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Modification of anti-bacterial surface properties of textile polymers by vacuum arc ion source implantation

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ABSTRACT

Ion implantation provides an important technology for the modification of material surface properties. The vacuum arc ion source is a unique instrument for the generation of intense beams of metal ions as well as gaseous ions, including mixed metal–gas beams with controllable metal:gas ion ratio. Here we describe our exploratory work on the application of vacuum arc ion source-generated ion beams for ion implantation into polymer textile materials for modification of their biological cell compatibility surface properties. We have investigated two specific aspects of cell compatibility: (i) enhancement of the antibacterial characteristics (we chose to use *Staphylococcus aureus* bacteria) of ion implanted polymer textile fabric, and (ii) the "inverse" concern of enhancement of neural cell growth rate (we chose Rat B-35 neuroblastoma cells) on ion implanted polymer textile. The results of both investigations were positive, with implantation-generated antibacterial efficiency factor up to about 90%, fully comparable to alternative conventional (non-implantation) approaches and with some potentially important advantages over the conventional approach; and with enhancement of neural cell growth rate of up to a factor of 3.5 when grown on suitably implanted polymer textile material.

Introduction

The generation of intense broad beams of metal ions by vacuum arc plasma-based ion sources is by now a well-developed technology [1]. These kinds of ion sources were developed in the 1980s, virtually simultaneously at the Lawrence Berkeley National Laboratory (LBNL), Berkeley, USA [1,2], and at the High Current Electronics Institute (HCEI), Tomsk, Russia [3,4]. Recent embodiments of such devices include the Mevva-V.Ru ("Metal vapor vacuum arc ion source, Russian version V") [5] at the Plasma Sources Department at HCEI, Russia, and the Mevva-V ion source [6] at Ege University, Izmir, Turkey. The work described here was carried out as a collaborative effort between research teams at Izmir and Tomsk. The Turkish team, at the Bioengineering Department of Ege University, is recognized as expert in modern surface science and surface modification technology, including the treatment of textile materials by ion beams and plasma flows. The Russian team, at the Plasma Sources Group at HCEI, specializes in the plasma physics of ion beam and plasma flow sources. The Izmir-Tomsk groups have more than a decade of successful collaborative history [6–8].

We describe here the results of exploratory research on the surface modification of polymer textile materials with respect to their biological properties in two specific ways. We have explored the suppression of *Staphylococcus aureus* bacterial growth (enhancement of antibacterial activity) by ion implantation into polymeric textile material; and quite conversely the enhancement or acceleration of the growth rate of Rat B-35 neuroblastoma cells on ion-implanted polymer textile material.

Experimental

The ion implantation for this work was carried out using the Mevva-V ion source implantation facilities at both Izmir and Tomsk. Photographs of both of these facilities are shown in Fig. 1. Both sources incorporate a multi-cathode arrangement whereby any one of sixteen separate cathodes (and thus cathode materials and ion species generated) can quickly and simply be brought into operation, thereby allowing rapid change of the implantation ion beam

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Fig. 1. Mevva-V.Ru ion implantation test bench at the Plasma Sources Group, HCEI, Tomsk, Russia (left); and the Mevva-V facility at the Bioengineering Department, Ege University, Izmir, Turkey (right).

species. The sources also incorporate a highly localized magnetic field (around the vacuum arc region) and injection of added gas (into the arc region), thereby providing the capability of generating not only purely metal ion beams but also mixed metal–gas ion beams. The sources can generate repetitively-pulsed beams (typically 250 μs pulses at up to 10 pps) of current up to about 1 A at extraction voltage of up to about 60 kV. (Note that since the metal ions formed in the vacuum arc discharge are typically multiply ionized with mean charge state $Q = 2+$ or 3+ or more, this corresponds to a mean ion energy of up to 150–200 keV, depending on the metal ion species used). The ion beam is a "broad beam", with diameter directly after the extractor of about 7–10 cm; after a relatively short distance from the source the radial beam profile evolves into a Gaussian shape with half-width (FWHM) of course depending on the distance from the source, and here about 20 cm [5] at the target, as is typical for vacuum arc ion sources. These parameters are eminently suitable for our exploratory investigation of ion implantation into polymers. The implantation facilities at both Izmir and Tomsk are equipped with time-of-flight charge-to-mass spectrometers [9], allowing real-time monitoring of ion beam composition during the beam pulse and throughout the implantation process.

Ion implantation into polymers is somewhat problematic compared to implantation into metallic or even ceramic materials. In contrast to non-organic materials, polymer chains can be easily destroyed by an energetic and intense ion beam. Polymers also have low thermal conductivity and can therefore be easily heated excessively by the beam. The absence of free conducting electrons in these materials is responsible for their high dielectric properties. Thus there is an important concern of the possibility of thermal destruction of the polymer by heating of its surface by the beam. For these reasons the mean beam current is kept low by using a relatively low pulse repetition rate during the implantation. Further, when the pulse repetition rate is sufficiently low any charge build-up on the insulating target can leak off in the inter-pulse period, thereby avoiding the accumulation of charge and the build-up of potential on the target surface.

For the present work, upper limits for the ion implantation dose and pulse repetition rate were determined as a compromise between overall processing time and the goal of producing significantly changed polymer surface properties. The lower dose limit provides only minor surface modification, though still enough for characterization and for some practical applications. We determined experimentally that the antibacterial properties of polymer surfaces begin to be apparent, though at very low level, at implantation doses as low as about 10^{14} ions/cm^2. Here we describe results obtained for implantation dose between 5×10^{15} and 5×10^{16} ions/cm^2. We also determined that the desired polymer modification effects start to appear at an ion beam energy of about 10–20 keV; further increase of the ion energy leads to unwanted surface overheating and hence was not used.

Testing procedure of implanted polymers

The bacterial species that we chose for investigation was *S. aureus* ("golden staph") because it is one of the most prevalent and dangerous of hospital bacteria [10]. Testing procedures for the antibacterial properties of the polymer surfaces were carried out according to specifications of the American National Standard [11].

All swatches of polyester (75% polyester and 25% cotton) were sterilized in an autoclave (120 °C, 15 min) before experiments. Rectangular samples (3×3 cm^2) of treated (ion implanted) and untreated sterile swatches were placed in sterile Petri dishes separately and inoculated in 400 μl bacterial suspension (Fig. 2). Bacterial suspension was prepared from activated culture according to the McFarland standard with $(1–2) \times 10^5$ CFU/ml (CFU = colony forming units). The dilution of the test bacteria was made in sterile saline solution (0.87% of NaCl in distilled water). Inoculated Petri dishes were covered to prevent evaporation. All dishes were incubated at 37 °C for 24 h and then the swatches were transferred aseptically to a jar containing 40 ml sterile saline solution. One series of untreated swatches was used for T_0 detection (contact time detection). As soon as possible after inoculation ("0" contact time, T_0), 40 mL of normal saline solution was added to each of the jars, which were then shaken vigorously for 1 min. Serial dilutions (1, 10, 100) were made with saline solution and were plated (100 μl) on nutrient agar plates in duplicate. This last step was applied to all the incubated swatches in a similar way. All plates were incubated for 24–48 h at 37 °C.

Meanwhile, all samples were washed 30 times with detergent at 49 °C while shaking, according to the AATCC (American Association of Textile Chemists and Colorists) 124 Test method [12]. The experiment was repeated for the washed samples to detect the effect of the washing on the antibacterial activity. Bacterial colonies were assessed by the number of bacteria counted per sample. The Antibacterial Efficiency Reduction factor, R, was calculated as:

$$R = 100 \times \frac{B - A}{B} \quad (1)$$

where B is the number of bacterial colonies counted from Petri dishes belonging to untreated swatches immediately after inoculation (T_0), and A is the number of bacterial colonies counted from Petri dishes belonging to treated swatches 24 h after inoculation

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