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Low temperature plasma for textiles disinfection

Justyna Szulc [a, *], Wiesława Urbaniak-Domagała [b], Waldemar Machnowski [b], Henryk Wrzosek [b], Karolina Łącka [a], Beata Gutarowska [a]

[a] Lodz University of Technology, Institute of Fermentation Technology and Microbiology, Wolczanska 171/173 St., 90-924 Łódź, Poland
[b] Lodz University of Technology, Department of Material Commodity Science and Textile Metrology, Zeromskiego 116 St., Łódź, Poland

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ABSTRACT

The aim of the study was to evaluate the effectiveness of low temperature plasma (LTP) disinfection and its impact on cotton, linen, and silk. Research included: optimization of LTP parameters (time: 5, 10 min, gases: oxygen, nitrogen, argon and their mixtures); antimicrobial effectiveness of LTP for artificially aged and 19th-20th century textiles; impact of LTP on the mechanical, optical and structural (SEM, FTIR) textiles properties, and their susceptibility to colonization by microorganisms after LTP. The effectiveness of LTP disinfection was evaluated for the following microorganisms: *Streptomyces* sp., *Bacillus megaterium*, *Pseudomonans fluorescens* (silk), *Aspergillus niger*, *Penicillium funiculosum* and *Trichoderma viride* (cotton and linen). LTP for 10 min with oxygen provided the highest antimicrobial effect, and the number of microorganisms was reduced by 1–4-fold on the logarithmic scale (R = 69.64–99.99%), depending on the strain and textile. LTP increased textiles' breaking strength. LTP did not caused significant changes in molecular structure of the fiber-forming polymers (cellulose and fibroin). In addition, it also lightened the colour and microdamaged the disinfected textiles. Nevertheless, LTP prevented microorganisms from colonizing the textiles for up to 21 days. Thus, this method can be a suitable alternative to currently used disinfection methods for textile, but should be used carefully for historical textiles.

1. Introduction

Natural fibres of plant and animal origin (cotton, flax, sisal, hemp, jute, fur, wool, silk and others) are present in many historical objects, e.g. carpets, tapestries, decorative fabrics, clothing and ecclesiastical vestments, which make up cultural heritage stored in museums all over the world.

Due to the chemical composition, historical textiles are easily colonized by microorganisms, leading to their biodeterioration. This process mainly depends on the origin and type of fabrics, contact with microorganisms and insects, as well as storage conditions, e.g. temperature and relative humidity of the air, light and dust (Garside, 2010). The problem of biodeterioration mostly affects natural fibres containing cellulose (cotton, linen) and keratin (wool), due to attack of moulds. The problem is less significant in case of fibroin and sericin (silk), which are mainly degraded by bacteria (Ahmed and Darwish, 2012; Bílková, 2012; Szostak-Kotowa, 2004). Moulds from the genera *Alternaria, Aspergillus, Chaetomium, Penicillium, Trichoderma, Cladosporium* and bacteria *Bacillus, Cellulomonas, Protemonas, Pseudomonas* and *Streptomyces* were previously isolated from natural textiles at high frequencies (Forlani et al., 2000; Montegut et al., 1991; Pangallo et al., 2013; Seves et al., 1998; Szostak-Kotowa, 2004). Biodeterioration usually begins due to carbon and nitrogen assimilation from fibres. The intensive microbial growth and metabolic activity - production of extracellular enzymes (cellulolytic and proteolytic), pigments and acids (Pekhtasheva et al., 2012) lead to changes in the structure, colour and pH, decrease in strength and production of Microbial Volatile Organic Compounds (MVOCs) (Bajpai et al., 2011).

Disinfection may inhibit the active growth of microorganisms and biodeterioration of textiles. It can be carried out using various chemical (ethylene oxide fumigation, formaldehyde, essential oils, silver nanoparticle misting) and physical methods (γ-irradiation, UV radiation, dehydration, freezing, autoclaving and refrigeration) (Pietrzak et al., 2016). Chemical disinfection methods are effective and easy to use, and therefore are very popular. However, they are associated with compounds which may be toxic to human health and the environment. Nowadays, there is a tendency to reduce the use of chemical disinfection methods and replace them with safe physical methods. It has already been shown that some physical

* Corresponding author.
E-mail address: justyna.szulc@p.lodz.pl (J. Szulc).

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methods can be successfully used for disinfection of historical objects (Garside, 2010; Pietrzak et al., 2016).

Currently, low temperature plasma (LTP) is becoming more popular in chemistry, for the decomposition of gaseous pollutants, surface modification, in medicine for the treatment of cancer cells, prevention of nosocomial infections and the therapy of infected wounds (Becker et al., 2005; Fridman et al., 2008; Morfill et al., 2009; Vandamme et al., 2012). This method works at low temperature and uses small amounts of non-toxic gases which reduce both environmental impacts and safety risks (Rossi et al., 2009). Moreover, in LTP the applied gas or gases are activated by electrical discharge and have a biocidal effect (Moisan et al., 2001). UV radiation, reactive oxygen species (ROS) and reactive nitrogen species (RNS), such as atomic oxygen (O), ozone (O_3), hydroxyl (OH), NO and NO_2 are relevant to the process, and play a major role in the antimicrobial activity of LTP (Brandenburg et al., 2007; Laroussi and Leipold, 2004). Miao and Yun (2011) indicated that ROS and RNS generated by plasma caused localized progressive disintegration of the cell wall of microorganisms.

Numerous applications of LTP in textile treatment are reported, e.g. shrink-resistant finish of wool fabrics, improvement in the dying properties of fibres and the modification of polymeric materials in a dry system (Rashidi et al., 2004).

The major problem for historical textiles is the lack of a disinfection method, which meets all requirements: has high antimicrobial activity, causes no changes of mechanical, structural and optical properties of materials, is safe for human health and the environment, and continues to prevent microbial growth even after the treatment (Pietrzak et al., 2016).

There is no study on the effectiveness of LTP disinfection of historical textiles, but it may be a promising alternative method for textile disinfection.

The aim of this study was to evaluate the effectiveness of LTP disinfection, and its impact on textile properties. Research included: the optimization of plasma disinfection parameters (time, gases); determination of the effectiveness of LTP for model textiles (unaged and aged) and historical objects; and evaluation of the impact of plasma on textile properties (mechanical, structural, optical). In addition, we checked if LTP changed the susceptibility of textiles to colonization by microorganisms.

2. Materials and methods

2.1. Textiles

Natural origin cotton, linen, and silk were used in the study. The textiles did not contain dyes or auxiliary agents. The cotton (130 g m^{-2}, Andropol S.A., Poland) and linen (225 g m^{-2}, Swiat Lnu, Poland) fabrics were not bleached, and had the colour of natural fibres. The silk fabric (52 g m^{-2}, Fei–Long Inc., China) was degummed, without sericin.

We used textile samples of 10 cm $^{-2}$ (2 cm × 5 cm) for microbiological analysis, and 30 cm^{-2} (2 cm × 15 cm) for determination of the effect on mechanical, optical and structural properties.

Aged textiles were used for microbiological analysis, as well as for mechanical, optical and structural tests. Textile ageing was conducted using a thermal process to simulate 50 years (El-Gaoudy et al., 2011). The process was conducted at 130 °C for 52 h (electronic convection oven, SLW 32STD; POL-EKO Aparatura, Poland).The effectiveness of plasma disinfection was evaluated for four historical textiles provided by the Department of Costume and Folk Textiles of the Archaeology and Ethnography Museum in Lodz, Poland. The textile samples (from 19th - 20th century) included: embroidered cotton pillowcase (1950), polyester ribbon (1980), men's cotton trousers (1940) and a starched silk headband (1900).

2.2. Microorganisms

Microorganisms used in this study were selected on the basis of high cellulolytic (moulds) and proteolytic (bacteria) activity, responsible for cotton, linen and silk biodeterioration (Montegut et al., 1991; Seves et al., 1998). Three bacterial strains and three mould strains obtained from Pure Culture Collection at Institute of Fermentation Technology and Microbiology, Lodz University of Technology (ŁOCK) and American Type Culture Collection (ATCC) were used: *Streptomyces* sp. (ŁOCK 0894), *Bacillus megaterium* (ŁOCK 105), *Pseudomonans fluorescens* (ŁOCK POM 2123) (silk tests); *Aspergillus niger* (ATCC 16404), *Penicillium funiculosum* (ŁOCK 0587) and *Trichoderma viride* (ŁOCK E153) (cotton and linen tests).

Microorganisms were cultured on TSA medium (Tryptic Soy Agar, Merck, Germany) at a temperature of 30 °C for 48 h (bacteria) and on MEA medium (Malt Extract Agar, Merck, Germany) at a temperature of 27 °C for 5 days (moulds). Bacterial and mould colonies were transferred into 10 ml of TSB (Tryptic Soy Broth, Merck, Germany) medium and MEB (Malt Extract Broth, Merck, Germany) media with 0.01% of Tween®80, respectively. The average densities of microorganisms in the inocula were 1.23 × 10^7 - 4.88 × 10^7 cfu cm^{-3} (moulds) and 5.57 × 10^8 - 3.18 × 10^9 cfu cm^{-3} (bacteria).

2.3. Microorganism cultures on textiles

Before disinfection, textile samples were inoculated with a 250 μl of inoculum. The microorganisms were cultivated on textiles with the addition of 100 μl M_0 medium ($MgSO_4$ $7H_2O$ - 5 g; (NH_4) $2SO_4$ - 3 g; KH_2PO_4 - 1 g; glucose - 20 g per 1000 ml H_2O). M_0 medium was added to the materials to initiate microbial growth and establish the maximum mass moisture of the tested textiles. Samples were incubated for 21 days in a climatic chamber KBF720 (Binder, Germany), at a temperature of 28 °C and relative humidity of the air RH = 80%.

In order to determine the bacterial and fungal growth on textiles, the quantitative method, AATCC Test Method 100-2012 (2012) was used. Samples after 0, 7, 14, 21 days of incubation (controls) and after plasma disinfection were placed in 50 ml of sterile saline (0.85% NaCl) with 0.01% Tween®80 and shaken for 10 min to wash out the microorganisms from the tested materials. After serial dilutions, the bacterial strains were plated on TSA (incubated for 48 h at 30 °C), and moulds on MEA (for 72 h at 27 °C). After incubation, colonies were counted and the results were expressed as cfu $sample^{-1}$. The analyses were conducted in triplicates.

The reduction in the number of microorganisms after plasma disinfection R(%) was determined using the formula: $R = \frac{N_0 - N_d}{N_0} \times 100\%$, where: N_0 is the number of microorganisms in the sample before disinfection (cfu per sample); N_d is the number of microorganisms in the sample after disinfection (cfu per sample).

2.4. Low temperature plasma disinfection

The disinfection was carried out using a commercial apparatus CD 400PLC ROLL CASSETTE (Europlasma, Belgium). The plasma was generated in RF 13.56 MHz electric field (C type discharge), under reduced pressure. The power was applied by a generator and regulated up to 200 W. During this process, pressure was measured using a Baratron probe, the media flow rate was measured using MFC controllers, the applied and reflected power, as well as, the temperature in the reactor were also controlled and measured. Each fabric sample was placed, in a free state, in the inter-electrode space and de-aerated for 60 min in vacuum. Next, the gas was introduced; when stable flow and pressure were reached, discharge

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