zone. But as it can be seen in Table 2, that shows the results of counting test, more reduction of survival bacteria were caused by Pre Plasma modification.

Cu sputtering on the fabrics causes 100% reduction of bacterial growth.

Samples	Percentage of Reduction(%)
Untreated cotton	15
Cu-Coated cotton	100
$AgNO_3$ treated cotton	80
$AgNO_3$ treated o2 plasma cotton	87
Untreated Nylon	22
Cu-Coated Nylon	100
$AgNO_3$ treated Nylon	85
$AgNO_3$ treated O2 plasma Nylon	92

Table 2: The result of Bacteria counting tests.

4 CONCLUSION

In this work, the effect of Pre-plasma functionalization on antibacterial activity of fabrics was investigated. The results showed Oxygen plasma treatment causes decrease of Ag particle size, and increase the amount of them. Antibacterial activities of cellulose fabrics were easily achieved with a DC magnetron sputtering device, by coating copper on the surface of a fabric, without any chemical or wet process. In addition, the duration of the process is much shorter than the time needed for the conventional process (more than 100 min) using a nonionic detergent, metallic salts, and at least three washing baths.

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