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Antifungal activity of ionic liquid applied to linen fabric

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ABSTRACT

This study aimed at improving the functionality of linen fabric by antimicrobial finishing with the use of ionic liquid, i.e., quaternary ammonium salt. Antimicrobial activity of ionic liquids strongly depends on their structure. An ammonium-based ionic liquid with nitrate anion named didecyldimethylammonium nitrate – [DDA][NO_3] –was tested. The study included testing the susceptibility of linen fabric protected with this salt to the biodeterioration process with special attention paid to fungi resistance. Finished linen fabric was tested in relation to the action of five mildew mixtures. The degree of microorganism growth and its effect on physical–mechanical properties of the fabrics were evaluated. The antimicrobial effectiveness of ionic liquid applied to linen fabric was determined by the use of SEM. Applying this biocide in the finishing processes of natural textile materials allows the attainment of antimicrobial barrier properties.

1. Introduction

Linen fabrics, due to their special properties, i.e., high hygroscopicity, cool and pleasant touch, excellent air permeability, and low accumulation of electrostatic charges on the surface, when used for clothing, provide optimum wearing comfort. Because linen products create the best microclimate for the skin, they have a positive effect on the human organism.

Unfortunately, though, natural fibers such as linen or cotton are more susceptible to microbial attack than are man-made fibers. Microbial growth on fabrics and other textile products becomes evident as surface changes, most often discoloration, and associated unpleasant odors (Szostak-Kotowa, 2004). The chemical changes occurring with the growth of microorganisms result in decreased fabric strength and lead to partial or total destruction of the material. Additionally, the increased vulnerability of textiles to microbial attack can cause cross infection, transfer of diseases, allergic reactions, and odor on humans due to infestation by microbes (Thilagavanthi et al., 2006).

These detrimental effects can be avoided or controlled through the efficient use of antimicrobial finishing of textiles with specific agents (Gao and Cranston, 2008). The most frequently studied and described agents for finishing of cellulosic textiles are chatoyant and silver nanoparticles (Gorensek and Recelj, 2007; Gouda and Keshk, 2010; Dastjerdi and Montazer, 2010; Silva et al., 2011; Wazed et al., 2011; Ibrahim et al., 2012). The literature also shows the antimicrobial functions of cellulose based-textiles treated with quaternary ammonium compounds (QACs) (Gao and Cranston, 2008). A number of recent studies have also demonstrated the potential of ionic liquids (ILs), which are QACs, to exhibit excellent antimicrobial activity (Pernak et al., 2003, 2004a; Gilmore, 2011). These compounds were successfully used to protect cellulose materials such as wood (Pernak et al., 2004b) and paper (Przybysz et al., 2005) against biodeterioration. Apart from antimicrobial properties, wood treated with ILs showed some useful properties, such as higher electrical conductivity, improved wettability, and low surface roughness, in comparison with untreated wood (Croitoru et al., 2011).

Ionic liquids are characterized by remaining liquid over a wide temperature range (about 300 °C), being non-volatile, having a high thermal stability, high ionic conductivity, anti-electrostatic properties, and easy recyclability. In addition, despite their profound antimicrobial activity, they belong to the class of compounds that are nontoxic for homeothermic organisms. They can be solvents for organic and nonorganic compounds, so have been described as alternative “green” solvents for clean technology (Seddon, 1997). New regulations definitely limit application of many commonly used biocides i.e., EU Directive 98/8/EC on introduction of biocidal products into the market and withdrawal of products based on substances exceptionally toxic to humans and the environment. Therefore, there is growing demand for replacing old and not always environmentally safe compounds with new, more ecologically benign ones.

The properties of ILs strongly depend on their structure, and anion and cation type. Interestingly, ILs with herbicidal anions –

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named herbicidal ionic liquids (HILs) have been synthesized (Pernak et al., 2011). The combination of two active chemicals in the form of cation and anion in a single moiety reduced the number of additional chemicals, such as adjuvants or surfactants, required per application. Herbicidal ionic liquids containing 4-chloro-2-methylphenoxyacetic acid (MCPA) as anion exhibited higher biological activity than currently used salts of MCPA, and involved pesticides with a multiorganism activity. The acute toxicity of HILs might be controlled by the appropriate selection of cation type.

The structure of the ILs determines their antimicrobial activity. $[NO_3]^-$ and $[NO_2]^-$ salts are very effective agents against bacteria and fungi (Pernak et al., 2006).

Didecyldimethylammonium nitrate [DDA][NO_3] is characterized by high antibacterial activity, which makes possible the antimicrobial barrier properties of linen fabric to keep human skin micro flora bacteria from growing (Foksowicz-Flaczyk and Walentowska, 2008). Linen fabric treated with as little as 8 μg [DDA][NO_3] showed high antibacterial activity against both Gram-positive and Gram-negative bacteria. A 100-times greater concentration caused an inhibition zone of bacteria growth that exceeded 5 mm around the sample.

Here we report on the application of [DDA][NO_3] in the finishing process of linen fabrics to improve their antifungal functionality.

2. Materials and methods

2.1. Materials and finishing method

One-hundred-percent linen fabric with a surface mass of 120 g/m^2 was used. Before testing, the fabric was washed in order to remove any residues from the surface and possible finishing agents applied during production.

The antifungal agent used in the finishing process was ionic liquid didecyldimethylammonium nitrate [DDA][NO_3] purchased from P.I.W. Delta company (Fig. 1). The investigated IL is easily soluble in water; thus it was applied by a padding process from a water solution. The padding process was carried out with the use of Mathis 2-Roll Laboratory Padder, which equipment allows for accurate control of the degree of padding (100%), which in turn enabled uniform application of a specific amount of the biocide on the fabric surface. The fabric samples, containing [DDA][NO_3] at levels of 8 μg, 80 μg, 800 μg, and 5000 μg per 1 g of the dry linen fabric, were prepared for the tests. After the padding process the linen fabric samples were dried at ambient temperature.

2.2. Evaluation of antifungal properties

The level of influence of added biocide on fungal growth was measured according to the EN 14119, 2003 Standard using the following mould fungi mixture: *Aspergillus niger* van Tieghem, *Chaetomium globosum* Kunze, *Gliocladium virens* Miller, *Paecilomyces variotii* Bainier, *Penicillium ochrochloron* Biourge. All microorganisms originated from the pure culture collection of the Institute of Fermentation Technology and Microbiology, Technical University of Lodz, Poland.

The samples of protected linen fabric were placed on agar medium and inoculated with a suspension of testing moulds. Incubation of the tested samples was conducted for 4 week at a temperature of 29 ± 1 °C and relative air humidity of 90%. After the test, evaluation of antifungal properties was done on the basis of visual assessment by determining degree of mould growth on the surface of linen fabric samples. The rating system for mould growth was as follows:

0 – no visible growth evaluated microscopically.

1 – no visible growth evaluated with the naked eye but clearly visible microscopically.

2 – growth visible with naked eye, covering up to 25% of tested surface.

3 – growth visible with naked eye, covering up to 50% of tested surface.

4 – considerable growth, covering more than 50% of tested surface.

5 – very intense growth, covering all tested surface.

Subsequently, the samples were cleansed and strength properties were evaluated. The microbial growth and changes in surface properties were also studied by scanning electron microscopy (SEM). All the measurements were performed six times.

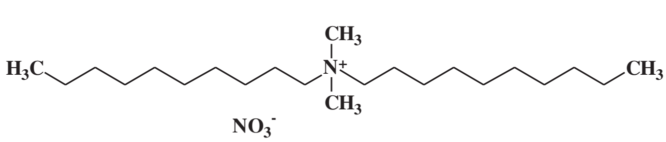

Fig. 1. Formulation of IL used in the study.

2.3. Evaluation of strength properties

Determination of the breaking force of finished fabrics after microbial exposure using the strip method was done according to the EN ISO 13934-1, 1999 Standard. The relative loss of breaking force (expressed as a percentage) caused by mould action was calculated from the mean value of six samples, using the formula:

$$S = 100 - \frac{\overline{A}}{\overline{B}} x100$$

where $\overline{A}$ is the arithmetical mean value of the breaking force for all samples exposed to mould action, and $\overline{B}$ is the arithmetical mean value of the breaking force for all samples not exposed to mould action. The samples were conditioned at 65 ± 2% relative air humidity and 29 ± 1 °C temperature for 24 h. The evaluation was also performed on the control sample, which was unfinished linen fabric.

2.4. SEM analysis

The microscopic evaluation of surface changes occurring during the biodegradation of finished and unfinished samples of linen fabrics after 4 week of exposure to the mould fungi was carried out using a Hitachi S-3400N scanning electron microscope, where samples were coated with a thin layer of gold before observation.

3. Results and discussion

The antifungal activity of linen fabric finished with [DDA][NO_3] was studied by visual evaluation of mould fungi growth on a scale from 0 to 5, as observed on each sample's surface. For comparison, the test was performed on a control sample, which was unfinished linen fabric. Moreover, the loss of breaking force was evaluated.

Earlier studies on bacteria indicated that the application of [DDA][NO_3] in amounts as small as 8 μg [DDA][NO_3] per 1 g of the dry fabric resulted in high antibacterial activity against both Gram-positive and Gram-negative bacteria (Foksowicz-Flaczyk and Walentowska, 2008). In the present paper on antifungal activity, 8 μg [DDA][NO_3] per 1 g of the dry linen fabric was also used as the basic concentration for comparison. The results demonstrated that the applied concentration did not show antifungal activity (Table 1). The 10-times-higher concentration also proved to ineffective in the current study. Only after using a 100-times higher concentration was an antifungal effect observed. The linen fabric protected with 5000 μg [DDA][NO_3] per 1 g of the dry fabric, which represents 0.5% application of ILs, reduced the growth of fungi.

These results are visible in Figs. 2 and 3. Fig. 2a demonstrates very intense growth of mould fungi, which covered all tested