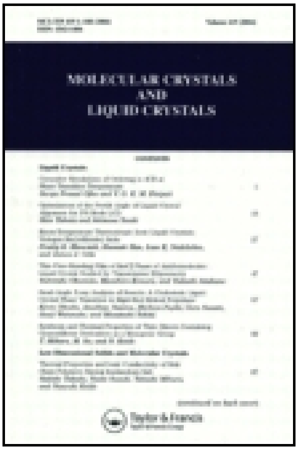

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Eco-Friendly Antimicrobial Finishing of Natural Fibres

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Natural fibres well protected against biodeterioration and with barrier properties can be used in many new applications. The study aims at using eco-friendly biocides, not used in textile industry so far, for antimicrobial finishing of natural fibres. The research was carried out on flax fibre and linen fabric protected with biocides based on amono-boron-copper compounds, natural biocides and ionic liquids as new QACs. The flax fibre was subjected to action of mixture of fungi most often causing decomposition of cellulose in high humidity conditions. Evaluation of antibacterial properties of treated fabrics was done using qualitative method in presence of synthetic sweat against groups of bacteria present on human skin.

Keywords: antimicrobial finishing; biodeterioration; ionic liquids; natural fibers

INTRODUCTION

Natural fibers are susceptible to biodeterioration caused by microorganizms especially in high humidity. Using proper antimicrobial finishing allowes to obtain wider area of their application. The biodeterioration caused by fungi affects finishing materials containing natural fibres, which are used in automotive or building industries. Moreover natural fibres especially applied in medical application should be resistant to bacteria attack. Additionally, new regulations definitely limit application of many commonly used biocides. Therefore there is growing demand for replacing old and not always envirомentaly safe compounds with new more ecological ones. Applying eco-friendly biocides in finishing processes of natural fibres allows

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for obtaining new ecological barrier properties, as: antibacterial and antifungal.

Quaternary ammonium salts (QACs) are widely known to be bioactive and have high anti-microbial activity. On the other hands, in case of toxicity of QACs, despite profound antimicrobial activity, they belong to compounds non toxic for homeothermal organisms. First quaternary ammonium salt was obtained by Menschutkin in 1890 [1]. In 1916, Jacobs discovered antibacterial activity of QACs [2]. In 1935, these compounds were first time usedin disinfection [3], and in 1977 in wood preservation [4,5]. In 1997, Seddon discovered ionic liquids which are new group of QACs [6]. Ionic liquids consist usually of an organic cation and a inorganic or organic anion, which are liquids at temperature below 100°C. Because of their interesting properties i.e., a wide liquid range about 300°C, non volatility, solvents for organic and non organic compounds, high thermal stability, high ionic conductivity, antielectrostatic properties, easy recyclibility, the interest in these salts increases every year.

Studies proved also that ionic liquids are characterized by antimicrobial activity [7,8]. These compounds were successfully used in protection of cellulose materials like wood [9] and paper [10] against biodeterioration. Antimicrobial activity of ionic liquids strongly depends on their structure, especially of anion type. $[NO_3]^-$ and $[NO_2]^-$ salts are very effective agents against bacteria and fungi [11]. Here, we report, applying ammonium based ionic liquid with nitrate anion in finishing process of natural fibres to improve their bactericidal functionality.

Natural biocides find increasingly wider application in protection e.g., of medical, cosmetic, food and packaging products. An important role is played by essential oils of plant origin. Active substances (alkaloids, flavonoids, terpenes) present in such essential oils as: oils of thyme, oregano, clove and mint are natural source of antimicrobial properties [12].

The use of essentials oils from clove, cinnamon and oregano as antimicrobial solutions in paper packaging was studied. Cinnamon oil used in paraffin coating totally inhibited *Aspergillus flavus* [13]. Also the influence of essential oils from sage, mint, hyssop, camomile and oregano was studied for growth of Gram-negative and Gram-positive bacteria. In case of mint oil bacteriostatic activity was observed [14]. Antifungal activity of mint oil was observed and what follows the possibility to apply it as natural protection of food against infections caused by e.g. mildew: *Aspergillus spp.* and *Penicillium spp.* [15].

MATERIALS AND METHODS

Evaluation of Antibacterial Properties

Evaluation of antibacterial properties was done using screening method according to AATCC 147/1998 standard in presence of synthetic sweat. 100% linen fabric was used in this study. Antibacterial agent used in finishing process was didecyldimethylammonium nitrate [DDA][NO_3] purchased from P.I.W. DELTA company. The investigated salt was applied by padding from water solution in amount of 8 μg; 80 μg and 800 μg on the 1 g of the dry linen fabric. Bacteria species present on human skin were chosen for the tests: *Corynebacterium xerosis* PCM555, *Bacillus licheniformis* Łock 0808, *Micrococcus flavus* Łock, *Staphylococcus haemolyticus* PCM 2113, *Staphylococcus aureus* ATCC 6538 as a Gram positive bacteria and *Escherichia coli* ATCC 10536, *Klebsiella pneumoniae* PCM 555, *Pseudomonas aeruginosa* Łock 0885 as Gram negative ones. Microogranisms were inoculated on nutrient agar using parallel streak method. The samples measuring 25×50 mm were soaked with synthetic sweat characterized by acidic pH (freshly prepared) in amount of 0.2 mL and allocated on inoculated nutrient agar perpendicularly to direction of bacteria inoculation. After 24 h of incubation in 37 ± 2°C inhibition zone of bacteria growth under the samples was evaluated.

Evaluation of Antifungal Properties

Flax fibre protected with biocides Amono-boron-copper compounds (MCB), mint oil (*Mentha piperita*) and mint extract (*Mentha piperita*) were tested. Amono-boron-copper compounds (MCB) were applied by padding from 20% concentration of water solution in amount of 5 mL on the 1 g of the dry flax fibre. Mint oil and extract were applied by padding from 20% concentration of methanol solution in amount of 5 mL/g. The tests on flax fibre protected with biocides were conducted according to EN 14119:2003. The tested samples of flax fibre were exposed to the action of the following fungi mixture: *Aspergillus niger* van Tieghem, *Chaetomium globosum* Kunze, *Gliocladium virens* Miller, *Paecilomyces variotii* Bainier, *Penicillium ochrochloron* Biourge. The samples of flax fibre were allocated on agar medium and inoculated with a suspension of testing fungi. Incubation of tested samples in temperature 29 ± 1°C and relative air humidity 90%, was conducted for 4 weeks. After the test, evaluation of antifungal properties was done on the base of visual assessment by determining degree of mildew growth and specific strength of the flax fibre.

RESULTS

The antibacterial activity of linen fabric treated with [DDA][NO_3] was studied by evaluation of inhibition zone of bacteria growth under the samples. In the literature, minimum inhibitory concentration in case of this salt against *E. coli* was established at 8 μg mL^{-1} [11]. Following this result, in the presented paper 8 μg [DDA][NO_3] on the 1 g of the dry linen fabric was used as a basic concentration and ten and hundred times bigger concentration. The studies were conducted on Gram positive and Gram negative bacteria present on human skin. The results demonstrate that using [DDA][NO_3] in antimicrobial finishing of linen fabric is a very effective method (Table 1). Addition of as little as 8 μg of this salt is effective and caused inhibition of both Gram-positive and Gram-negative bacteria growth under sample. Hundred times bigger concentration caused that inhibition zone of bacteria growth exceeded 5 mm around the sample.

The degree of biological activity of the ionic liquid applied in smaller concentration depends on the kind of microbial organisms. Results showed higher antibacterial activity against Gram positive bacteria and lower but still effective against Gram negative. Generally, the mechanism of biological effect of the QACs lies in affecting synthesis

TABLE 1 Antibacterial Properties of Linen Fabric Treated with [DDA][NO_3]

	Bacterial growth under sample			
Bacteria species	Untreated linen fabric	Linen fabric with 800 μg [DDA][NO_3] on the 1 g of the dry fabric	Linen fabric with 80 μg [DDA][NO_3] on the 1 g of the dry fabric	Linen fabric with 8 μg [DDA][NO_3] on the 1 g of the dry fabric
Corynebacterium xerosis	+	--	–	–
Bacillus licheniformis	+	+/–	+/–	+/–
Micrococcus flavus	+	--	–	–
Staphyloccocus haemolyticus	+	--	–	–
Staphyloccocus aureus	+	--	–	+/–
Escherichia coli	+	--	+/–	+/–
Klebsiella pneumoniae	+	--	+/–	+/–
Pseudomonas aeruginosa	+	--	+/–	+/–

+ bacterial growth.
– no bacterial growth.
-- inhibition zone of bacteria growth exceeded 5 mm.
+/– inhibition of bacterial growth.

of bacteria cell walls [16]. Protection mechanism of Gram positive bacteria is based on creating clusters or bacterial resting forms, so they can be easier destroyed. Gram negative bacteria are characterized by a very complex structure of cell wall, and especially *Pseudomonas*, are more resistant to all presently used biocide preparations. On the other hand, there is correlation between hydrophobic character of bacteria cell surface and their susceptibility to QACs action [17]. Surface of Gram negative bacteria cell is characterized by higher hydrophobicity, than Gram positive. Therefore, QACs as a hydrophilic compounds can be easier adsorbed on the cells of Gram positive bacteria. Linen fabric treated with 800 μg [DDA][NO_3] on the 1 g of the dry fabric showed strong biological effect against both Gram positive and Gram negative bacteria. These results show that [DDA][NO_3] is potentially applicable in finishing process of lignocellulosic textiles. The antifungal activity of flax fibre protected with biocides was studies by visual evaluation of fungi growth in scale from 0 to 5, with using stereoscope microscope. Moreover, the loss of specific strength was evaluated. Flax fibre protected with MCB (amono-boron-copper compounds) showed very high antifungal activity – no visible growth evaluated microscopically (0 degree) and no loss of specific strength (0%). In comparison with MCB biocide, mint oil used for protecting flax fibre showed slightly lower antifungal activity – growth was not visible with naked eye, but single traces of fungi were visible microscopically (1 degree) and slightly higher loss of specific strength was observed (22%). Mint extract did not show antifungal properties (Table 2).

Thanks to application of the eco-friendly biocides, studied in this paper, for finishing process of lignocellulosic textiles, it is possible to obtain a multifunctional product with antibacterial and antifungal properties. Therefore this application allows to improve the functionality of the natural fibres.

TABLE 2 Antifungal Properties of Flax Fibre Protected with Biocides

Biocide	Degree of fungi growth (scale from 0 to 5)	Loss of specific strength (%)
MCB (amono-boron-copper compounds)	0	0
Mint oil (*Mentha piperita*)	1	22
Mint extract (*Mentha piperita*)	4	83
Control–unproteced	5	100

CONCLUSION

1. Ionic liquid [DDA][NO_3] is very promising and may replace old and not always enviromentaly safe compounds, commonly used in finishing processes of fibres.
2. Linen fabric treated with [DDA][NO_3] showed high antibacterial activity and distinctly inhibition zone of growth both Gram positive and Gram negative bacteria. Addition of 8 μg [DDA][NO3] on the 1 g of dry fabric is effective.
3. Flax fibre protected with MCB (amono-boron-copper compounds) showed very high antifungal activity-no mildew growth and no loss of specific strength.
4. The essential oil – mint oil – used for protection of flax fibre is very promising-fungi growth is not visible with naked eye.
5. The essential oils, including mint oil for obtained antifungal properties of natural textiles will be continued.

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