Renewable antimicrobials for textile finishing

The goal of this research was to introduce new sustainable materials in textile finishing, requiring minor optimization for industrial use and up-scaling. Since finishes aim to functionalize the textiles, there is need for bio-additives. Much attention is paid to antimicrobial textiles due to the new biocide regulation. The application of renewable antimicrobials on textiles is described.

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There is a constant need for the improvement of materials applied in textile industries. Nowadays there is a tendency for "bio, eco, natural and environmentally friendly" consciousness of the consumer resulting in various textile labels. The Kyoto regulations prescribe a reduction of CO_2 emission. Materials, totally based on CO_2 neutral renewable resources (biopolymers), constitute a significant enhancement in respect of ecological and procedural aspects. The development of bio-based formulations for finishing textiles is still a challenge and demands the elaboration of novel formulations. Key drivers for changes in coating and finishing formulations include increasing levels of legislations to protect the environment and human and animal health. The REACH regulation for chemical substances has a large impact on textile coating and finishing industry. Next to this a new biocidal products regulation 528/2012 (BPR) is installed replacing the biocidal products directive 98/8/EC. According to the regulation, articles can only be treated with biocidal products containing active substances approved in the EU. The BPR requires manufacturers and importers of treated articles to label treated articles when a claim that the treated article has biocidal properties is made. Treated articles with a primary biocidal function will be considered as a biocide and need to be approved.

Fabrics are susceptible to microorganisms. Infestation by microbes can cause cross infections by pathogens and odor. With increasing awareness of the importance of hygiene, antimicrobial finishing of textiles has received much attention in recent years. A lot renewable materials with different functional properties can be obtained from nature, including antimicrobials. For example, chitosan is a natural, biodegradable product introducing antimicrobial properties. The antimicrobial activity of chitosan treated textile is reported in many publications and will not be discussed here [1-4]. This paper discusses the results of the implementation of renewable antimicrobials, besides chitosan, in textile finishing. The evaluated antimicrobial renewable additives include tannic acid and corresponding hydrolysis products, fatty acids, salicylic acid, fatty acid esters, thymol and carvacrol. Many of these compounds are already used in food and cosmetics.

Experimental

Materials

Radiamuls MG2549K (2,3-dihydroxypropyl laurate) and Radiasurf 7157 by Oleon NV, Ertvelde/Belgium. Gallic acid, alkyl gallates, octanoic acid, lauric acid, thymol and carvacrol were purchased from Sigma-Aldrich BVBA, Diegem/Belgium. Tannic acid was kindly donated by S.A. Ajinomoto Omnichem N.V., Louwain-la-Neuve/Belgium. Itofinsih LJGF and Itofinish LJSYF New were bought from LJ Specialties, Chesterfield/UK. Amipreserve (salicylic acid) was kindly donated by Alban Muller International, Vincennes/France. Cotton knitted fabric was kindly donated by Plastibert, Wielsbeke/Belgium. Suprapein and Neopein were purchased from Bio-Botanica, Hauppauge, NJ/USA.

Methods

The renewable antimicrobials were dissolved in water. Additives, not soluble in water, were dispersed in water using Radiasurf 7157 or were first dissolved in ethanol before being diluted with water up to a water: ethanol ratio 4:1. Cotton knitted fabrics were immersed in the antimicrobial solution/dispersion and squeezed. Fabrics were dried 2 minutes at 110 °C.

The antibacterial activity of the finished textiles was evaluated according to the agar diffusion plate test (ISO 20645) towards *E. coli* and *S. aureus*. Specimens of the material to be tested are placed on 2-layer agar plates. The lower layer consists of a culture medium free from bacteria and the upper layer is inoculated with the selected bacteria. The textiles are tested on both sides. The level of antibacterial activity is assessed by examining the extent of bacterial growth in the contact zone between the agar and the specimen and, if present, the extent of the inhibition zone around the specimen after 24 hours.

The antifungal activity of the finished textiles was evaluated according DIN EN 14119 B2 towards *Aspergillus repens*, *Aspergillus niger*, *Chaetomium globosum* and *Hormoconis resinae*. Immersed specimens were

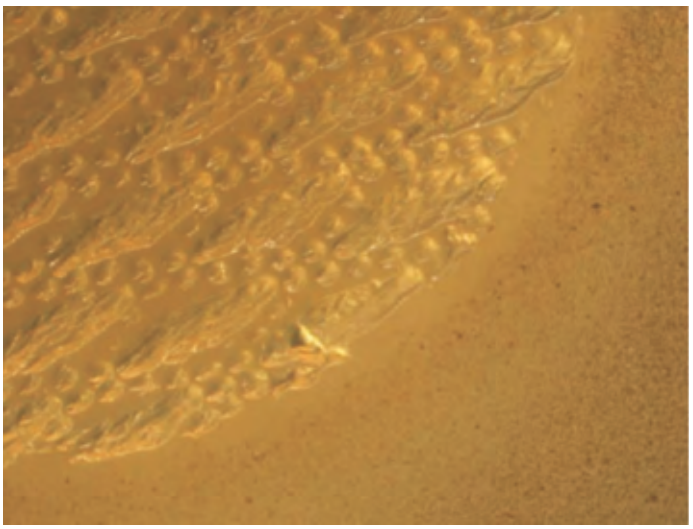

Fig. 1
Antibacterial effect of knitted fabric with 2 % tannic acid

Table 1
Antibacterial effect of cotton knitted fabric treated with thymol and carvacrol towards S. aureus and E. coli

S. aureus	Test specimen	Zone of inhibition (mm)	Bacterial growth beneath substrate
Side A	1	(9-7) 1**	No
	2	(10-9) 1**	No
Side B	1	(10) 0.5**	No
	2	(11) 1**	No

E. coli	Test specimen	Zone of inhibition (mm)	Bacterial growth beneath substrate
Side A	1	(<1) 0	No
	2	(<1) 0	No
Side B	1	(<1) 0	No
	2	(<1) 0	No

Concerning the zone of inhibition: numbers in brackets correspond to the zone where an effect is observed with the eye, the other numbers represent the real inhibition zone observed with the binocular. **: Some colonies were observed in the inhibition zone.

Table 2
Overview of the antibacterial effect of cotton knitted fabric treated with monolaurin towards S. aureus

S. aureus	Test specimen	Zone of inhibition (mm)	Bacterial growth beneath substrate
Side A	1	0-1	No
	2	1	No
Side B	1	0-1	No
	2	1	No

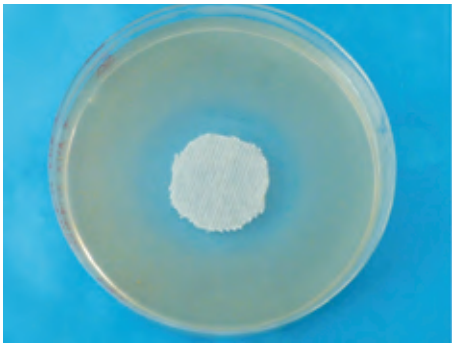

Fig. 2
Zone of inhibition of S. aureus around cotton knitted fabric treated with a mixture of thymol and carvacrol

placed on culture media and incubated for 28 days at 30 °C for *A. repens*, *A. niger* or *C. globosum* and 24 °C for *H. resinae*. After 28 days the mold growth on samples and possible inhibition zones were determined.

Results and discussion

The concentration of the different antimicrobial additives in the padding solution was calculated according to the dry pick-up (0.3, 0.5, 1, 2 or 3 %). Therefore the wet pick-up of the cotton knitted fabric was calculated before determining the concentration of the additives in the solution. Dry pick-up percentages of maximum 3 % of antimicrobial additive on the textile were evaluated.

Tannic acid treated cotton (2 % dry pick-up) exhibited antibacterial activity towards *S. aureus*, but not towards *E. coli* [5]. No growth of *S. aureus* bacteria underneath the specimen was observed as well as a small zone of inhibition (Fig. 1). The small zone of inhibition indicated that tannic acid migrated in small extent out of the specimen. Gallic acid and alkyl gallates are hydrolysis products from tannic acid. In vitro experiments indicated that these compounds are potential antimicrobials [6-7]. However cotton treated with gallic acid or alkyl gallates did not show significant antibacterial effects towards *S. aureus* and *E. coli*.

Thymol and carvacrol are natural compounds found in essential oil of thyme. Cotton knitted fabric was immersed in a thymol and carvacrol containing water:ethanol (4:1) solution. Dry pick-up was 0.3 %. The samples showed significant antibacterial activity towards *S. aureus* and *E. coli* (Table 1).

Cotton knitted fabric padded in a dispersion of thymol or in a dispersion of carvacrol showed no antibacterial activity towards *S. aureus* and *E. coli*. However padding the cotton knitted fabric in a dispersion mixture of thymol and carvacrol resulted in antibacterial activity towards *S. aureus* (Fig. 2). Thymol and carvacrol are synergetic. Further it was noticed that the water:ethanol solution of thymol and carvacrol is more effective compared to the corresponding dispersion [5].

Monolaurin or glycerol monolaurate is naturally found in coconut oil. Cotton knitted fabric with 3 % monolaurin showed significant antibacterial activity towards *S. aureus* [5]. No growth of *S. aureus* bacteria underneath the specimen was observed as well as a small zone of inhibition (Table 2). Textiles treated with the fatty acids octanoic and lauric acid or the commercial formulations Itofinish LJSYF New and Itofinsih LJGF showed no antibacterial activity towards *S. aureus* and *E. coli*. Concentrations up to 3 % were evaluated. Itofinish LJSYF New is based on chitosan, while Itofinish LJGF is derived from the extract from grapefruit seeds and Citrus grandis.

Salicylic acid occurs in a range of fruits and vegetables. Fabrics containing 0.5 % Amipreserve (salicylic acid) exhibited no antibacterial effect regarding *S. aureus* and *E. coli*. However contrary to the previous antimicro-

Fig. 3
Incubation of textile on Aspergillus niger inoculated media (28 days)
R1: growth control on media, R2: growth control on untreated textile. 0.05-100 % carvacrol

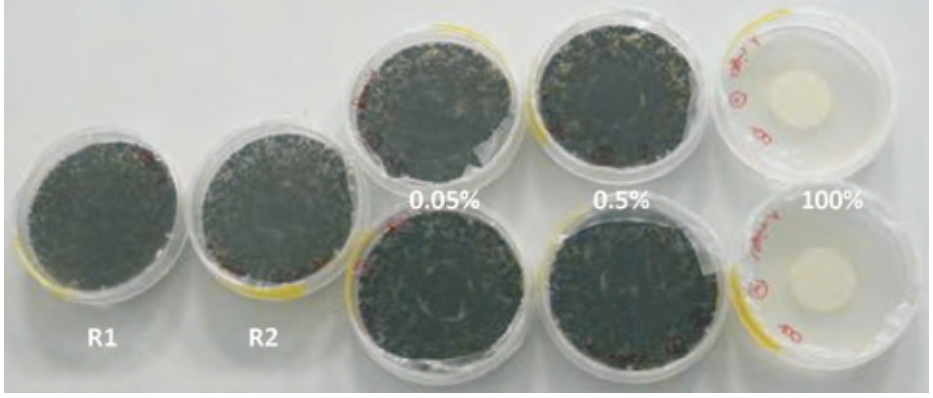

Table 3
Growth of fungi on textile with 0.5 % salicylic acid after 28 days

Aspergillus niger	100
Aspergillus repens	5
Chaetomium globosum	100
Hormoconis resinae	100

bials, salicylic acid treated textiles showed antifungal effect only towards *Aspergillus repens* (Table 3 and Fig. 3).

Antifungal effects of carvacrol treated textiles were observed only at a concentration of 100 %. Concentration of 0.05 % and 0.5 % carvacrol are insufficient. The same results were obtained for herbal extracts Suprapein and Neopein. Although the data sheet indicates an antifungal effectiveness from 0.45 % Suprapein or 0.55 % Neopein, even 2 % did not suppress the mold growth. 100 % Suprapein or Neopein prevented completely the growth of fungi.

Conclusion

Renewable materials were used as antibacterial agent for textiles. Textiles finished with monolaurin or tannic acids were antibacterial towards *S. aureus*. Padding cotton knitted fabric in thymol and carvacrol mixture containing water:ethanol (4:1) solution resulted in antibacterial activity towards *S. aureus* and *E. coli*. Thymol and carvacrol have a synergetic antibacterial effect. An antifungal effect could be achieved by treatment of textiles with carvacrol, Suprapein or Neopein. The MIC (minimal inhibition concentrations) could not be determined exactly up to now. However, previous attempts show that the MIC are far above the expected concentrations. ■

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