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Optimisation of fragrance finishing on cotton by grafting of β-cyclodextrin based microcapsules: Application of the experimental design methodology

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The grafting reaction of β-cyclodextrin-based microcapsules containing neroline onto pure cotton jersey knitted fabric is studied. The influence of the concentrations of microcapsules, citric acid (CA) crosslinking agent and catalyst on the fabric mass gain was studied to determine the optimum operating conditions. For this purpose, an experimental design based on response surface methodology (RSM) was used leading to the development of a predictive statistical model. The optimal grafting conditions were thus determined: 107.6 g $\cdot$ L^{-1} for microcapsules concentration, 111.9 g $\cdot$ L^{-1} for CA concentration and 50 g $\cdot$ L^{-1} for disodium hydrogen phosphate (DHP) catalyst concentration (CAT). Morphology, tensile properties, air permeability and washing fastness of finished textile were studied to evaluate the effectiveness of the optimised grafting process.

Keywords: *microcapsules, β-cyclodextrin, grafting process, optimisation, response surface methodology, cosmetotextile*

1. Introduction

Manufacturers are paying a growing interest to the functionalisation of textiles for innovative applications. Among the most emerging technologies are those based on microencapsulation [1]. This high-tech approach for the global market allows the improving of intrinsic properties or providing entirely new functionalities, which would not be possible or would be too expensive by using other processes [2]. Encapsulation creates a physical barrier that protects the active ingredient from the external environment, enabling the possibility of its controlled release [3]. Such finish allows a broader usability and higher market value of garments in a vast range of applications [4].

In the beginning, functional textiles focused only on individual value-adding properties. Nevertheless, recent research has targeted combinations of multiple properties and their effects, allowing the development of new multifunctional smart textiles with various functionalities in one product, such as simultaneous aromatic [5], antibacterial [6], superhydrophobic [7] and UV-protective effects [8]. With regards to encapsulated materials, microparticles have been in use for a long time in many fields, involving applications such as carbonless copying paper [9], adhesives, insecticides, acaricides [10], pharmaceutics, medicine [11], coatings [12], liquid crystals and cosmetics, and others [13]. For the latter newly emerging sector, encapsulated products are designed to transfer an active material upon contact with the human body for cosmetic purposes like perfuming, moisturising, slimming, refreshing, relaxing, revitalising or/and UV-protecting [14].

As a current trend, researchers nowadays tend to go further by producing cosmetic-loaded microparticles from renewable resources such as cyclodextrins (CDs) [14], which leads to the usage of green and bio-sourced materials [15].

CDs are a simple and relatively affordable material [16] that result from the degradation of starch by α-1,4-glucan-glycosyltransferases [17]. These

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compounds are cyclic oligosaccharides comprising of at least six D-(+)-glucopyranose units linked by α-(1,4)-glucoside bonds [18]. With lipophilic inner cavities and hydrophilic outer surfaces, these macromolecules can interact with a variety of guest molecules to form non-covalent inclusion complexes that provide protection and improve solubility, bioavailability and safety of active compounds [19]. Natural α-, β- and γ-cyclodextrins (with six, seven and eight glucose units, respectively), differing in ring size and solubility, are the most frequently used [20].

In the textile field, CDs frequently used to be chemically grafted to cotton with polycarboxylic acid in the presence of a catalyst. According to Sharkawy et al. [21] and Yang et al. [22], citric acid (CA) was used as a safe crosslinker to covalently bind the microcapsule wall material to hydroxyl groups of cotton via ester bonds. During curing, the binder forms a thin, elastic and transparent layer on the textile surface in which the microcapsules are bound. Hence, the adhesion between the bound layer and the textile substrate plays a crucial role [13].

In a previous study, the functionalisation of cotton fabric by fragrant β-cyclodextrin-based microcapsules using an impregnation process was studied using a polyurethane (PU) binder [23]. The adhesion to cotton fabric was quite good. However, the binding of microcapsules relied on the film-forming properties of the PU binder emulsion instead of covalent linkage. The present process relies on chemical attachment brought about by a chemical reaction with a crosslinking agent. To the best of the author's knowledge, no research articles about optimisation processes are available in the literature about grafting of β-cyclodextrin-based microcapsules in the cosmetotextile field despite CDs and their derivatives being frequently grafted onto different textile supports, as reported in the studies of Shown and Murthy [24], Martel et al. [25] and El Ghoul et al. in 2007 [26], 2008 [27] and 2014 [28].

The paper reports on the application of Response Surface Methodology (RSM) on β-cyclodextrin-based microcapsules deposition and binding on pure cotton fabric using grafting process for the elaboration of the cosmetotextile product. The effect of the composition of the grafting bath (concentrations of microcapsules, CA crosslinking agent and disodium hydrogen phosphate [DHP] catalyst) on the fabric mass gain are studied. Modelling and optimisation of the experimental conditions are then investigated so as to improve the performance of the grafting process. Finally, several grafted textile properties are assessed, namely morphology, tensile strength, air permeability and washing fastness.

2. Experimental Part

2.1. Materials

Pure cotton jersey knitted fabric, bleached, mercerised of specific area 138 g $\cdot$ m^{-2} was supplied by Esprit Maille (Bouhjar, Tunisia). CA (Sigma-Aldrich, 99.5%) was used as a crosslinking agent and DHP (Sigma-Aldrich, 99%) was used as a catalyst. Microcapsules of spherical shape and a mean particle size of 29 µm with good thermal stability were synthesised according to our previous published procedure [23]. PU neroline loaded microcapsules have been achieved by the classical process of interfacial polycondensation between β-cyclodextrin and hexane diisocyanate in an o/w emulsion. The PU polymer forming the microcapsules shell is shown in Figure 1.

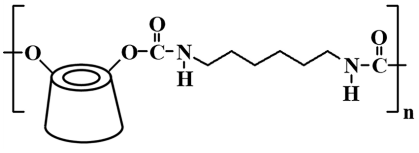


Fig. 1. Molecular structure of the PU polymer based on β-cyclodextrin forming the microcapsules shell. PU, Polyurethane

2.2. General Methods and Instrumentation

2.2.1. Textile finishing

Cotton was impregnated into an aqueous solution containing fragrant microcapsules mixed with CA and DHP for 5 min at 195°C. Fabric samples were then squeezed and dried at 90°C for

Table 1. Experimental range and levels of independent process variables

Coded variable	**Natural variable**	**Unit**	**Levels**		
			−1	**0**	**+1**
X_1	U_1: microcapsules concentration	$(g \cdot L^{-1})$	90	100	110
X_2	U_2: CA crosslinking agent concentration	$(g \cdot L^{-1})$	80	100	120
X_3	U_3: DHP CAT	$(g \cdot L^{-1})$	50	60	70

CAT, catalyst concentration; CA, citric acid; DHP, disodium hydrogen phosphate

Table 2. Box-Behnken design and experimental results

Experiment N°	**Coded values**			**Real values**			**Mean response**
	X_1	X_2	X_3	U_1	U_2	U_3	G (%) (n = 3)
1	−1	−1	0	90	80	60	2.25
2	+1	−1	0	110	80	60	3.68
3	−1	+1	0	90	120	60	2.75
4	+1	+1	0	110	120	60	4.11
5	−1	0	−1	90	100	50	3.85
6	+1	0	−1	110	100	50	4.72
7	−1	0	+1	90	100	70	1.88
8	+1	0	+1	110	100	70	2.11
9	0	−1	−1	100	80	50	3.45
10	0	+1	−1	100	120	50	5.22
11	0	−1	+1	100	80	70	1.50
12	0	+1	+1	100	120	70	1.47
13	0	0	0	100	100	60	4.23
14	0	0	0	100	100	60	4.26
15	0	0	0	100	100	60	4.28

15 min. Functionalised textiles were finally rinsed and dried again to remove non-grafted microcapsules.

The functionalisation rate of the fabrics was assessed by the mass gain of the samples upon treatment with β-cyclodextrin based microcapsules (expressed as wt.%). The fabric mass gain G was reported as the ratio of the mass difference of dry fabric after and before the treatment with the fragrant microcapsules to the initial mass of dry fabric. It was calculated as a percentage using Eq. (1) as follows:

$$G(\%) = \frac{m' - m}{m'} \times 100 \qquad (1)$$

where (m) and (m') are the masses of the dry fabric before and after functionalisation, respectively.

2.2.2. Design of experiments (DOE)

RSM was used to optimise the impregnation process as reported by Box et al. [29], D'Agostino and Stephens [30] and Khuri and Cornell [31]. The studied experimental factors were the concentrations of the microcapsules (X_1), the CA crosslinker (X_2) and the Na_2HPO_4 catalyst (X_3). The investigated experimental domain and the corresponding coded levels (−1, 0 and +1) are defined for each factor as shown in Table 1 according to Kumar et al. [32], and Singh et al. [33, 34]. The choice of the levels of each factor is made according to results obtained in section 3.1. A Box–Behnken design was built to fit a second-order quadratic model to experimental data, allowing the prediction of the fabric mass gain G [29]. Fifteen experiments were

carried out, including three repetitions of the central point (Table 2). All these experiments were done in triplicate. The Minitab software (Version 19, State College, PA, USA) was used for multiple linear regression, analysis of variance (ANOVA) and statistical analysis.

2.2.3. Scanning electron microscopy

The shape and surface features of textile fabrics before and after functionalisation were observed by scanning electron microscopy (SEM) after drying using a Jeol JCM 5000 (Jeol, Japan) microscope. Specimens were examined at room temperature without surface metallization at 5 kV and 10 kV acceleration under moderate vacuum.

2.2.4. Tensile strength

Tensile test measurements of untreated and treated fabrics were carried out based on the ISO 13934-1 standard by using a Lloyd dynamometer LS series (Ametek STC, France) under standard conditions (20 ± 2°C and 65 ± 2% of relative humidity) after preconditioning all samples in a standardised conditioning room for 24 h. Measurements in column and row directions were performed using a specimen with dimensions of 200 mm length and 50 mm width. The distance between clamps and the movement speed were 50 mm and 10 mm · s^{-1}, respectively. Three samples were tested for each type of fabric.

2.2.5. Air permeability

Air permeability of untreated and treated fabrics was measured based on the EN ISO 9237 standard by using a FX3300-III instrument (TEXTEST AG) under standard conditions (20 ± 2°C and 65 ± 2% of relative humidity). Preconditioning of all samples was done in a standardised conditioning room for 24 h. Measurements were performed under an air pressure of 100 Pa per 100 cm^2 fabric surface. Tests were done in triplicate and the measurements were carried out by scanning the entire textile surface on both sides in order to ascertain the reproducibility of the results. Results were expressed as rates of air flow per unit area and time expressed in "mm · s^{-1}".

2.2.6. Wash fastness

Wash fastness was studied in accordance with ISO Standard 105-C10 of 2010. Functionalised fabrics were washed for 30 min at 40°C in an Autowash device. Then, specimens were rinsed with water for 5 min and dried under ambient conditions.

The fate of bound microcapsules and the residual amount of fragrance were estimated by SEM observations and gas chromatography (GC) analysis using a 7,890 A Gas Chromatograph from Agilent Technologies (USA) equipped with a flame ionisation detector (FID). Residual neroline after washing was extracted using chloroform. Analytes from the 1 μL samples were injected at a split ratio of 1:20 and separated on a 19091J HP-5 column (length, 30 m; internal diameter, 0.32 mm; film thickness, 250 mm). The oven temperature was initially set at 200°C for 10 min and the detector temperature was 280°C. Nitrogen was used as the carrier gas with a constant flow rate of 20 mL · min^{-1} and an inlet pressure of 1.5 bar.

3. Results and Discussion

3.1. Factors Affecting Grafting Process

Functionalisation of mercerised cotton jersey fabric with neroline-loaded microcapsules based on β-cyclodextrin was investigated. This surface modification was carried out by a condensation reaction between hydroxyl groups of cellulose and β-cyclodextrin through the polycarboxylic acid crosslinking agent, CA. The finishing procedure was applied by standard methods – analogous to those of reactive dyeing – on conventional equipment. Microcapsules were drawn up from a dipping bath, the textile was squeezed and thus, β-cyclodextrin was fixed on the fiber at an elevated temperature. Unattached microparticles were simply removed by washing [35].

The studied variables were the main operating conditions influencing the grafting process, the microcapsules concentration, the CA crosslinking agent concentration and the DHP CAT. The studied response was the mass gain of the functionalised textile (G). Throughout this study, each experiment

was carried out in triplicate and each experimental data is an average of them. Since this was a preliminary study, the influence of the variables was initially investigated independently while keeping the other variables constant. Thereafter, a full optimisation was performed using RSM.

3.1.1. Effect of the microcapsules concentration

The microcapsules concentration varied between 90 g · L^{-1} and 120 g · L^{-1} for a CA crosslinking agent concentration of 80 g · L^{-1} and a DHP CAT of 50 g · L^{-1}. The variation of G in Figure 2 shows that the mass gain increased with respect to the concentration of microcapsules according to obvious expectation. However, there was no further mass gain for concentrations >110 g · L^{-1}as the excess microcapsules clumped together in the reaction medium.

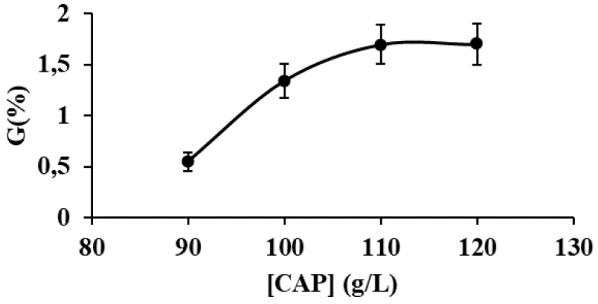


Fig. 2. Effect of the microcapsules concentration (CAP) on the mass gain G

3.1.2. Effect of the concentration of CA crosslinking agent

For a microcapsules concentration of 110 g · L^{-1} and DHP CAT of 50 g · L^{-1}, the effect of the CA crosslinking agent concentration on the mass gain (G) was studied at different concentrations, from 80 g · L^{-1} to 140 g · L^{-1}.

As shown in Figure 3, the mass gain increased with respect to the concentration of CA at levels above [CA] = 120 g · L^{-1}. However, this 'optimum' concentration depends on both the quantity of microcapsules introduced and the textile surface area to be treated. As a polycarboxylic acid, CA acts as a crosslinking agent by reacting with the hydroxyl groups of the β-cyclodextrin molecules in the microcapsules shell on the one hand and the hydroxyl groups of the cellulose on the other.

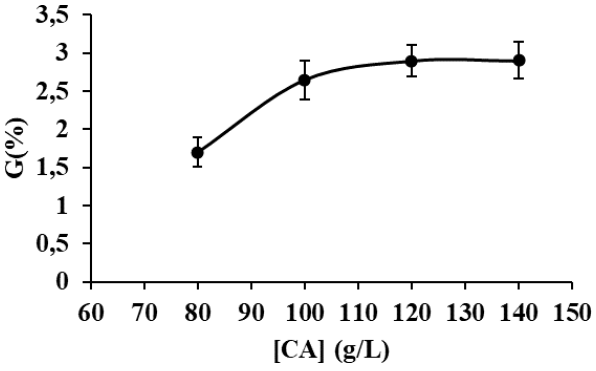


Fig. 3. Effect of the CA crosslinking agent concentration on the fabric mass gain. CA, citric acid

3.1.3. Effect of the DHP CAT

For a microcapsules concentration of 110 g · L^{-1} and a CA crosslinking agent concentration of 120 g · L^{-1}, the mass gain percentage (G) was assessed for DHP CATs varying between 50 g · L^{-1} and 70 g · L^{-1} (Figure 4).

It appears that the optimum CAT is about 60 g · L^{-1}. Indeed, the mass gain decreases for higher concentrations. This may be due to the fact that, at higher concentrations, the reaction takes place mainly between the microcapsules instead of between the microcapsules and the cellulose.

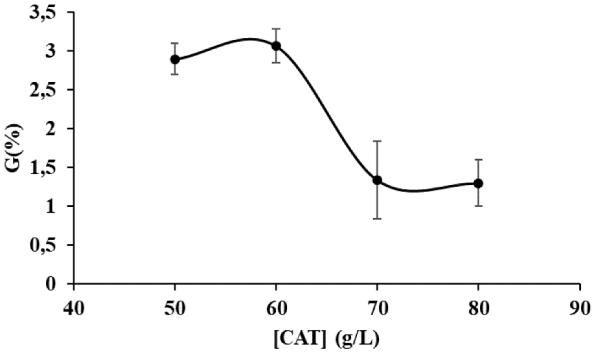


Fig. 4. Effect of the DHP CAT on the mass gain. CAT, catalyst concentration; DHP, disodium hydrogen phosphate

Table 3. ANOVA

Source	Degrees of freedom	Sum of squares	Variance	*F*	*p*-value
Regression	9	20.4000	2.2667	18.98	0.002
Residuals	5	0.5971	0.1194	–	–
Total	14	20.9971	–	–	–

ANOVA, analysis of variance

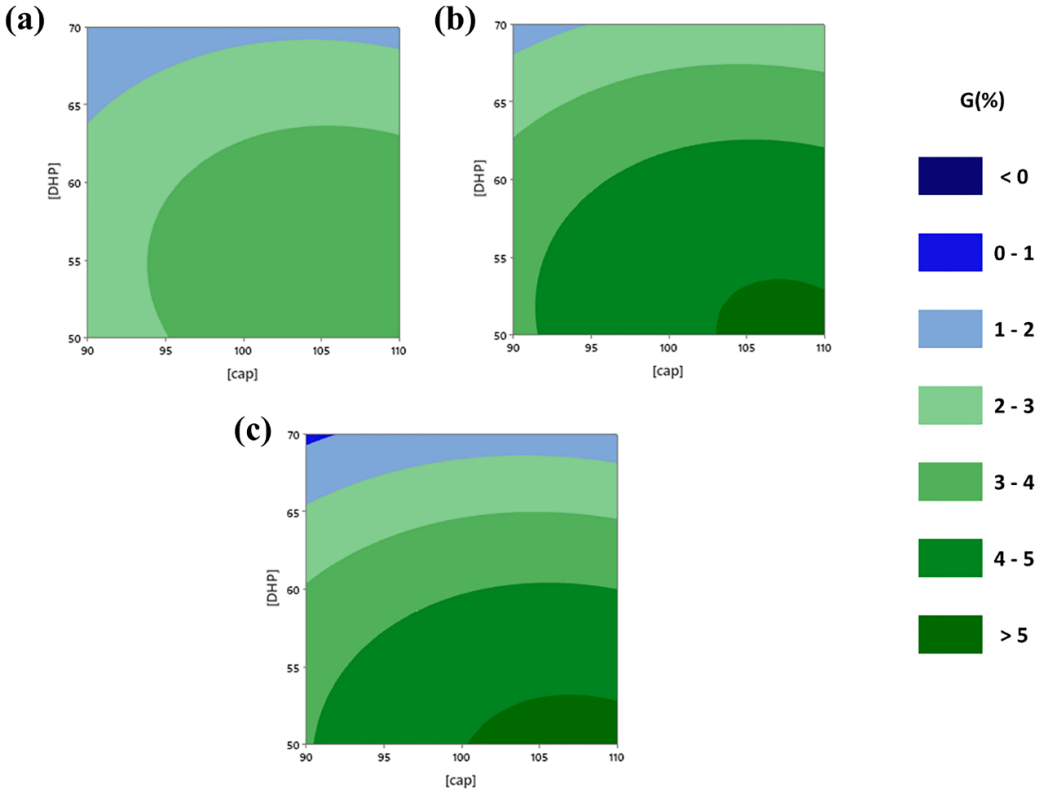


Fig. 5. Contour plots showing the combined effect of microcapsules and DHP CATs on the mass gain (G) using different CA crosslinking agent concentrations: **(A)** 80 g · L^{-1}, **(B)** 100 g · L^{-1} and **(C)** 120 g · L^{-1}. CAT, catalyst concentration; DHP, disodium hydrogen phosphate

3.2. Optimisation of the Grafting Process by RSM

3.2.1. Model validation

Since the preliminary experiments showed that the variations of mass gain with respect to variables were not linear, and that there was a maximum, a second-order quadratic model has therefore been developed to explain the mass gain. To reach this goal, the three experimental factors were simultaneously varied according to a Box–Behnken design. Results were investigated using the software Minitab 19 which led to Eq. (2), where X_i are the coded factors:

$$G(\%) = -101.4 + 0.983X_1 + 0.483X_2 + 1.099X_3 - 0.00415{X_1}^2 - 0.001611{X_2}^2 - 0.00702{X_3}^2 - 0.000087X_1X_2 - 0.00160X_1X_3 - 0.002250X_2X_3 \quad (2)$$

with Adjusted R^2 = 0.9204 and Predicted R^2 = 0.5458. At the 5% level in the Student *t*-test, all the regression coefficients were significant. The usual determination coefficient R^2 of the regres-

sion equation (Eq. (2)) was 0.9716. All these R^2's proved the satisfactory adequacy of the model. The mass gain ranges from 1.47% up to 5.22% depending on the applied operating conditions (Table 2). Each experiment was carried out in triplicate and the 95% confidence interval of G has been estimated at about $\pm 0.1\%$ (standard deviation ~0.04%) indicating high reproducibility of the G measurements.

ANOVA was first used to evaluate the fitting quality of the model [36]. The assessment is based on an F-test. Results of ANOVA in Table 3 shows the high significance of the regression model for the mass gain prediction (Eq. (2)) (p-value < 0.01).

To finally evaluate the validity of the model, the residuals were also determined by calculating the difference between the experimental G and the G predicted by the model (Eq. (2)). These residuals $<0.8\%$ indicated that the mass gain G was satisfactorily explained by the regression model.

3.2.2. Response surfaces

Once validated, the model was used to visualise the response surfaces as bi-dimensional plots of two factors (X_1 and X_3), while keeping the third one (X_2) constant. Figure 5 shows the contour plots of the response surface for G at CA crosslinking agent concentrations of 80 g · L^{-1}, 100 g · L^{-1} and 120 g · L^{-1}.

The contour plots in Figure 5 confirm the results drawn by varying parameters one by one: the concentrations of microcapsules and CA should be maximum and the concentration of catalyst should be minimum within the studied window. There are synergistic effects, however. The most relevant ones are those between the concentration of catalyst on the one hand and either the concentration of microcapsules or CA on the other hand. The optimum concentration of catalyst drawn from the one parameter at a time study was 60 g · L^{-1} for a microcapsules concentration of 110 g · L^{-1} and a CA crosslinking agent concentration of 120 g · L^{-1}. The quasi-symmetrical feature of the contour plots with respect to the diagonal in Figure 5 shows that the optimum of CAT shifts from 60 g · L^{-1} to 50 g · L^{-1} as the concentration of microcapsules increases. The same trend is observed for an increase of CA concentration.

3.2.3. Response optimisation

The optimal conditions of the cotton grafting process using fragrant microcapsules were predicted by the response optimiser tool of Minitab 19 software for maximum response. Response optimisation described in Figure 6 shows that optimal experimental conditions are a microcapsules concentration of 107.6 g · L^{-1}, a CA crosslinking agent concentration of 111.9 g · L^{-1} and a DHP CAT of 50 g · L^{-1}, which yields a mass gain of 5.32%.

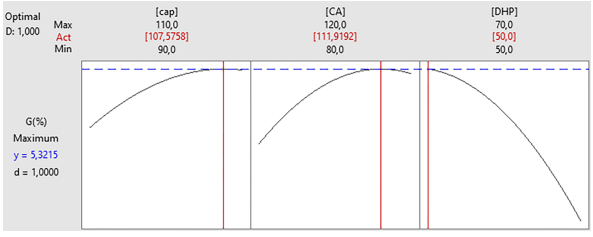


Fig. 6. Response optimisation of the grafting process. CA, citric acid; DHP, disodium hydrogen phosphate

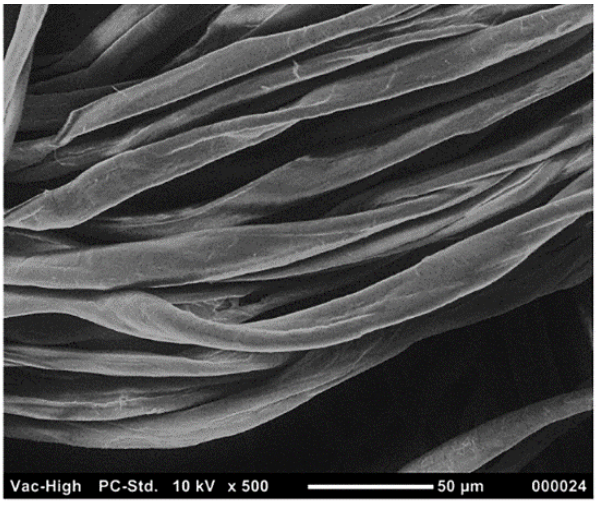
To verify the validity of the model, the corresponding experiment was performed to compare the experimental results with the response predicted by the model. The theoretical optimal value of mass gain under these optimised conditions is 5.32% while the experimental one is 5.58%. The difference between these two values is well within the 95% confidence interval of the experimental error, thus proving the good predictive performance of the developed model.

3.3. Effect of the Grafting Process on Textile Properties

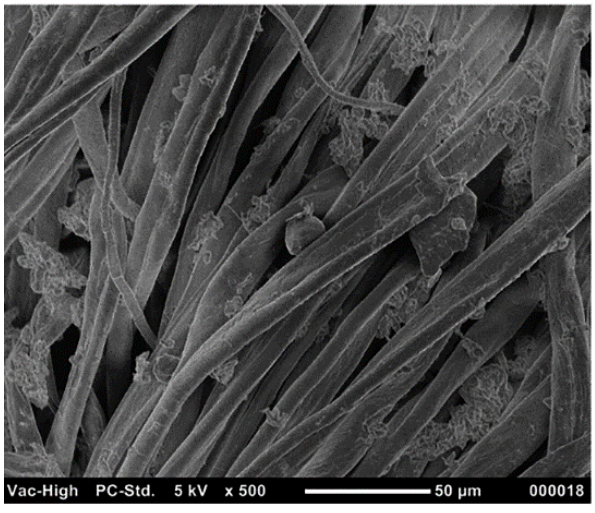
After functionalisation of cotton knitted fabric by the grafting process under optimised conditions, several textile properties were measured namely morphology, tensile strength, air permeability and wash fastness.

3.3.1. Morphology

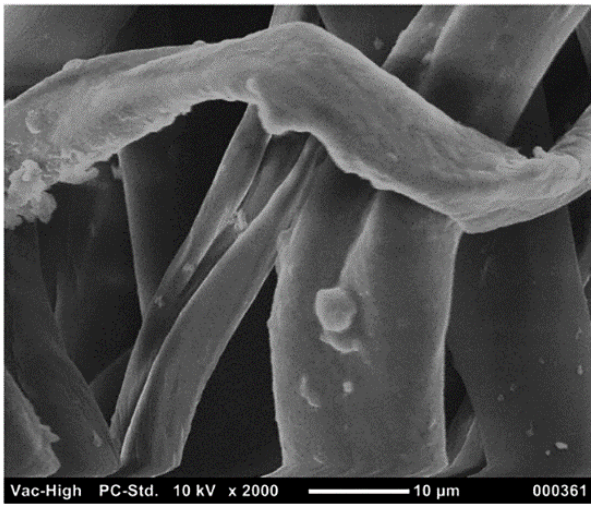
Grafted cotton fabric was analysed by SEM after being treated in a bath containing fragrant β-



(a)



(b)



(c)

Fig. 7. SEM micrographs of: **(A)** untreated cotton knitted textile at ×500 magnification and **(B, C)** treated cotton knitted textile at ×500 **(B)** and ×2,000 **(C)** magnifications. SEM, scanning electron microscopy

cyclodextrin based microcapsules, CA crosslinking agent and DHP catalyst, under optimised conditions. Figure 7 shows SEM micrographs of the treated textile at ×500 and ×2,000 magnifications (Figure 7B) via the previously optimised grafting protocol compared to the non-treated one at ×500 magnification (Figure 7A). These observations confirm the efficacy of the optimised grafting process designed from the ANOVA results. Nevertheless, the present SEM data does not provide a visual comparison allowing an assessment of the optimised efficacy of the process since pictures were collected on fibers grafted using the optimised process only. Indeed, it is difficult to infer binding density of microcapsules from SEM images because it requires a large number of images of the same sample for obtaining statistical significance. We did collect several pictures for ensuring that the pictures shown in Figure 7 were representative; the number of pictures we collected was not sufficient

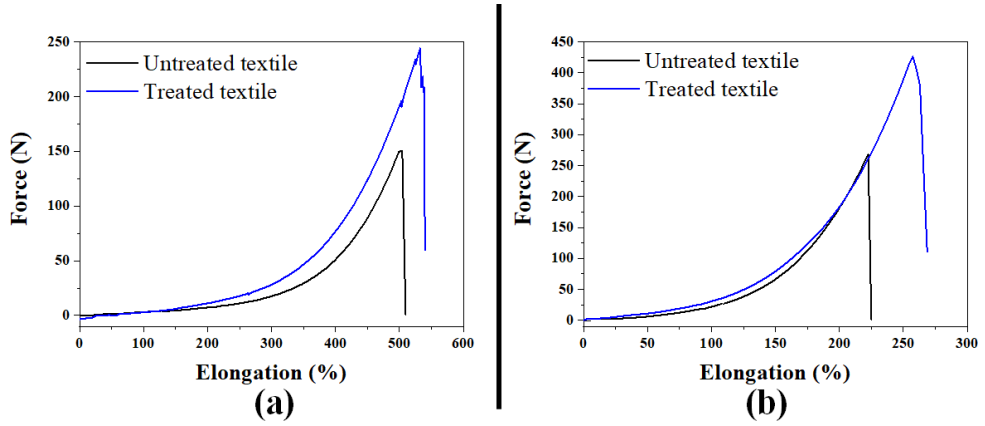


Fig. 8. Tensile behaviour of untreated and treated knitted fabric in both directions: **(A)** row direction and **(B)** column direction

for performing a statistical analysis. Owing to these constraints, the determination of grafting density by SEM is not to be done.

Though SEM does not provide a quantitative analysis, SEM pictures show that a sufficiently high density of grafting has been reached. Pictures reveal a large collection of grafted microparticles distributed evenly onto the cotton textile fabric: between the textile yarns, the fibers and in the cotton cavity. The density of grafted microcapsules was similar to that of previous work obtained by the impregnation process using PU or epoxy resin [37] shell microparticles based on β-cyclodextrin [14, 23] or isosorbide [38, 39].

Fragrant microcapsules are not damaged following the heat treatment undergone during the process (grafting and drying temperatures of 195°C and 90°C respectively). The microparticles are also tightly fixed by means of covalent bonds after the reaction and a simple rinse.

3.3.2. Tensile strength

The effect of the optimised grafting treatment on the tensile properties was evaluated by a comparison between the tensile curves of the treated and the non-treated samples in both knitting directions (row and column directions), and in particular, the maximum force, the elongation at maximum force as well as the stiffness (Figure 8).

The general tensile behaviours of the different knitted fabrics were similar in the two stress directions and whether they were measured before or after functionalisation. Tensile strength at low loads mainly originates from the friction resistance of yarns in the wales [40]. Meshes progressively line up leading to fabric elongation. The yarns get deformed at higher loads and eventually neck and break.

A comparison between the maximum force, the elongation at maximum force as well as the stiffness of the untreated and the treated fabrics is shown in Figure 9.

The treatment of grafting the microcapsules to the cotton knitwear increased the maximum force in both directions. The establishment of new covalent bonds contributes, in some way, to the improvement of the tensile strength. The elongation at maximum force is slightly higher for the grafted textile than that of the untreated textile. The cause of such changes could be the treatment at high temperatures and without applied tension during grafting that increases the amorphous areas of already mercerised cotton. Hence, the rate of crystallinity decreases and the strain at maximum force increases slightly in both directions of stress.

Examination of Figure 9 shows that the grafting treatment increases the stiffness of the textile stressed in both directions. This increase is more accentuated in the column direction rather than in the row direction, which is probably due to the establishment of new bonds, inter-fibers and inter-yarns, of covalent types by the grafting process.

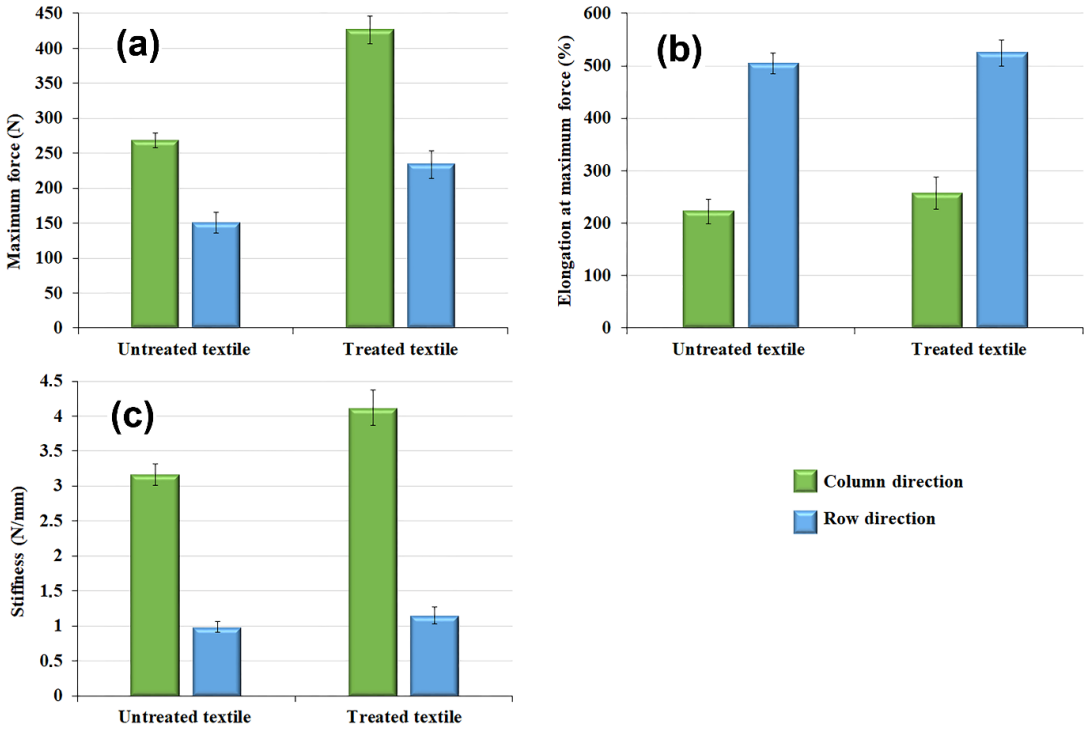


Fig. 9. Variation of: **(A)** maximum force, **(B)** elongation at maximum force and **(C)** stiffness before and after grafting treatment in row and column directions

According to these results, it appears that the optimised grafting treatment slightly modifies the mechanical properties of the textile without altering them.

3.3.3. Air permeability

The assessment of air permeability was investigated by measuring the rate of air flow through the fabric under differential pressure.

The air permeability properties of knitted cotton fabrics before and after treatment are displayed in Figure 10. The treatment of grafting microcapsules decreased the air permeability of the functionalised textile by 50% for a mass gain of 5.58%. The textile support is not yet saturated and occluded with bound microcapsules, since porosity between the fibres was clearly seen in SEM pictures. There is no excess of the grafted microcapsules forming an occlusive layer right side up and on the other side of the textile substrate. Microcapsules are well distributed inside the textile sample in the sites between the thread and in statements between the fibers.

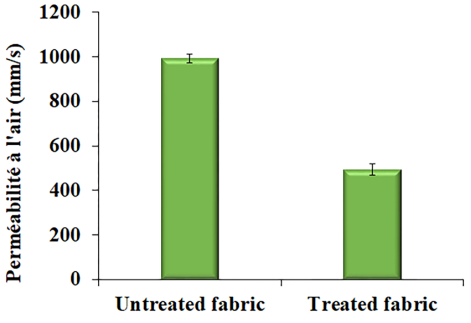


Fig. 10. Air permeability of knitted cotton fabrics before and after grafting

Misra et al. [41] in 2020 reported that fabrics become less permeable to air upon increasing the mass per unit area of the textile. Although the air permeability decreased from 992 mm $\cdot$ s^{-1} to 492 mm $\cdot$ s^{-1}, the wearing comfort is not compromised. Given the low mass per unit area of the jersey structure, the very high level of openness and air permeability of the textile support before treatment allows for a large mass gain without loss of sensory properties.

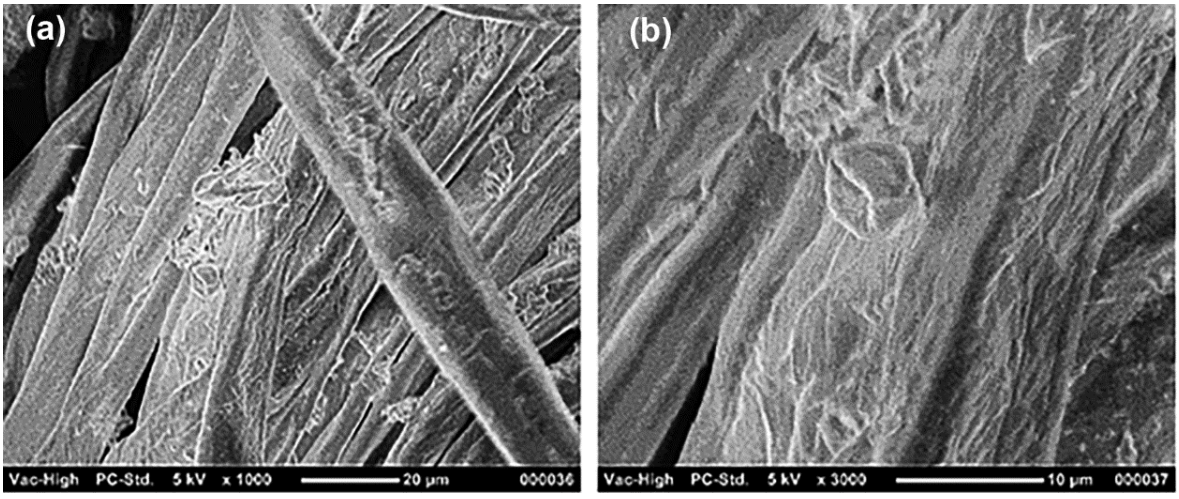


Fig. 11. SEM micrographs of knitting grafted with fragrant microcapsules after 40 washing cycles at **(A)** ×1,000 and **(B)** ×3,000 magnification. SEM, scanning electron microscopy

The uniformity of grafted microcapsules was confirmed by air permeability measurements performed at different points of the fabric. All tests presented similar air permeability behaviour. The present treatment is efficient in, not only promoting a high level of material attachment but also ensuring the coating uniformity [42].

3.3.4. Effect of washing test on the treated fabric efficiency

The effect of washing cycles on grafted textile was investigated according to the ISO 105-C10 standard of 2010 to evaluate the efficiency and the durability of the microcapsules application to the knitted fabric. SEM observations and GC analysis were used to assess the lifetime of scent textiles both as qualitative and quantitative evaluations.

SEM micrographs of the functionalised knitted fabric after 40 washing cycles (Figure 11) show the presence of microcapsules remaining bound to the textile. The amounts of microparticles on the fabric before and after washing are similar; no noticeable fall could be detected. Thus, unlike the impregnation treatment, the grafting treatment provides a good wash fastness. Indeed, grafted microcapsules still remain attached to the textile support by means of covalent bonds. Compared to their original shape in the dispersed state, β-cyclodextrin -based microcapsules are slightly deformed following the release of the active ingredient by diffusion through the capsule membrane. For such a finishing process, in addition to the release of the encapsulated product, there is the possibility for the capture of sweat or cigarette smoke by the β-cyclodextrin, which considerably reduces the intensity of odours on the clothes. These encapsulated substances are removed in the washing machine, and the β-cyclodextrin is again free to trap odours. Textiles grafted with β-cyclodextrin-based microcapsules can also be selectively reloaded with a large diversity of guest substances by dipping or spraying methods. 4Particular interest is the treatment with perfume, antimicrobial or pharmaceutical products which can be released continuously over a long period of time upon exposure to moisture. The higher the humidity level, the more the encapsulated substance that is released. Such modified textiles may 'respond' to a variety of environmental conditions [35]. These two methods of reloading the β-cyclodextrin prolong the effect of the functionality of the studied grafting process [43].

The presence and the quantification of residual encapsulated neroline after washing cycles were studied by GC analysis. The area of the fragrance peak decreased as repeated washing cycles have been applied. The amount of residual neroline was determined based on a calibration curve.

Figure 12 shows that the residual neroline concentration decreased slowly, confirming that the microcapsules remained loaded with perfume along subsequent washing cycles.

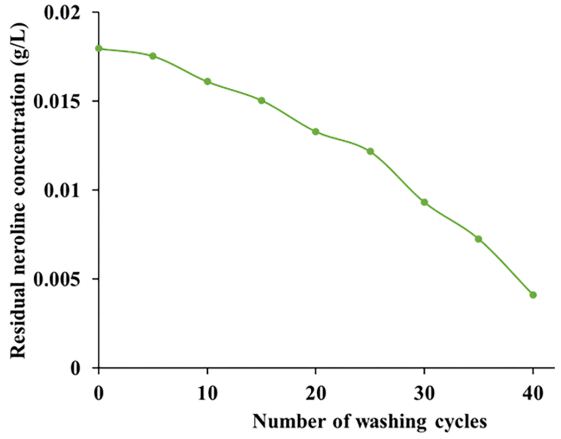


Fig. 12. Residual neroline concentration after subsequent washing cycles

Residual neroline concentration on the textile treated with β-cyclodextrin-based microcapsules is lower than that obtained by the impregnation process for the same mass gain. The high grafting temperature causes a partial loss of about 37% of the encapsulated perfume during the polycondensation reaction (temperature of 195°C). However, the effectiveness of the textile grafted with β-cyclodextrin-based microcapsules appeared higher than that of in our previous works [39] and those of Rodrigues et al. [44, 45] since the present fragrance loss was about 2% after five washes and 77% after 40 washes. This can be attributed to the fact that in the case of the grafted textile, there is no significant loss of the microcapsules following the washing cycles.

Thereby, this decrease in perfume concentration is essentially due to a diffusion phenomenon of the active material through the pores of the PU microcapsules and the cavity of the β-cyclodextrin. These results confirmed not only the efficient encapsulation of neroline and the features of a controlled release of the active material but also the efficiency of the grafting process. Microencapsulation is an effective method that allowed the control of neroline diffusion through the pores of the microparticles shell protecting the active ingredient from the environment on one hand. On the other hand, it appears that the grafting process further contributes to improving the lifetime of scent textiles.

4. Conclusions

After the successful application of neroline-loaded β-cyclodextrin based microcapsules on cotton using the impregnation technique previously reported, this study demonstrates the possibility of finishing textile support by grafting microcapsules to the textile fibers. This technique is a good candidate for the production of cosmetotextile articles. Indeed, this process requires a classical textile finishing equipment, the use of nontoxic chemicals that are environmentally friendly, not expensive and does not involve any organic solvent.

The effect of the composition of the grafting bath on the efficiency of the microcapsules deposition shows a clear optimum. The RSM allows optimising the odorous functionalisation of pure knitted cotton. Using the developed model, the maximum possible mass gain reached was 5.32%. The optimal grafting conditions are as follows: 107.6 g $\cdot$ L^{-1} for microcapsules concentration, 111.9 g $\cdot$ L^{-1} for CA crosslinking agent concentration and 50 g $\cdot$ L^{-1} for DHP CAT.

There is justification for optimisation because there is a pronounced maximum mass gain of the cotton knitted fabric according to the variables studied. Specifically, there is an optimum concentration of microcapsules. This disclosure goes against a kind of 'common sense' belief that one should deposit more microcapsules for obtaining greater binding to the fabric. It has been shown that RSM is an efficient tool for performing such optimisation.

Some properties of cosmetotextiles produced via the optimised grafting protocol have been measured. SEM micrographs revealed effective adhesion between the microcapsules and the cotton fibers. The tensile strength tests in both directions of stress showed that the grafting treatment slightly modified the mechanical properties of the textile, without dramatically altering them. Such al-

terations may be viewed as improvements or deterioration of properties depending on the type of end-use of the fabric and its properties before treatment. The air permeability decreased by 50% after functionalisation. Overall, the studied grafting treatment appears adequate for the development of a wide range of other cosmetotextile articles since it makes it possible to add a specific functionality to the textile support without altering its intrinsic properties. The optimised treatment appears to be effective not only in promoting a high level of adhesion of the material but also in ensuring uniformity of the coating. The wash fastness resistance of grafted fabric was quite satisfactory since there was no loss of microcapsules following successive washing cycles. The amount of neroline component decreased slowly with a fragrance loss of 2% after five washes and 77% after 40 washes. After the release of the encapsulated active principle, reloading the microcapsules through β-cyclodextrin cavities might be possible.

Thus, microencapsulation appeared to be an effective method to control the diffusion of fragrances through the pores of the microparticles shell, protecting the active principle from the environment. Of noteworthy interest, the grafting technique as well as the presence of β-cyclodextrin in the macromolecules further contribute to improving the lifetime of the olfactory textiles.

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