

STUDY ON PERFUME SUSTAINED-RELEASE FROM COTTON FABRIC TREATED WITH POLYSTYRENE MICROSPHERES

Azizi N.^{1,1}, Ladhari N.², Chevalier Y.³, Majdoub M.¹

¹Laboratoire des Interfaces et Matériaux Avancés (LIMA), Faculté des Sciences de Monastir, Université de Monastir, bd de l'Environnement, 5019 Monastir, Tunisia.

²TEXTILE ENGINEERING LABORATORY, UNIVERSITY OF MONASTIR, TUNISIA

³Laboratoire d'Automatique et de Génie des Procédés (LAGEP), Université Claude Bernard Lyon 1, UMR CNRS 5007, 43 bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France.

ABSTRACT

Encapsulation is a suitable way to control fragrance release and to make perfumed textiles more durable. Polystyrene-based microparticles containing fragrance were produced by *in-situ* polymerization technique with neroline as a core material and polystyrene as wall material. The chemical structure of the microspheres was confirmed by IR and ¹H NMR spectroscopies. Spherical shape and particle size distributions of microparticles were revealed by means of optical microscopy, scanning electron microscopy (SEM) observations and small-angle light scattering measurements. The encapsulation efficiency of perfume, determined by using ¹H NMR analysis, accounts for 55%. Neroline-loaded microspheres have been investigated for their properties and their suitability for cosmetotextile applications. The microspheres were deposited onto cotton fabrics by an impregnation process with about 76 % yield. The durability and the perfume release behaviour of the impregnated textile were evaluated through SEM observations and UV-visible spectroscopy.

KEYWORDS

Cosmetotextile ; impregnation; microparticle; neroline ; polystyrene.

1. INTRODUCTION

Microencapsulation technology has recently been introduced into the textile field. Microspheres can be defined as microscopic containers enclosing functional materials with a polymer matrix (Sánchez et al., 2011). The encapsulating membrane is composed of natural or synthetic polymers with varying thickness and degrees of permeability (Benita, 1996; Kim, Suh, 1998; Jabbari, 2001).

The membrane of the capsule protects volatile products from light and oxygen, therefore, providing a highly stable product with extended shelf-life (Suryanarayana et al., 2008; Specos et al., 2010). The coating materials must not react with the core materials (Hwang et al., 2006; Jyothi et al., 2010). The most common method used for encapsulation is interfacial polymerization which allows for the manufacture of microcapsules from an o/w emulsion by the formation of thick polymer walls around liquid droplets. Other commonly used methods are Pickering emulsion polymerization, In-situ polymerization, spray drying and coacervation (Babil et al., 1977; Archady, 1992; Urakawa, 2005; Sánchez et al., 2007; Sawada, Specos et al., 2010; Chen et al., 2010).

Microparticles have been in use for a long time in many fields such as carbonless copying paper, liquid crystals, adhesives, cosmetics, insecticides, pharmaceuticals and medicine (Green, 1957; Nelson, 2002;

¹ : Corresponding author. Email : azizinedra@yahoo.fr

Marinkovic et al., 2005; Suryanarayana et al., 2008). In textiles the major interest in microencapsulation is currently in the application of durable fragrances and skin softeners (Rodrigues et al., 2009). If a fabric is treated with microencapsulated functional agents, higher durability of functionality is expected (Shulkin et al., 2002; Sarier et al., 2007).

The evolution by the developed countries to more sophisticated textiles has encouraged the industry to use microencapsulation processes as means of imparting finishes and properties to textiles that were not possible or cost-effective using other technologies (Nelson, 2002; Marinkovic et al., 2005). Microencapsulation of essential oil flavors has led to many innovative applications, particularly for children's garments. The microcapsules can be applied by stamping works, exhaustion dyeing, impregnation, spraying and coating or by direct incorporation in the fibre (Nelson, 2002; Monllor et al., 2007; Rodrigues et al., 2009).

Up to now, there have been some attempts to develop a cheap and technically easy process for the encapsulation of fragrances. The present work aims at the elaboration of the neroline-loaded polystyrene-based microspheres by *in-situ* polymerization technique. Given that polystyrene is widely used for encapsulating phase change materials (Sánchez et al., 2007), in our study we are going to test the possibility of encapsulating another active product (neroline) for other textile applications. In fact, the microencapsulation method developed in this work is simpler than other methods referred to in literature. The elaborated microspheres were characterized for their chemical composition, morphology and particle size distribution. Their behaviour on cotton fabrics finishing was checked continuously.

2. EXPERIMENTAL

2.1. Materials and methods

2.1.1. Materials

Styrene (99 wt%) was of technical grade reagent. Styrene was washed with sodium hydroxide to remove the inhibitor. Sodium persulfate (97 wt%, Acros) was used as an initiator. Sodium dodecyl sulfate (SDS, purity 98%, Sigma Aldrich) was used as emulsifier. The purification of the water was accomplished by distillation and deionization. 2-ethoxynaphthalene (neroline) was synthesized by O-ethylation of β -naphthol with ethyl bromide. In order to bind the microspheres to the cotton fabric, an acrylic cross-linking agent (RESACRIL BD CONC; supplied by Prochimica Novarese SPA, Italy) was used. Microencapsulation processes were carried out in a thermostated double-jacketed 1 L glass reactor, (Sovirel), equipped with an anchor blade mixer, a digital control of stirring rate and an oil thermostated bath. The emulsion droplets were dispersed by Ultra-Turrax T 25 Basic homogenizer equipped with a S25N 25F shaft rotating at 12000 rpm.

2.1.2. Methods

$^1\text{H-NMR}$ spectra were recorded on a Bruker AV300 spectrometer. IR analyses were carried out in transmission mode with a Shimadzu FT-IR spectrometer on KBr pellets with sample concentration of 1wt%. Optical microscopy pictures of microspheres were taken with a Leica DMLM microscope equipped with Colour view camera and soft imaging system. A drop of the aqueous suspension placed between a glass plate and a cover slip was observed in transmission mode. Scanning Electron Microscopy (SEM) analyses of the surface morphology were performed using a Jeol JCM 5000 microscope operating at 10kV acceleration and under moderate vacuum. Particle size distribution was studied by small-angle light scattering using a Coulter 13320 laser-diffraction particle size analyzer. UV-vis absorption spectra were recorded with a Cary 50 Probe spectrophotometer of Hellma quartz cuvettes in 10 mm optical path.

2.2. Preparation of the microspheres

Polystyrene-based microspheres containing fragrances were prepared by in-situ polymerization, according to previous reports (Hiroyuki et al., 2002; Sánchez et al., 2007; Li et al., 2011).

The synthesis process involved two phases: a continuous phase containing 160 mL of water and 1.38 mmol of SDS and 0.67 mmol of sodium persulfate, and a dispersed phase containing 348.4 mmol of styrene, 47.6 mmol of neroline.

The solution was stirred in the reactor at room temperature for 5 min. Agitation was regulated by a homogenizer Ultra-Turrax T 25, at a speed of 12000 rpm. Then, the speed was decreased to 900 rpm. The temperature was maintained at 90°C during 6 hours. The obtained microspheres were separated by centrifugation (Gyrozen 416G) at a speed of 3000 rpm for 20 min, then rinsed with methanol to eliminate the residual monomer and non-encapsulated neroline and finally dried under vacuum at room temperature during 24h.

2.3. Application of microspheres to textile finishing

Impregnation was chosen as the most suitable process to apply neroline-loaded polystyrene microspheres on textile fibers. The bleached pure cotton fabric (250 g m⁻²) was impregnated with encapsulated active product (Jing et al., 2011; Rodrigues et al., 2009; Monllor et al., 2007). Microspheres were suspended in bath containing acrylic cross-linking agent (RESACRIL BD CONC, 50 g L⁻¹). Fabric was impregnated in the bath for 15 min at room temperature. Then, the impregnated textile was dried for 5 min at 100 °C, followed by a polymerization at 120°C during 5 min.

3. RESULTS AND DISCUSSIONS

3.1. Chemical analysis of the neroline-loaded microspheres

Dry microspheres were analyzed by IR and ¹H NMR spectroscopy in order to check against the polymerization reaction and to determine the encapsulation rate of neroline.

IR analysis

Dry microspheres were mixed with KBr and pressed as pellets for recording the IR spectrum in transmission mode.

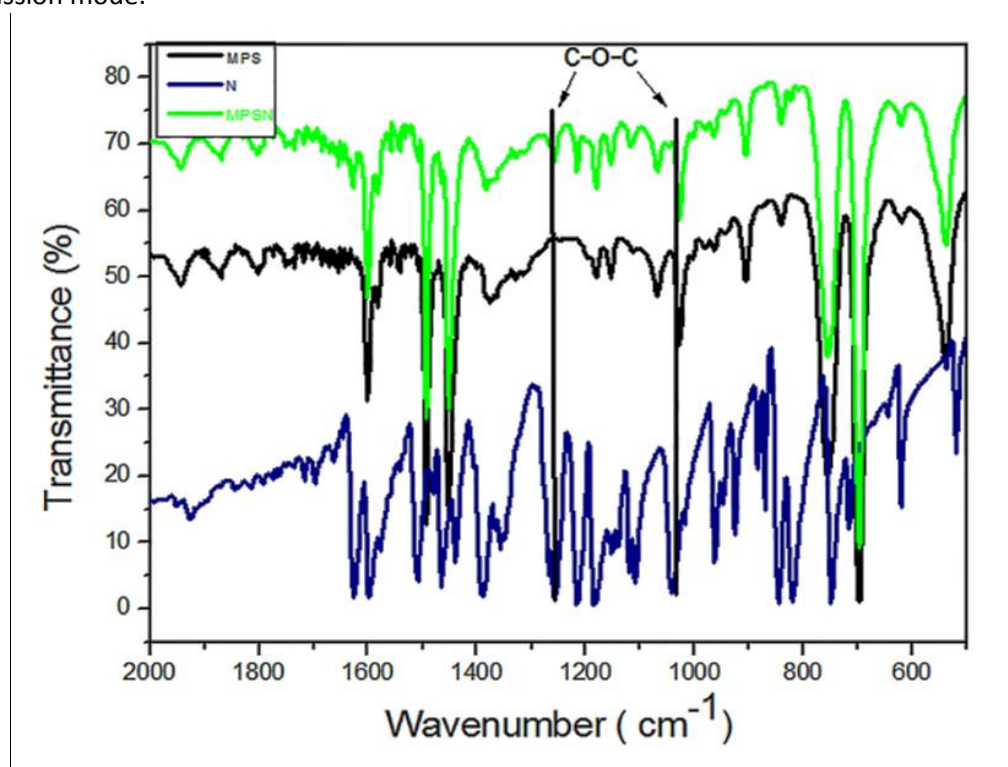


Figure 1: Identification of neroline encapsulation by IR spectroscopy

Figure 1 shows the IR spectrum of the loaded polystyrene microspheres (MPSN), compared to spectra of hollow polystyrene microspheres (MPS) and that of neroline. In particular, the well-resolved bands in the microsphere spectrum corresponded to the neroline C-O-C stretching vibrations, which confirmed that the perfume was successfully encapsulated.

¹H NMR analysis

The figure 2 shows the ¹H NMR spectrum of the loaded polystyrene microspheres that have been dissolved in CDCl₃, compared to hollow microspheres spectrum. The ¹H NMR spectrum of the loaded polystyrene microspheres shows the characteristic peaks of neroline: The peaks between 7.8 and 7.1 ppm were assigned to the aromatic protons; the peaks at 4.1 ppm and 1.4 ppm were attributed to the -OCH₂- and -CH₃ protons respectively. Quantitative comparison between the integral intensities of the polystyrene shell peaks and those of neroline was used to estimate a neroline encapsulation rate of 55%.

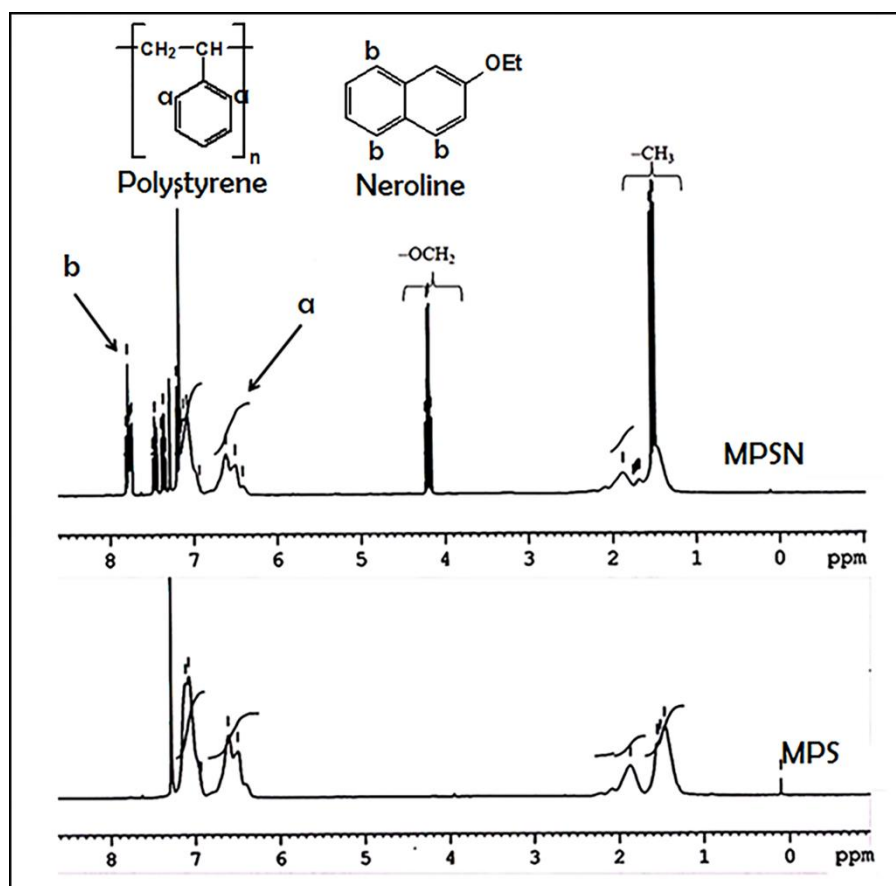


Figure 2: ¹H NMR spectra (CDCl₃, 300 MHz) of the hollow (MPS) and loaded (MPSN) microspheres dissolved in CDCl₃.

3.2. Morphology of the microspheres

Optical microscopy

Aqueous suspensions of the microspheres were observed by optical microscopy at different magnifications. The obtained optical micrograph (Figure 3) shows that the perfume microparticles had a spherical shape and different sizes. It also shows spherical shapes and many small particles of 1 μm and large particles of about 30 μm. The microspheres were well-dispersed without significant agglomeration. The polymer shells appeared as continuous membranes all around the oil droplets.

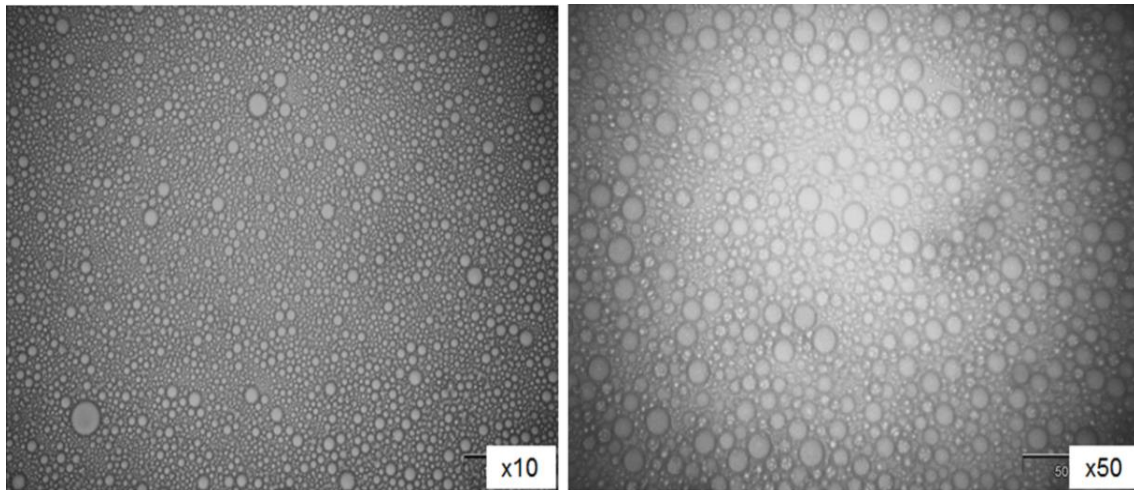


Figure 3: Optical pictures of neroline-loaded microspheres.

Scanning electron microscopy (SEM)

Surface morphology of microspheres obtained was studied by SEM (Fig.4). SEM pictures of the microspheres show different morphologies: microparticles with a soft and smooth surface (a) and others with rough surface (b).

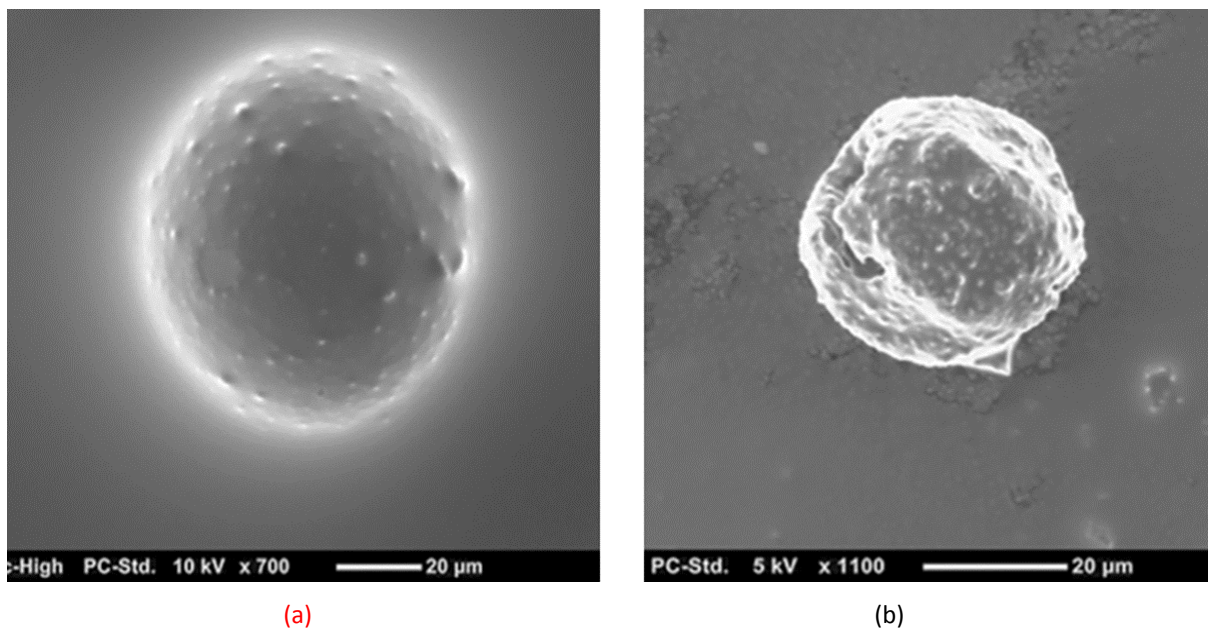


Figure 4: Scanning Electron Microscopy photographs of the loaded microspheres.

Particle size distribution

Particle size distribution (PSD) of the neroline loaded microspheres was measured by small-angle light scattering (Figure 5). The microspheres mean size was 31 μm , with 50% of the particles had a diameter lower than 26 μm . Hence, such PSD was considered as appropriate for the application of the microspheres to a textile impregnation process (Madene et al., 2006).

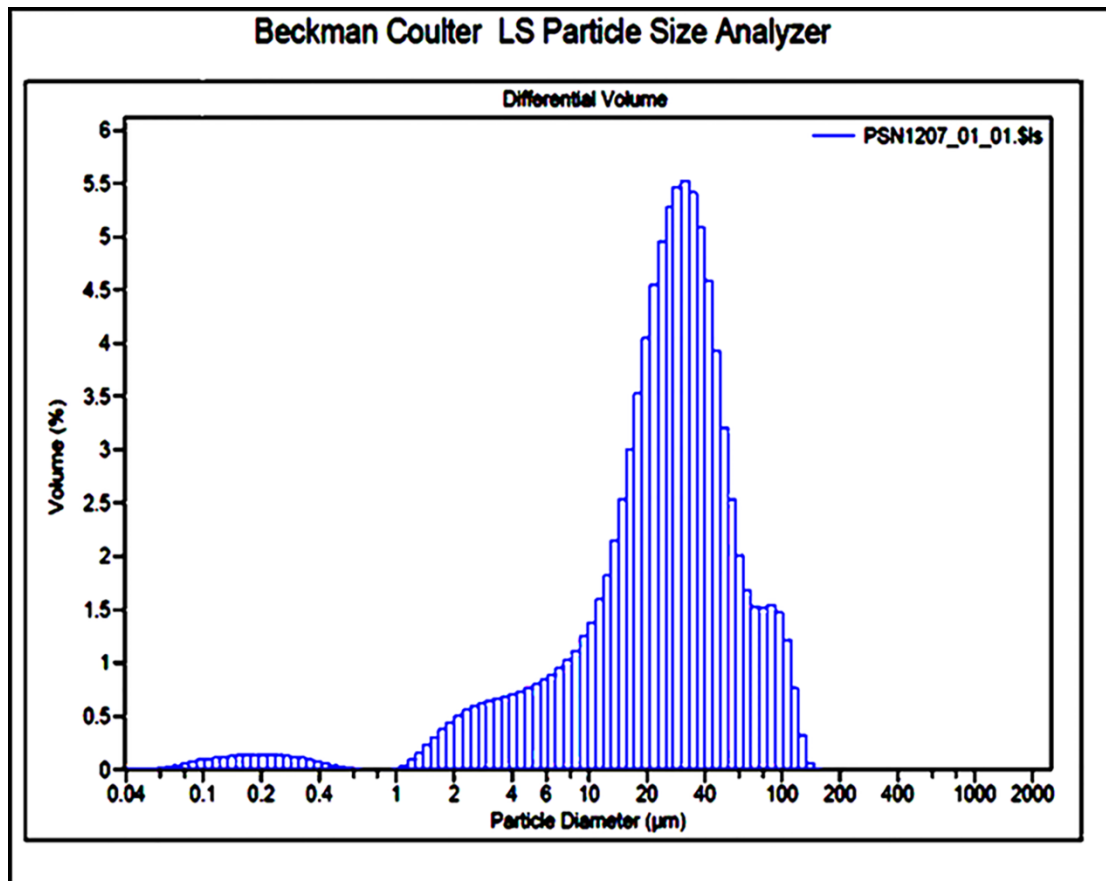


Figure 5: Particle size distribution of polystyrene-based microspheres.

3.3. Characterization of textile impregnated with microspheres

Neroline-loaded polystyrene-based microspheres were added to fabrics by impregnation (Monllor et al., 2007; Jing et al., 2011; Rodrigues et al., 2009). Adhesion of the microspheres to the cotton fabric was ensured by an acrylic cross-linking agent present in the bath and thermal curing at 120 °C for 5 min. The remaining microspheres in the bath after impregnation were separated by centrifugation in order to quantify the non-fixed microspheres. The impregnation yield was about 76% and this result was in the same range as was found in literature (Monllor et al; 2007). The extent of microspheres deposition was assessed by means of Scanning Electron Microscopy observations. The presence of microspheres adhering on impregnated textile was obvious. SEM micrograph showed the favorable adhesion of microspheres to the fabrics and also confirmed the spherical morphology of the microspheres (Figure 6).

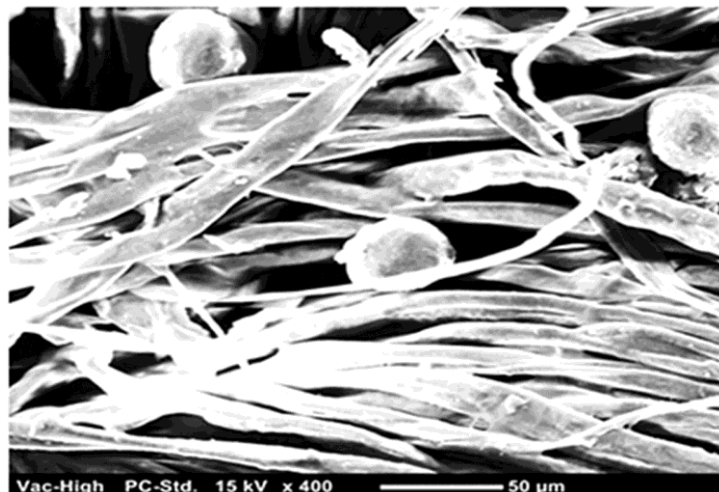


Figure 6: Scanning electron microscopy photograph of textile impregnated with microspheres.

The resistance of microspheres to washing was studied, according to the ISO 105-C10 standard of 2010, in order to improve the lifetime of scent textiles. The washing time was for 15 min and the final rinse was for 5 min. It was observed that, after cleaning, the amount of the microspheres on the fabric had decreased. Nevertheless, the pictures show that the capsules remained intact after several washing cycles, which suggested that the mechanism of neroline release did not involve the capsules' break up by full degradation of their walls or by their total elimination (Figure 7). On this basis, it is presumable that the release of neroline was caused by passive diffusion through the capsules walls rather than by degradation of the walls.

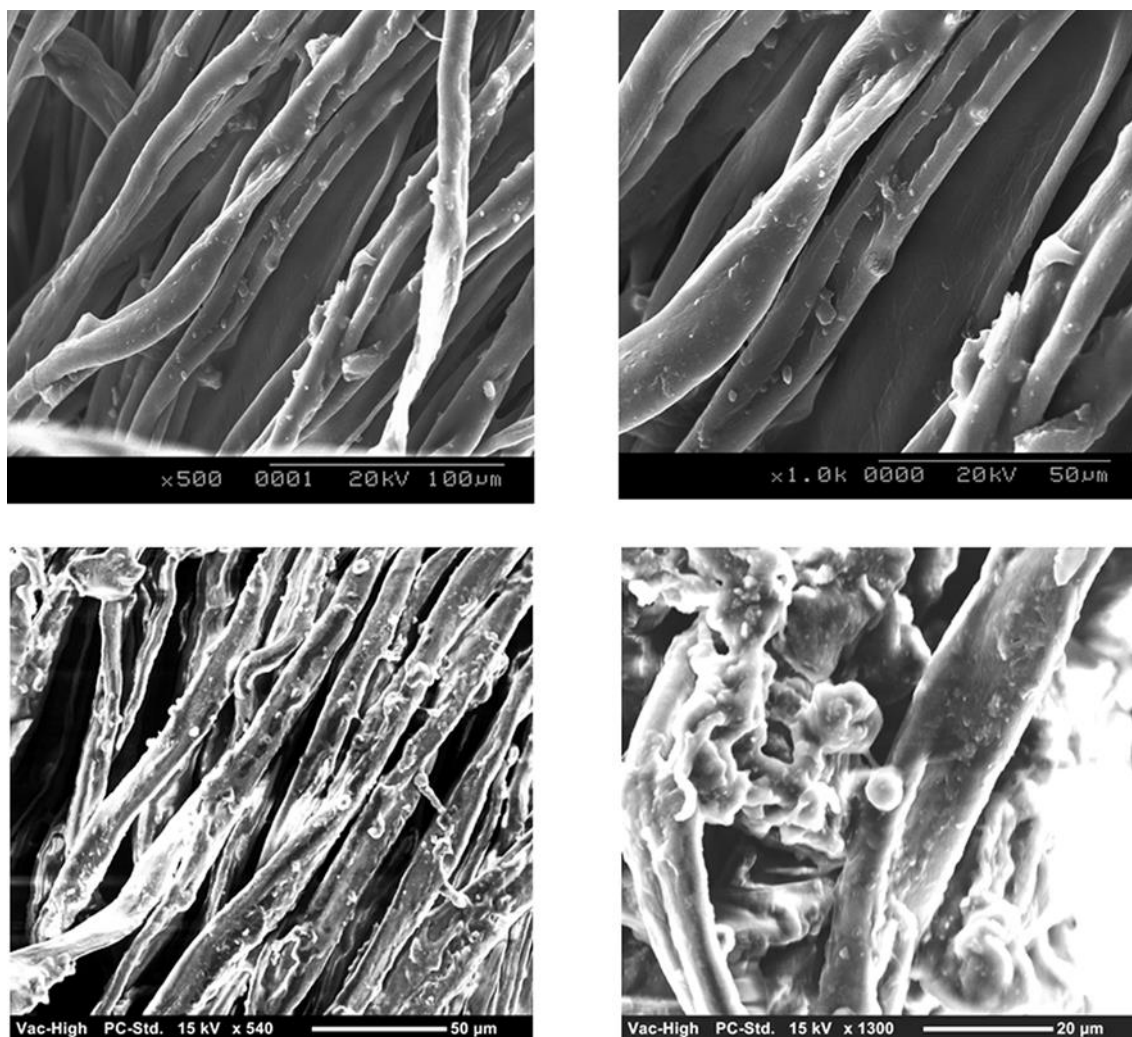


Figure 7: SEM photographs of textile impregnated with microspheres, after washing cycles, at different magnifications.

The effect of the number of washing cycles on the concentration of neroline inside the microspheres in the impregnated textile substrate was assessed by UV-visible absorbance. After every washing cycle the remaining encapsulated neroline in the textile substrate were extracted with diethyl ether and analyzed by UV-visible absorption spectroscopy, to check against the existence of residual neroline. The UV-vis spectrum of the diethyl ether solution showed two absorption maxima at 262 and 272 nm which were characteristic of the neroline (Azizi et al. 2014).

The figure 8 shows the absorbance ratio variation (A_i/A_0) at 272 nm as a function of the number of washing cycles. A_0 and A_i are respectively the absorbance of the extracted encapsulated neroline solution before and after i washing cycles.

A slow decrease of neroline amount according to the number of washing cycles was observed. The impregnated textile fabrics with perfume microcapsules showed higher resistance to washing cycles

compared with Rodrigues et al. (2009) works, where the resistance to washing was only of five cycles, while in our study the loss of neroline was of 15% after the fifth cycle and of 65% after the thirtieth washing cycle. These numbers confirm the efficient encapsulation of neroline. This had indeed the features of a controlled release of the perfume. In fact, the microcapsule shell represents a barrier acting against the diffusion of the encapsulated substance to the external environment. It can be explained by the fact that the microparticles with sustained-release are distinguished from one another by their structure (Jing et al., 2011; Sánchez et al., 2011). The results of release experiments by successive washings, demonstrated that microencapsulation allowed the control of the release kinetics of neroline through the pores of the encapsulating matrix.

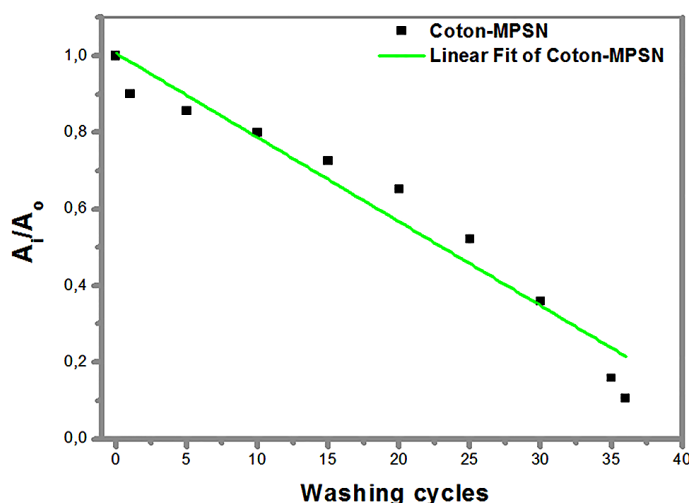


Figure 8: Amount of neroline present in textiles substrate according to the number of washing cycles.

4. CONCLUSIONS

Thanks to microencapsulation, fragrances can be retained on a garment during a significant part of their lifetime. Polystyrene-based microspheres were produced by in-situ polymerization technique. Careful analysis of the microparticles by means of NMR and IR showed that the chemistry could be performed satisfactorily with regards to expectations from the literature on microencapsulation and similar polymerization processes. The observation of microparticles by optical microscopy and SEM showed the absence of agglomerates, and a regular spherical shape. The particle size distribution of microspheres showed an average particle size of 31 μm . The impregnation of the neroline-loaded microparticles onto cotton fabrics was successful and allowed assessing them in an application to cosmetotextiles. SEM photographs confirmed the spherical morphologies of microspheres and also an effective adhesion of microspheres to fibers. The amount of neroline component decreased slowly when the impregnated textile substrates were subjected to washing cycles. However, the loss of neroline was only 15% after the fifth washing cycle. Resistance to wash fastness test of impregnated fabrics proved that the loaded microparticles retained their efficiency after more than 35 washing cycles.

Finally, encapsulation methods based on in-situ polymerization are open to health concerns resulting from the fear of the possibility that residual monomers might not reach complete conversion. As an alternative it would be better to utilize bio-based materials of renewable sources.

5. REFERENCES

- Archady, R. (1992).** *Suspension, emulsion, and dispersion polymerization: A methodological survey*, Colloid Polym. Sci., 270, 717–732.
- Azizi, N., Chevalier, Y., Majdoub, M. (2014).** *Isosorbide-based microcapsules for cosmeto-textiles*, Ind. Crops Products, 52, 150–157.
- Babil, S., Claar, J.-A., Temple, R.-G. (1977).** *In situ production of microcapsules on a substrate*. United States Patent. 4064294 A.
- Benita, S. (1996).** *Microencapsulation. Methods and Industrial Applications*. Marcel Dekker, New York.
- Chen, W., Liu, X., Liu, Y., Kim, H. I. (2010).** *Synthesis of microcapsules with polystyrene/ZnO hybrid shell by Pickering emulsion polymerization*. Colloid Polym. Sci., 288, 1393–1399.
- Green, B. K. (1957).** *Oil-containing microscopic capsules and method of making them*. US patent US 2, 800-458.
- Hiroiyuki, K., Hideaki, K., Naomichi, H., Tsutomu, K., Hironao, O. (2002).** *Operating conditions and microcapsules generated by in situ polymerization*, Adv. Powder Technol., 13, 265–285.
- Hwang, J.-S., Kim, J.-N., Wee, Y.-J., Jang, H.-G., Kim, S.-H. Ryu, H.-W. (2006).** *Factors affecting the characteristics of melamine resin microcapsules containing fragrant oils*. Biotechnol. Bioproc. Eng., 11, 391–395.
- Jabbari, E. (2001).** *Morphology and structure of microcapsules prepared by interfacial polycondensation of methylene bis(phenyl isocyanate) with hexamethylenediamine*. J. Microencapsulation, 18, 801–809.
- Hu, J., Xiao, Z., Zhou, R., Ma, S., Wang, M., Li, Z. (2011).** *Properties of aroma sustained-release cotton fabric with rose fragrance nanocapsule*. Chin. J. Chem. Eng., 19, 523–528.
- Jyothi, N. V. N., Prasanna, P. M., Sakarkar, S. N., Prabha, K. S., Ramaiah, P. S., Srawan, G. Y. (2010).** *Microencapsulation techniques, factors influencing encapsulation efficiency*, J. Microencapsulation, 27, 187–197.
- Kim, J.-W., Suh, K.-D. (1998).** *Highly monodisperse crosslinked polystyrene microparticles by dispersion polymerization*. Colloid Polym. Sci., 276, 870–878.
- Li, J., Wang, S., Liu, H., Wang, S., You, L. (2011).** *Preparation and characterization of polystyrene/polycarbonate composite hollow microspheres by microencapsulation method*. J. Mater. Sci., 46, 3604–3610.
- Marinković, S. S., Bezbradica, D., Škundrić, P. (2005).** *Microencapsulation in the textile industry*. Chem. Ind. Chem. Eng. Quart., 1, 58–62.
- Monllor, P., Bonet, M. A., Cases, F. (2007).** *Characterization of the behaviour of flavor microcapsules in cotton fabrics*. Eur. Polym. J., 43, 2481–2490.
- Nelson, G. (2002).** *Application of microencapsulation in textiles*. Int. J. Pharm., 242, 55–62.
- Rodrigues, S. N., Martins, I. M., Fernandes, I. P., Gomes, P. B., Mata, V. G., Barreiro, M. F., Rodrigues, A. E. (2009).** *Scentfashion®: Microencapsulated perfumes for textile application*. Chem. Eng. J., 149, 463–472.
- Sánchez, L., Sánchez, P., de Lucas, A., Manuel, C., Rodríguez, J. F. (2007).** *Microencapsulation of PCMs with a polystyrene shell*. Colloid Polym. Sci., 285, 1377–1385.
- Sánchez-Silva, L., Rodríguez, J.-F., Carmona, M., Romero, A., Sánchez, P. (2011).** *Thermal and morphological stability of polystyrene microcapsules containing phase-change materials*. J. Appl. Polym. Sci., 120, 91–297.

Sarier, N., Onder, E. (2007). *The manufacture of microencapsulated phase change materials suitable for the design of thermally enhanced fabrics.* *Thermochim. Acta*, 452, 149–160.

Sawada, K., Urakawa, H. (2005). *Preparation of photosensitive color-producing microcapsules utilizing in situ polymerization method.* *Dyes Pigments*, 65, 45–49.

Shulkin, A., Stöver, H. D. H. (2002). *Microcapsules from styrene–maleic anhydride copolymers: study of morphology and release behavior.* *J. Membrane Sci.*, 209, 433–444.

Suryanarayana, C., Chowdoji Rao, K., Kumar, D. (2008). *Preparation and characterization of microcapsules containing linseed oil and its use in self-healing coatings.* *Prog. Org. Coatings*, 63, 72–78.

Specos, M. M. M., Escobar, G., Marino, P., Puggia, C., Victoria M., Tesoriero, D., Hermida, L. (2010). *Aroma finishing of cotton fabrics by means of microencapsulation techniques.* *J. Ind. Textiles*, 40, 13–32.