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Deterioration of contemporary and artificially aged cotton by selected fungal species

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ABSTRACT

The scope of this study was an analysis of the deterioration of cotton fibres caused by selected strains of fungal species from historical cotton textile objects. Aged and non-aged cotton fabric specimens were inoculated with representative strains of the six highest frequency fungal species isolated from museum textile objects from different Slovene museums. The selected fungi were *Aspergillus clavatus*, *Cladosporium cladosporoides*, *Fomes fomentarius*, *Hypoxylon fragiforme*, *Penicillium chrysogenum* and *Penicillium corylophilum*. Their effects on contemporary and artificially aged cotton was examined by Raman spectroscopy, infrared spectroscopy, scanning electron microscopy, and tensile behaviour. These fungal species affected the cellulose structure and fabric properties differently. Among the fungi analysed, *P. chrysogenum* was least harmful to cotton-cellulose samples, while *C. cladosporoides*, *F. fomentarius* and *H. fragiforme* showed the greatest effects. The main structural changes were hydrolysis, depolymerisation, and decreased molecular order. Although not all of these fungal species are dangerous to cotton fibres, and hence to museum objects, they all cause visible changes that can lead to disintegration of these objects. Another important factor that accelerates the depolymerisation of cellulose macromolecules in cotton fibre is inappropriate storage conditions, which should be avoided at all costs, to preserve historical objects and artefacts.

1. Introduction

Biodeterioration of organic and inorganic materials is a natural process. However, in the case of historical objects that have social, historical, cultural and educational value for the generations of both today and the future, this natural circle is not desirable. Several professions that work hard to preserve objects that are a part of our cultural heritage are therefore working against strong natural forces, among which are fungi, causing deterioration and visible changes on historical textile objects.

Cotton is a widespread natural textile material that has been commonly used over the last few thousands of years [8]. Although known already to the ancient Greeks, cotton became popular in Europe only in the Middle Ages [26]. Cotton is a cellulose fibre that is made of almost pure cellulose [8]. Cellulose is a macromolecule made up of a long chain of glucose molecules. The number of glucose molecules linked together in macromolecule is referred to as degree of polymerization. The arrangement of cellulose macromolecules varies from completely ordered (crystalline) to completely unordered (amorphous). In crystalline regions, the glucose macromolecules are closely packed, parallel to one another and with intermolecular (mainly hydrogen) bonds linked to a crystal-like entities. Whereas in amorphous regions the macromolecules are more arbitrary arranged with less intermolecular bonds.

Slovene museums store many textile objects that are made of cotton [21]. Since the histories of the use of these objects differ, they are in different states of preservation. Their biodeterioration is influenced by the chemical and physical properties of the fibres [36], and this is promoted by further deterioration via the actions of microorganisms [37], which can be facilitated by inappropriate storage conditions.

In summary, historical textiles are very sensitive organic materials, and their preservation is a very complex and demanding task.

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Amongst the invading microorganisms on cotton, fungi are the most severe degraders, and particularly of historical objects [40,41]. To prevent the growth of fungi [17,23], special measures need to be taken in storage and exhibition rooms; e.g., low relative humidity and low temperature. However, some known air-borne contaminant fungal species from the genera *Aspergillus* and *Penicillium* are xerotolerant and can grow under conditions of low relative humidity. Thus the right balance between storage conditions of historical textiles and conditions that prevent the growth of the most important contaminant fungi needs to be established.

The aim of the present study was to analyse the influence of six different fungal species on contemporary non-aged and artificially aged cotton fabrics. These fungi represented the prevailing species among isolates from 37 museum textile objects across five different Slovene museums and several religious institutions (churches and monasteries). The biodeterioration properties of these individual species were investigated through observations of the chemical and morphological structure of the cotton fibres, as well as the mechanical properties of the cotton yarn.

2. Materials and methods

2.1. Materials

Desized, non-bleached contemporary cotton fabric (plain weave, 44 × 31 threads/cm) was selected for analysis. The large (2.5 cm × 5.0 cm) cotton specimens were prepared from this fabric.

2.1.1. Accelerated ageing

Half of the cotton specimens were artificially aged to simulate conditions that resemble those of naturally aged fabrics. These cotton specimens were attached to Whatman paper (Whatman) and aged at 80 °C and 65% relative humidity for 25 days in a type VC 0020 Vötsch Climatic chamber (Vötsch).

2.1.2. Isolation and inoculation of fungi

The fungi were isolated from historical objects using sterile cotton swabs that were either soaked in sterile physiological solution, or were dry in the case of more sensitive objects. These fungi were inoculated onto solid media (malt extract agar = MEA according to Blackeslee [34], oatmeal agar = OA (Difco), potato dextrose agar = PDA (Biolife), and incubated for 21 days at room temperature. Upon isolation of pure cultures, the fungi were stored under cryoprotection at −80 °C. All of the strains are stored in the EX Culture Collection of the Department of Biology of the Biotechnical Faculty, University of Ljubljana (www.ex-genebank.com).

The aged and non-aged cotton specimens were inoculated with single strains of the six different fungal species that were selected from 25 fungal species isolated from textile objects from different Slovene museums [18]. These selected fungi were: *Aspergillus clavatus* (EXF-5895), *Cladosporium cladosporoides* (EXF-5883), *Fomes fomentarius* (EXF-5903), *Hypoxylon fragiforme* (EXF-5882), *Penicillium chrysogenum* (EXF-5913), and *Penicillium corylophilum* (EXF-5897). The strains of *A. clavatus*, *C. cladosporoides*, *P. chrysogenum* and *P. corylophilum* were the four dominant species isolated from infected cotton textiles stored and exhibited in Slovene museums and religious institutions, while *F. fomentarius* and *H. fragiforme* were isolated during the same investigation, but only from non-cotton objects that contained wood, as well as proteinaceous and cellulose textiles [20,21].

For inoculation of the cotton specimens, the fungi from the stored stock cultures were freshly grown in test-tubes containing MEA, for 14 days at room temperature. The inoculum was then prepared by suspending spores or mycelium pieces in a mixture of 5 ml physiological solution (0.9% NaCl solution) and 15 ml distilled water [20]. Spore/mycelium suspensions (250 μl) of each fungus were inoculated onto two pieces of the cotton, which were then incubated in sterile moist chambers, in Petri dishes with wet filter paper (Fig. 1). Four moist chambers were used that were each designed to contain two pieces of the cotton specimens inoculated with the suspension of a single fungal strain. The fungal strains were prepared for the aged and non-aged cotton. Eight cotton specimens of each type (aged and non-aged) were inoculated with each fungal strain. The Petri dishes were incubated at a constant temperature of 25 °C. The moisture of each chamber was carefully checked and maintained throughout the whole incubation period.

A set of control samples that were aged and non-aged were incubated under the same conditions after being soaked in sterile distilled water, instead of the spore suspension.

2.1.3. Termination of fungal growth

The biodeterioration process was stopped using sterilisation by autoclaving at 121 °C for 20 min, which was also designed to prevent contamination of the working environment with these fungi. As indicated in Table 1, half of the inoculated samples were autoclaved after 8 weeks incubation, and the other half after 20 weeks incubation. By observing these inoculated samples by Fourier transform infrared (FTIR) spectroscopy prior to and after autoclaving, it was initially shown that the process of sterilisation itself did not cause additional damage to the cotton material, and thus did not influence the results. Nevertheless, the non-inoculated reference samples were also autoclaved.

2.2. Methods

2.2.1. Raman spectroscopy

Raman spectroscopy was performed using a HR 800 dispersive LabRam spectrometer (Horiba Jobin-Yvon) with an air-cooled CCD detector attached to an optical microscope. A diode laser in the near infrared region (785 nm) was used. All of the samples were scanned under the microscope at 10× magnification to cover the Raman shift between 100 cm^{-1} and 2000 cm^{-1} wavenumbers. The hole was 1000 μm and the grating was 600 g/mm. The laser energy varied from 8.9 mW to 17.9 mW and the acquisition time varied from 50 s to 300 s, depending on the characteristics of each sample. Before the data acquisition, drench quenching was performed, to diminish the luminescence effects and to reduce the background noise. Drench quenching involves prolonged exposure to a reduced

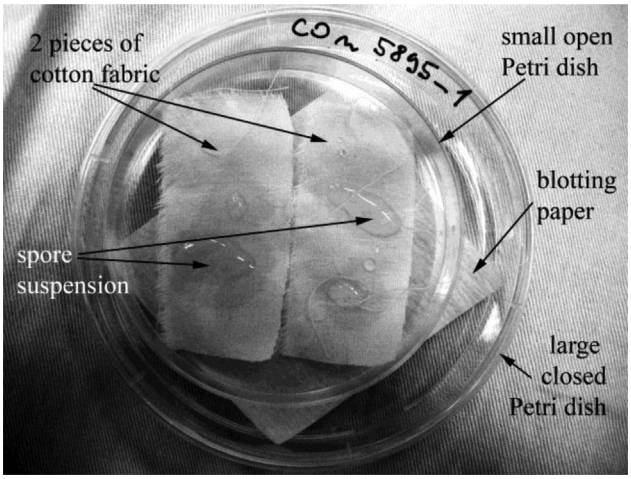

Fig. 1. Moist chamber used for the incubations of the inoculated cotton specimens.