Elaboration and Characterization of Polyurethane-based Microcapsules: Application in Textile

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ABSTRACT
The aim of this study was to elaborate a textile odorous or a fireproof one using microcapsule. Polyurethane (PU)-based microcapsules containing the diammonium hydrogen phosphate (DAHP) as a flame retardant or the neroline as an odorant entity were prepared and characterized. The microcapsules were synthesized by interfacial polycondensation of toluene disocyanate and triethylene glycol. Microcapsules were characterized by optical microscopy and FT-IR spectroscopy. The thermal properties of membrane were analyzed by differential scanning calorimetry and results showed that PU microcapsules were thermally stable till 280°C. The study of inflammability of the cotton fabrics coated with DAHP-loaded microcapsules showed a decrease of flame propagation speed, compared to the untreated fabric. In order to evaluate the adhesion of microcapsules to textile, washing and rubbing tests, had been investigated. Neroline/DAHP-loaded microcapsules showed a good fastness and remained after a six cycle washing. In the case of DAHP-loaded microcapsules the flame retardant action is significant.

Key words: Polyurethane microcapsule, flame retardant, neroline, cotton fabrics, coating, fastness

INTRODUCTION
Microcapsules are small particles with sizes between 1 and 100 μm that contain an active agent surrounded by a natural or synthetic polymeric membrane (Giraud et al., 2005; Nelson, 2001). In fact, all the interest of microcapsule resides in the membrane. The shell can be formed by chemical or physical process (Dihayati et al., 2007; Mellati et al., 2010). Microencapsulation has attracted much attention due to the large number of potential applications (Toure et al., 2007; Su et al., 2007). They were used widely in a number of industries including pharmaceutical, agricultural, bulkchemical, food processing (Davido-Fardo et al., 2008), cosmetics and particularly in textile domain (Nelson, 2002; Leelajariyakul et al., 2008; Lolodi, 2011).

The encapsulation is used to protect fragrances or other active agents from oxidation caused by heat, light, humidity and exposure to other harmful substances over their lifetime (Rad, 2010; Salaun et al., 2011). It has been also employed to prevent the evaporation of volatile compounds and to control the rate of release (Monllor et al., 2007; Rodrigues et al., 2008). The microcapsules could be applied to textile using coating, padding, spraying, impregnation and exhaust or screen-printing techniques (Giraud et al., 2005; Nelson, 2002; Rodrigues et al., 2009). Binding agent had
been used to fix the microcapsule on the woven and to allow a good fastness in wash. The woven can be silk, synthetic or cotton fiber. The microcapsules fixed into textile should not modify the material, the touch and the colour of textile (Rodrigues et al., 2008; Sarier and Onder, 2007).

Our main purposes are to synthesize and to characterize the microcapsules. Then, microcapsules were used to coat cotton fabrics. The polyurethane capsules were synthesized by interfacial reaction and studied using two active substances: flame retardant (diammonium hydrogen phosphate) and odorant entity (neroline).

MATERIALS AND METHODS
Materials: This study was carried out during 2009-2011. The emulsion (water/oil) was maintained by an homogenizer ULTRA-TURRAX® T25 Basic. Microencapsulations were carried out in glass reactor, Sovirel® (1 l), equipped with digital control of stirring rate and an oil thermostat bath.

The polyurethane shell of microcapsules were synthesized from toluene diisocyanate (TDI, purity 97%, Aldrich) as aromatic polycosocyanate, triethylene glycol (TEG, purity 98%, Aldrich) as polyol. Sodium dodecyl sulfate of (SDS, purity 98%, Sigma) is used as well as emulsifier, dibutyltin dilaurate (DBDL, Aldrich, purity 95%) as catalyst. Diammonium hydrogen phosphate (DAHP, purity 99%, Aldrich) and 2-ethoxynaphthalene (neroline) were used as additives. The neroline is synthesized in our laboratory from β-naphtol. Obtained Microcapsules were characterized by optical microscopy; Infrared analysis was carried out with a SHIMADZU Fourier Transform IR Spectrometer using a resolution of 4 cm⁻¹. A potassium bromide (KBr) pellet technique was employed. A pure cotton fabric (143 g m⁻²) was coated by a binder loaded with neat or encapsulated active product. Coatings were carried out by using a coating table; this technique is similar to the scraper coating, except that the coated support is fixed and the coating paste is spread with a threaded rod.

Preparation of the microcapsules
DAHP-loaded microcapsules: The interfacial polycondensation of TDI and TEG in inverse emulsion was adopted (Giraud et al., 2005). Three solutions were prepared separately: In solution I, 6.25 mmol of SDS were solubilized in 225 mL of toluene. In solution II, 8.70 mmol of TEG and 42.40 mmol of DAHP were dissolved in 45 mL of water. In solution III, 38 mL of solution I were taken, to which 7.08 mmol of TDI and 0.40 mL of DBDL were added.

The remainder of solution I and solution II were placed in the reactor. The mixture was initially stirred at room temperature. Agitation was started, regulated at a speed of 1200 rpm in order to carry out the emulsion water/oil. After 5 min, solution III was added, speed was maintained to 1200 rpm for 5 min. Then, speed was decreased to 400 rpm and the temperature was maintained at 60°C during 4 h.

The mixture was centrifuged during 15 min or filtered with a sintered glass filter. The microcapsules were rinsed with toluene to eliminate the traces of monomer, then with water to solubilize the non-encapsulated particles of DAHP. They were finally dried in vacuum.

Neroline-loaded microcapsules: Polyurethane-based neroline-charged microcapsules were prepared by interfacial polycondensation reaction and a direct emulsion technique was adopted. Three solutions were prepared separately. In solution I, 12.50 mmol of SDS were solubilized in 225 mL of water. In solution II, 7.08 mmol of TDI and 42.40 mmol of neroline were dissolved in 45 mL of toluene. In solution III, 38 mL of solution I were taken, to which 8.70 mmol of TEG and
0.40 mL of DBDL were added. The remainder of solution I and solution II were placed in the reactor and we proceed with the same conditions described in case of DAHP-loaded microcapsules.

RESULTS AND DISCUSSION

Characterization of DAHP-loaded microencapsules: The particle shapes were observed by the optical microscope and their images were depicted in Fig. 1. The microcapsules were well separated and they had spherical shapes. The microcapsule average diameter was about 30 μm. The FT-IR spectra of polyurethane, neat DAHP and synthesized DAHP-loaded microcapsules were presented in Fig. 2. The microcapsules spectrum, showed an absorption band at 2364 cm⁻¹ attributed to the DAHP (O-H) and (NH₂⁺) stretching vibrations. The P = O stretchings were observed at 1400 cm⁻¹ and PO₄ vibrations were at 1074 cm⁻¹ (Saihi et al., 2006).

![Image of microcapsules](image1.jpg)

**Fig. 1(a-b):** Structure of the polyurethane microcapsules containing DAHP. Magnification (a) 400x; (b) 1000 x

![FT-IR spectra](image2.jpg)

**Fig. 2:** Identification of DAHP encapsulation by FT-IR spectra

Characterisation of the neroline-loaded microcapsules: The particles shape was observed by optical microscope and the obtained images were shown in Fig. 3. Homogeneous distribution of microcapsules was obtained and no agglomerates were observed. The microcapsule average size was about 25 μm, compared with results of Rodrigues et al. (2008) sized were in the same range, the difference could be due to the elaboration and condition process.
FT-IR spectra of polyurethane (PU), neat neroline and neroline microcapsules are presented in Fig. 4. The microcapsule spectrum showed absorption two bands at 1254 and 1038 cm\(^{-1}\) attributed to the neroline C-O-C asymmetrical and symmetrical stretchings.

![Image 1](image1.png)

**Fig. 3 (a-b):** Structure of the polyurethane neroline-containing microcapsules, Magnification: (a) 100 x; (b) 1000 x

![Image 2](image2.png)

**Fig. 4:** Identification of the neroline encapsulation by FT-IR spectra

**Fixation of DAHP- loaded microcapsules on the fabric:** Cotton fabric was coated using a coating table with a deposited-coating weight of about 210 g m\(^{-2}\). The coated fabric was then dried. Diverse formulations were prepared with different DAHP rates (Table 1). The mass rate of the Active Product (AP) and the microencapsulated active product (\(\mu\)AP) was calculated with the following formula:

\[
\% (\text{AP}) = \frac{100 \times m(\text{AP})}{m(\text{AP}) + m(B)}
\]
Table 1: Coating formulations of the (neat/microencapsulated) DAHP

<table>
<thead>
<tr>
<th>Formulation name</th>
<th>Composition of coating on cotton fabrics</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Binder (a reference sample)</td>
</tr>
<tr>
<td>B+10% µDAHP</td>
<td>Formulation B with 10% DAHP microcapsules</td>
</tr>
<tr>
<td>B+20% µDAHP</td>
<td>Formulation B with 20% DAHP microcapsules</td>
</tr>
<tr>
<td>B+30% µDAHP</td>
<td>Formulation B with 30% DAHP microcapsules</td>
</tr>
<tr>
<td>B+10% DAHP</td>
<td>Formulation B with 10% neat DAHP</td>
</tr>
<tr>
<td>B+20% DAHP</td>
<td>Formulation B with 20% neat DAHP</td>
</tr>
<tr>
<td>B+30% DAHP</td>
<td>Formulation B with 30% neat DAHP</td>
</tr>
</tbody>
</table>

Where: M (B): Mass of the binder, m (AP): Mass of the active product, m (µAP): Mass of the microencapsulated active product. The obtained fabrics present a glossy visual aspect with a hard touch and a thicker surface, compared to the original fabric.

\[
\% \ (µAP) = \frac{100 \times m \ (µAP)}{m \ (µAP) + m \ (B)}
\]

**Effect of the DAHP encapsulation on the propagation speed of flame:** The different fabric prepared samples were tested with referring to the French Norm NFG 07-100. Figure 5 describes the variation of flame propagation speed via fabric, depending in DAHP charge rate. The results showed an improvement in the flame-retardant action of the DHAP via the encapsulation. Indeed, for all DAHP rates, a lower propagation speed was observed for the encapsulated DAHP-based formulations, compared to the neat DAHP-based samples. A dependence of the encapsulation improvement effect with the DAHP rate was also observed. We could explain the speed decreasing by the combination of the PU shell/encapsulated DAHP which leads a complete fireproof system. The speed reduction presented a linear evolution and their equations were mentioned following.

![Graph showing the variation of flame propagation speed with DAHP rate](image)

Fig. 5: Variation of the flame propagation speed with DAHP rate

**Washing fastness test:** Washing fastness was evaluated according to the norm ISO 105-C01 of 1989. Figure 6 showed that propagation flame speed increases after each cycle due to removal of DAHP into the textile in both neat and encapsulated DAHP cases. For the microcapsule coated samples, the mechanism of DAHP remove can be explained by a spread of the active product through microcapsules or the disappearance of the loaded microcapsule (PU+DAHP) by the detergent action.
Fixation of neroline-loaded microcapsules on the fabric: Diverse samples were prepared using different formulations of coating applied into cotton fabric (Table 2).

<table>
<thead>
<tr>
<th>Formulation name</th>
<th>Composition of coating on cotton fabrics</th>
</tr>
</thead>
<tbody>
<tr>
<td>B+10% µNeroline</td>
<td>Formulation B with 10% neroline microcapsules</td>
</tr>
<tr>
<td>B+20% µNeroline</td>
<td>Formulation B with 20% neroline microcapsules</td>
</tr>
<tr>
<td>B+30% µNeroline</td>
<td>Formulation B with 30% neroline microcapsules</td>
</tr>
<tr>
<td>B+10% neat Neroline</td>
<td>Formulation B with 10% neat neroline</td>
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<tr>
<td>B+20% neat Neroline</td>
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Washing fastness test: Fabrics were maintained at mechanical stirred in a detergent solution during 30 min, rinsed with distilled water and then immersed in methanol solution.

The control of microcapsules fixation into the fabric and the diffusion of the neroline through the microcapsule pores after each washing cycle was carried out by Thin Layer Chromatography (TLC).

The results showed that washing fastness improves with the encapsulation of the odorant entity he number of cycle could attain six cycles (Table 3) better than results of Rodrigues et al. (2009) where the number of cycle is five. Moreover, a dependence of the encapsulation effect with the neroline rate was observed. In fact, the microencapsulation allowed the control of the diffusion of neroline through the pores of the membrane which forms a barrier between the encapsulated substance and his environment.
Rubbing fastness test: Rubbing test has been used to study the performance of the fixation technique according to the ISO 105-X12: 1993. Results showed that fabrics coated by the formulation with encapsulated neroline had a better resistance than those coated with the neat one. In fact with encapsulated neroline coat, the resistance could attain more than 17 cycles however in neat coat the resistance is 10 cycles (Table 4). On the other hand, after rubbing test a lower deterioration of the microcapsules was obtained, microcapsule persists either after 17 cycles. These results are better than the results found in the literature (Kim and Cho, 2002). The rubbing test damaged the encapsulated membrane. The active product is liberated slowly. The smell of the neroline was intensified after each rubbing cycle which proves a controllable liberation of the neroline. The rubbing fastness test had a less effect than washing one; this could be explained by a more important mechanical aggression in wash. The treated textile could be used in fabrics furnishing which do not be washed very well.

CONCLUSIONS

In the present study we have successfully synthesized polyurethane microcapsules by interfacial polycondensation technique. We have used ammonium phosphate and neroline as active products for textile applications. The elaborated microcapsules exhibited good thermal stability and showed an average diameter of 25 μm. Such diameter facilitates the implementation of microcapsules on the textile and let fixation without bursting. The behavior to fire of fabric coated by DAHP microcapsules was evaluated. The DAHP microcapsules give to the cotton fabric a good solidity to fire. It is worth noting that coatings with 30% of DAHP-loaded microcapsules evolve the decreases of flame propagation speed, compared to the virgin binder and all other coating formulations. Rubbing and wash fastness of fabric coated with neroline were studied and the number of cycles had attempt 6 in the case of sample with 30% of neroline-loaded microcapsules.
REFERENCES


