

**MICROENCAPSULATED NEROLINE WITH NEW EPOXY RESIN SHELL BASED ON ISOSORBIDE: PREPARATION, CHARACTERIZATION AND APPLICATION TO COSMETOTEXTILE**BEN ABDELKADER M.<sup>1\*</sup>, AZIZI N.<sup>1</sup>, CHEVALIER Y.<sup>2</sup>, MAJDOUB M.<sup>1</sup><sup>1</sup> LABORATOIRE DES INTERFACES ET MATERIAUX AVANCES (LIMA), FACULTE DES SCIENCES DE MONASTIR, UNIVERSITE DE MONASTIR, TUNISIA.<sup>2</sup> LABORATOIRE D'AUTOMATIQUE ET DE GENIE DES PROCEDES (LAGEP), UNIVERSITE CLAUDE BERNARD LYON 1, UMR CNRS 5007, FRANCE.*Received 08 October 2013; Accepted 12 December 2013***ABSTRACT**

New core shell microparticles made of a bio-based epoxy resin wall and having the neroline fragrance as a core material have been investigated for their preparation and properties, and their suitability for cosmetotextile applications has been evaluated. The wall material was made of a polycondensate of a bio-based epoxy-isosorbide prepolymer and methylene bisphenyl-isocyanate produced by interfacial polymerization. The prepolymer was diglycidyl ether of 1,4:3,6-dianhydro-D-sorbitol (DGEDAS) synthesized from isosorbide and epichlorohydrin in the presence of concentrated aqueous NaOH. It was characterized in details by means of chemical analyses by <sup>1</sup>H NMR and IR spectroscopy, measurement of the molar mass distribution by size exclusion chromatography and mass spectrometry. Its interfacial polycondensation with methylene bisphenyl-isocyanate led to the formation of the isosorbide-based epoxy-urethane shell monitored by IR and TGA. The core-shell morphology of the microparticles was confirmed using optical microscopy and scanning electron microscopy. The microparticles were deposited onto textile fabrics by an impregnation process using a binding agent. The durability and the perfume release behaviour of the impregnated textile were evaluated through microscopic observations and Thin Layer Chromatography (TLC).

**KEYWORDS**

Epoxy resin; isosorbide; neroline; interfacial polycondensation; cosmetotextile.

**1. INTRODUCTION**

First microencapsulation applications dated from the 60th years when it was used for the manufacture of carbonless copying paper (Cheng, 2008) coated with microcapsules containing colorless chemically reactive color-forming dye precursor in their core. The manifold set was designed such that a colored mark formed when a marking pressure caused by a typewriter, pen, or other instrument was applied to the sheet (Chao, 1986). Thanks to its excellent properties known in coating, adhesive, and composite materials applications, epoxy resin has been extensively used as a wall material of microparticles (Chao, 1991). Thus, the diglycidyl ether of bisphenol A (DGEBA) was the most commonly used starting monomer for the formulation of epoxy thermosets: it represents 75% of all epoxy precursors (Chrysanthos et al., 2011). However, DGEBA-based

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materials are suspected to release the harmful bisphenol A. Therefore, epoxy prepolymers prepared from renewable resources are currently the subject of many researches and developments as safe and sustainable alternatives to the classical DGEBA. One way relies on the utilization of natural polysaccharides in the synthesis of bio-derived epoxy prepolymers (Lukaszczuk et al., 2011). Another alternative to DGEBA is polyglycidyl ether derived from 1,4:3,6-dianhydrohexitols, especially isosorbide (1,4:3,6-dianhydro-D-sorbitol (DAS)) that is commercially available in large quantities (Feng et al., 2010; Chrysanthos et al., 2011; Lukaszczuk et al., 2011; Catalani et al., 2008; East et al., 2010).

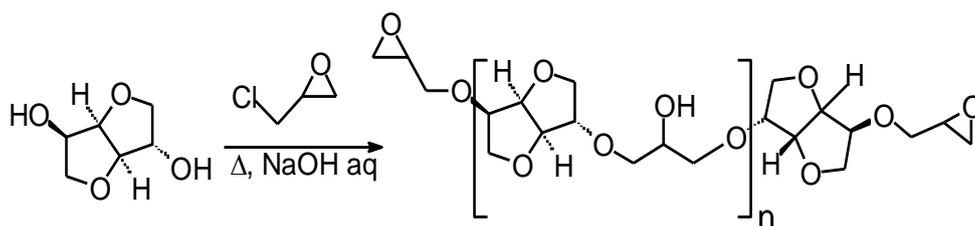
The aim of the present work is to investigate the synthesis of the bio-based prepolymer epoxy resin, Diglycidyl ether of isosorbide (DGEDAS), and its utilization for the elaboration of new microparticles prepared by interfacial polycondensation with methylene bisphenyl isocyanate (MDI) for cosmetotextile application. It includes three parts: the synthesis and characterization of the epoxy prepolymers, the preparation of microparticles by interfacial polycondensation with MDI, and finally the elaboration of impregnated textile substrates and their evaluation in terms of their resistance to wear and to dry cleaning cycles.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Following chemicals are used as received for the preparation of epoxy prepolymer: isosorbide (DAS, Acros, 98%); epichlorohydrin (Epi, Acros, 99%); sodium hydroxide (NaOH, Sigma-Aldrich); chloroform (CHCl<sub>3</sub>, Prolab). Materials used to prepare microparticles are as follow. Synthesized epoxy prepolymer Diglycidyl ether of isosorbide (DGEDAS) and methylene bisphenyl-isocyanate (MDI, Sigma-Aldrich, 98%) as wall materials, 2-ethoxynaphthalene (neroline) as core material. The neroline has been synthesized from  $\beta$ -naphthol (Acros, 98%). Polysorbate 80 (Tween<sup>TM</sup>-80, Sigma-Aldrich) was used as an emulsifier and dibutyltin dilaurate (DBDL, Aldrich, 95%) as a catalyst for polycondensation. Toluene (Sigma-Aldrich) was used as the dispersed phase of the oil-in water. Emulsion was prepared using an ULTRA-TURRAX<sup>®</sup> T25 Basic homogenizer. Microencapsulation was carried out in glass reactor, Sovirel<sup>®</sup> (1L), equipped with digital control of stirring rate and an oil thermostat bath. In order to bind the microparticles to the cotton fabric, an acrylic cross-linking agent (RESACRIL BD CONC; supplied by Prochimica Novarese SPA, Italy) was used.

### 2.2. Preparation of epoxy prepolymer (DGEDAS)



Scheme 1: Reaction route for the synthesis of the epoxy prepolymer (DGEDAS)

The synthesis of DGEDAS was adapted from the work by East et al. (Feng et al., 2010; Chrysanthos et al., 2011; Lukaszczuk et al., 2011; Catalani et al., 2008; East et al., 2010) that involves the direct reaction of isosorbide with epichlorohydrin. It is similar to the classical industrial route to produce DGEBA. A flask fitted with a Dean-Stark water-separator tube and a condenser was loaded with isosorbide and epichlorohydrin. The mixture was heated to reflux in stirred and inert environment. After cooling the reaction mixture to the azeotropic point of water and epichlorohydrin, an aqueous solution of sodium hydroxide (50%) was added dropwise during 30 minutes. Then, the temperature was risen again to 180 °C for the excess of

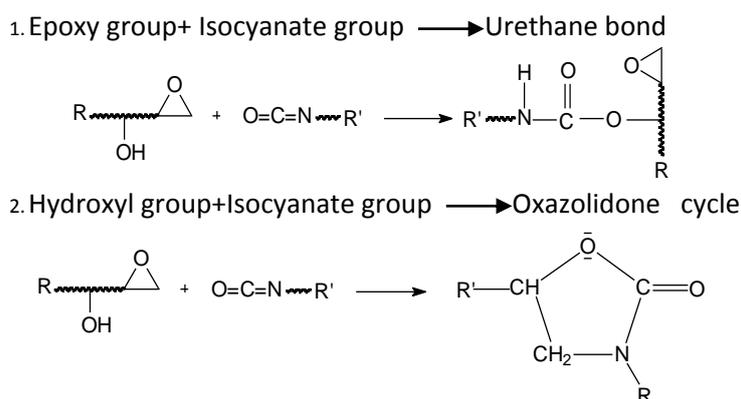
epichlorohydrin and water were progressively eliminated in the Dean-Stark trap. The Dean-Stark distillation was run for 30 minutes so as to ensure complete removal of epichlorohydrin. The cooled crude was filtered, the precipitate was washed several times with chloroform, first dried under reduced pressure in a rotary evaporator, and finally dried under high vacuum at 50 °C. The reaction shown in scheme 1; the reagents amounts are given in Table 1.

Table 1: Reagents characteristics and amounts

	Formula	M <sub>n</sub> (g/mol)	n(mol)
Isosorbide	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	146	0.24
Epichlorohydrin	C <sub>3</sub> H <sub>5</sub> ClO	92.5	1.2
Sodium hydroxide	NaOH	40	0.48

### 2.3. Preparation of epoxy microparticles

Epoxy microparticles were prepared by the interfacial polymerization process (Giraud et al., 2005, Rodrigues et al., 2009 and Azizi et al., 2011). A first aqueous phase (S1) containing water and Polysorbate 80 emulsifier and an organic phase (S2) containing neroline and MDI in toluene were used for the preparation of an o/w emulsion. Emulsification was performed by adding (S2) into (S1) under stirring with an Ultra-Turrax mixer rotating at 11,000 rpm during 5 min. A third aqueous phase (S3) containing 16% of (S1), DGEDAS and the DBDL catalyst, was subsequently transferred to the previously mentioned emulsion to start the interfacial polycondensation that forms the epoxy wall.



Scheme 2: Synthetic route for the formation of epoxy shell microparticles

Interfacial polymerization was performed in the reactor at 60 °C using a stirring rate of 700 rpm during 4h. Microparticles thus prepared were washed and dried under reduced pressure during 48h. The reactions involved in the formation of epoxy shell are shown in scheme 2.

### 2.4. Impregnation of microparticles on textile substrate

Pure cotton fabric (250g.m<sup>-2</sup>) was impregnated with perfume microparticles by the bath exhaustion method (Šiler Marinković et al., 2005; Rodrigues et al., 2009). Briefly, perfumed microparticles (4%) were suspended in the bath (RdB=1/4) at atmosphere temperature containing the acrylic crosslinking agent (20g.L<sup>-1</sup>), and the fabric was impregnated in the bath. The impregnated textile was dried for 5 min at 100 °C and cured at 120 °C during 15 min.

### 2.5. Characterization

Epoxy number (EN) and equivalent epoxy weight (EEW) of the product were measured by reaction with pyridine in excess of hydrochloric acid under nitrogen at 100 °C for 20 minutes, and subsequent back titration with sodium hydroxide using pH-meter.

Nuclear Magnetic Resonance spectra were recorded with a Bruker DRX 300 spectrometer operating at 300 MHz (for  $^1\text{H}$  NMR). Deuterated chloroform ( $\text{CDCl}_3$ ) was used as a solvent. Infrared (IR) spectra of the products in KBr pellets were collected in absorbance mode on a Shimadzu Fourier Transform IR spectrometer. Electro Spray Ionization Mass Spectrometry (ESI-MS) analysis was carried out on Termol LCQ, ion trap device, source mass range from 50 to 2000 Th. Samples were dissolved in  $\text{CH}_2\text{Cl}_2$ . Size Exclusion Chromatography (SEC) analysis was carried out on Viscotek instrument. The separation was done on column type GMHxl. THF was used as the eluent at a flow rate of  $1\text{ mL}\cdot\text{min}^{-1}$ . Thermo Gravimetric Analysis (TGA) measurements are carried out on a TG 209 F1 Netzsch instrument. The samples were heated at rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$  under nitrogen atmosphere. The distribution, diameter and surface morphology of the microparticles in solution were assessed by observation with a Scanning Electron Microscopy (SEM) using a Jeol JCM 5000 microscope operating at 10kV acceleration under moderate vacuum, thus avoiding the need for metallization of the samples. A Sodemat microscope equipped with VisioCal software application was used to visualize microparticles in the impregnated textile substrates.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Epoxy prepolymer characterization

The reaction of isosorbide with an excess of epichlorohydrin in the presence of 50% aqueous NaOH (scheme 1) yielded the prepolymer as a light yellow, viscous and water soluble liquid.

#### Determination of Epoxy Number and Equivalent Epoxy Weight

Epoxy Number (EN) and Equivalent Epoxy Weight (EEW) determined by titration were respectively equal to 0.39 mol/100g and 252.

#### $^1\text{H}$ NMR analysis

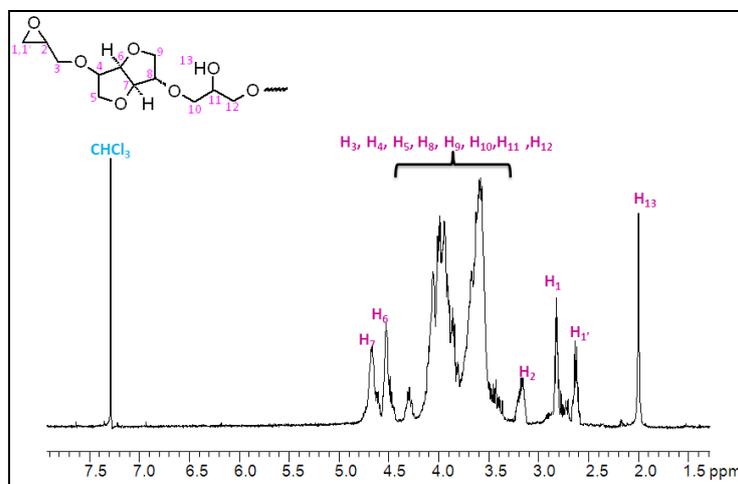


Figure 1:  $^1\text{H}$  NMR spectrum of DGEDAS (25 °C,  $\text{CDCl}_3$ )

The  $^1\text{H}$  NMR spectrum of DGEDAS shown in Figure 1 reveals three multiplet signals typical of glycidyl group protons at  $\delta=2.6\text{ ppm}$ ,  $\delta=2.8\text{ ppm}$ , and  $\delta=3.2\text{ ppm}$ , as well as two broad signals at  $\delta=4.5\text{ ppm}$  and  $\delta=4.7\text{ ppm}$  which were assigned to the protons present in the isosorbide junction. Because of the conformation of the cycle and the non-equivalence of the protons in the isosorbide cycle (Chrysanthos et al., 2011), the assignment of the peaks between  $\delta=3.3\text{ ppm}$  and  $\delta=4.4\text{ ppm}$  corresponding to these protons was of low accuracy.

## IR analysis

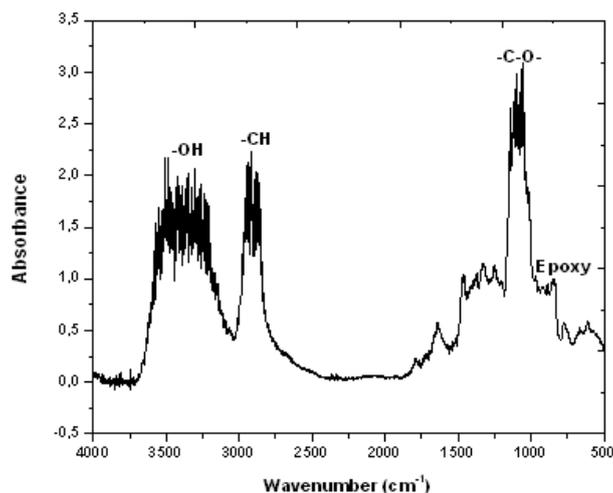


Figure 2: IR spectrum of DGEDAS

The IR spectrum of DGEDAS shown in Figure 2, displays the different bands centred at  $3500\text{ cm}^{-1}$  and  $2920\text{ cm}^{-1}$  indicating the presence of -OH and -CH groups respectively, the band at  $845\text{ cm}^{-1}$  of epoxy groups, as well as the band at  $1056\text{ cm}^{-1}$  of the -CO- group from the aliphatic ether (Chrysanthos et al., 2011).

## ESI-MS analysis

The ESI-MS spectrum of DGEDAS (Figure 3) shows a high number of peaks which indicated the presence of numerous oligomers. The molar masses and formula of some of these species are given in Table 2. Scheme 3 shows the chemical structures of these molecules.

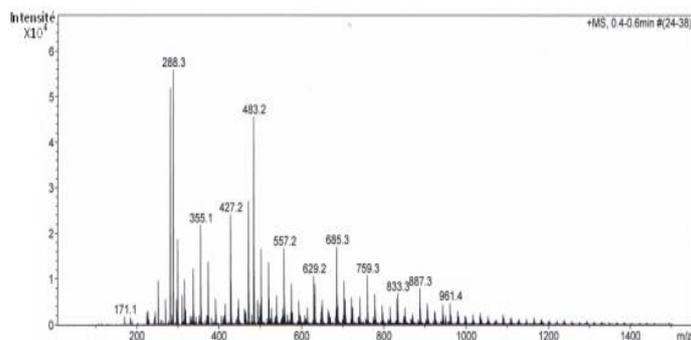
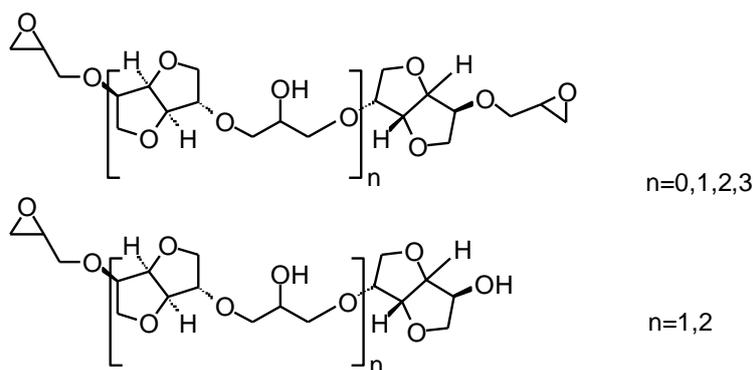


Figure 3: ESI-MS spectrum of DGEDAS

Table 2: Molar mass values and formulas of some DGEDAS oligomers revealed by ESI-MS

Peak (m/z)	$M_n$ (g.mol <sup>-1</sup> )	Formula
281.1	258	C <sub>12</sub> H <sub>18</sub> O <sub>6</sub>
427.2	404	C <sub>18</sub> H <sub>28</sub> O <sub>10</sub>
483.2	460	C <sub>21</sub> H <sub>32</sub> O <sub>11</sub>
629.2	606	C <sub>27</sub> H <sub>42</sub> O <sub>15</sub>
685.3	662	C <sub>30</sub> H <sub>46</sub> O <sub>16</sub>
887.3	864	C <sub>39</sub> H <sub>60</sub> O <sub>21</sub>



Scheme 3 : Structures of DGEDAS oligomers revealed by ESI-MS

### SEC analysis

The DGEDAS prepolymer was analyzed by SEC to determine its molar mass distribution. The average molar masses were low and the polydispersity index was 1.64 (Table 3).

Table 3: Average molar masses of epoxy prepolymer determined by SEC

$(M_p)$ ( $\text{g}\cdot\text{mol}^{-1}$ )	$(M_n)$ ( $\text{g}\cdot\text{mol}^{-1}$ )	$(M_w)$ ( $\text{g}\cdot\text{mol}^{-1}$ )
614	522	857

### TGA analysis

The mass loss as a function of temperature for DGEDAS prepolymer is shown in Figure 5. The TGA curve of diglycidyl ether of isosorbide shows a continuous single step degradation process contrary to the DGEDAS studied by Chrysanthos et al. (2011) for which degradation took place as two distinct stages. The initial mass loss started at 322°C. However, degradation took place at 360 °C, a higher temperature than for the epoxy prepolymer synthesized by Chrysanthos et al. (2011) (the maximum rate of degradation was observed at 320°C). At 800°C, the mass loss was about 92%. These thermal stability results will affect the thermal properties of the epoxy-urethane polymer constituting the microparticle's wall to be synthesized.

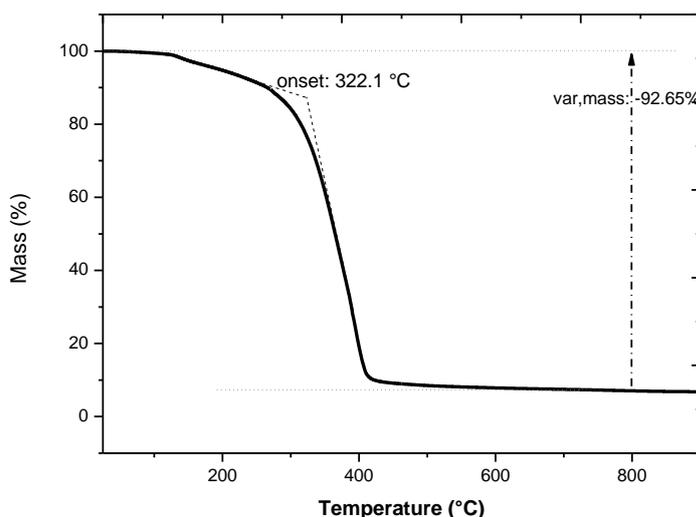


Figure 4: TGA thermogram of DGEDAS

### 3.2. Microparticles characterization

#### Scanning electron microscopy (SEM)

The surface morphology of microcapsules was observed using SEM; the results were presented in Figure 5. The size was about 20  $\mu\text{m}$ . It is clear that the shape of the microparticles was spherical and rough and their surface was rough.

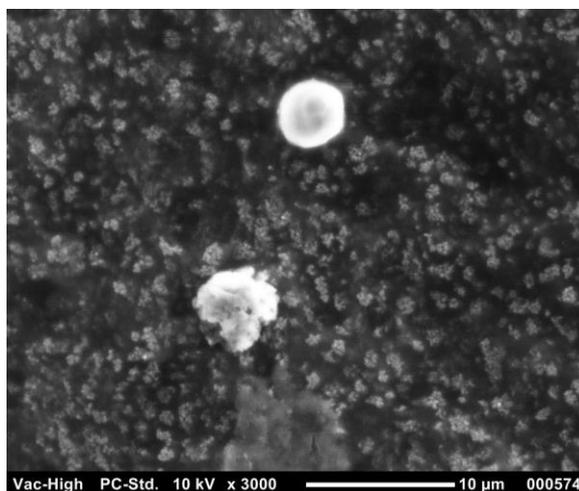


Figure 5: SEM micrograph of microparticles containing perfume

#### IR analysis

Figure 6 shows the IR spectra of epoxy resin, neroline and microparticles. The bands at  $1724\text{ cm}^{-1}$  and  $3311\text{ cm}^{-1}$  were assigned respectively to C=O and N-H bonds pertaining to the epoxy resin. The typical absorption peaks of neroline appeared at  $1266\text{ cm}^{-1}$  and  $1033\text{ cm}^{-1}$  corresponding to the C-O-C asymmetrical and symmetrical stretching vibrations (Azizi et al., 2011). The IR spectrum of perfumed microparticles confirmed the encapsulation of neroline by the epoxy resin shell.

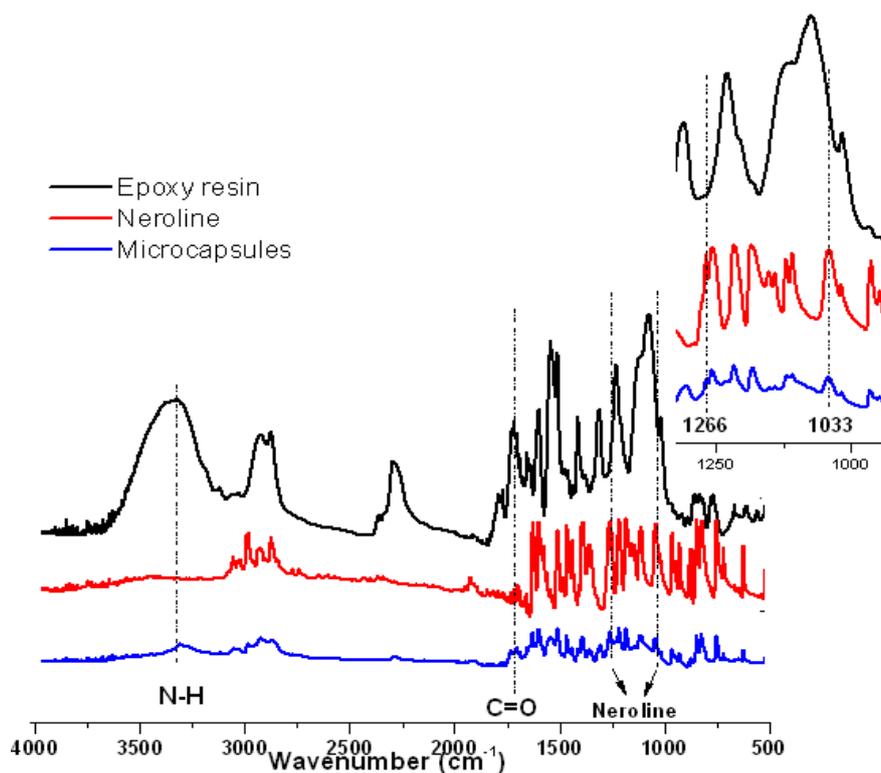


Figure 6: Identification of neroline encapsulation by IR spectroscopy

## TGA analysis

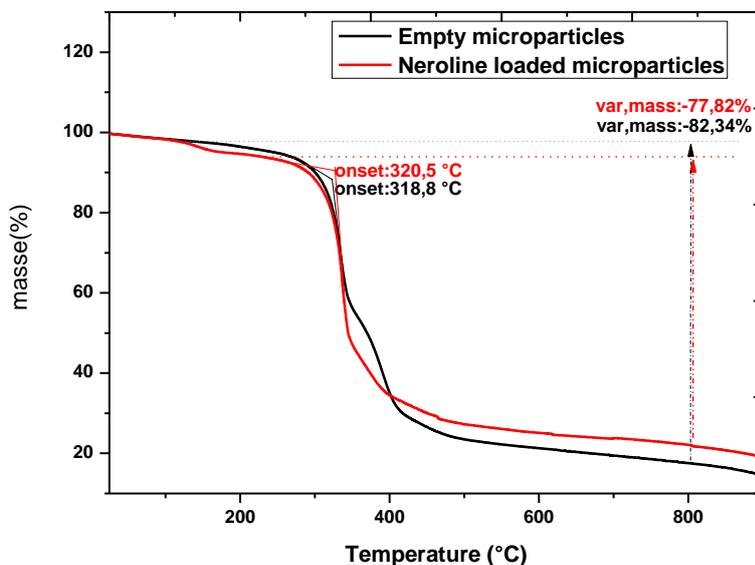


Figure 7: TGA thermograms of empty and loaded microparticles

TGA thermograms of blank (free of neroline) and loaded microparticles are shown in figure 7. The initial mass loss, the degradation temperature and the mass loss in a molten state at 800 °C of these two samples showed the formation of the microparticles with different levels of resistance to heat, which is related to the presence of encapsulated neroline. However, these values are close to each other. Results are summarized in table 4.

Table 4: Thermal properties of empty and loaded microparticles

	Temperature of initial mass loss (°C)	Td(°C)	Mass loss at 800°C (%)
Blank microparticles	318.8	346.73	82.34
Loaded microparticles	320.5	336.77	77.82

As shown, all the specimens have a high thermal stability upon the formation of polymer wall. The thermal properties of epoxy-urethane microparticles are higher than those of other urethanes shells reported in the literature (Giraud et al., 2005).

### 3.3. Textile impregnated with microparticles

SEM and optical micrographs of fabric after being impregnated with microparticles solutions are given in Figures 8 and 9 respectively. These pictures confirm that adhesion of microparticles to the textile fibres is effective. However, due to the presence of the acrylic resin, microparticles tend to agglomerate.

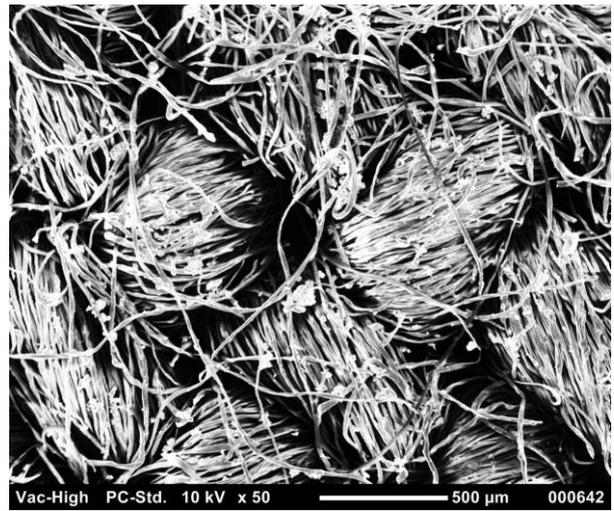
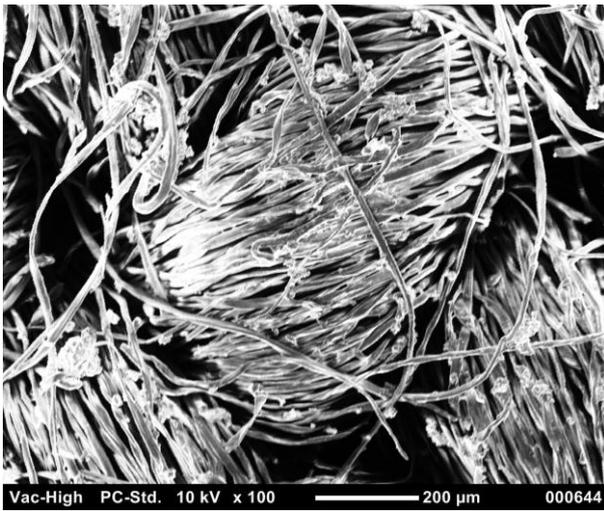


Figure 8: SEM micrographs of impregnated textile substrates

Figure 9: Optical micrograph of impregnated textile substrates (200X)

The effect of washing cycles on impregnated textile substrates was studied, in order to assess the life time of scent textiles. Washing fastness is evaluated according to the norm ISO 105-C10 (2006) using an Autowash machine. The control of microparticles fixation onto fabric and the diffusion of the neroline through the microparticles membranes after each washing cycle were carried out by titration of the release neroline by Thin Layer Chromatography (TLC).

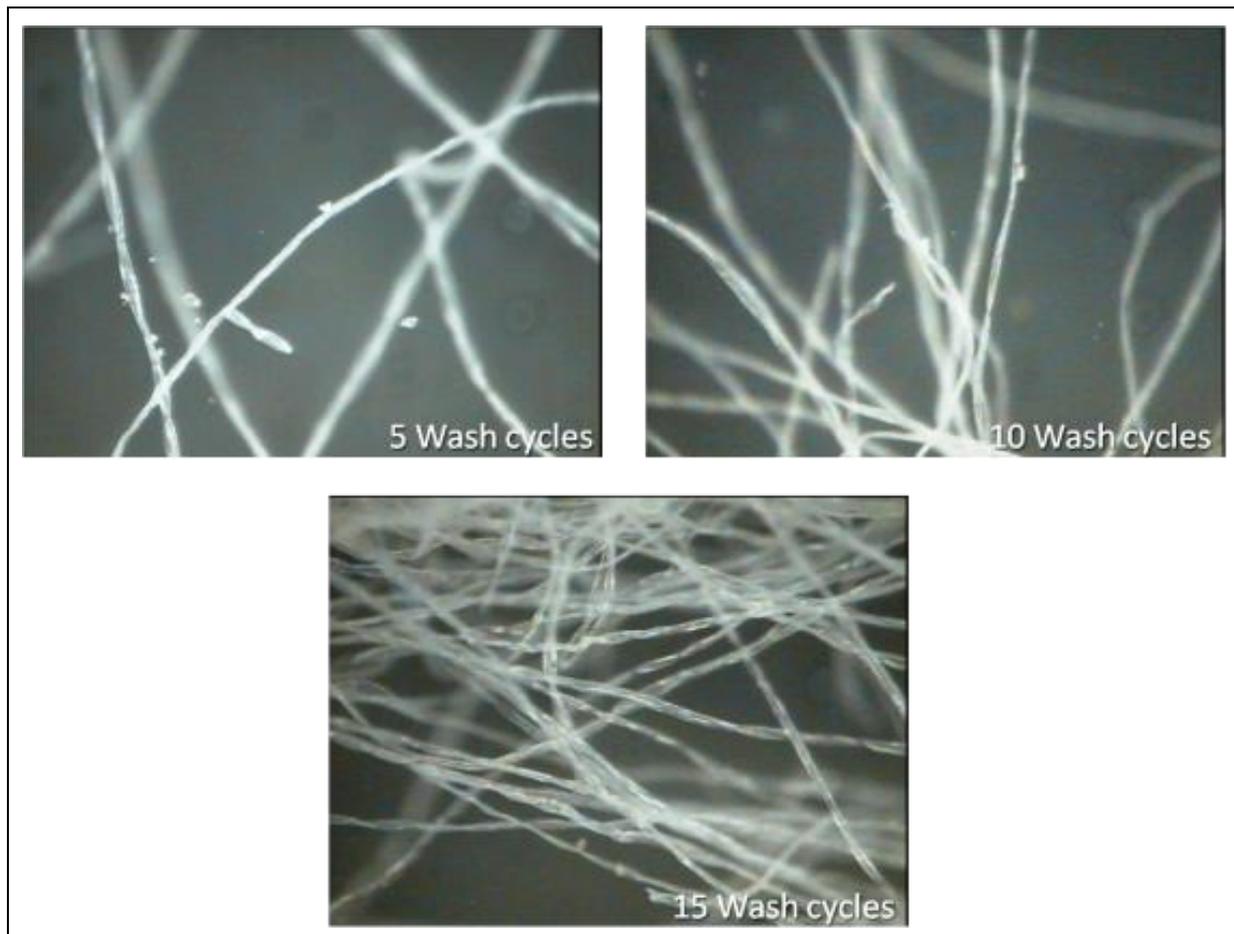


Figure 10: Optical micrograph of impregnated textile substrates after different wash cycles (200X)

A reduction of the microparticles amount fixed on the clothes after cleaning was observed. Figure 10 shows microscopic photographs of fabrics impregnated with perfumed microparticles after 5, 10 and 15 washing cycles. 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. However, the resolution of optical microscopy did not allow to detect any possible degradation of the capsules wall that would have converted the tight wall barrier into a more permeable (porous) material. On this basis, it was presumed that the release of neroline was caused passive diffusion through the capsules walls better than degradation of the walls. According to these optical micrographs, microparticles are attached yet to the treated fabric and subsequently the treatment performed retained its effectiveness for more than 5 wash cycles. To make sure of the neroline existence, washed perfumed textile was impregnated in the appropriate solvent for the core material. Results evaluated through TLC confirm the presence of neroline after the fifth washing cycles. Thus, microencapsulation is an effective method that allowed the control of neroline diffusion through the pores of the microparticles membrane which represents an effective diffusion barrier separating the active ingredient and the environment.

Tests of resistance to wear of impregnated textile substrates were carried out in a Martindale apparatus according to the Swiss norm BS 5690. Fabric was submitted to 1,500, 3,000, and 4,500 rubbing cycles. The control of microparticles fixation onto fabric and the diffusion of the neroline through the microparticles membranes were carried out by Thin Layer Chromatography (TLC). Figure 11 shows microscopic photographs of fabrics impregnated with perfumed microparticles after rubbing cycles. The wear resistance test and TLC evaluation, showed that the treatment performed retained its efficiency more than 4 500 rubbing cycles.

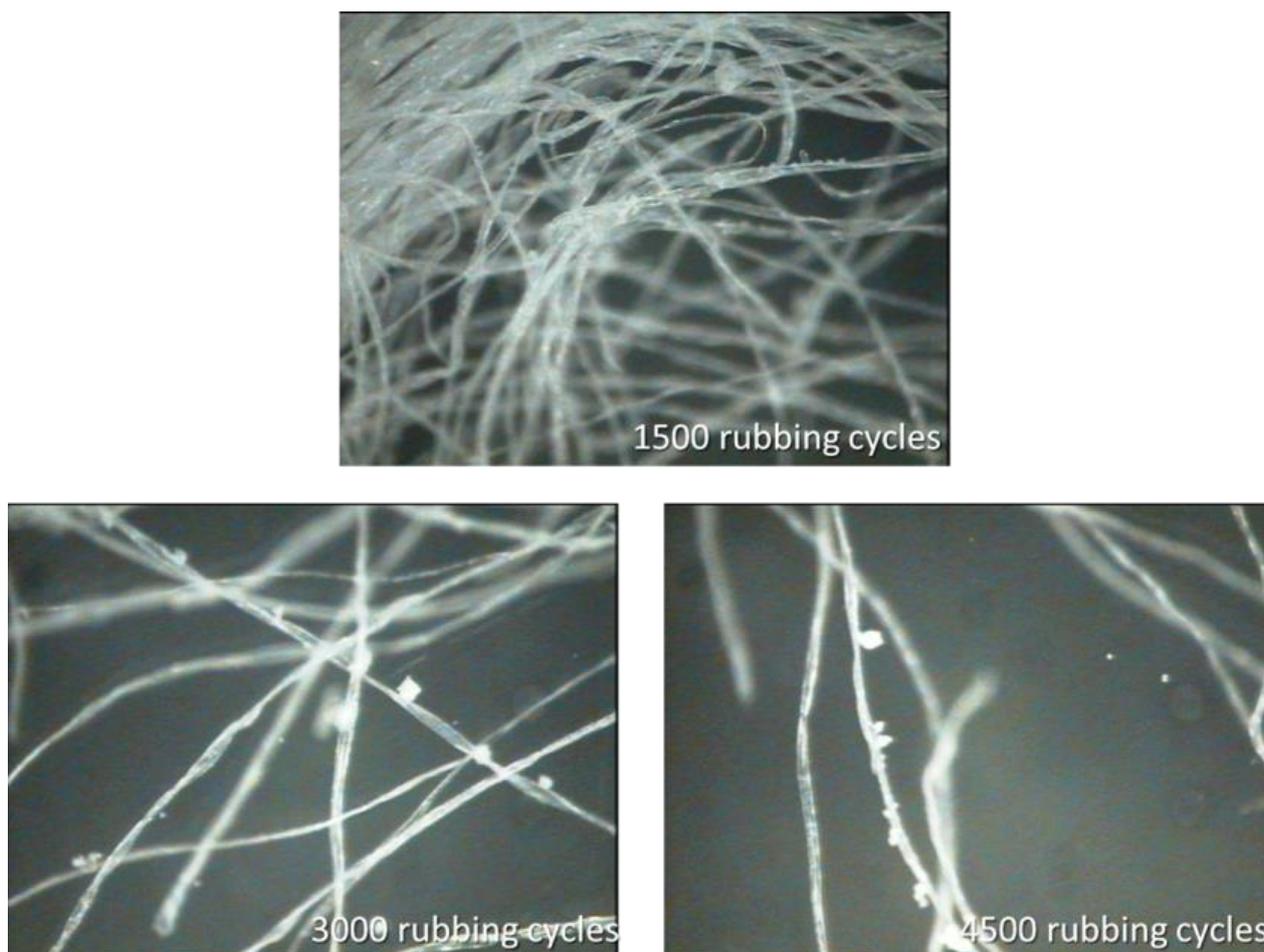


Figure11: Optical micrograph of impregnated textile substrates after different rubbing cycles (200X)

#### 4. CONCLUSION

A new epoxy prepolymer based on isosorbide as an alternative to the bisphenol A- based DGEBA has been used for the preparation of microcapsules for means of interfacial polycondensation. This successful substitution was demonstrated by the encapsulation of the neroline perfume and application to cosmetotextile. Careful analyses of the microparticules by means of NMR, IR, ESI-MS and SEC showed that the chemistry could be performed satisfactorily with regards to expectations from the literature on microencapsulation and similar polycondensation chemistry. The good thermal properties of DGEDAS and microparticles showed an improved thermal stability of the isosorbide-based materials.

The, epoxy microparticles of neroline perfume produced by interfacial polymerization technique were impregnated onto textile fabrics in order to assess them in an application to cosmetotextile. Resistance to wear and wash fastness test of impregnated textile substrates proved that the microparticles deposited by this treatment retained their efficiency after more than 5 washing cycles and 4,500 rubbing cycles.

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