ASSESSMENT OF ACTIVE PRINCIPLE IN MICROCAPSULES APPLIED BY PAD-DRY SYSTEMS

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SUMMARY

The use of micro encapsulation techniques to incorporate active principles into fabrics has been widely used in textile industry. Pad-dry is one of the most used processes in industrial applications due to the easy control on the physical parameters that permits to work with a wide variety of substrates and micro-encapsulated formulations.

Once the product has been incorporated into the fabric the problem of determining the yield of the process arises. It's necessary to ensure a specific quantity of active principle if we want to accomplish with the commercial conditions that market demands.

Although each system ***substrate-microcapsules-active principle*** needs to define the requirements of delivery and the specific instrumental techniques to be applied, we can offer a methodology to face the problem.

In this work we propose for several textile substrates and active principle, how can be determined the exact amount that has been applied into the fabric. The methodology used in these cases has been validated by the use of different analytical techniques.

INTRODUCTION

The adaptation to social and industrial needs forces textile industry to make changes and modifications of the finishing procedures in order to obtain better and different functions.

Textile substrates play a very important role in all these changes. The modification of their functionality is one of the ways to incorporate new properties. The functionality of a polymer chain is related directly with its chemical structure and, therefore, any change on it can modify the whole properties of the structure.

The incorporation of substances on to the surface or into the inner structure of fabrics is also useful to modify this functionality. In this way, microencapsulation has shown an important potential. In textile, the major interest in microencapsulation is currently the application of durable fragrances and skin softeners. Other applications include insect repellants, dyes, vitamins, antimicrobial agents, phase change materials and medical applications, such as antibiotics, hormones and other drugs (1).

The move by the more developed countries into textiles with new properties and added value, into medical textiles and technical textiles, for example, has encouraged industry to use microencapsulation processes as mean of imparting finishes and properties on textiles that were not possible or cost-effective using other technologies(2).

Smart or bioactive textiles can act as “repository systems” and are capable of continually release small doses of active substances from the textile onto the skin, reacting in front of external stimulus as temperature, pH or simply concentration gradients.

When active substances are administrated from the modified textiles, only a very small fraction of the applied microencapsulated system, actually hits relevant receptors or sites of action. One important part of the dose onto the fabric is wasted either by being taken up into the “wrong” tissue, removed too quickly from the “right” tissue or destroyed before arrival.

Due to this important fact, the exact amount of active substances incorporated into the structure of the fabric using microencapsulation mean should be considered as the most important parameter on the process. Moreover, the doses that biological tissues will take, depends strongly of the amount of active substance capable to be delivered.

The main objective of this work is to develop a methodology to face this problem. A microencapsulated molecule (EthylHexyl-Methoxycinnamate) will be applied using pad-dry system and the amount of active principle present on to the fabric will be determined using several analytical methods.

Microencapsulation in textiles

Microencapsulation is a micropackaging technique that has traditionally involved the deposition of thin polymeric coatings or small particles of solids, droplets of liquids or dispersion of solids in liquids (3).

This process was primarily established as the bases of carbonless copy paper industry and is now used widely in a number of industries including pharmaceutical, agricultural, bulk chemical, food processing, cosmetic and toiletries.

A wide variety of materials are encapsulated and a number of different types of microcapsules are available (4).

The potential applications of microencapsulated active substances in textiles are as wide as the imagination of textile designers and manufacturers. Early success for some companies in producing microencapsulated finishes for textiles have come about from collaboration and adaptation of technology from other industrial sectors (5).

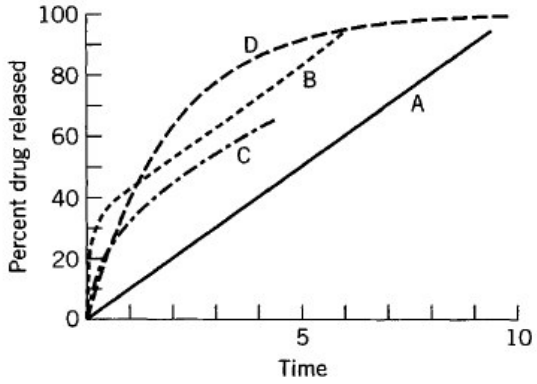
The textile industry must continue to be outward looking and developing the textiles that consumers desire in the first decade of the new century.

Bioactive molecule release

A microcapsule is a system that contains a well defined core and a well-defined envelope: the core can be solid, liquid or gas; the envelope is made of a continuous porous or non-porous, polymeric phase. The bioactive molecule, or

active principle, can be dispersed inside the microcapsule as solid particulates with regular or irregular shape.

Release of the core material from non-erodible microcapsule can occur in several ways, as is shown in the Figure 1:



A: Steady-state diffusion

B: Migration-burst effect

C: Higuchi Model

D: Pseudo-first order diffusion

Fig. 1: Mechanisms of drug delivery (6)

Basically four different mechanisms can be considered:

- Microcapsule which releases the encapsulated material by steady-state diffusion through a coating of uniform thickness. The rate of release remains constant as long as the internal and external concentrations of the core material and the concentration gradient through shell membrane are constant (A)

- In some cases, some of the encapsulated material, migrates trough the microcapsule membrane during storage and then a burst effect occurs (B)

- If the microcapsule acts as an inert matrix particle in which material is dispersed, the Higuchi model is valid up to 60% release (7). In this case, a plot of the percentage of drug released versus square-root of time is linear, as show in graphic in curve C

- Pseudo first-order release is presented by curve D. The curve is linear if log percent of core material left in the capsule is plotted versus time.

Many microcapsules samples can experience an unusually rapid rate of release when first immersed in an in vitro release medium, i.e: they have an intense burst effect. That means a total discharge, difficult to fit in one of the former classification mechanisms.

Application of microcapsules onto textiles

With the vast variety of microencapsulation techniques currently available, nearly any active agent can be, successfully incorporated into a microencapsulation formulation.

Microcapsules solution can be applied by spraying to obtain a uniform thickness coating on the fabrics. Various factors of the spraying process, such as spraying

distance, flow rate, and atomizing air pressure, affected the release properties when applied into textile substrates.

It has been pointed out (8) that the variables governing solvent evaporation and spreading of the microcapsules solution droplets during the coating process are also, very important to obtain films with the desired properties.

Another option, studied in this work, is to use a well known system in textile processing industry by padding the fabric between squeezing rolls. The use of this system, offers several advantages that have to be considered:

- Uniformity of the microcapsules solution application
- Easy to use in textile industry
- Control on the exact amount of solution retained by the fabric, through the pressure of the rolls over the fabric,
- Reproducibility of the concentration of microcapsules onto the fabric
- Wide range of adaptation to different textile substrates and to different active principles microencapsulated

Nevertheless, the problem of the application of microcapsules onto textiles substrates is always the same; the assessment of the exact amount of active principle that can be delivered from it to the target surface or to the skin.

When drugs, biomolecules or active principles are allocated into microcapsules and these coated on to a textile substrate, there exists more inconveniences for them to reach the “right” place in the adequate dose (9).

The composition of microcapsules solution can change the sensibility of the discharge mechanism due to the influence of the characteristics of the own substrate, and therefore the amount of active principle to be delivered is underdose.

The mechanism of the active principle migration to the matrix of the microcapsule shell structure can combine with other lateral diffusion phenomena to the fabric. Then, underdose amount is released from the system (10).

All these facts make necessary to establish methodologies that permit to asses the exact amount of active principle that is capable to pass through all these barriers to accomplish with the function for which has been designed .

Then, the need, first of all, to get a reproducible applying industrial method, and an easy measuring control system of the real amount of active principle remaining into the fabric, to adjust the delivering conditions to the desirable target.

EXPERIMENTAL

Material

Formulations of microcapsules containing ethyl hexyl methoxycinnamate (EHMC) (38%) were prepared by the company Lipotec Group (Spain). A

standard cotton fabric (Style 400, Test Fabrics, Inc.) as described in ISO 105 F02 was used as a textile substrate to apply EHMC formulations.

A given amount of the EHMC formulations used (38% concentration) was applied by pad-dry process on the cotton fabric in an exposure area of about 1.86 cm^2. The cotton fabric was dried at 50ºC temperature for 10 minutes in a Benz Lab tenter frame.

All chemicals used were of analytical grade. Isopropylic alcohol (HPLC grade) and distilled water were used for high-performance liquid chromatography (HPLC) analysis.

Methods

Application of microcapsules solution by pad-dry

Samples of standard Cotton fabric were processed in a Benz Lab Foulard of 30 cm with a corresponding pressure to obtain a pick-up of 80%, from a 200 g/L microcapsules solution concentration, prepared from the original (38% of EHMC)

HPLC method: EHMC Analysis

The microencapsulated EHMC was extracted from 0.7g of applied cotton fabric using an extractor system ASE 200 (DIONEX) after sample conditioning at 60%Hr and 20ºC during 24h. The solvent used was isopropylic alcohol at the temperature of 50ºC and 1500psi of pressure, with two cycles. The extracts were dried in a Turbo Vap LV Concentration Workstation (Caliper Life Science).

The analyses of the EHMC from different extracted samples were determined by HPLC using a VWR-Hitachi Elite LaChrom instrument (Darmstadt, Germany). The apparatus is equipped with an L-2130 Pump, an L-2200 Autosampler and an L-2400 UV-Vis Detector working at 271 nm. The system was operated from the software Merck EZChrom Elite v3.1.3. The column used was a LiChrocart 125-4/Lichrosorb RP-18 (5 µm) (Darmstadt, Germany). The mobile phase was a mixture of methanol and water (20:80 v:v) at 1 mL/min flow rate. The analytical method was validated in terms of limit of detection, limit of quantitation, and reproducibility (intra- and interday).

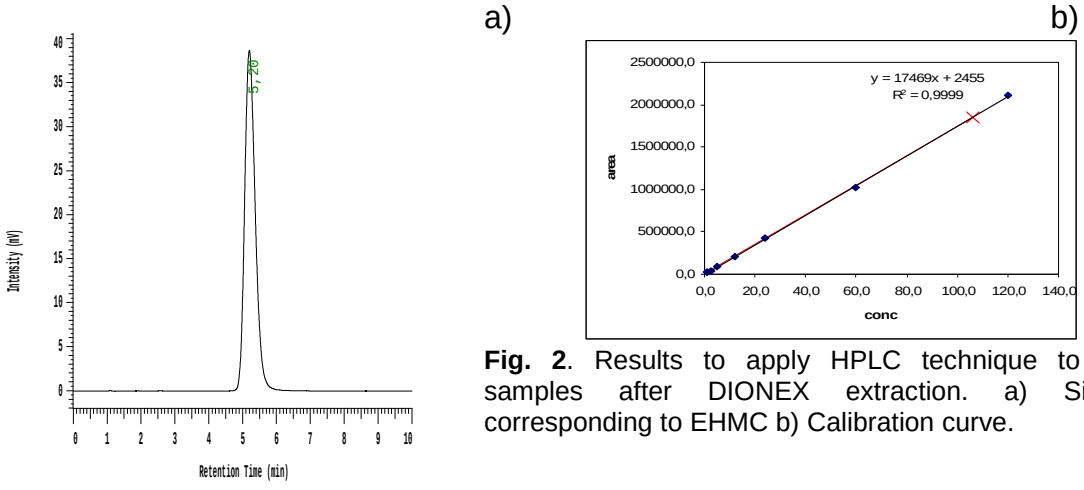


Fig. 2. Results to apply HPLC technique to the samples after DIONEX extraction. a) Signal corresponding to EHMC b) Calibration curve.

UV Spectrophotometry

Samples of 1 g of cotton pad-dryed were used as substrate for the extraction with a 50% mixture of water/isopropyl alcohol in a Soxhlet system during 1 h (5 cycles).

The resulting solution was measured in a 1 mm cuvette (quartz) in a Shimadzu UV-Vis 240 Spectrophotometer, using a λ_{max}= 310 nm.

a) b)

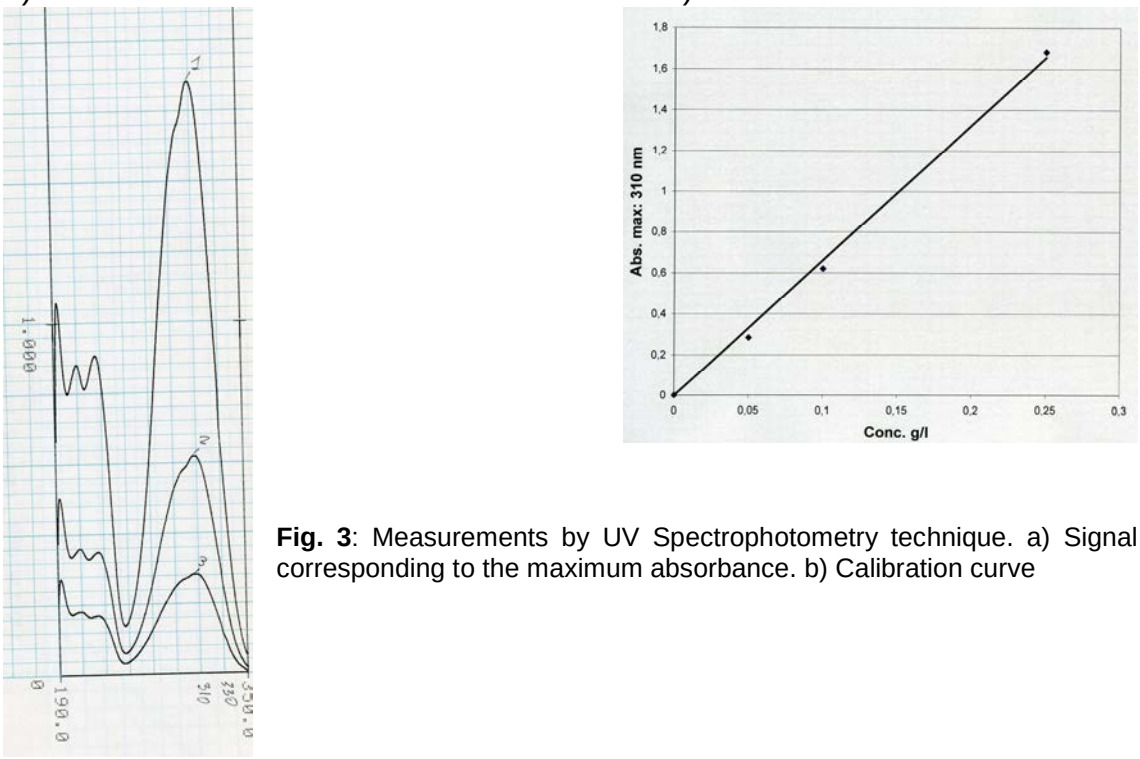


Fig. 3: Measurements by UV Spectrophotometry technique. a) Signal corresponding to the maximum absorbance. b) Calibration curve

Calibration curves

In order to quantify the exact amounts of EHMC extracted in both methods, calibration curves for each instrumental technique were built. (Fig. 2 b) and Fig 3 b))

RESULTS AND DISCUSSION

According to the main objective of this work, two experimental analytical methods have been used to analyze the solutions from two different microcapsules extraction systems.

It must be pointed out that either HPLC or UV-Spectrophotometry give excellent correlation between concentration of active substance and instrumental signal. Therefore, results obtained from both techniques can be compared one each other.

From the same cotton fabrics sample two samples of each one, were submitted to the treatment and measured.

Results obtained are shown in the following table:

Table 1: Weight increase, and concentration of EHMC

Sample	Weight % *	Expected Soxhlet extraction** (g/L)	UV measurements (g/L)	HPLC Measurements (g/L)
1	13,04	1,043		1,017
2	16,61	1,329	1,329	1,399
3	16,29	1,303		1,305
4	15,33	1,226		1,208

*Nominal increase 16 %; nominal concentration on Soxhlet extraction 1,6 g/L
** Calculation from the fabric weight lost after Soxhlet extraction

As it can be seen from the results on Table 1, two aspects must be commented:

- The uniformity of padding fabric must be increased, being acceptable for samples 2 and 3 but not for sample 1
- The expected values in Soxhlet extraction agree with the measured concentrations obtained for sample 2 by UV Spectrophotometry and for the values of HPLC

CONCLUSION

We can conclude that, padding method of application of microcapsules on fabrics can be industrially acceptable, and that the two analytical techniques used, soxhlet extraction and UV-Spectrometry analysis, and ASE extraction and HPLC analysis, give enough accuracy to measure the real amount of active principle that can be delivered from the fabrics treated.

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