

## Fragrant Microcapsules Based on $\beta$ -Cyclodextrin for Cosmetotextile Application

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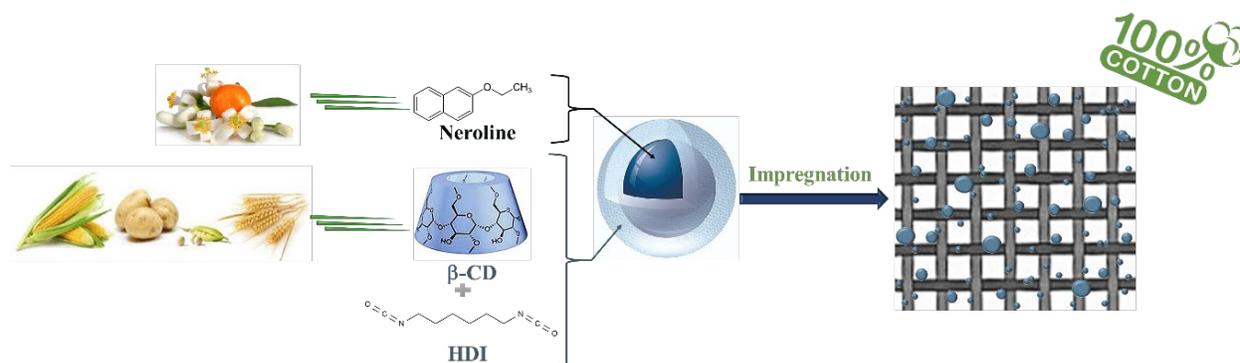
**Abstract:** Microencapsulation of neroline inside microcapsules having a polyurethane shell based on  $\beta$ -cyclodextrin ( $\beta$ -CD) and hexane diisocyanate was performed by interfacial polycondensation. The polyol nature of  $\beta$ -CD caused tight crosslinking of microcapsules wall. Microcapsules of neroline were characterized for their chemical composition and structure of the polyurethane shell by FTIR spectroscopy, thermogravimetric analysis, optical and electron microscopy, light scattering and electrophoresis measurements. Core content and encapsulation yield were 15% and 60%, respectively. Spherical microcapsules of mean diameter 29  $\mu\text{m}$  were slightly cationic with an isoelectric point of 6.3. Neroline-loaded microcapsules were fixed on cotton fabric using an impregnation technique. The functionalized fabric showed improved resistance to washing cycles in comparison with previously reported diol-based microcapsules. Such microcapsules display great potential for the long-lasting release of fragrance in the framework of cosmetotextile.

**Keywords:** Microcapsules; interfacial polycondensation;  $\beta$ -cyclodextrin; neroline; cosmetotextile

### Highlights

- New microencapsulation material based on interfacial polycondensation of  $\beta$ -cyclodextrin and diisocyanate was designed.
- Multiple hydroxy groups of  $\beta$ -cyclodextrin provide high cross-linking density.
- Microcapsules show long lasting release of fragrance.
- Microcapsules were suitable for textile application.

## Graphical abstract



## 1 Introduction

Fragrances show up several features that provide consumers with pleasant effects such as relieving anxiety, alleviating suffering, hypnose, uplifting spirit and enhancing efficiency at work [1]. To such ends, they are added to various products widely used in daily life like laundry detergents, soaps, personal care products (body washes, shampoos, deodorants, ...) and fabric softeners [2,3]. As a current trendy, fragrances and other volatile compounds can also be used in perfumed finishing agents to produce cosmetotextile items designed for aroma therapy [4], antibacterial [5] and insecticide [6,7] textiles. One way to do so is physical absorption of active substances onto textile fibers. Release rate relies on physical diffusion of fragrance molecules inside inter-fiber spaces. The manufacture process consists in either impregnation with a perfume solution or coating using a mixture of binder and fragrance. A drawback is a poor resistance to wash; only two wash cycles can be resisted at maximum [1]. Perfume products are highly volatile, and their odor is rapidly lost after application [3,8]. Exposed to open air, fragrances that contain reactive functional groups are sensitive to environmental elements including water, warmth, oxygen, and light. As a result, serious stability issues are faced such as color changes and alteration of olfactory profile [9]. To overcome these limitations and enhance fragrance effectiveness, encapsulation allows not only protection and controlled release of the active substance but also supplementary beneficial properties such as efficient deposition of perfume onto target surfaces [3].

Microcapsules are made of a core material containing an active ingredient surrounded by a shell (wall material) that acts as a separation barrier against external medium and controls release kinetics [10]. The diameter of microcapsules may vary from 1 to 1000  $\mu\text{m}$  and the encapsulating membrane can be made of natural or synthetic polymers with variable thickness and permeability [11,12].

Various microencapsulation techniques have been used for perfume encapsulation such as coacervation processes [13] and *in situ* polymerization [14-16]. The most widely used method is interfacial polycondensation. Depending on the hydrophilicity of the active material, microcapsules are prepared from an oil-in-water (o/w) or water-in-oil (w/o) emulsion by formation of a thick polymer wall around liquid droplets [11,17-24]. Interfacial polycondensation involves the reaction of two multifunctional monomers present in the two phases of the emulsion. The polycondensation reaction takes place at the interface, yielding a polymer wall around emulsion droplets [25]. Different polymer materials have been used like poly(urea-formaldehyde), poly(melamine-formaldehyde), poly(urethane-urea) and especially polyurethane [3,26,27,29]. As a current trend to include more non-fossil fuel-based polymers, attention is paid worldwide to polymers derived from biomass [28]. Though polyurethane materials based on  $\beta$ -cyclodextrins have been reported for various applications [30-34], the use of  $\beta$ -cyclodextrins as monomer for interfacial polycondensation has received poor attention to date.

Taking inspiration from above concepts, the present work addresses the microencapsulation process of neroline as model perfume with a biomass-derived polyurethane shell using  $\beta$ -cyclodextrin as monomer

in interfacial polycondensation. Besides its use as a complexing agent [35], the choice of this reagent was made regarding its high functionality (21 hydroxyl groups per  $\beta$ -cyclodextrin molecule), interesting features such as low toxicity, low price and availability in large quantities. This study deals with the preparation of such cyclodextrin-based microcapsules, their chemical and physicochemical characterization, and their properties as fragrance encapsulating particles. Finally, the behavior of microcapsules applied to a cotton fabric was evaluated in order to assess their use in cosmetic textile application.

## 2 Experimental

### 2.1 Materials and Chemicals

The following chemicals were used as received for the preparation of microcapsules: 1,6-hexane diisocyanate (HDI, Fluka, 98%) and  $\beta$ -cyclodextrin ( $\beta$ -CD, Kleptose<sup>®</sup>, Roquette Frères, Lestrem, France) as monomers, Polysorbate 80 (Tween<sup>™</sup> 80, Aldrich, 98%) and dibutyltindilaurate (SnDBDL, Aldrich, 95%) respectively as emulsifier and catalyst. Neroline (2-ethoxynaphthalene), employed as core material, was obtained by O-ethylation of  $\beta$ -naphthol with ethyl bromide [36]. Toluene (Sigma-Aldrich, 99.8%) was used without further purification as the dispersed phase of the oil-in-water emulsion. Emulsification was achieved using an Ultra-Turrax<sup>®</sup> T25 Basic homogenizer equipped with a S25N 25F shaft (IKA, Germany). Microencapsulation process was carried out in a thermostated double-jacketed glass reactor (Sovirel, 1 L) equipped with a half-moon blade mixer, a mechanical digital control of stirring rate and an oil thermostat bath.

For textile application, a knitted fabric (jersey, 100% cotton) bleached and mercerized, with a mass of 138 g·m<sup>-2</sup>, was used. It was supplied by Esprit Maille (Bouhjar, Tunisia). A polyurethane cross-linking agent (Politex SW/N) was supplied by Prochimica Novarese SPA (Italy). Dodecylamino Diglycidyl Ether of Isosorbide (DoDGEDAS) was synthesized as previously reported and used as a cationic surfactant [37]. The application of microcapsules was carried out using a Continuous Hot Air Dryer (Mathis KTF, Switzerland).

### 2.2 Synthesis of Microcapsules

Polyurethane microcapsules containing neroline were synthesized by interfacial polycondensation according to previous reports [36,38-41]. The synthesis process involved the preparation of three solutions as following: Solution 1 (S1) contained 0.63 mmol of Polysorbate 80 diluted in 225 mL of water. An organic solution containing 74.34 mmol of HDI and neroline previously solubilized in 45 mL of toluene corresponded to solution 2 (S2). The third solution (S3) contained 7.08 mmol of  $\beta$ -CD and 0.67 mmol of SnDBDL dissolved in 35 mL of S1.

The microencapsulation starts with the first step corresponding to the emulsification of the dispersed phase (S2) in the continuous one (S1) at 12,000 rpm during 5 min in order to prepare an o/w emulsion. Then, after decreasing stirring rate to 600 rpm, S3 was added. Thereby, the reactive step began when the temperature was maintained at 80°C during 6 h under inert atmosphere. Finally, microcapsules were recovered by centrifugation (Gyrozen 416G), washed once with toluene and twice with water to remove the residual monomer and non-encapsulated neroline. The drying of resulting microcapsules obtained was carried out under ambient conditions during 48 h.

The overall yield  $\eta$  was calculated as the ratio of the mass of recovered microcapsules to the mass of monomers and neroline introduced. It is expressed as:

$$\eta(\%) = 100 \times \frac{\text{Mass}(\text{microcapsules})}{\text{Mass}(\text{monomers} + \text{neroline})} \quad (1)$$

The loading capacity (LC) was defined as

$$LC(\%) = 100 \times \frac{\text{Mass of encapsulated neroline}}{\text{Mass}(\text{polymer} + \text{neroline})} \quad (2)$$

The encapsulation efficiency (EE) was defined as the ratio of encapsulated neroline to the full amount used to feed the encapsulation process

$$EE(\%) = 100 \times \frac{\text{Mass of encapsulated neroline}}{\text{Mass of neroline feed}} \quad (3)$$

### 2.3 Textile Application

Cotton fabric was impregnated with dry neroline-loaded microcapsules as previously reported [38,40,42-46]. Fragrant microcapsules were mixed with a polyurethane cross-linking solution ( $31 \text{ g}\cdot\text{L}^{-1}$ ) in distilled water containing a cationic surfactant ( $0.7 \text{ g}\cdot\text{L}^{-1}$ ). The cotton fabric was impregnated into this solution under ambient conditions during 20 min. Then the fabric was dried without squeezing during 6 min at  $140^\circ\text{C}$  in air at atmospheric pressure to allow the cross-linking agent to polymerize.

### 2.4 Methods

The chemical composition of synthesized microcapsules was studied by Fourier Transform InfraRed spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR) using a Nicolet™ iS 50 FT-IR spectrometers (Nicolet Instrument Corp., USA). Spectra were recorded at room temperature, under nitrogen atmosphere, in the range  $500\text{-}4000 \text{ cm}^{-1}$  at a resolution of  $4 \text{ cm}^{-1}$  and using 32 scans for each spectrum. They were displayed in absorbance mode.

The microcapsules suspension was firstly observed for their size and shape by optical microscopy using a Zuzi optical microscope (Leica, Germany) equipped with different Epiplan objectives, an integrated camera and controlled by the TSView software. A drop of sample placed between a slide and a cover glass was observed in transmission mode under  $\times 4$ ,  $\times 10$ ,  $\times 40$  and  $\times 100$  magnifications of the objective.

The shape and surface features of both synthesized microparticles and treated textile were observed by Scanning Electron Microscopy (SEM) after drying using a Jeol JCM 5000 (JEOL, Japan) microscope. The samples were examined at room temperature without metallization and operating at 5 and 10 kV acceleration under moderate vacuum.

Particle Size Distribution (*PSD*) of microcapsules was measured by small-angle light scattering using a MasterSizer 3000 particle size analyzer (Malvern Instruments Ltd, Malvern, UK). The instrument reservoir was filled with 125 mL of water circulating during the analysis. The microcapsules dispersion was added dropwise until the obscuration was above 5%. Refractive indices used for the calculation of the particle size distribution using the Mie theory were 1.33 for water and 1.58 for the dispersed phase made of polyurethane and neroline (the refractive index of neroline is 1.59). The *PSD* was evaluated on a volume average basis.

Thermo Gravimetric Analysis (TGA) measurements were performed using a TG 209 F1 Iris Netzsch instrument (Netzsch Gerätebau, Germany). The samples were heated from 20 to  $900^\circ\text{C}$  at a rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ , under nitrogen atmosphere.

Zeta potential was determined by measurements of the electrophoretic mobility. All measurements were carried out using a Nano Zetasizer instrument (Malvern Instruments Ltd, Malvern, UK). NaCl 0.1 M was used as background electrolyte. The pH was varied between 3 and 12 using 1 M NaOH and HCl solutions. All measurements were carried out at  $25^\circ\text{C}$ .

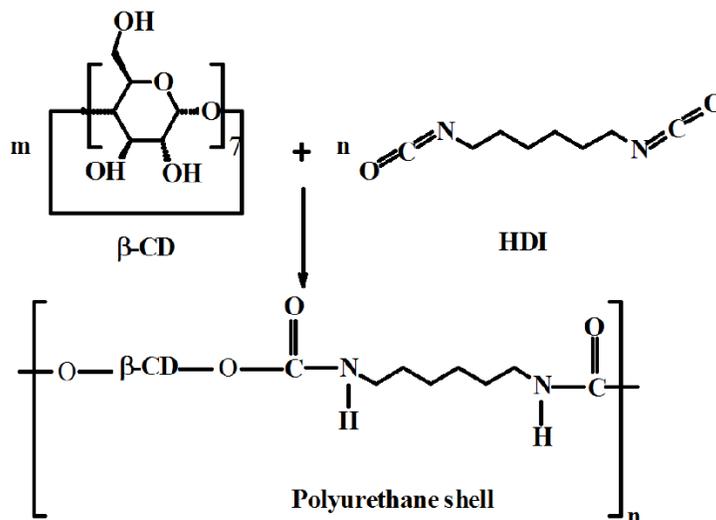
Wash fastness was assessed in accordance with ISO Standard 105-C10 of 2010, functionalized fabrics were washed during 30 min at  $40^\circ\text{C}$  in an Autowash device. Then, the specimen was rinsed with water for 5 min and dried under ambient conditions. The fate of bound microparticles and residual amount of neroline were estimated by SEM observations and GC analysis using a 7890A Gas Chromatograph from Agilent Technologies (USA) equipped with a flame ionization detector (FID). Chloroform was used as solvent to extract the residual neroline after washing. Samples were injected at a split ratio of 1:20. Analytes from the  $1 \mu\text{L}$  samples were 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  $200^\circ\text{C}$  for 10 min. Nitrogen was used as the carrier gas with an inlet pressure of 1.5 bar and a constant flow rate of  $20 \text{ mL}\cdot\text{min}^{-1}$ . The detector temperature was  $280^\circ\text{C}$ .

## 3 Results and Discussion

### 3.1 Microcapsules Synthesis

The synthesis of polyurethane neroline loaded microcapsules has been achieved by the classical

process of interfacial polycondensation in an o/w emulsion, fairly adjusted in order to get high-quality microcapsules in large quantities. Fragrant microcapsules synthesized by interfacial polymerization between  $\beta$ -CD and HDI resulted in the formation of the encapsulating polyurethane shell surrounding the neroline core (Fig. 1). Accordingly [12], the polyol present in the aqueous phase reacted at the interface of emulsion droplets with the diisocyanate present in the organic phase.



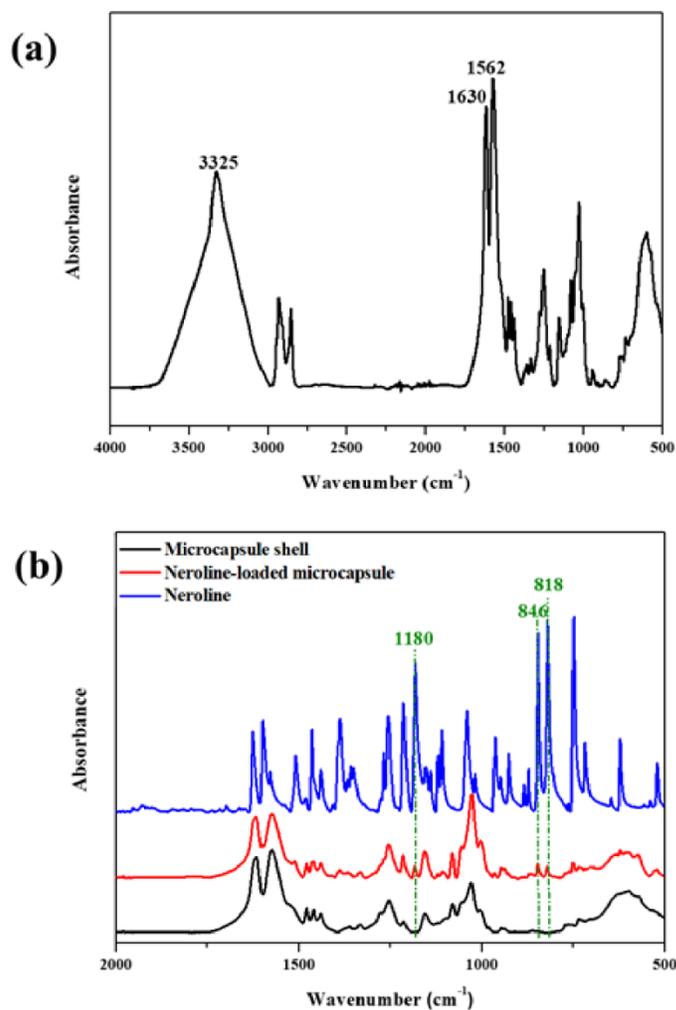
**Figure 1:** Polycondensation reaction scheme

Microcapsules were manufactured in several steps: i) emulsification of HDI, neroline and toluene in water using the Polysorbate 80 emulsifier; ii) addition of  $\beta$ -CD and SnDBDL catalyst; iii) heating at 80°C for 6 h. The o/w emulsion was stable during the whole process that was kept under stirring till completion of hardening the walls by polycondensation.  $\beta$ -CD was added in a second step for its presence does not interfere with emulsification. Indeed  $\beta$ -CD is known to form inclusion complexes with surfactants [47] and oils [48] and might have detrimental effects as it might cause too slow adsorption of the emulsifier during emulsification. The catalyst was also added in the second step just before starting the polycondensation reaction for it retains its full activity. Polymerization started when the temperature was raised to 80°C. Polyurethane formed at the interface since HDI was soluble in the oil phase and  $\beta$ -CD was soluble in the aqueous phase. The resulting polymer stayed at the interface during the polymerization since it was recovered as a wall at the surface of oil droplets at the end of the process. Microcapsules were recovered by centrifugation, washed for removing non-encapsulated materials and dried at room temperature for 48 h. The overall yield was  $\eta = 60\%$ , slightly higher than the result obtained in previous work using isosorbide diol [41] where the same amount of polyol was introduced in both cases. The polymeric shell material was highly crosslinked because  $\beta$ -cyclodextrin contains 21 hydroxyl groups per molecule.

### 3.2 Characterization of Fragrant Microcapsules

#### 3.2.1 Chemical Analyses

The chemical characterization of microcapsules composition was performed by FTIR-ATR spectroscopy. To check the shell formation and the perfume encapsulation, the spectrum of synthesized microcapsules was compared with the spectra of polyurethane material and neroline (Fig. 2).



**Figure 2:** (a) FTIR spectrum of the polyurethane material of the microcapsules shell; (b) FTIR spectra of microcapsules shell, neroline loaded microcapsules and neroline

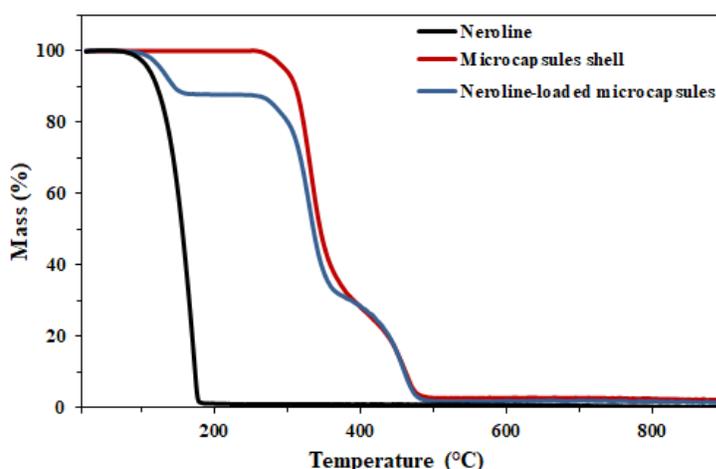
The formation of the polyurethane shell was demonstrated by the characteristic IR absorption bands of the urethane bond at 3325 cm<sup>-1</sup>, 1630 cm<sup>-1</sup> and 1562 cm<sup>-1</sup>, corresponding to NH, C=O and NHCO, respectively [49,50], and the disappearance of the isocyanate peak at 2270 cm<sup>-1</sup> [31,40] both in the spectra of the microcapsules shell (Fig. 2(a)) and the same polyurethane material prepared by classical bulk polycondensation (data not shown). The spectrum of fragrant microcapsules also showed the neroline characteristic bands at 1180 cm<sup>-1</sup>, 846 cm<sup>-1</sup> and 818 cm<sup>-1</sup> in addition to the microcapsules shell spectrum (Fig. 2(b)). The first band corresponds to the ether group and the other two peaks are relative to the monosubstituted naphthalene [41,51]. Thereby, neroline was successfully encapsulated in the polyurethane shell.

Besides the qualitative report showing the all IR bands meet expectations, the full incorporation of HDI into the polyurethane material remains an open question. Indeed, HDI might have been either involves in the polycondensation reaction or hydrolyzed by the water of the dispersing phase, so that disappearance of the isocyanate bands is not conclusive with regards to possible full conversion of HDI into polyurethane. Indeed, interfacial polycondensation of polyols and diisocyanates does yields polyurethane at the interface because hydroxyl groups are more reactive than water. But the formation of a thin polyurethane membrane at low conversion makes a barrier against diffusion of  $\beta$ -CD and/or HDI molecules for their further reaction with their partner. Diffusion and reaction continued either until complete conversion of one of the monomers or until diffusion through the polymer membrane became so slow that hydrolysis side-reaction can occur. Since

hydrolysis releases carbon dioxide gas, it should generate porosity in the polymeric shell [52,53]. Such porosity was not observed in the present case. Indeed, hydrolysis of HDI was unlikely owing to the low reactivity of aliphatic isocyanates. Conversely, more reactive aromatic isocyanates do undergo hydrolysis as side-reaction. Thus, aromatic polyurethane formed by interfacial polycondensation are porous materials as given evidence by BET experiments measurements showing a significant part of the specific area located inside the porosity using a *t*-plot analysis of the nitrogen adsorption isotherm : it was  $\leq 1 \text{ m}^2 \cdot \text{g}^{-1}$  for HDI-based polyurethane against  $\sim 10 \text{ m}^2 \cdot \text{g}^{-1}$  for aromatic isocyanate-based materials) [54]. On this basis, hydrolysis of HDI was presumed limited, suggesting that HDI has been fully converted into polyurethane by reaction with  $\beta$ -CD.

### 3.2.2 Thermal Properties

TGA analysis allowed estimating the core content and an assessment of thermal properties of microcapsules (Fig. 3).



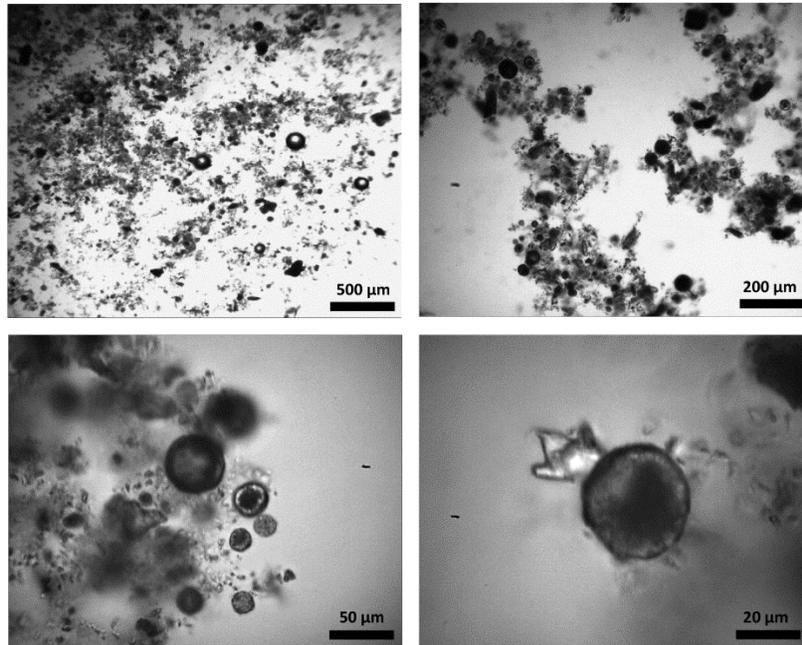
**Figure 3:** TGA thermograms of neroline, microcapsules shell and neroline-loaded microcapsules

TGA thermograms of neroline, microcapsules shell and neroline-loaded microcapsules are shown in Fig. 3. The thermal degradation of pure neroline took place in a single step at 121°C. The degradation of the pure polyurethane material of the microcapsules shell took place in two steps starting at about 305°C and 443°C with a mass loss of 62% and 30%, respectively. A progressive mass loss took place at higher temperature and there was no residual ash at the end of the experiment.

The TGA thermogram of neroline-loaded microcapsules showed three steps. The first starting at 125°C corresponded to the degradation of neroline. The mass loss was 15%, which corresponded to the core content (loading capacity). Combined with the overall yield ( $\eta = 60\%$ ), this allowed the calculation of the encapsulation efficiency  $EE = 23\%$ . The second and third thermal decompositions started at about 305°C and 438°C, which corresponded to polyurethane. The first thermal event at 305°C was probably due to urethane bond rupture [30,31], and the third degradation starting at 438°C corresponded to the degradation of  $\beta$ -CD [49]. Full mass loss was reached at 900°C; there was no residual ash. TGA did not show a mass loss around 110°C relative to toluene evaporation. Hence, the organic solvent has been previously removed during washing and drying steps. The microcapsules membrane had an excellent thermal stability compared to other wall materials reported in the literature [39]. According to Marin et al. [55,56], this is due to the higher stability of aliphatic polyurethanes based on HDI than aromatic ones.

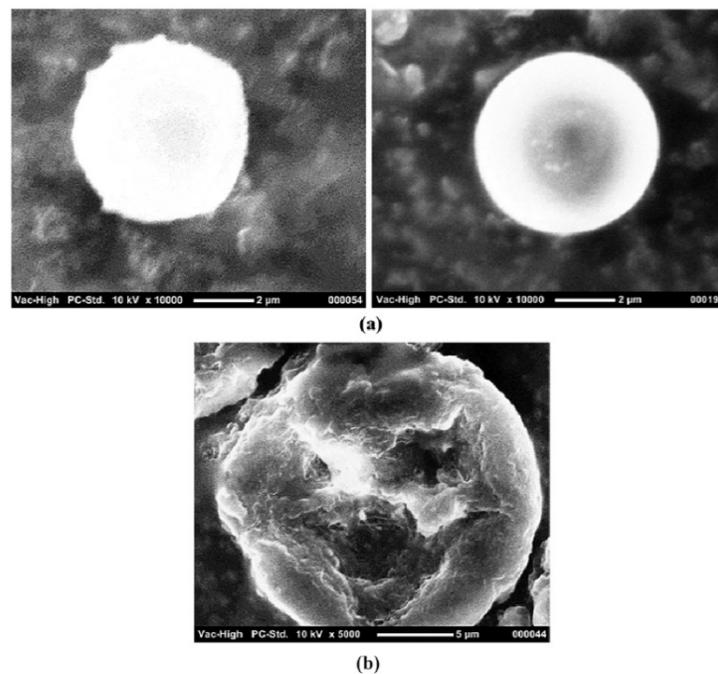
### 3.2.2 Morphological Characterization

The surface and shell morphology of neroline-loaded microcapsules were examined by optical microscopy and SEM observations (Fig. 4 and Fig. 5).



**Figure 4:** Optical micrographs of neroline-loaded microcapsules at different magnifications

Optical micrographs show well-individualized microparticles with a regular spherical shape and a broad size distribution. There was no significant number of aggregated particles. However, it was difficult to specify the surface morphology by optical microscopy. A better visualization of the surface state of the microcapsules shell was obtained by scanning electron microscopy (SEM).



**Figure 5:** SEM micrographs of synthesized microcapsules: (a) fully formed and (b) with the shell broken

SEM pictures (Fig. 5(a)) confirmed that microcapsules shape was regularly spherical. Their surface

shell was rather smooth. In fact, it could be controlled by the mechanical stirring rate, the concentration and/or nature of the reagents, and the polyol feeding rate [20].

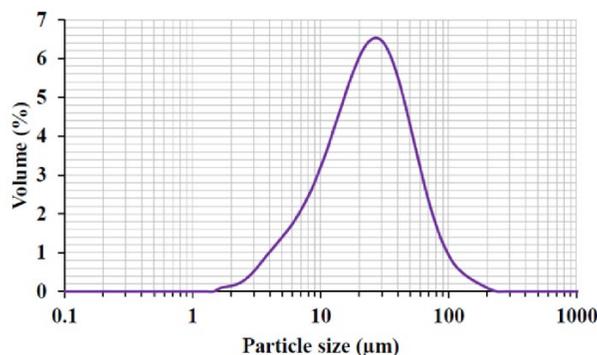
Few microcapsules were damaged with their shell wall fractured (Fig. 5(b)). The shell thickness of such capsules could be estimated from the pictures as about 2.5  $\mu\text{m}$ . Assuming perfect spherical symmetry of the morphology, the mean thickness of microcapsules wall can be estimated from their overall radius  $R$  and the volume fraction of the neroline core  $\phi_{\text{core}}$  as

$$t = R(1 - \phi_{\text{core}}^{1/3}) \quad (4)$$

If all materials have the same density,  $\phi_{\text{core}}$  is identical to the loading capacity (Eq. (2)). Taking  $\phi_{\text{core}} = 0.15$  and  $R = 12.5 \mu\text{m}$  (see next Section 3.2.3), the mean thickness is  $t \approx 6 \mu\text{m}$ . This is much larger than the thickness observed on fractured microcapsules, showing that damaged microcapsules were those having the thinnest wall.

### 3.2.3 Particle Size Distribution

The particle size distribution (PSD) of the microcapsules containing neroline is shown in Fig. 6. The PSD was unimodal, with sizes ranging from 1.5  $\mu\text{m}$  to 240  $\mu\text{m}$ . It is worth noticing that microcapsules described by Rodrigues et al. [57] had a bimodal PSD. The volume-average diameter was 29  $\mu\text{m}$  and  $d(50)$  was 25  $\mu\text{m}$ . The present unimodal PSD is considered appropriate for application of microcapsules to a textile impregnation process [38].

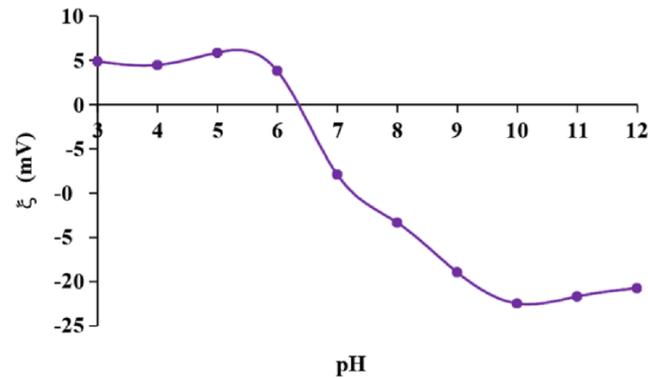


**Figure 6:** Particle size distribution of neroline-loaded microcapsules

### 3.2.4 Zeta potential and IsoElectric Point

The zeta potential ( $\zeta$ ) is an important physicochemical characteristic of the microparticles as it reflects the presence of charged species at the surface of them. In fact, the particle charge affects the suspension stability and it also conditions the application to fabric.

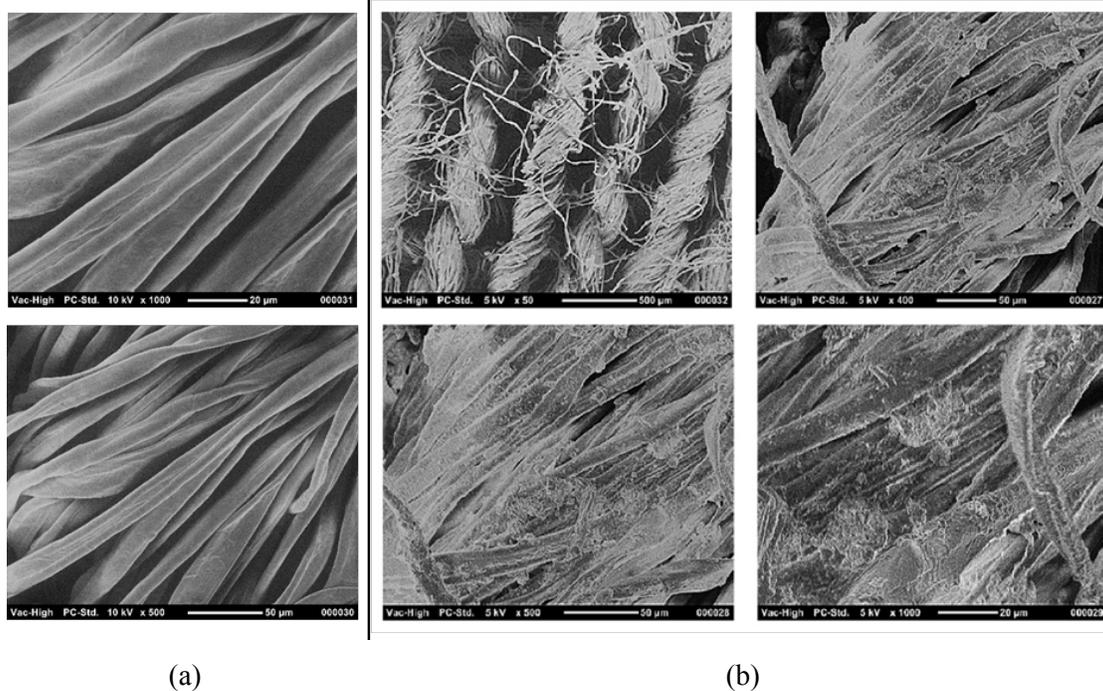
Changes of microcapsules  $\zeta$  potential as a function of pH are shown in Fig. 7. The pH was 5.9 when the microparticles were immersed in the electrolyte (NaCl) solution; neroline-loaded microcapsules were slightly cationic as the  $\zeta$  potential of the original dispersion was +3.7 mV. A positive charge is essential for efficient binding of microcapsules to the negatively charged cotton fabric. The positive charge comes from the protonation of amino groups of polyurethane in acidic medium. It is counterbalanced by negative charges coming from deprotonation of hydroxyl groups of  $\beta$ -CD in alkaline medium [58,59]. The isoelectric point (IEP) was reached at pH 6.3. Amino groups of polyurethane come from hydrolysis of isocyanate that has been claimed of limited extent because of the weak reactivity of HDI. Such amino groups are present for the IEP is shifted to high enough pH. Amino groups were probably generated at the outer surface of the polyurethane wall exposed to aqueous environment; they are concentrated there and can efficiently contribute to the surface charge.



**Figure 7:**  $\xi$  potential of neroline-loaded microcapsules as a function of pH

### 3.3 Textile Application

Fragrant functional fabric was prepared by an impregnation treatment of microcapsules on pure cotton fabric [38,40-46]. The microcapsules adhesion to knitted fabric was ensured by the presence of a polyurethane crosslinking agent in the impregnation bath and its thermal curing at 140°C during 6 min. The DoDGEDAS was used as a cationic surfactant to improve the microcapsules adhesion to the textile surface and avoid agglomeration troubles. SEM was used to observe surface morphology of the microcapsule-treated fabrics and results are illustrated in Fig. 8.

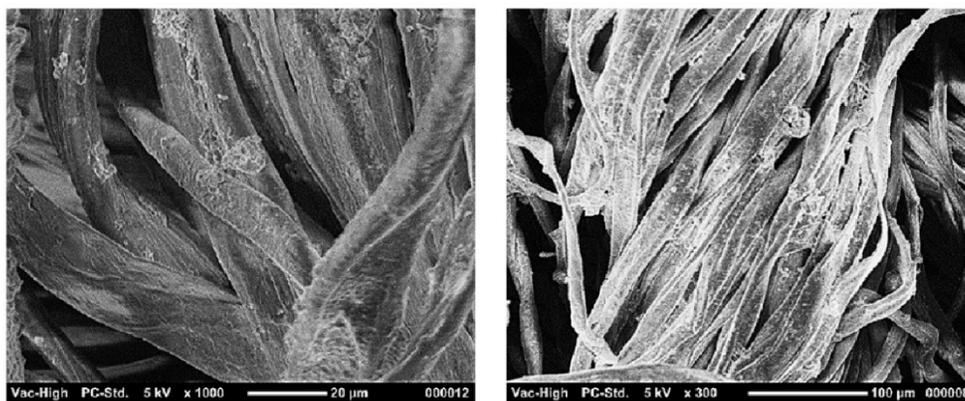


**Figure 8:** SEM micrographs of textile fabric: (a) before and (b) after functionalization

As shown in Fig. 8, SEM micrographs of the treated cotton fabrics confirmed that adhesion between textile fibers and microparticles was effective. The later were located within the interstices between fibers, on the open part of the fiber surface and even inside cavities of the cotton fiber. The fixed microcapsules had kept their spherical shape. Their morphology remained unchanged after impregnation, which highlighted their good mechanical strength and thermal properties. Such results could not be achieved in previous works by Rodrigues et al. [40] or Azizi et al. [38] where the microcapsules shape changed after

impregnation in comparison to their original shape in the dispersed state. It is also clear from these observations that the processing did not modify the treated fabric surface since the microparticles size was of the same order of magnitude as that of the cotton fiber.

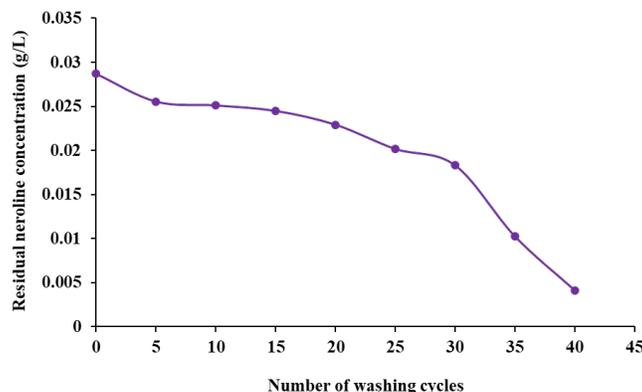
The durability of the microcapsules application to textile fabric was evaluated by measuring the effect of washing cycles on treated cotton according to the ISO 105-C10 standard of 2010. A qualitative study of the microparticles fixation was carried out by SEM observations (Fig. 9).



**Figure 9:** SEM micrographs of fragrant functional fabric after 40 washing cycles

Compared to Fig. 8, Fig. 9 shows a decrease of the number of fixed microcapsules. However, it is clear that a significant number of microcapsules remained on the fabric after 40 washing cycles. Most of them were of smaller sizes, intact and mostly stuck in the polyurethane resin which provided them some protection. The absence of broken microcapsule should also be noticed. Unlike the results obtained in previous work [41], it is important to point out the absence of deformed microcapsules after washing. Indeed, polyurethane shell material based on  $\beta$ -CD and HDI seems to own high crosslinking density and therefore its mechanical resistance is better than his counterpart based on isosorbide and HDI.

Wash fastness was improved by microencapsulation with polyurethane based on  $\beta$ -CD. The neroline concentration in the wash decreased slowly along subsequent washing cycles (Fig. 10). Long lasting release of neroline from the fabric treated with perfumed microcapsules was better than in previous works [38,40,41,57] as 50% of the present fragrance was retained after 35 washes. These results confirmed the efficient encapsulation of neroline inside tight microcapsules that strongly adhered to the cotton fabric. Microencapsulation with polyurethane based on  $\beta$ -CD appeared quite an effective method for the manufacture of perfumed cosmetotextile.



**Figure 10:** Residual neroline after subsequent washing cycles

#### 4 General Discussion

The present encapsulation process using  $\beta$ -CD-based crosslinked polyurethane brings about definite improvements with respect to previously reported materials. There are also few drawbacks. It is difficult to compare experimental results from several literature reports because the experimental protocols always show differences. The purpose of this section is a comparison with our previous report of polyurethane microcapsules prepared by interfacial polycondensation of HDI and isosorbide diol (Ben Abdelkader et al. [41]), because the design of the research work was closely similar. Tab. 1 gives this information. The ratio HDI/Polyol was different because isosorbide is a diol whereas  $\beta$ -CD bears 21 hydroxy groups. A 10-fold lesser amount of  $\beta$ -CD than isosorbide corresponds to twice higher number of hydroxy groups. The choice of a 10-fold decrease of  $\beta$ -CD polyol was rather arbitrary; it was not possible to keep the same concentration as for HDI because of the limited solubility of  $\beta$ -CD in water ( $18 \text{ g}\cdot\text{L}^{-1}$ ). The overall yields were similar for both systems. However, the nature of lost materials was not the same. The specific material losses were the encapsulation efficiency  $EE$  for neroline, and the polymer yield defined as the ratio of the masses of polymer in microcapsules to the mass of monomers introduced in the reaction. Both  $EE$  and polymer yield were calculated from the overall yield ( $\eta$ ) and neroline content ( $LC$ ) determined experimentally. Thus, the full neroline was encapsulated in Isosorbide-HDI microcapsules, so that the lost materials during the preparation were only monomers and/or soluble polymers. Indeed, the polymer yield was 22%. Conversely in case of  $\beta$ -CD-HDI microcapsules, the polymer was recovered inside microcapsules with high yield (polymer yield = 83%) and lost materials was mainly neroline ( $EE = 23\%$ ).

**Table 1:** Comparative account of  $\beta$ -CD-HDI and Isosorbide-HDI microcapsules encapsulating neroline

	HDI/Polyol/Neroline mole ratio	Overall yield ( $\eta$ )	Neroline content ( $LC$ )	Encapsulation efficiency ( $EE$ )	Polymer yield ( $\eta_{\text{polym}}$ )	Concentration of released neroline in the 1 <sup>st</sup> wash	Number of washes for 50% loss of neroline
<b>Isosorbide/HDI</b>	1 / 1 / 3	53%	73%	100%	22%	$0.055 \text{ g}\cdot\text{L}^{-1}$	15
<b><math>\beta</math>-CD/HDI</b>	1 / 0.1 / 1	60%	15%	23%	83%	$0.029 \text{ g}\cdot\text{L}^{-1}$	35

One benefit of crosslinking by  $\beta$ -CD is a large yield of polyurethane present inside microcapsules that allows for a thicker capsule wall. Conversely, interfacial polycondensation of isosorbide diol and HDI yields linear polymers that may have a significant solubility in water, especially at the early time of polycondensation when the polymers are of low molar mass. Indeed, polycondensation takes place at the surface of emulsion droplets. But formed macromolecules are not attached at the surface; they may leave it and migrate into the aqueous phase.

A drawback of  $\beta$ -CD-based microcapsules is a low encapsulation efficiency of neroline. Neroline probably left the capsules by evaporation during the drying stage, at first sight because the polyurethane wall was porous or permeable. The excellent resistance to wash fastness test of  $\beta$ -CD-HDI microcapsules shows that their walls are not permeable to neroline. Neroline was easily lost during manufacture process and could be strongly retained during washes. Such contradictory behaviors call for more sophisticated explanation, as the tentative one that follows. Since the hydroxyl/isocyanate stoichiometry was larger than one on case of  $\beta$ -CD polyol and almost the full monomers were polymerized and retained in microcapsules, the microcapsule walls contain hydroxy groups that may cause swelling by water, thereby making walls permeable. Drying causes shrinkage of the walls that might initiate the formation of cracks in the stiff crosslinked material; part of neroline could escape at that stage. Prolonged drying finally caused a kind of curing that healed the cracks and stopped leakage of neroline.

The amount of neroline deposited on cotton fabric was estimated from the neroline concentration found in the first wash. It was twice lower for  $\beta$ -CD-HDI than Isosorbide-HDI microcapsules. The lower amount obviously came from the lower encapsulation efficiency of  $\beta$ -CD-HDI microcapsules. However,

the deposited neroline was only twice lower although the encapsulation efficiency of  $\beta$ -CD-HDI microcapsules was four times lower than Isosorbide-HDI microcapsules. A better yield of capsule deposition onto fabric partly compensated the detrimental effect of the low neroline content of  $\beta$ -CD-HDI microcapsules. Neroline was probably lost from Isosorbide-HDI microcapsules during deposition. The higher mechanical strength of crosslinked  $\beta$ -CD-HDI microcapsules possibly allowed a deposition process with lower damage and higher yield.

Finally, neroline release was much slower from fabric impregnated with  $\beta$ -CD-HDI microcapsules. Crosslinking the microcapsules wall obviously allowed a long-lasting performance of the perfumed fabric. This is the most promising result that opens the door to improved perfumed cosmetotextile provided the loading capacity of fragrance inside capsules can be significantly increased.

## 5 Conclusions

The neroline fragrance has been microencapsulated with polyurethane shell by the interfacial polycondensation technique and then fixed onto cotton knitted fabric by impregnation. The originality of this study was the use of the  $\beta$ -CD as an alternative bio-sourced polyol in place of the conventional fossil fuel-based one. As a continuation of a previous study (Ben Abdelkader et al. [41]), it has been focused on the elaboration of a crosslinked polymeric shell material to improve mechanical resistance and therefore slow down release of active ingredient.

Both the chemical structure of the wall material and the perfume encapsulation have been confirmed by FTIR spectroscopy. Microcapsules of spherical shape and a mean particle size of 29  $\mu\text{m}$  exhibited good thermal stability. These microparticles were slightly cationic with an *IEP* of 6.32. Then, a cosmetotextile article was prepared by applying neroline-loaded microcapsules on cotton by impregnation technique using a cationic surfactant that increases the positive charge and a polyurethane crosslinking agent. SEM micrographs revealed an effective adhesion between textile fibers and microcapsules. The microparticles shape remained spherical after treatment thanks to their good mechanical strength and thermal properties. The wash fastness resistance of treated fabric was quite satisfactory as a significant amount of non-damaged microcapsules of small size resisted several washing cycles. Such microcapsules-treated cotton fabrics meet several criteria for their application as functional textile.

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