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Textile Materials Functionalised with Natural Biologically Active Compounds

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Abstract

Due to their properties (good sorption, softness, and good vapour permeability) the natural fibres are well suited for medical or cosmetic products. The paper targets the production of woven and knitted fabrics with aromatherapy characteristics by applying on their surface chitosan–lavender essential oil and monochlorotriazinyl-β-cyclodextrin–lavender essential oil systems. The treated samples were characterised by IR spectroscopy. The presence of the biologically active compound on the textile support was confirmed through qualitative and odour tests. The comfort characteristics of the treated and untreated samples were also studied viz. hygroscopicity, water vapour permeability and air permeability. The antimicrobial activity of the fabrics was tested for both Gram positive (Staphylococcus aureus ATCC-6538) and Gram negative bacteria (Escherichia coli ATCC-10536).

Keywords: *cotton, lavender essential oil, monochlorotriazinyl-β-cyclodextrin, chitosan*

Introduction

The aroma essential oils have lately become particularly interesting for therapeutic purposes. The functioning of ether oils, which act both at local level and through odour, has not been completely understood. In the last years, the possibility of obtaining fabrics with antimicrobial properties based on essential oils has come into focus [1-6]. Due to their volatile nature the essential oils are introduced in natural polymers such as chitosan or in cyclic oligosaccharides such as cyclodextrin and its derivatives [7-10]. The application of chitosan-essential oil and cyclodextrin-essential oil systems on textile supports allows a controlled release of the active substance in time, as well as a prolonged antimicrobial effect. Most frequently the textile supports are made of natural cellulose fibres, the resulting products being used as wound dressings, bandages, absorbent items, suturing products, hygiene products. These materials present good liquid sorption (water and exudate), softness and good permeability and they are commonly known as biomaterials with improved comfort indexes.

This paper aims at obtaining aromatic and antibacterial materials by applying chitosan–lavender essential oil and monochlorotriazinyl-β-cyclodextrin – lavender essential oil systems on three types of textile support which are to be used in medical applications, in treatments at skin level for single use items.

Experimental work

The experiments were conducted on three types of textile supports, made of 100% cotton yarns that were washed and bleached. The samples were produced through weaving and knitting. The woven fabric used had a plain weave structure. The first knitted fabric had a sandwich structure with connection through yarns. The fabric was produced with yarn count Nm 28/1/4, while for the connecting yarns the count was Nm 28/1/2. The second fabric had a jersey structure and was produced with blend single yarns, count Nm 14/1. The specific structural parameters are presented in Tables 1 and 2.

Table 1. Structural parameters for the woven fabrics

Textile support	Weight (g/m^2)	Count (yarns/cm)		Yarn count (dtex)	
		Warp	Filling	Warp	Filling
Woven fabric (T)	104	305	240	140/2	40/1

Tabel 2. Structural parameters for the sandwich fabrics

Code	Structure	Raw material	Stitch density		l_m [mm]	M/m^2 [g]
			Dh [w/5 cm]	Dv [r/5 cm]		
$T_{1\ gros}$	Sandwich with connection through yarns	Cotton Nm 28/4 Nm 28/2	19	32	l_{stitch} = 9.3 $l_{connect\ yarn}$ = 6.1	790
T_2	Jersey	Cotton Nm 14/1	30.5	43.5	l_{stitch} = 6.18	220

The biologically active compound was applied by embedding it in chitosan and monochlorotriazinyl-β-cyclodextrin.

Application of the chitosan-lavender essential oil system

The samples were padded twice with the chitosan emulsion (0.225 % chitosan, 1 % Tween 80, 0.9 % essential oil), with 110% extraction degree, 24 hours relaxation at room temperature and drying at 60^0C.

Application of the monochlorotriazinyl-β-cyclodextrin -lavender essential oil system.

The samples were impregnated for 5 minutes with a solution containing 10% monochlorotriazinyl-β-cyclodextrin, 20g/l sodium carbonate, and then dried at 80^0C and fixation was performed at 140^0C for 4 minutes. The samples were then impregnated for 5 minutes with an alcoholic solution of lavender (0.9% essential oil), subjected to extraction and stored for 24 hours at room temperature. The codification of the experimental variants is presented in Table 3.

Table 3. Codification of the experimental variants

Textile support and the applied system	Code
Woven fabric treated with the chitosan/essential oil system	V.1.
Woven fabric treated with the monochlorotriazinyl-β-cyclodextrin / essential oil system	V.2.
Knitted fabric T2 treated with the chitosan/essential oil system	V.3.
Knitted fabric T2 treated with the monochlorotriazinyl-β-cyclodextrin / essential oil system	V.4.
Knitted fabric T1 treated with the chitosan/essential oil system	V.5.
Knitted fabric T1 treated with the monochlorotriazinyl-β-cyclodextrin / essential oil system	V.6.

Embedding efficiency of the essential lavender oil in the considered systems.

The embedding efficiency of the biologically active compound (E) was calculated with relation (1):

$$E\ (\%) = X/Y \times 100\% \qquad (1)$$

Where: X = quantity of the essential oil extracted from the textile support in a Tween 80% solution, 0.3% concentration, under 48 hours stirring; Y = initial quantity of essential oil in the treatment system.

The solution absorbencies were measured using a spectrophotometer UV/VIS for λ_{max} = 260 nm, the calibration being carried out with the Tween 80 solution, 0.3% concentration. The unknown concentrations had to be calculated and the Lambert Beer law was used.

FTIR analysis

The chemical changes occurring at the surface of cotton fibres after treatment with chitosan/essential lavender oil and monochlorotriazinyl-β-cyclodextrin / essential lavender oil systems were recorded using FTIR – ATR spectroscopy. The FTIR spectra were recorded on a FTS 2000 Digilab spectrophotometer, in the range 4000 – 250 cm^{-1} for a resolution of 4 cm^{-1} using Merlin Digilab programme.

Sensorial evaluation

The samples treated with essential lavender oil were kept at room temperature and smelled at a 5-day interval. The evaluation was conducted on 10 subjects.

Chromatic measurements

The controlled release of the lavender essential oil was highlighted through chromatic measurements. Both treated and untreated samples were dyed with Sudan Red dye dissolved in chloroform (2g/l). The measurements were carried out on a DATACOLOR apparatus (Model Spectroflash 300®).

Analysis of comfort indexes

The comfort characteristics of the treated and untreated samples (variants V.1 to V.6), viz. hygroscopicity, water vapour permeability and air permeability were studied using standards STAS 12749-89, ISO 15496:2004 and SR EN ISO 9237-1999.

Hygroscopicity H was determined with the following relation:

$$H = \frac{M_u - M_c}{M_c} \cdot 100 \text{ (\%)}, \qquad (2)$$

Where: M_u – average mass of the samples stored in 100% humidity atmosphere (g); M_c – average mass of the conditioned samples – humidity 65% (g).

Vapour permeability P_v was calculated with the relation:

$$P_v = \frac{\Delta M}{S \cdot t}\left(\frac{g}{m^2 \cdot h}\right) \qquad (3)$$

Where: $\Delta M = M_0 - M_f$ (g);
M_0 = average mass of initial samples (g)
M_f = average mass of the samples after 24 h storage in a dehumidifying apparatus with sulphuric acid (ρ = 1.84 g/cm^3); S – vaporisation area (m^2); t - time (h);

The air permeability was determined on a METEFEM apparatus (Hungary), for Δp = 10 mm water column, using samples with 10 cm^2 area, measuring the air flow passing through the fabrics. The air permeability P_a was calculated with relation:

$$Pa = \frac{q.10^{-3}}{60.A}(m^3 / \min .m^2) \qquad (4)$$

Where: q –air flow (l/h) and A – sample flow area (cm^2)

Antimicrobial analysis

The sensibility of the *Staphylococcus aureus* ATCC – 6538 and *Escherichia coli* ATCC – 10536 bacteria to the lavender essential oil was tested „in vitro" under optimal and standardized conditions of inoculation (culture medium, inoculum, incubation time, etc). The testing method was based on the Kirby-Bauer disc diffusion method [11]. By placing the round samples impregnated with the tested oil on the surface of a solid medium inoculated with a bacterial culture, the active antimicrobial substance will be diffused, having a constant decrease in concentration gradient directed from the edge of the samples to their centre. After an incubation period of 24 hours at 37º C, the presence or absence of bacteria infestation can be demonstrated.

Results and discussions

FTIR analysis

Figures 1 and 2 present the FTIR spectra for variants V.1 and V.2.

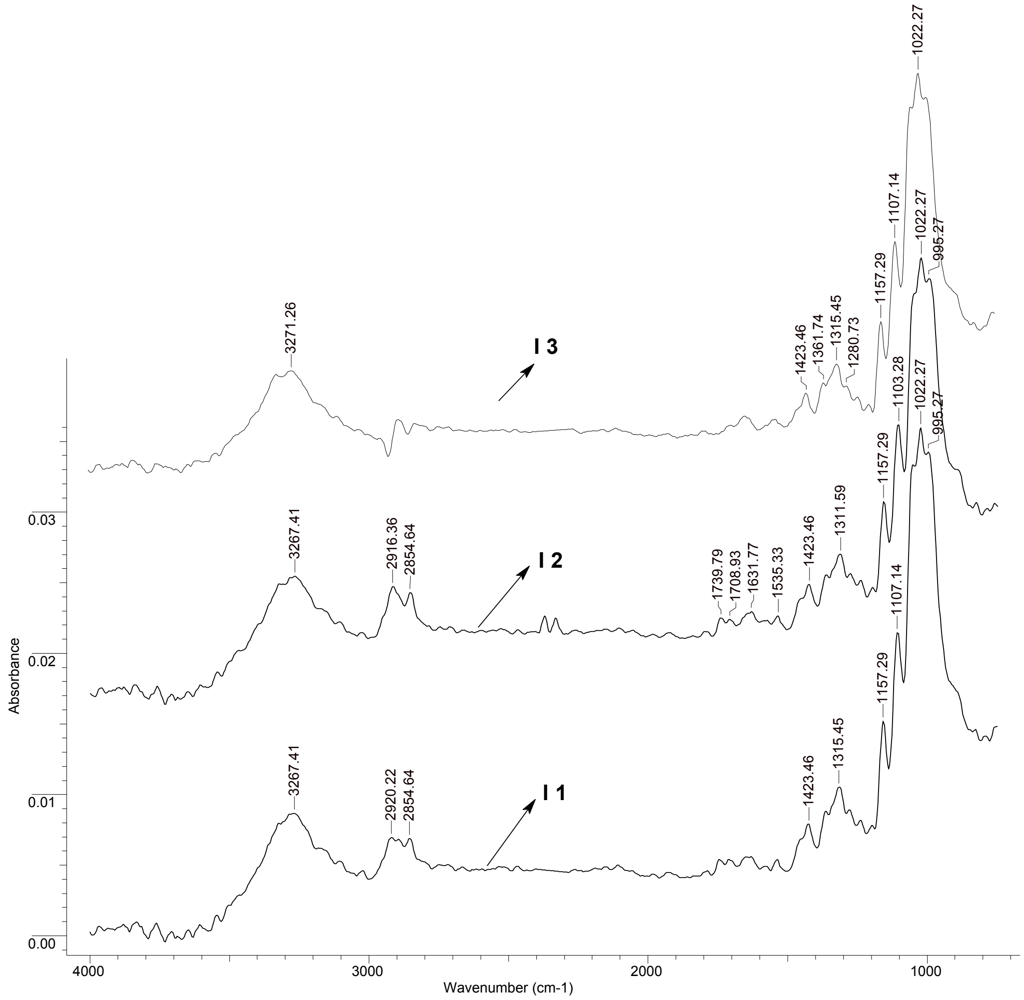

Figure 1. FTIR spectra for cotton (I 1), cotton treated with chitosan (I 2) and cotton treated with chitosan/essential oil system (I 3)

Figure 1 shows that the cotton spectrum contains characteristic bands at 1423.46 cm^{-1} and 1315.45 cm^{-1} (CH wagging), at 1157.45 cm^{-1} at 1107.14 cm^{-1} (asymmetrical bridge C–O–C) and at 995.27 cm^{-1} (C–O stretch).

The shifting of peaks from 3267.41 cm^{-1} to 3444.3 cm^{-1} is due to the insertion of NH_2 groups involved in the formation of hydrogen bonds from the chitosan. The shifting of peaks from 2920.22 to 2883.6 is attributed to the overlapping of CH stretching vibrations from cotton and chitosan, while the change of vibration frequency from 1535.33 cm^{-1} to 1598 cm^{-1} can be explained by the formation of hydrogen bonds.

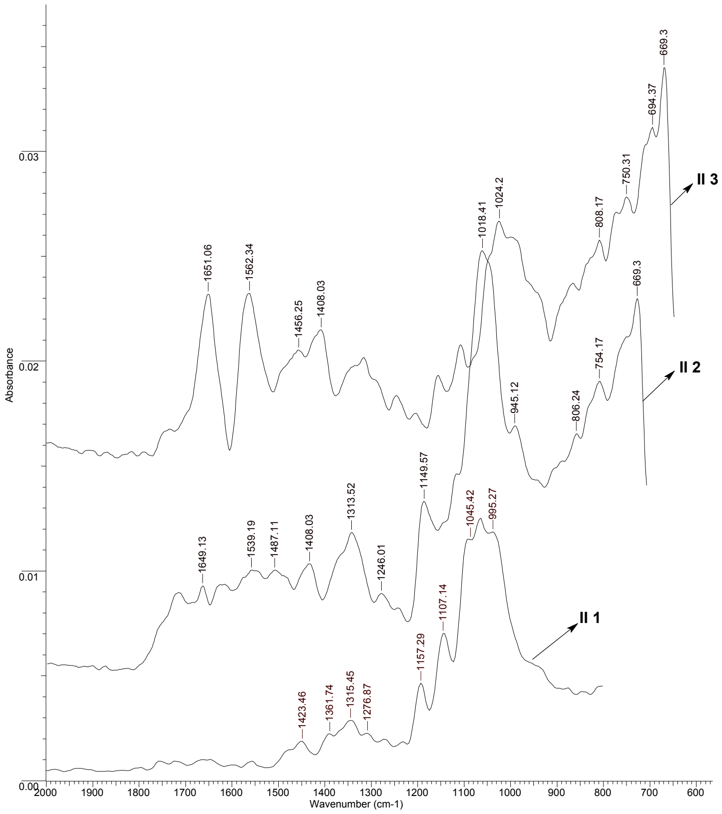

Figure 2. FTIR spectra of cotton (II 1), cotton treated with monochlorotriazinyl-β-cyclodextrin (II 2) and cotton treated with monochlorotriazinyl-β-cyclodextrin/essential oil system(II 3).

The formation of the etheric bond following the reaction between cellulose and monochlorotriazinyl-β-cyclodextrin is emphasised by the disappearance from the cotton fibre of 754.17 cm^{-1} vibration bands characteristic to the C-Cl bond from the chlorotriazinic nucleus, as well as by the 1051.2 cm^{-1} and 1423.46 cm^{-1} vibration bands specific to the –OH (CH_2OH) groups. It is also evinced by the presence of the 1024.2 cm^{-1} vibration band that characterises the etheric bond. The presence of the monochlorotriazinyl-β-cyclodextrin on the cellulose support is shown by the 1408.03 cm^{-1} vibration band corresponding to the -C=N- group from the triazinic nucleus (Fig.2).

Embedding efficiency of the lavender essential oil

The analysis of the experimental values regarding the embedding efficiency of the lavender essential oil shows that the best results were obtained in the case of the monochlorotriazinyl-β-cyclodextrin/lavender essential oil system for all three types of textile support (see Table 4). Another conclusion is that the knitted support retains the highest quantity of oil. One explanation could be the specific 3D geometry and the voluminosity of these fabrics that are characterised by high thickness. Furthermore, it seems that the oil penetrates the entire volume of the fabric, the presence of the connecting yarns increasing the oil embedding.

Table 4. Influence of the textile support on the embedding efficiency

Experimental variant	Embedding efficiency (%)
V.1.	15.440
V.2.	22.066
V.3.	20.089
V.4.	36.161
V.5.	36.038
V.6.	43.500

Sensorial evaluation

Table 5 presents the average values obtained from the sensorial evaluation.

Table 5. Sensorial evaluation of the odour intensity for the treated samples

Variant	Odour intensity*						
	1 day	5 days	10 days	15 days	20 days	25 days	30 days
V.1.	+++++	+++++	+++++	++++	+++	++	+
V.2.	+++++	+++++	+++++	++++	+++	++	++
V.3.	++++	++++	++++	++++	+++	++	+
V.4	+++++	+++++	+++++	+++++	++++	++++	+++
V.5.	++	++	++	++	++	+	+
V.6.	+++++	++++	++++	+++	+++	+++	++

** very strong odour +++++ ; strong odour ++++; medium intensity odour +++; low intensity odour ++; very low intensity odour +*

The experimental data show that the odour is strong for 15 days, after which it decreases gradually. The odour intensity is stronger in the case of the samples treated with the monochlorotriazinyl-β-cyclodextrin /lavender essential oil system in comparison with the ones treated with the chitosan/ lavender essential oil system. The best aromatic behaviour is obtained for the first knitted fabric (T1). This fabric presents the highest stitch density, therefore it is more compact and this can be the reason why it retained the aromatic odour longer.

Chromatic measurements

The results referring to the colour differences that appear between treated and untreated samples after dyeing them with Sudan Red are illustrated in Fig. 3 and 4.

The results confirm the release of the lavender essential oil in time. The gradual release decreases the amount of lavender oil in the textile support, thus explaining the differences in colour between the dyed treated and untreated samples. Comparing the two systems, it results that the monochlorotriazinyl-β-cyclodextrin /oil system releases a higher quantity of oil. As far as the textile support is concerned, the hierarchy concerning oil release is knitted fabric T1> knitted fabric T2> woven fabric.

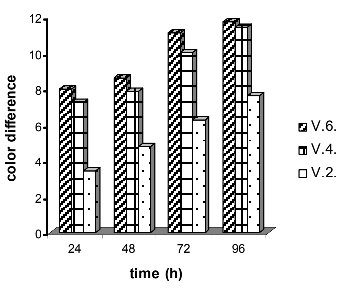

Figure 3. Variation of colour difference with time for the monochlortriazinil ß-ciclodextrine/lavender essential oil system.

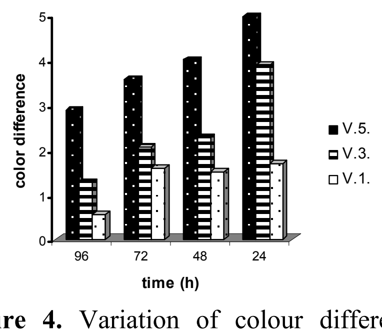

Figure 4. Variation of colour difference with time for the chitosan/lavender essential oil system.

Evaluation of the comfort indexes

The results demonstrate that the comfort indexes depend on the type of the textile support and the treatment applied (see Table 6).

The treated samples have lower vapour permeability and higher hygroscopicity in comparison with the untreated samples. This situation can be justified by the higher amount of hydrophilic groups introduced at fibre surface level through the chitosan and monochlorotriazinyl-β-cyclodextrin treatments. As to the differences between the two types of treatments, they can be explained through the higher number of polar groups generated by the monochlorotriazinyl-β-cyclodextrin /oil system. The lower values determined for the air permeability of the treated samples in comparison with the untreated ones are justified by the yarns in the treated samples being more rigid and having smaller cross section, which increases the free volume within the textile fabrics.

Table 6. Comfort indexes

Variant	Vapour permeability [g/m^2 . h]	Hygroscopicity [%]	Air permeability [m^3/m^2 · min]
V.1.	10.383	13.255	0.339
V.2.	9.854	13.874	0.421
Witness T	11.286	12.011	0.307
V.3.	14.011	14.0123	0.639
V.4.	12.058	14.6983	0.659
Witness T_1	15.295	13.024	0.522
V.5.	9.953	14.9879	0.082
V.6.	8.593	15.1231	0.096
Witness T_2	17.194	14.202	0.077

Antimicrobial analysis

Table 7 presents the experimental results for the antimicrobial study. Only the untreated (witness) samples presented contaminations with *Escherichia coli* and *Staphylococcus aureus* bacteria.

Table 7. Microorganisms development on treated and untreated samples

Treatment variant	Bacteria	
	Escherichia coli	*Staphylococcus aureus*
V.1.	-	-
V.2.	-	-
V.3.	-	-
V.4.	-	-
V.5.	-	-
V.6.	-	-
Witness	+	+

Legend: + increase and development of bacteria; - lack of increase and development of bacteria

Conclusions

The experimental study of aromatic and antibacterial materials with textile support presented in this paper took into consideration two systems - monochlorotriazinyl-β-cyclodextrin/lavender essential oil and chitosan /lavender essential oil embedded in woven and knitted textile fabrics. The resulted materials were evaluated considering embedding efficiency, sensorial characteristics, as well as antimicrobial behaviour.

The analysis of the experimental values regarding the embedding efficiency of the lavender essential oil has shown that the best results are obtained in the case of the monochlorotriazinyl-β-cyclodextrin/lavender essential oil system.

The odour intensity is stronger in case of the samples treated with the monochlorotriazinyl-β-cyclodextrin /lavender essential oil system in comparison with the ones treated with the chitosan/ lavender essential oil system. The odour decreases gradually after the first 15 days. Out of the three types of textile support used in these studies, the best aromatic behaviour is obtained for the first knitted fabric (T1).

The chromatic measurements confirm the release in time of the essential oil. The present study demonstrates that the monochlorotriazinyl-β-cyclodextrin /oil system releases a higher quantity of oil. Comfort indexes depend on the type of the textile support and the treatment applied. The treated samples have lower air permeability and higher hygroscopicity in comparison with the untreated samples.

All treated samples present antibacterial properties against both gram positive (*Staphylococcus aureus* ATCC-6538) and gram negative (*Escherichia coli* ATCC-10536) bacteria.

FTIR analysis confirms the presence of chitosan and monochlorotriazinyl-β-cyclodextrin systems in the textile material.

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