

Textile Functionalisation by Printing Fragrant, Antimicrobial and Flame-Retardant Microcapsules

Funkcionalizacija tekstilij s tiskanjem dišečih, protimikrobnih in protigorljivih mikrokapsul

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Abstract

The procedure of applying microcapsules to a cotton fabric using screen printing was investigated. The aim was to explore whether the printing of microcapsules might be a universal approach to functionalise textiles. Fragrant (lavender, rosemary and sage essential oil core), antimicrobial (triclosan core) and flame-retardant (triphenyl phosphate core) microcapsules with a melamine-formaldehyde wall were used. The optimal concentration of microcapsules in the printing paste to achieve the desired effect was investigated. The mechanical properties of the treated fabrics were analysed before and after the washing. The results showed that different functionalities of fabrics can be achieved using this printing technique. The optimal concentration of microcapsules to produce the desired fragrant or antibacterial textile product was 100 g of suspension (32 g of microcapsules) per kg of fabric. The optimal concentration of microcapsules to produce the desired fire-retardant material was very high and could not be achieved using the pigment system.

Keywords: microcapsules, fragrance, flame retardant, antimicrobial agent, screen printing, cotton

Izvleček

Raziskan je bil postopek nanašanja mikrokapsul na bombažno tkanino s pomočjo filmskega tiska. Naš cilj je bil raziskati, ali je tisk mikrokapsul lahko univerzalni postopek za funkcionalizacijo tekstilij. Uporabljene so bile dišeče (jedro iz eteričnega olja sivke, rožmarina in žajblja), protimikrobne (jedro iz triklosana) in protigorljive (jedro iz trifenilfosfata) mikrokapsule z melamin-formaldehidno ovojnico. Iskana je bila optimalna koncentracija mikrokapsul v tiskarski pasti za dosego ustreznega učinka. Lastnosti obdelane tkanine so bile analizirane pred pranjem in po njem. Rezultati so pokazali, da so s tehniko tiskanja lahko dosežene različne funkcionalne lastnosti tkanin. Optimalna koncentracija mikrokapsul za izdelavo zelene dišeče ali protibakterijske tekstilije je bila 100 g suspenzije (32 g mikrokapsul) na kg tkanine. Optimalna koncentracija mikrokapsul za izdelavo materiala, ki bi zaviral gorenje, pa je bila zelo visoka in je ni bilo mogoče doseči z uporabo pigmentnega tiska.

Ključne besede: mikrokapsule, dišava, zaviralec ognja, protimikrobno sredstvo, filmski tisk, bombaž

1 Introduction

The functionalisation of textiles can be achieved with the use of microcapsules (MCs) [1, 2], which can represent a universal procedure for the application of different substances to fabrics, thus enabling different types of textile substrates to have special properties. These properties increase their utility and

market value. Materials with special properties are of great importance in research and commercial use.

MCs are a product of the microencapsulation process, which is defined as “a technology of packaging solids, liquids or gaseous materials in miniature sealed capsules that can release (or not) their contents at controlled rates under the influence of specific conditions [3–6].” In this way, the active compounds are

safely stored inside the capsules, isolated from their surroundings, and they are protected from any degrading factors [7–12]. MCs can be physically applied to textiles from solutions, dispersions or emulsions by padding, coating, spraying or bath exhaustion. The durability to washing and handling can be improved by incorporating suitable binders. Alternatively, screen printing can be introduced as a method for applying microcapsules to textile fibres [6]. The advantage of printing is that the microcapsules can be applied to target areas on a fabric or textile product.

The aim of this research was to demonstrate that the printing of MCs might be a universal approach to functionalise textiles.

Three different types of MCs were used, i.e. MCs with fragrance, with an antimicrobial agent and with a flame retardant. Fragrant MCs imbue the fabric with a scent; antimicrobial agents protect the user from pathogen microorganisms [13, 14] and fire retardants protect the user from fire. Such agents are very important for medical and technical textiles, as well as for textiles in public use [14, 15]. The crucial characteristics of these fabrics are that they are safe for the producer and the user, show good fastness to washing, work efficiently at the terms of use and do not significantly change the original technological properties of the fabric. The mentioned agents applied to the fibres in the form of microcapsules meet all these requirements.

In this study, all used MCs had the same melamine formaldehyde wall. In the core, the fragrant MCs contained a mixture of lavender, rosemary and sage essential oil (LRS). The antimicrobial MCs contained triclosan (TCS) and the fire-retardant MCs contained triphenyl phosphate (TPP). The latter were prepared specifically for this purpose [16]. The use of identical MCs has not been found anywhere in the literature.

TCS is a chlorinated bisphenol, as well as synthetic, non-ionic, antimicrobial agent with antibacterial activity (effective against many types of Gram-positive and Gram-negative bacteria). Additionally, TCS has some antifungal and antiviral properties [17]. The mechanism of TCS blocks the active site of the enoyl-acyl carrier protein reductase enzyme (ENR), which is a significant enzyme in fatty acid synthesis in bacteria. By blocking the active site, the inhibition of the enzyme and the prevention of fatty acid synthesis, which is necessary for building the cell membrane and for reproduction, are achieved [18, 19].

TPP is an effective fire retardant based on phosphorus. It breaks down in the flame to produce chemical species such as P_2 , PO, PO_2 and HPO_2 . These reactions reduce the hydrogen atom concentration in the vapour phase, thus extinguishing the flame [20]. In addition, the intention of our work was to identify a simple and universal procedure for the application of MCs to textiles. Screen printing with a pigment printing system was chosen to achieve this objective. The MCs by mass were synthesised in a partner laboratory.

In this study, the optimal MC concentration in the printing paste and, consequently, on the fabric was investigated to achieve a fabric with a lasting aroma, lasting antimicrobial properties and flame-retardant properties. One of the objectives was also to study the changes in the mechanical fabric properties (air permeability, stiffness, mass per unit area and thickness) after the application of MCs. A cotton fabric was used for the application of MCs. The MC presence on the fabric, as well as distribution, shape and size were analysed using SEM micrographs. The changes in the properties of treated fabrics and the MC fastness to washing were tested using standardised methods of textile research. The presence and fastness of the aroma were investigated using the panel procedure (Lewis) of fragrance evaluation. The effect of antimicrobial MCs was monitored using microbiological tests and a burial in soil test. The effect of flame-retardant microcapsules was monitored by analysing their burning and thermal properties (DSC, TGA).

2 Experimental

2.1 Materials

A bleached and mercerised 100% cotton woven fabric (124 g/m² in weight, supplied by Tekstina d. d., Slovenia) was used for the study. Suspensions of MCs 2–8 µm in size with a pressure-sensitive melamine-formaldehyde wall and three different cores were prepared in Aero d. d. Celje, Slovenia by *in situ* polymerisation of melamine-aldehyde prepolymers [7, 21–24]. The mass fraction of the cores in all MCs was 75%, and the mass fraction of the walls was 25%. The mass fraction of the MCs in suspensions was 32%. The cores of MCs contained the following active substances:

- fragrant MCs: an industrial mixture of sage, rosemary and lavender essential oils (1 : 2 : 7) in isopropyl

- myristate as a solvent (25% essential oil and 75% isopropyl myristate),
- antimicrobial MCs: triclosan (20% triclosan in 80% isopropyl myristate),
 - fire-retardant MCs: solid triphenyl phosphate (100%).

The MC suspensions were added to the printing pastes which were composed of a synthetic polyacrylate thickener (Tubivis DRL 300), a polyacrylate binder (Tubifast AS 30), both of which were obtained from CHT, Germany. The pigment Bezaprint (Bezema, Switzerland) was also added.

2.2 Printing

Table 1 presents the recipes for the printing pastes. Different concentrations of MC suspensions in the printing paste were tested. The printing, drying and curing conditions are presented in Table 2.

Table 1: Printing pastes recipes

Component	Quantity [g]
Thickener	34
Binder	150
Pigment	2
Suspension of MCs	x^*
Distilled water	y^{**}
Sum	1000

* 25–600 (concentrations of individual suspensions of MCs in printing pastes are given as c_{sp} in Table 3)

** difference to 1000

Table 2: Printing, drying and curing conditions

Phase	Conditions
Printing	Flat screen stencil: mesh 43 threads/cm Printing speed: 80% Squeegee diameter: 8 mm Magnet pressure: level 5 No. of strokes: 2
Drying	Air drying
Curing	Ernst Benz TKF 15-M500 drier, $T = 150^\circ\text{C}$, $t = 3$ min

Flat screen printing was performed on a laboratory magnetic printing machine MINI MDF R 390 (Johannes Zimmer AG, Austria). The coverage area of the printing paste on the cotton cloth was approximately 25×35 cm.

Different quantities of MC suspensions were added to the printing pastes, resulting in different concentrations of active substances on the fabric after the printing. The mass fraction of the active substance in the MC cores, the concentration of the MC suspension in the printing paste, the amount of the printing paste applied to the fabric, the concentration of the suspension on the fabric and the concentration of MCs on the fabric are presented in Table 3.

Table 3: Mass fraction of active substance in core (x_a), concentration of suspension of MCs in printing paste (c_{sp}), share of printing paste application to fabric (N), concentration of suspension on fabric (c_s), concentration of MCs on fabric (c_m) and concentration of active substance on fabric (c_a) after printing

Type of MCs	x_a [%]	c_{sp} [g/kg]	N [%]	c_s [g/kg]	c_m [g/kg]	c_a [g/kg]
Fragrant	25	100	100	100	32	6
		150	90	135	43.2	8.1
		200	88.2	176.4	56.54	10.6
Anti-microbial	20	25	76	19	6,08	0,9
		50	65.6	32.8	10.5	1.58
		100	100	100	32	4.8
Fire retardant	100	100	100	100	32	24
		200	90	180	57.6	43.2
		400	54.4	218	69.76	52.32
		600	58.6	351.6	112.5	84.37

The abbreviations of all treated samples used in this study are gathered in Table 4.

Table 4: Sample abbreviations according to treatment (printing)

Abbreviation	Sample
CO	untreated sample
CO0	sample printed without MCs
LRS100 150 200	sample printed with different concentrations of fragrant MCs
TCS25 50 100	sample printed with different concentrations of antimicrobial MCs
TPP100 200 400 600	sample printed with different concentrations of fire retardant MCs

Washing

Some printed (cured) samples were washed for 30 min at 40 °C according to the ISO 105-C01:1989 (E) [25] standard using a soap solution (5 g/L of soap) with pH 7 and a liquor-to-fabric ratio 50 : 1. After the washing, the samples were air-dried.

2.3 Analysis

SEM observation

Using a scanning electron microscope (Jeol JSM 6060 LV), the uniformity of the deposit, as well as the size and morphological characteristics of different MCs on printed fabrics were observed. Moreover, the quantity and condition of MCs that remained on the fabric after the washing were investigated. The printed samples were coated with gold prior to the observation with a microscope.

Fragrance evaluation

Fragrance evaluation was performed on the samples printed with four different quantities of fragrant MCs (0, 100, 150 and 200 g of MCs per kg of printing paste). The method for fragrance evaluation was based on the Lewis procedure [26, 27]. A portion of fabrics was removed after 10 wash cycles (ISO 105-C01:1989 (E) standard), air dried for 24 h and tested for the presence of fragrance using a panel of five judges. The samples were first hung on a clothesline in a room for 1 hour to stabilise fragrance evaporation. Then, the samples were brought to a judge in an evaluation room. A printed fabric was placed on a flat, hard board on a table. A judge used their fingernails to scratch an "X" (approximately 3 × 3 cm in size) on the fabric to break some of the capsules and then immediately smelled the swatch. Then they recorded "Yes" according to the presence of strong, medium or weak fragrance, or "No" according to the absence of the fragrance. No judge was performing the testing for more than 15 minutes.

Antibacterial activity testing

Antibacterial activity testing was performed on the samples printed with four different quantities of TCS MCs (0, 25, 50 and 100 g of MCs per kg of printing paste). The antibacterial activity was estimated for the Gram-negative bacteria *Escherichia coli* (ATCC 25923) and for the Gram-positive *Staphylococcus aureus* (25922) according to the standard SIST EN ISO 20645:2005, "Determination of antibacterial activity –

Agar diffusion plate test [28]." Circular fabric pieces (diameter of 25 ± 5 mm) were placed on two-layer agar plates. The lower layer consisted of a bacterial-free culture medium and the upper layer was inoculated with the selected bacteria. The level of antibacterial activity was assessed by examining the extent of bacterial growth in the contact zone between the agar and the specimen, and the width of the inhibition zone around the specimen. The tests were performed in a certified laboratory.

Fungicidal activity

The fungicidal activity testing was performed on the samples that showed the best antibacterial activity (100 g/kg). The activity was estimated for the fungi *Aspergillus brasiliensis* according to the DIN 53931 standard method [29]. The nutrient malt-extract agar (MEA) was prepared to which the fungi was inoculated. The inoculated plates were incubated at 29 °C for 24 h. Afterwards, cotton fibre samples 5 × 5 cm in size were placed on the medium and were incubated at 29 °C for 7 and 14 days. After the incubation, the fungicidal activity was determined in terms of mycelia growth on and below the surface of the cotton fibres and the sporulation intensity. The degree of fungal growth was ordered in eight grades from 00 to 5, where 00 indicated no growth, 0 indicated fungal growth outside the inhibition zone surrounding the cotton specimen, (0) indicated fungal growth up to the specimen's edge, (1) indicated fungal growth only on and below the specimen's edge, (2) indicated fungal growth on and below less than 25% of the specimen, (3) indicated fungal growth on and below 25–75% of the specimen, (4) indicated fungal growth on and below more than 75% of the specimen and (5) indicated 100% overgrowth of the specimen. The sporulation intensity was assessed using the following symbols: – meant clear, without mycelium; + meant weak, only mycelium; ++ meant noticeable growth, partly with spores; and +++ meant strong overgrowth, extensive spore formation.

Combustion test

Combustion testing was performed on the samples printed with five different quantities of TPP MCs (0, 100, 200, 400 and 600 g of MCs per kg of printing paste). The combustion performance was studied using the vertical burning test. The vertical burning test was performed in a burning chamber according to the DIN 53906 standard [30].

Thermal properties of MCs and fabrics treated with TPP MCs – TGA and DSC analysis

The samples were examined using a 449c Jupiter Instrument (NETZSCH). The samples were placed on Al_2O_3 carriers. They were heated in a protective atmosphere (air) and the measurements were performed from 35–650 °C at the heating rate of 10 K/min. The samples were then cooled at 10 K/min to room temperature.

3 Results and discussion

3.1 SEM micrographs

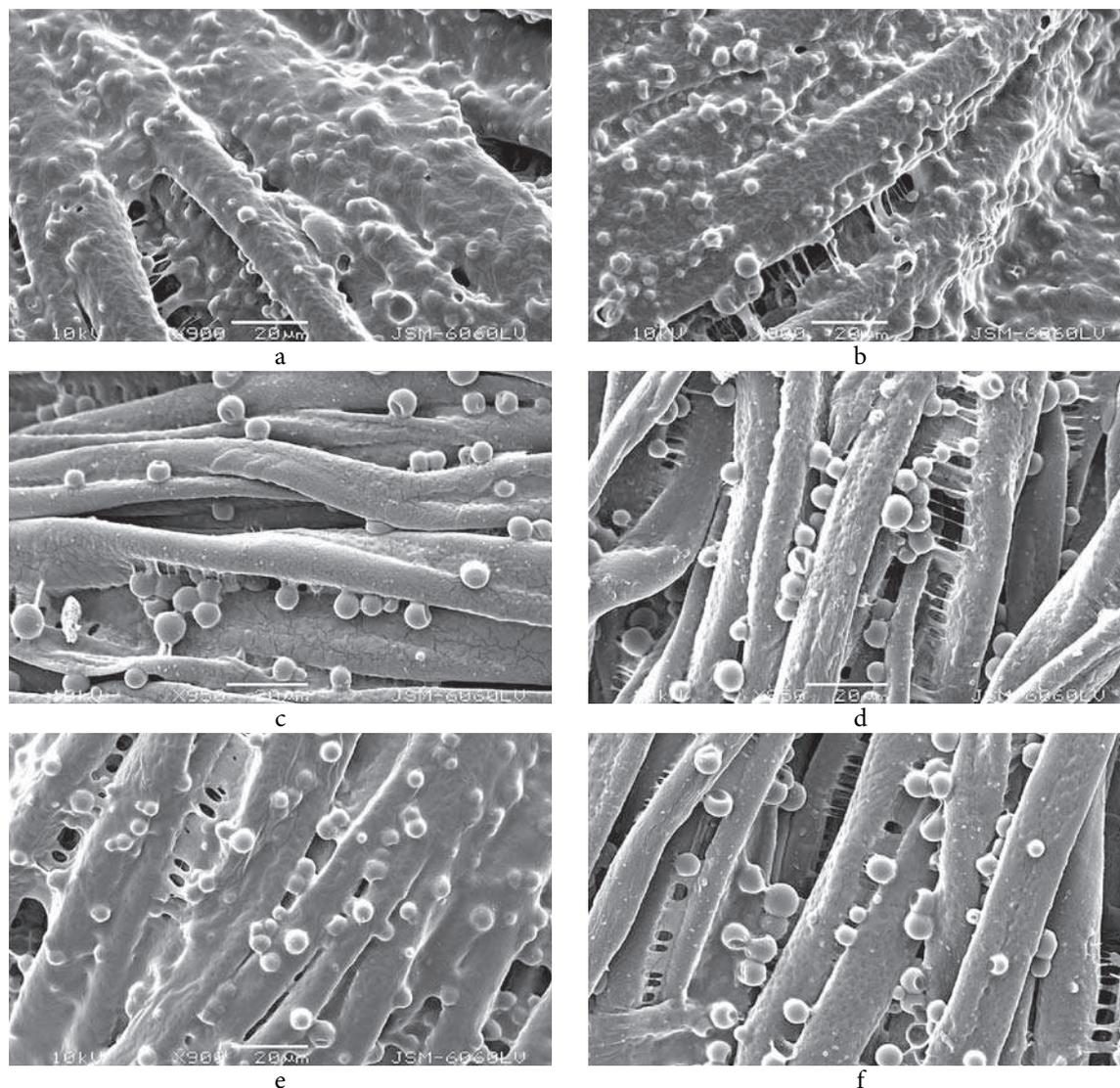


Figure 1: SEM micrographs of printed, one time washed and unwashed samples with MCs (100 g/kg); LRS100 (a), LRS100 – washed (b), TCS100 (c), TCS100 – washed (d), TPP100 (e), TPP100 – washed (f); magnification: 900×, 950×

Fabric properties

The properties of untreated samples and samples printed with different types of MCs were examined. The fabric mass per unit area was determined according to the standard SIST EN 12127:1999 [31], the fabric stiffness was evaluated using the ASTM D-1388-64 method A [32], the fabric thickness was measured according to the standard SIST EN ISO 5084:1999 [33], and the fabric air permeability was determined according to the standard SIST EN ISO 9237:1999 [34].

SEM micrographs (Figure 1) show that there are no morphological differences between the samples printed with different MCs. All MCs were round in shape and evenly distributed over the fibres. There were no aggregates or ruptured MCs. The micrographs of washed samples reveal that the fastness to washing of all samples was very good. Similar to pigments (pigments and MCs are the same size), MCs were firmly bound to the fibres due to the printing system and remained on them after the laundering.

3.2 Fragrance evaluation

The fragrance on the fabric before and after a selected number of washing cycles was evaluated using a panel of five judges (Table 5).

Table 5: Number of judges evaluating fragrance intensity

	Sample	Number of judges per fragrance intensity			
		Strong	Medium	Weak	No
Before washing	CO0				5
	LRS100	4	1		
	LRS150	5			
	LRS200	5			
After 10 washings	CO0				5
	LRS100			3	2
	LRS150			4	1
	LRS200			5	

Before the washing, a strong fragrance was present on all samples with MCs. Even after 10 washings, the fragrance was judged to remain weakly noticeable (regardless of the quantity of the applied MCs) by the majority of the panel. The fragrance was detected as stronger on the samples containing a higher quantity of capsules. The difference between lower and higher concentrations remained evident even after up to 10 washing cycles.

It can be concluded that fragrant MCs work efficiently if they are applied to a fabric in the concentration of at least 100 g of suspension (32 g of MC or 6 g of essential oil) per kg of fabric.

3.3 Antibacterial efficiency

The antibacterial activity levels of fabrics printed with different quantities of MCs (0, 25, 50 and 100 g/kg) was assessed by examining the extent of bacterial growth in the contact zone between the agar and the specimen, and the width of the inhibition zone around the specimen. The activity of printed and washed samples was estimated for one Gram-negative (*E. coli*) and one Gram-positive (*S. aureus*) bacteria. The printed microcapsules were not activated by pressure prior to the testing. The results are shown in Table 6.

Table 6: Widths of inhibition zones of printed samples

Sample	Inhibition zone [mm]	
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>
CO	0	0
CO0	0	0
CO0-W*	0	0
TCS25	0	15
TCS25-W	0	15
TCS50	0	20
TCS50-W	0	35
TCS100	25	40
TCS100-W	25	40

*one time washed sample

It can be observed that the unprinted sample (CO) and the sample printed without MCs (CO0) showed no antibacterial action, as expected. There was no inhibition zone present (Figure 2a). The samples with lower quantities of MCs (TCS50, TCS25) showed satisfactory antibacterial activity only for *S. aureus*. Excellent antibacterial activity of the samples printed with the highest quantity of TCS MCs (TCS100) was evidenced for both bacteria, although it was better for *Staphylococcus aureus*, which had a 40-mm-wide inhibition zone. The inhibition zone remained the same (25 mm for *E. coli* (Figure 2b) and 40 mm for *S. aureus*) even after the washing. It can be concluded that fabrics printed with the highest quantity of TCS MCs (100 g/kg of printing paste) are resistant to *E. coli* and *S. aureus* bacteria.

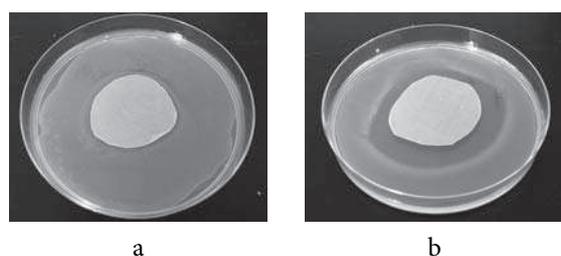


Figure 2: Activity against *E. coli*: (a) sample printed without MCs, CO0, with no inhibition zone; and (b) printed and one time washed sample, TCS100-W, with inhibition zone

3.4 Fungicidal activity

The results of the fungicidal activity test of samples printed with TCS MCs are shown in Table 7.

Table 7: Evaluation results of fungal growth and intensity of sporulation (for code explanations see Methods section)

Sample	Duplicate 1	Duplicate 2
CO0	5+++	5+++
CO0-W	5+++	5+++
TCS100	5+	5+
TCS100-W	5++	5++

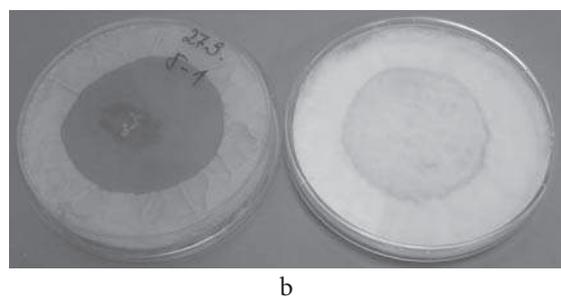
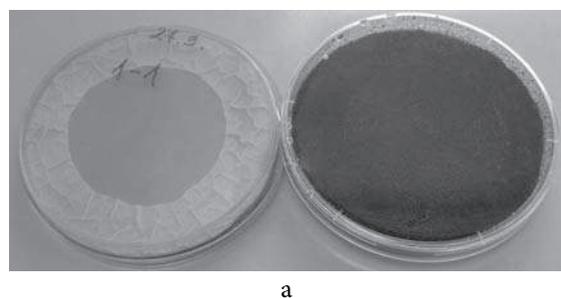


Figure 3: Photographs of samples before and after fungicidal activity testing: (a) sample printed without MCs (CO0); (b) sample printed with TCS MCs (TCS100)

The results of the fungal growth evaluation (Table 7) and the photographs (Figure 3) show that all samples are overgrown with fungi. On the sample printed without MCs, rich mycelium development and strong sporulation (black colour) was observed, whereas the sample with MCs exhibited mycelium spread all over the sample but without sporulation. It can be concluded that there is no fungicidal activity on the printed sample. However, due to the different medium on this sample, the process of fungal growth was slower compared with the sample without MCs. The washing of samples did not have a significant influence on the accelerated fungal growth; on some samples, the intensity was reduced or remained the same as before the laundering.

TCS is a good antibacterial agent (*Staphylococcus aureus*, *Escherichia coli*); however, in the case of the fungi *Aspergillus brasiliensis*, it did not show satisfactory activity.

3.5 Combustion test

Table 8 and Figure 4 represent the results of the influence of printed MCs on the flammability of the CO samples. The upward burning behaviour shows that most samples glow for a longer period of time than they burn. The addition of TPP MCs did not have a substantial influence on the burning time of cotton samples. The untreated sample and the samples printed without MCs burned through their whole length, and only a small quantity of residue remained (Figure 4a). The samples printed with higher quantities of MCs (400, 600 g/kg) also burned through their whole length; however, a significant increase in the amount of the final residue indicates that the printed MCs were able to retard the further degradation process of the char formed during the burning (Figure 4b). None of the samples can be considered as a flame-resistant material. The reason for this result is the concentration of applied MCs, which is too low. The highest possible concentration of microcapsules used for the preparation of the printing paste (that still allowed its preparation) was only 600 g/kg. In contrast, we showed in our previous research that the impregnation of a fabric with the MC concentration of 800 g/kg protects the fabric from burning.

Table 8: Results of vertical burning test of printed samples with different quantity of applied microcapsules

Sample	Burning time [s]		Glow time [s]	
	unwashed	washed	unwashed	washed
CO	<12	<9	20	7
CO0	<5	<3	20	30
TPP100	<6	<4	31	34
TPP200	<5	<5	40	44
TPP400	<19	<9	9	15
TPP600	<15	<10	10	13

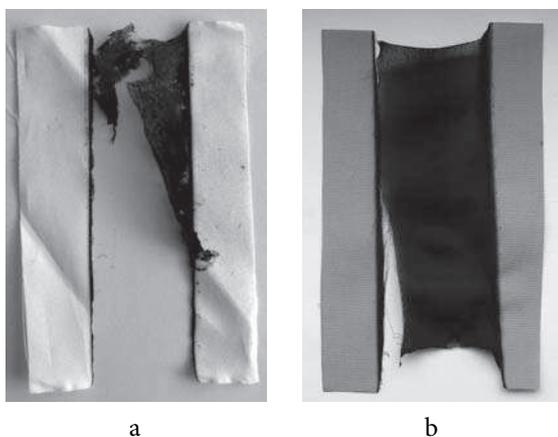


Figure 4: Samples of untreated (a) and printed fabrics with TPP MC (600 g/kg), (b) after vertical burning test

3.6 TGA and DSC analyses

Figures 5 and 6 show the TGA and DSC curves of untreated cotton and the sample printed with TPP MCs. All diagrams also present the curves of the TPP MCs suspension.

The TGA curve of the suspension deviates from the dry sample due to the evaporation of water at temperatures below 180 °C. The CO samples lost 60% of their weight at 330 °C. The printed sample started to degrade earlier (at 190 °C) than the raw material. TPP MCs start to degrade at lower temperatures than the surrounding material, and the degradation products, such as P₂, PO, PO₂ and HPO₂, in the vapour phase extinguish the flame. Consequently, if there are MCs present on the material, more fabric remains unburned (Figure 4).

The DSC curve in Figure 6 confirms that the presence of MCs on the textile material changes its properties. The printed cotton fabric has lower exothermic peaks that start at lower temperatures than the raw cotton fabric. The MCs decrease the heat released from the cotton fabric. Figure 6 also demonstrates the behaviour of cotton at high temperatures. Natural CO fibres gradually degrade in several oxidation reactions, represented by several broad peaks on the DSC curve. It can be concluded that the applied MCs increase the thermo-oxidative stability of cotton; however, they do not prevent the burning. The pigment system does not allow using higher concentrations of MC; therefore, its application is not appropriate to produce fire-retardant materials.

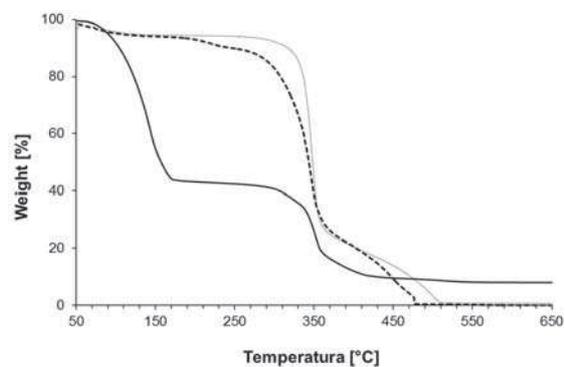


Figure 5: TG curves of samples: TPP MC (—), CO (.....), TPP400 (----)

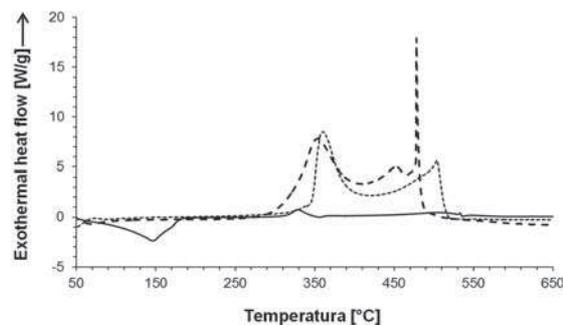


Figure 6: DSC curves of samples: TPP MC (—), CO (.....), TPP400 (----)

3.7 Fabric properties

The mechanical properties of fabrics (mass, thickness, stiffness and air permeability) printed with the same quantity of different MCs was investigated and compared with the properties of the unfinished sample and the sample printed without MCs. The mass per unit area of samples is presented in Figure 7.

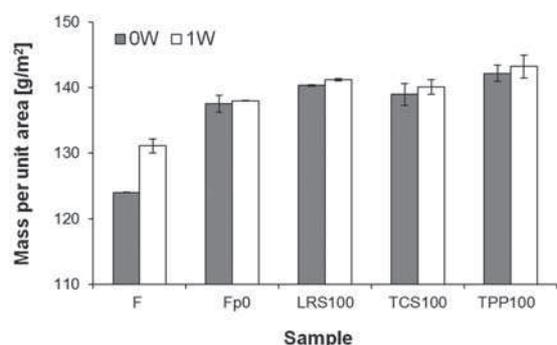


Figure 7: Mass per unit area of untreated sample, sample printed without MCs, sample printed with LRS MCs, sample printed with TCS MCs and sample printed with TPP MCs

Figure 7 reveals that all printed samples had higher masses than the unprinted fabric. The MCs further increased the mass but not significantly. The differences between the samples printed with different MCs were negligible. The sample printed with TPP MCs had the highest mass per unit area. We assume that the reason for this result is a solid core without a solvent, which could not evaporate from some of the MCs that broke during the printing process. After the washing, the mass of all samples increased, which is a consequence of the fabric thickness increase after the laundering.

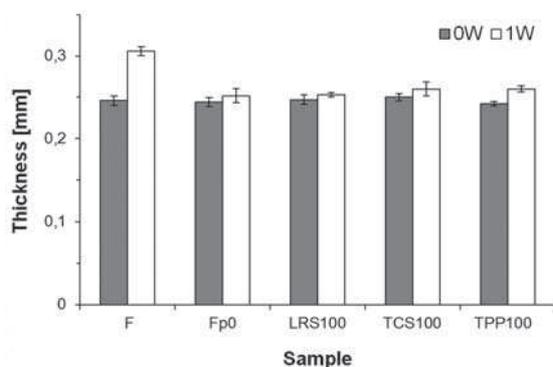


Figure 8: Thickness of untreated sample, sample printed without MCs, sample printed with LRS MCs, sample printed with TCS MCs and sample printed with TPP MCs

Figure 8 shows the thicknesses of samples. The results show that the printing on a fabric without or with MCs does not cause differences in thickness. The fact that the thickness of the printed fabric is similar or even slightly lower than the unprinted

fabric is a consequence of the printing process, in which the fabric is compressed. The thickness of all samples printed with different MCs was almost the same. This result was expected since all MCs were in the same size range and the deposit of the printing pastes on the fabric was similar in all cases. After the washing, the thickness of all samples increased. This result is an issue of fabric shrinkage and thickening of threads in material.

Considering the stiffness of samples (Figure 9), it is evident that according to the expectations, all printed (with and without MCs) samples were more rigid than the unfinished sample. It can also be seen that MCs further increased fabric stiffness. There were no essential differences between the samples printed with different MCs. The sample with TPP MCs was slightly stiffer. After the washing, the stiffness of printed samples decreased as the polymer thickener softened and some MCs were removed.

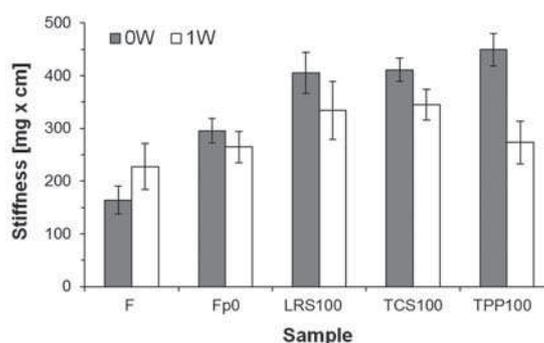


Figure 9: Stiffness of untreated sample, sample printed without MCs, sample printed with LRS MCs, sample printed with TCS MCs and sample printed with TPP MCs

The air permeability results are presented in Figure 10. As expected, all printed samples show lower permeability than the unfinished fabric. The applied printing paste itself caused a considerable decrease in the permeability, whereas the addition of MCs led to a further decrease. The air permeability of samples printed with different MCs was similar.

It can be clearly seen that the printing of MCs changes the fabric properties. Even the printing without microcapsules increased the fabric mass per unit area and stiffness, as well as decreased the thickness and air permeability. This result is due to the presence of a thickener and binder in the printing paste, which resulted in an additional stiff layer on the fabric. The

addition of MCs further increased the changes in fabric properties.

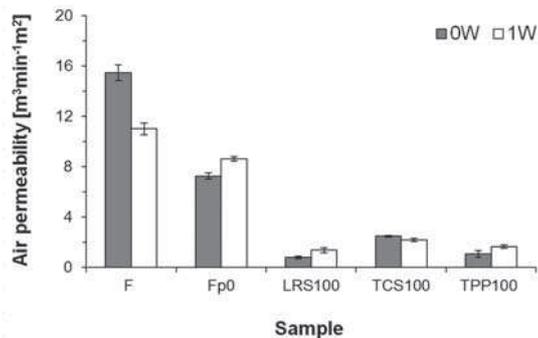


Figure 10: Air permeability of untreated sample, sample printed without MCs, sample printed with LRS MCs, sample printed with TCS MCs and sample printed with TPP MCs

4 Conclusion

Fragrant, antimicrobial and fire-retardant MCs were successfully applied to cotton fabrics using screen printing. The fastness to washing of all MCs was very good. The fragrant MCs worked best when they were applied to the cotton fabric at the concentration of 100 g suspension per kg of fabric (32 g of MCs or 6 g of oil) and the antibacterial MCs worked best also at the concentration of 100 g suspension per kg of fabric (32 g of MC or 4.8 g of TCS). The latter had no fungicidal activity. In the case of fire-retardant MCs, the MCs had some influence on the burning of the cotton sample; however, higher concentrations of MCs applied to the fabric would be needed to substantially inhibit the burning. This result could not be achieved by using the pigment system. The printing of MCs changed the mechanical properties of all samples to some extent. The properties of the samples printed with the same concentration (100 g/kg) of different MCs were similar. It was shown in this study that with the use of aminoaldehyde MCs, textiles with different functional properties can be achieved. The MCs of this type can be used for the application of a wide range of substances to fabrics since they represent a suitable carrier for different water-immiscible compounds. It was also shown that the printing with synthetic swelling thickeners and polymeric binders (pigment system) is appropriate for the application of melamine-formaldehyde microcapsules.

MCs applied this way are able to achieve the desired properties, show good fastness to washing and do not significantly change the mechanical properties of the fabric.

It can be concluded that the system (model) for the functionalisation of textiles with MCs which can improve the quality, functionality and value of textile products was successfully established.

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References

- BOH PODGORNIK, Bojana, STAREŠINIČ, Marica. Microencapsulation technology and applications in added-value functional textiles. In *Microencapsulation : innovative applications*. Edited by GIAMBERINI, Marta, FERNANDEZ PRIETO, Susana, TYLKOWSKI, Bartosz. Berlin, Munich, Boston : De Gruyter, 2015, 37–75.
- BOH PODGORNIK, Bojana. Aplikacije mikrokapsuliranja v proizvodnji funkcionalnih tekstilij. In *Proceedings of Slovenski kemijski dnevi*, Ljubljana, 2015.
- BOH PODGORNIK, Bojana, KNEZ, Emil. Microencapsulation of essential oils and phase change materials for applications in textile products. *Indian Journal of Fibre and Textile Research*, 2006, **31**, 72–82
- ANAL, Anil Kumar, STEVENS, WF, REMUÑÁN-LÓPEZ, C. Inotropic cross-linked chitosan microspheres for controlled release of ampicillin. *International Journal of Pharmaceutics*, 2006, **312**, 166–173, doi: 10.1016/j.ijpharm.2006.01.043.
- NELSON, Gordon. Application of microencapsulation in textiles. *International Journal of Pharmaceutics* 2002, **242**(1–2), 55–62, doi: 10.1016/s0378-5173(02)00141-2.
- MIRÓ SPECOS, Maria, ESCOBAR, German, MARRINO, Patricia, PUGLIA, Cesar, DEFRAIN, Maria Victoria, HERMIDA, Laura. Aroma finishing of cotton fabrics by means of microencapsulation techniques. *Journal of Industrial Textiles*, 2010, **40**(1), 13–32, doi: 10.1177/1528083709350184.

7. OCEPEK, Barbara, BOH PODGORNIK, Bojana, ŠUMIGA Boštjan. Printing of antimicrobial microcapsules on textiles. *Coloration Technology*, 2012, **128**, 95–102, doi: 10.1111/j.1478-4408.2011.00349.x.
8. BADULESCU, Roxana, VIVOD, Vera, JAUŠOVEC, Darja, VONČINA, Bojana. Grafting of ethylcellulose microcapsules onto cotton fibres. *Carbohydrate Polymers* 2008, **71**(1), 85–91, doi: 10.1016/j.carbpol.2007.05.028.
9. PONCELET, Denis. *Surface Chemistry in Biomedical and Environmental Science*. Netherlands : Springer, 2006, 23–34.
10. NELSON, Gordon. Microencapsulation in textile finishing. *Coloration Technology*. 2001, **31**(1), 57–64, doi: 10.1111/j.1478-4408.2001.tb00138.x.
11. LESKOVŠEK, Mirjam, JEDRINOVIĆ, Gordana, STANKOVIĆ ELESINI, Urška. Properties of polypropylene fibres with incorporated microcapsules. *Acta Chimica Slovenica*, 2004, **51**(4), 699–715.
12. VAN PARYS, M. *Functional coatings: by polymer microencapsulation*. Weinheim : Wiley-VCH Verlag GmbH & Co. KgaA, 2006, 2218.
13. BOH PODGORNIK, Bojana, KNEZ, Emil. Microencapsulated antimicrobials on non-woven textiles for shoe insoles. In *Proceedings of the XVth International Workshop on Bioencapsulation, Vienna, 2007*, 1–4.
14. TOMŠIČ, Brigita, SIMONČIČ, Barbara, OREL, Boris, ŽERJAV, Metka, SCHROERS, Hans, SIMONČIČ, Andrej, SAMARDŽIJA, Zoran. Antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric. *Carbohydrate Polymers*, 2009, **75**(4), 618–626, doi: 10.1016/j.carbpol.2008.09.013.
15. KLEMENČIČ, Danijela, TOMŠIČ, Brigita, KOVAČ, Franci, SIMONČIČ, Barbara. Antimicrobial cotton fibres prepared by in situ synthesis of AgCl into a silica matrix. *Cellulose*, 2012, **19**, 1715–1729, doi:10.1007/s10570-012-9735-z.
16. ŠUMIGA, Boštjan, STEPANČIČ, L., BOH, Bojana. *Mikrokapsule z zaviralcem gorenja in postopek za njihovo pripravo*. Patent SI 23760 A, SLO, 2011.
17. ORHAN, Mehmet, KUT, Dilek, GUNESOGLU, Cem. Use of triclosan as antibacterial agent in textiles. *Indian Journal of Fibre and Textile Research*, 2007, **32**, 114–118.
18. GLASER, Aviva. The ubiquitous triclosan: a common antibacterial agent exposed. *Pesticides and You*, 2004, **24**(3), 12–17.
19. BHARGAVA, HN, LEONARD P. A. Triclosan: applications and safety. *American Journal of Infection Control*, 1996, **24**(3), 209–218.
20. HORROCKS, AR, PRICE, D. *Fire retardant materials*. Cambridge : Woodhead Publishing Limited, 2001, 50.
21. ŠUMIGA, Boštjan. *Information approaches in the design of chemical microencapsulation processes : PhD thesis*. University of Ljubljana, 2012.
22. GOLJA, Barbara, ŠUMIGA, Boštjan, FORTE TAVČER, Petra. Fragrant finishing of cotton with microcapsules – comparison of printing and impregnating. *Coloration Technology*, 2013, **129**(5), 338–346, doi: 10.1111/cote.12044.
23. ŠUMIGA, Boštjan, KNEZ, Emil, VRTAČNIK, Margareta, FERK SAVEC, Vesna, STAREŠINIČ, Marica, BOH, Bojana. Production of melamine-formaldehyde PCM microcapsules with ammonia scavenger used for residual formaldehyde Reduction. *Acta Chimica Slovenica*, 2011, **58**, 14–25.
24. BOH PODGORNIK, Bojana, ŠUMIGA, Boštjan. In situ polymerisation microcapsules. *Bioencapsulation Innovations*, 2013, 4–6.
25. *ISO 105-C01:1989, Textiles – Tests for colour fastness – Part C01: Colour fastness to washing: Test 1*. Geneva : ISO, 1989.
26. LEWIS, J. *Effect of curing method on the durability of microencapsulated fragrant finishes : master's thesis*. Institute of Textile Technology, Manchester, England, 2003.
27. Van SOEST JGJ. *Flavours and fragrances – chemistry, bioprocessing and sustainability*. Berger, Berlin; Heidelberg New York : Springer, 2007, 439.
28. *SIST EN ISO 20645:2005, Determination of antibacterial activity – Agar diffusion plate test*. Brussels : CEN, 2004.
29. *DIN 53931 – Testing of textiles; Determination of the resistance of textiles to mildew, growth test*. Berlin : DNA, 1969.
30. *DIN 53906: 1974-02, Testing of textiles – Determination of the burning behaviour. Vertically method; Ignition by application of flame to base of specimen*. St. Gallen : SNV, 1971.
31. *SIST EN 12127:1999 Textiles – Fabrics – Determination of mass per unit area using small samples*. Brussels : CEN, 1999.
32. *ASTM D-1388-64 Method A: Standard test method for stiffness of fabrics*. New York : ASTM, 1975.
33. *SIST-EN ISO 5084:1999 Determination of thickness of textiles and textile products*. Brussels : CEN, 1996.
34. *SIST-EN ISO 9237:1999 Determination of permeability of fabric to air*. SIST, 1999.