Controlled release of the essential oil of citronella microencapsulated using cotton and polyester matrix

Fabricio Maestá Bezerra[1,2], Oscar Garcia Carmona[3], Carlos Garcia Carmona[3], Manuel José Lis[3]
Flavio Faria de Moraes[2]

ABSTRACT

Microencapsulated finished fabrics are among the major resources to develop new textiles. In this context, a large area to be explored is the use of essential oil in textiles, through microencapsulation. Such technique offers the possibility of developing new products with many advantages compared to traditional fabrics, some traditional finishing may be ineffective for reasons related to its uncontrolled release of the active principle, microencapsulation aims to change that allowing increased duration of the finishing effect. However, many studies present only the application of microcapsules in the textile and do not show how the release of the encapsulated material occurs and the influence of the textile matrix. This paper reports the mechanism and kinetics of controlled release of microencapsulated citronella oil applied in cotton and polyester. The microencapsulation was done by complex coacervation with gelatin and Arabic gum as shell material. The formed microcapsules were analyzed by optical microscopy, scanning electron microscope, thermogravimetric analysis and dynamic light scattering. After, they were applied in cotton and polyester and evaluated by Fourier transform infrared spectroscopy attenuated total reflection and, finally, the controlled release of citronella from the microcapsules deposited on the fabrics was studied *in vitro*. It was found that the release was directly influenced by the type of fiber, the microcapsules applied in polyester article presented diffusion by the Fickian mechanism, while the kinetic model fitted to the modified cotton presented non-Fickian. The comprehension of the process of controlled release is fundamental for the creation and development of more durable finishing.

Keywords: Cotton, polyester, citronella, microcapsule, controlled release.

1. INTRODUCTION

The finishing of textile products is a fundamental factor for its commercialization [1]. It is in this stage of the process that the textile stops having only characteristics of protection for the human body and starts to have functions that allow it to interact with the skin [2-4]. When a textile starts interacting with the body, it becomes more interesting and attractive to the consumer.

Some finishes, applied to textile products present great limitations in what refers to application and durability. These limitations involve the sensibility of substances, which can oxide, may be inhibited and evaporate by mere contact with the environment [5-8], there exists a need to protect them from the environment, to extend their service life and to control the release of these products. According to Desai and Park [9], Jamekhorshid, Sadrameli and Farid [10], Leclerq, Harlander and Reineccius [11], Nesterenko *et al.* [12], this can be obtained by creating an envelope over the products through microencapsulation.

[1] Federal University of Technology – Paraná, 635 Marcilio Dias Street, Apucarana, Parana, Brazil
Phone: +55 43 3162-1200
Email: fabriciomb@gmail.com
[2] State University of Maringa, 5790 Colombo Ave, Maringá, Paraná, Brazil
[3] INTEXTER-UPC, C/Colom, 15,08222 Terrassa, Barcelona, Spain

Microencapsulation is a technique commonly used in the food and pharmaceutical industries. In the textile industry it has been little explored. In the 90s some commercial applications appeared [13] and with the advance of the years, manufacturers of the textile articles have demonstrated more and more interest in fabrics with new properties, due to the possibility of its ennoblement.

The application of microcapsules in the textile field ranges from the utilization as fire retardant agents [13], protection against atmospheric agents [14-16], to functional finishes [3, 17-20]. The utilization of the microencapsulated active substances applied in cotton and polyester fabrics has attracted more and more attention with the development of functional fabrics that can have some effects and solve problems that the traditional process could not [18, 21, 22].

Currently, among these possibilities, according to Frederiksen, Kristensen and Pedersen [23], in relation to the active principle, the biggest interest in microencapsulation for the textile industry is related to the application of durable essential oils in fabrics, aiming at obtaining the controlled released in medical applications [24]. The controlled liberation allows the extension of the oil's service life, thus avoiding its rapid evaporation and improving its performance [25-27].

When it comes to the medical effect, it depends on the type of oil utilized. Several essential oils have already been used, such as lavender, rosemary and jasmine, showing medicinal properties [20, 28-32] and protection against disease vectors [33-36].

An oil that draws attention because of its functionality and contribution is the citronella essential oil (CIEO), *Cympobogonnardus* [33, 35]. The CIEO, according to the results of Specos *et al.* [36], shows the characteristic of a mosquito repellant, especially the *A. aegypt*. On the other hand, some researchers report that this oil may be ineffective for reasons related to its uncontrolled release, that is, one expects it to be released in small quantities, or excessively released with reduced protection duration. Therefore, controlling the release of these essential oils is a research area of great importance [37].

Consequently, producing microcapsules with CIEO and applying them to textile products can be an alternative to the controlled release. Chatterjee, Salaün and Campagne [24], note that after the microcapsule has been applied to a textile substrate, if it can be loaded with essential oil then it can effectively interact with the skin, thus allowing the functionalization of the material.

The novelty of this work is to produce arabic-gum/gelatin microcapsules with Citronella oil as the core active principle and to study the way in which citronella is retained by microcapsules. This study is a preliminary work to clearly establish the possibilities of using citronella microcapsules in cellulosic substrates without binder. Binders usually change a lot of properties of the fabric and modify the mechanisms of delivery.

The specific goals of this work are to microencapsulate citronella essential oil and apply the microcapsules to two textiles, cotton and polyester, and model the controlled release of the oil from each fabric, using Higuchi's [38] and Korsmeyer-Peppas'[39] kinetic models [39-41].

2. MATERIALS AND METHODS

2.1. Materials

Materials used to prepare the microcapsules were type A gelatin (GE), (*Sigma Chemical*, Germany), Arabic gum (GA) (*Sigma Chemical*, Germany) as shell materials and citronella essential oil (*WNFt*, Brazil) as the core material. Glutaraldehyde (50%), sodium lauryl sulfate (SLS), citric acid, sodium hydroxide and all other

chemicals used were of analytical grade. The standard woven fabrics used were: cotton fabric (COT) (Bleached and desized Cotton Print Cloth, Style 400, 100 g m^{-2}, ISO 105-F02) and spun polyester type 54 fabric (PES) (Style 777, 126 g m^{-2}, ISO 105-F04),both from Test Fabrics Inc. (USA).

2.2. Methods

2.2.1. Preparation of microcapsules by complex coacervation

The complex coacervation protocol was based on the works of Wang, Adhikari and Barrow [31], Piacentini *et al.* [29], LV *et al.* [42], Leclerq, Harlander and Reineccius [11], and Desai & Park [9], which are characterized by the insertion of two biopolymers, pH correction and the insertion of a cross-linking agent.

The process begins with the formation of three emulsions prepared separately in aqueous solution. The first one has 3 g of gelatin in 50 ml of water under stirring and temperature of 50 °C. In the second emulsion it was used 50 ml of water at 50 °C under stirring with 5 ml of citronella essential oil and 0.3 g of sodium lauryl sulfate (SLS). The third emulsion was prepared with 100 ml of water and 3 g of gum arabic at ambient temperature under stirring.

First and second emulsions were mixed until complete dissolution. In this stage, agitation was increased up to 500 rpm to guarantee a thorough dispersion of the oil and to obtain small diameter droplets. Then, the third emulsion was added to the main mixture and adjusted the pH to 4 with citric acid, leaving this preparation for 90 minutes until total stabilization.

The resulting solution was cooled to the temperature of <8 °C leaving it for 1 hour. Then the pH of the solution was adjusted to 8-9 with NaOH and 1 g of glutaraldehyde (50%) added, dropwise. The system was left for 12 hours under stirring at room temperature. After, the microcapsules were prepared and could be applied to the substrates fabric.

The application of microcapsules on the fabrics was done by the *foulard* process, followed by drying at room temperature [3]. Textile articles of COT and PES were impregnated for 1 minute in the solution of microcapsules, 30 g L^{-1}, and then passed through a *foulard*, the pressure used was 2 - 3 bar and the speed 2 m min^{-1}. The treated fabric samples were finally conditioned at 20±2°C and 65±5% relative humidity for 24 h before weighing and proceeding to perform subsequent experiments.

2.2.2. Assessment of the microcapsules' morphology

Optical microscopy and scanning electron microscope (SEM) were performed to verify the distribution of the microcapsules, as can be seen in the pictures of Fig. 1, one can notice the homogeneity of the solutions, as well as the size distribution of the microcapsule shells. The equipment BX43-OLYMPUS was used with an amplification magnitude of: 500x and 1,000x and the scanning electron microscope, JEOL-JSM 5610, was set to an increase of $\approx 1{,}820x$.

2.2.3. Efficiency of encapsulation

The efficiency of encapsulation was obtained following the methodology presented by Wang, Adhikari, Barrow [31], indirectly, in the liquid phase by UV/VIS, equipment UV-240 LPC, Shimadzu with Software UVProbe [photometric] version 2.43.

Absorbance readings were taken for the solution prepared according to section 2.2.1 and the maximum peak absorbance used was 333 nm. Efficiency of the encapsulation process was determined with equation (1):

$$E(\%) = \frac{C_t - C_d}{C_t} \times 100 \quad (1)$$

where C_t is the theoretical concentration of the microencapsulated essential oil and C_d being the concentration of the essential oil that remained in the bath solution.

2.2.4. Thermogravimetric analyses

The thermal stability study of the microcapsules was done by the utilization of a Thermogravimetric Analysis, TGA.SDTA851 – Mettler Toledo, *Software* STARe (Version SW 9.01). It was assessed the thermal behavior of the following products: gelatin, gum Arabic, citronella essential oil, and microcapsules (dry).

The method used a warming-up rate of 10 ºC min^{-1}, temperature range of 30 ºC to 800 ºC, and a nitrogen atmosphere.

2.2.5. Distribution of the size of the microcapsules and complexes

The analysis of the microcapsule's size was done by the method of Dynamic Light Scattering (DLS) with the equipment Nanoplus (EDS) *Software* nanoplus common, coxtin method. It was calculated using 70 accumulations for each of the samples.

2.2.6. Assessment of the finishes over the substrates by FTIR-ATR

For the investigation of the functional groups, it was used infrared spectroscopy with the Fourier transform (FTIR). The equipment employed in this analysis was the FT-IR (Frontier – Perkin Elmer), with a resolution of 1 cm^{-1} and 64 accumulations, and the selected technique was the attenuated total reflectance (ATR), in the medium infrared range between 650 and 4000 cm^{-1}.

2.2.7. Quantification and fitting of a mathematical model to the controlled release of essential citronella oil

The profiles for the release of the citronella essential oil from the textile substrates were determined by the technique *in vitro*, by triplicate. The cotton and polyester fabrics, after the application of the treatment (microcapsule), were taken to a thermostatized bath at 37 ℃ ± 0.5 ℃, under agitation in a Shaker, WNB14 Memmert. Aliquots of 2 mL were extracted and filtered at pre-determined times and their absorbances were determined by spectroscopy in the ultraviolet range with a UV-240LPC – Shimadzu, at 333 nm (oil). The mathematical adjustments to describe the release drug release from the polymeric matrices are derived from the equation of Higuchi for planar films [38]:

$$\frac{M_t}{M_\infty} = K\sqrt{t} \quad (2)$$

Where $\frac{M_t}{M_\infty}$, is the percentage of drug released at each interval of time relative to the percentage of release at the equilibrium, K is the Higuchi constant of drug release, *t* is the time measured.

Other aspects of the release mechanism were evaluated using the model of Korsmeyer-Peppas [39]:

$$\frac{M_t}{M_\infty} = Kt^n \quad (3)$$

Where n is the diffusion exponent which indicates the type of system mechanism: Fickian diffusion mechanism (n=0.5), anomalous diffusion (0.5<n<1.0) and non-Fickian diffusion mechanism (1.0).

Statistical analysis, all the data was taken in triplicate and presented as a mean value with the standard deviation (mean ± SD). Statistical significance ($p < 0.05$) was determined with one-way analysis of variance (ANOVA) using the OriginPro version 8.5.1.

3. RESULTS

3.1. Morphology

It can be observed a homogenous distribution of microcapsules in relation to the size and format, mostly spherical seen on Fig. 1(a). After the microcapsules were dried, they were well defined without the formation of clusters. It can also be observed at Fig. 1(a) that the formed microcapsules are multi-core, cores separated by coacervates, according to the results obtained by Jamekhorshid, Sadrameli and Farid [10].

The multi-core microcapsules generally possess properties of more regular controlled release than the ones with a single core, as observed in the work of Wang, Adhikari, Barrow [31]. This happens due to multi-core microcapsules being capable of releasing the active substance encapsulated slowly over time, while the single-core normally release their fundamental ingredients in a *burst*, that is, in a single short instant.

Another factor that one can point out is the reduced size of the formed microcapsules, which facilitates the absorption and penetration in the fabric's surface during the finishing process. Li *et al*. [18] also relate to this reduced size the advantage concerning the controlled dosage and the increase in the durability of the textile finish.

In Fig. 1(b) is presented the scanning electron microscopy (SEM) of microcapsules. In these micrographs it is possible to verify the uniform distribution and reduced size that also has been seen in optical microscopy. It is also noted in Fig. 1(b) that there is a small amount of microcapsules that have not a perfect spherical geometry; are elongated spheres, similar images to the microcapsules found in the work of Krishnan, Kshirsagar and Singhal [43]. According to Leclercq, Harlander and Reineccius [11], this occurs by high stirring during the coacervation stage, and by limiting the concentration of negatively charged colloid, in this case gum Arabic.

182 3.2. Analysis of the yield of the encapsulation process of citronella oil

183 To assess the efficiency of the microencapsulation, it was necessary to find the maximum absorbance
184 peak for the citronella essential oil and the wavelength scanning was done from 250 to 550 nm, giving 333 nm as
185 the peak absorbance for the CIEO. Then the oil concentration was calculated with equation (4):

$$C_{oil} = 0.08309 \times abs_{333} + 0.0008864 \quad (4)$$

186 where C_{oil} is the concentration of the citronella essential oil, in mL mL^{-1}; *abs* is the absorbance read at 333 nm, in
187 %.

188 The measured yield of the microencapsulated oil gave the average of $51.37 \pm 3.33\%$, a value that is
189 within the range of results presented by Solomon *et al*. [35], who performed the microencapsulation citronella oil
190 through the simple coacervation method and obtained 36.20 – 62.80% yield. And also, this yield is within the
191 range of results presented by Yang *et al*. [8], who microencapsulated vanilla oil through complex coacervation.
192
193 3.3. Thermogravimetric evaluation (TGA) of the microcapsules

194 Thermograms are essential to the analysis of micro-capsule formation, with them it is possible to obtain
195 information from each constituent that form the microcapsule and compare them. Fig. 2 shows the
196 thermogravimetric curves (Fig. 2a) and the first derivative curve of the thermogravimetric curve in function of
197 time (Fig. 2b). Table 1 shows the summary of the most important results for the thermographic data.

198 As can be noted by the profile of the thermogravimetric curves, Fig. 2a, and seen on Table 1, there are
199 distinct zones of mass loss for each component, meaning that the thermal decomposition goes through different
200 stages. Citronella presents mass loss in a single stage, while gelatin and gum arabic presents two, and the
201 microcapsules present three stages. These are equivalent thermal events shown by Otálora *et al*. [44] for the
202 microencapsulation of *betalains* obtained from cactus fruit (*Opuntia ficus-indica*).

203 The mass loss of the essential oil of citronella starts at about 30 °C and ends at around 200 °C, which
204 according to El Asbahani *et al*. [33] is close to the temperature range of citronella essential oil evaporation that is
205 201-207 °C. The analysis of the thermogram curves and its first derivative show that the analysis of the thermogram
206 curves and its first derivative show that the oil evaporates completely. Thus, this oil has high volatility and there
207 is the need of protection for extending its durability when applied to surfaces. This is analogous to the thermal
208 analysis behavior of jasmine oil observed by LV *et al.* [2] that has shown a single parable, which meant that most
209 of the mass of the sample have been lost before 150 °C, showing thus no heat resistance.

210 Concerning gelatin and arabic gum, the first mass loss stage, is an indicative of the evaporation of all
211 the residual water present in these compounds [45]. The liberation of humidity seen on Fig. 2, in the TGA and
212 dTGA curves as mass loss, occurs in the initial temperature range of the analysis approximately up to the water's
213 ebullition temperature. In this case, the loss extends to 124ºC for the gelatin and to 116.2ºC for gum arabic.
214 Quantitatively, 7.7% (m/m) and 8.5% (m/m) have been lost, respectively.

215 The pyrolysis of gelatin and of gum arabic happens at the same range of decomposition, 200 – 500ºC,
216 denominated stage two. Both compounds present similar behavior in the decomposition zone regarding mass loss,
217 61.7% and 61.4%, and the residual mass percentage, 19.6% and 18.7%, respectively.

218 In relation to the microcapsule's thermogram, three thermal events are observed: the first stage of mass
219 loss occurred in a temperature 2.4% higher than the ebullition of water, which is close to that found in the work of

Yang *et al.* [8], which was 2.2% higher, when the microcapsules were prepared using chitosan and gum arabic as shell materials.

The second stage loss of mas occurs in the upper temperature range, beginning at 233 ºC and going up to 272 ºC. At this stage it was lost about 53.1% by mass, value close to that presented in the paper of Fei *et al.* [46] that made microencapsulation of the essential oil of roses and the mass loss was 56%. This value refers to the amount of microencapsulated active principle released due to the initial degradation of the constituent chains shell materials, around 53.1% mass. This loss is also close to the microencapsulated active substance released due to the degradation of protein shell chains, verified by LV *et al.* [42].

Fig. 2 shows that the curve of the second stage in the case of the microcapsules happens in a few seconds, due to the citronella oil high volatility and this can also be observed in corresponding first derivative curve. A similar result was obtained in the work of Yang *et al.* [8], when the microcapsules were prepared using chitosan and gum arabic as shell materials.

On stage three, occurs the pyrolysis of the microcapsules, which has a range of decomposition from 280-429 ºC. This range coincides with the pyrolysis temperatures of gelatin and gum arabic, it should be stressed that only in this stage both materials have been totally decomposed, as shown by Al-Shannaq *et al.* [47].

The overall results of thermal analysis show that the incorporation of citronella essential oil by the microencapsulation process form a complex with high thermal stability when compared to the free oil, indicating that microencapsulation protects the oil, making it more resistant to evaporation.

3.4. Estimative of the diameter of the microparticles by dynamic light scattering

Fig. 3 shows the histogram of the microcapsule and the accumulated distribution. The results demonstrate that the microcapsules of citronella essential oil present a restrict distribution of diameter in the range from 1 to 18 µm, and that the highest proportion of particles in the distribution lies in the range from 3.5 to 7.5 µm. Around 90% of the microcapsules are in this range of diameter. This homogeneous distribution is confirmed by Fig. 1 and by the cumulative distribution of particle size analysis (Fig. 3), which show that there are only small proportions of microcapsules with small and large diameters.

The average diameter of the microcapsules was 5.435 µm, Table 2, a result that agrees with the work presented by Jamekhoshid *et al.* [10] who points out that the range of average diameter of the microcapsules made by coacervation is from 2 – 1,200 µm and further, according Prata & Grosso [48]. also, the diameter is inferior to the one presented by Qv, Zeng and Jiang [7], who microencapsulated lutein through complex coacervation obtaining an average diameter for the microcapsules of 14.98 µm.

Application in textile substrate

The results of the applications of the microcapsules can be seen in Table 3.

The data recorded imply that at the end of the process it is possible to observe microcapsules on the surface of the fabrics. Cotton the most hydrophilic fiber has higher retention of microcapsules (o.w.f. %), (7.10 ± 0.22). This is due to the functionality of COT, which can be seen in the results of FTIR-ATR, Fig 4.

3.5. Evaluation of finishes on the substrates by Fourier transform infrared spectroscopy attenuated total reflection

The FTIR-ATR analysis was done in cotton, Fig. 4, and in polyester, Fig. 5, with no previous surface treatment and in the treated textile products. Fig. 4a (COT) shows the spectra of the original cotton fabric, and Fig. 4b (COT-MIC) after the application of the finish with microcapsules. Equivalently, Figs. 5a (PES) and 5b (PES-MIC) show the spectra of the original polyester fabric and after the application of the finish with microcapsules, respectively.

In the product which received the treatment, Fig. 4b (COT-MIC), it can be seen the appearance of the band at 1,545.55 cm^{-1}, characteristic of the amide II group [49], which confirms the presence of microcapsules. During the process of coacervation, the carboxylic groups of the polysaccharide (gum arabic) interact with the amine groups of the protein (gelatin). Same result has been presented by Rocha-Semi *et al*. [50] in the microencapsulation of aspartame with gelatin and gum arabic. The disappearance of the band at 1,734 cm^{-1}, C-O-C bond, characterizes the interaction between the substrate and the finishing. Also, it can be observed the displacement of the axial aliphatic deformation CH, from 2,922 to 2,900 cm^{-1}, this displacement, according to Carrera *et al.* [51] gives the idea of possible interactions due to the hydrogen bonds. This hints at the formation of hydrogen bonds between the cotton fiber and the microcapsules.

For the polyester fabric, Fig. 5a (PES) and Fig. 5b (PES-MIC) compared, the presence of new bands can be verified in the regions of: 661 and 900 cm^{-1} which are characteristics of the CH bond, present in gum arabic [52]. It can also be noticed the presence of the band at 1,450 cm^{-1}, concerning aromatic alkenes C=C, present in gelatin [52] showing that there was treatment, though only superficial without any interaction.

3.6. Kinetics of the release of citronella essential oil

Many mathematical models have been developed with the aim to describe the release of the active substance from microcapsules, however, the most frequently used are Higuchi's and Korsmeyer-Peppas' [53], equations (2) and (3). The *in vitro* studies were done over 24 hours and the modeling of the release profile was done with the software Origin 8.0®.

When analyzing the profiles of controlled release (Fig. 6), it is possible to observe that the process of liberation of the CIEO occurs in two distinct steps: on the first step, the oil that is free in the surface of the fabric is lost by evaporation. As observed in Fig. 4 and 5, this step corresponds to the disappearance of the band of the aldehyde group. The second step, though, corresponds to the release of the microencapsulated oil. However, each textile product presents a different behavior that is strictly related to the specific interactions between each fiber and the microcapsules.

When observing Fig. 6a it can be seen that after 35 minutes there is a change in the inclination of the release curve, which highlights the change in the control of the release mechanism. Similarly, in Fig. 6b, the controlled release of oil from the polyester fabric shows also two steps and its first stage ends up after 15 minutes.

It can be observed that in the controlled release of the citronella essential oil applied to cotton (Table 4), Korsmeyer-Peppas' model gives the best correlation coefficient R^2=0.9540 and Chi-sqr 0.0053. In this stage of release Korsmeyer-Peppas model gave n=0.5833±0.0573, which means that the system shows an anomalous mechanism of diffusion, i.e. a non-Fickian transport [39,53]. According to Lee [53] this is due to the relaxation of polymeric matrix, giving rise to more than one type of liberation of the active principle.

The double release becomes evident, since the cotton fiber is a hydrophilic fiber, the greater affinity for water swells the textile matrix when in contact with water [1], causing the relaxation of the chains and modifying the interaction between the fiber and the essential oil, and consequently the water becomes unavailable for release so easily.

In relation to the liberation of the essential oil applied to the 100% polyester fabric, it can be verified that in the first stage occurs the release of about 40% of the active substance. This leads to a greater kinetic constant than the one for cotton (K=0.2189±0.0304 for polyester versus K=0.0611±0.0015 for cotton, Table 4), this is explained as a consequence of the high hydrophobia of the polyester fiber [55]. On the other hand, the diffusion coefficient for the release of oil in both fabrics is relatively close, for polyester D_f is approximately 0.20×10^{-2} min^{-1}, and for cotton 0.15×10^{-2} min^{-1}. .

The high affinity of the active substance to the medium as opposed to the fiber is explained by Salem [1], due to the fact that the polyester fiber does not interact in any way, then there is repulsion of chemical products in contact with its fiber surface, facilitating the removal of the finishing. The microcapsules do not interact with the polyester matrix, staying only on the fabric surface.

It can be observed that in the case of polyester (Table 4), the Korsmeyer-Peppas's model also gives the best correlation coefficient R^2= 0.9477 and Chi-sqr 0.0056. When analyzing the exponential parameter of the Korsmeyer-Peppas' equation, the release mechanism is Fickian, with n=0.3177±0.0329, which does not depend on the relaxation of the chains [55], the contact with water does not cause the swelling and inter slip. Sóti *et al*. [56] show in their work that the hydrophobicity of the matrix can change the release mechanisms, as well as influence the release constant.

Carreras *et al*. [51] show in their work that the microcapsules applied to polyester displayed the highest kinetic constant of 2.90 min^{-1}, while for cotton the kinetic constant was 0.09 min^{-1}, showing low interaction for the polyester and finishing, as seen in this study.

4. CONCLUSION

The results show that the microencapsulation of the essential oil of citronella has shown a close perfect spherical geometry, which allows better penetration into the interstices of the fibers. In addition, the cotton, a hydrophilic fiber, was shown to be more apt to receive the citronella oil microcapsules. In the FTIR-ATR it suggested the possible emergence of hydrogen bonds between the cotton fiber and the microcapsules, which strengthen the controlled release of oil from the cellulose matrix, even without the use of binders. This comes as an innovation, since there would be no change in essential physical characteristics of the fabric, such as strength, touch and resilience, which are usually modified in the presence of ligands.

As seen in the thermal analysis microencapsulation of the oil improves its thermal characteristics making it less volatile and can thus be applied to textile substrates in high temperature processes. The protection of the essential oil of citronella is also important so that you can prolong its release, because excessively released with reduced protection duration, would make it an inefficient repellent application.

The low diffusion coefficients obtained indicate the release control based on the substrate, just as the different kinetic mechanisms of release were also influenced by the type of fiber. Therefore, depending on the characteristics desired in the final product, textile fibers can be selected from a wide variety of natural or synthetic polymers to provide different release properties.

5. REFERENCES

1. Salem V (2010) Tingimentos têxteis: fibras, conceitos e tecnologias. Blucher, São Paulo
2. Lv Y, Yang F, Li X, Zhang X, Abbas S (2014) Formation of heat-resistant nanocapsules of jasmine essention oil via gelatin/gum arabic based complex coacervation. Food Hydrocolloid 35: 305–314
3. Rubio L, Alonso C, Coderch L, Parra JL, Martí M, Cebrián J, Navarro JA, Lis M, Valldeperas J (2010) Skin delivery of caffeine contained in biofunctional textiles. Text Res J 80: 1214–1221
4. Wang JM, Zheng W, Song QW, Zhu H, Zhou Y (2009) Preparation and characterization of natural fragrant microcapsules. J Fiber Bioeng Inform 4: 293–300
5. Feczkó T, Kokol V, Vončina B (2010) Preparation and characterization of ethylcellulose-based microcapsules for sustaining release of a model fragrante. Macromol Res 18:636–640
6. Özdemir K, Gökmen V (2015) Effect of microencapsulation on the reactivity of ascorbic acid, sodium chloride and vanillin during heating. J Food Eng 167: 204-209
7. Qv XY, Zeng ZP, Jiang JG (2005) Preparation of lutein microencapsulation by complex coacervation method and its physicochemical properties and stability. Food Hydrocolloid 25: 1596–1603
8. Yang Z, Peng Z, Li J, Li S, Kong L, Li P, Wang Q (2014) Development and evaluation of novel flavor microcapsules containing vanilla oil using complex coacervation approach. Food Chem 145: 272–277
9. Desai KGH, Park HJ (2005) Recent developments in microencapsulation of food ingredients. Drying Technol 23: 1361 – 1394.
10. Jamekhorshid A, Sadrameli SM, Farid M (2014) A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium. Renew Sust Energ Rev 31:531–542
11. Leclercq S, Harlander KR, Reineccius GA (2009) Formation and characterization of microcapsules by complex coacervation with liquid or solid aroma cores. Flavour Frag J 24: 17–24
12. Nesterenko A, Alric I, Silvestre F, Durrieua V (2013) Vegetable proteins in microencapsulation: a review of recent interventions and their effectiveness. Ind Crop Prod 42: 469– 479
13. Nelson G (2002) Application of microencapsulation in textiles. Int J Pharm 242: 55–62
14. Annan NT, Borza AD, Hansen LT (2008) Encapsulation in alginate-coated gelatin microspheres improves survival of the probiotic bifidobacterium adolescentis 15703t during exposure to simulated gastro-intestinal conditions. Food Res Int 41: 184–193
15. Souza FN, Gebara C, Ribeiro MCE, Chaves KS, Gigante ML, Grosso CRF (2012) Production and characterization of microparticles containing pectin and whey proteins. Food Res Int 49: 560–566
16. Zimet P, Livney YD (2009) Beta-lactoglobulin and its nanocomplexes with pectin as vehicles for Ω-3 polyunsaturated fatty acids. Food Hydrocolloid 23:1120–1126
17. Cheng SY, Yuen MCW, Kan CW, Cheuk KKL, Chui CH, Lam KH (2009) Cosmetic textiles with biological benefits: gelatin microcapsules containing vitamin C. Int J Mol Med 24: 411– 419
18. Li L, Song L, Hua T, Au WM, Wong KS (2013) Characteristics of weaving parameters in microcapsule fabrics and their influence on loading capability. Text Res J 83: 113–121
19. Hassan MM, Sunderland M (2015) Antimicrobial and insect-resist wool fabrics by coating withmicroencapsulated antimicrobial and insect-resist agentes. Progress in Organic Coatings 85: 221-229

20. Martin A, Tabary N, Leclercq L, Junthip J, Degoutin S, Aubert-Viard F, Cazaux F, Lyskawa J, Janus L, Bria M, Martel B (2013) Multilayered textile coating based on a β-cyclodextrin polyelectrolyte for the controlled release of drugs. Carbohydrate Polymers 93: 718-730.

21. Ma ZH, Yu DG, Branford-White C. J (2009) Microencapsulation of tamoxifen: application to cotton fabric. Colloid Surface B 69: 85–90

22. Sanchez P, Sanchez-Fernandez MV, Romero A (2010) Development of thermoregulating textiles using paraffin wax microcapsules. Thermochim Acta 498: 16–21

23. Frederiksen HK, Kristensen GH, Pedersen M (2003) Solid lipid microparticle formulations of the pyrethroid gamma-cyhalothrin - incompatibility of the lipid and the pyrethroid and biological properties of the formulations. J Control Release 86: 243– 252

24. Chatterjee S, Salaün F, Campagne C (2014) Development of multilayer microcapsules by a phase coacervation method based on ionic interations for textile applications. Pharmaceutics 6: 281–297

25. Martins IM, Barreiro MF, Coelho M, Rodrigues AE (2014) Microencapsulation of essential oils with biodegradable polymeric carriers for cosmetic applications. Chemical Engineering Journal 245: 191-200

26. Tzhayik O, Cavaco-Paulo A, Gedanken A (2012) Fragrance release profile from sonochemically prepared protein microsphere containers. Ultrason Sonochem 19: 858–863

27. Gillij YG, Gleiser RM, Zygadlo JA (2008) Mosquito repellent activity of essential oils of aromatic plants growing in Argentina. Bioresource Technology 99: 2507-2515

28. Karaman S, Digrak M, Ravid U, Ilcim A (2001) Antibacterial and antigungal activity of the essential oils of Thymus revolutus CelaK from Turkey. Journal of Ethnopharmacology 76: 183–186

29. Piacentini E, Giorno L, Dragosavac MM, Vladisavljevic GT, Holdich RG (2013) Microencapsulation of oil droplets using cold water fish gelatine/gum arabic complex coacervation by membrane emulsification. Food Res Int 53: 362–372

30. Fei X, Zhao H, Zhang B, Cao L, Yu M, Zhou J, Yu L (2015) Microencapsulation mechanism and size control of fragrancemicrocapsules with melamine resin shell. Colloids and Surfaces A: Physicochem. Eng. Aspects 469: 300–306

31. Wang B, Adhikari B, Barrow CJ (2014) Optimisation of the microencapsulation of tuna oil in gelatin-sodium hexametaphosphate using complex coacervation. Food Chem 158: 358–365

32. Shahid-ul-Islam, Shaid M, Mohammad F (2013) Perspectives for natural product based agents derived from industrial plants in textile applications – a review. Journal of Cleaner Production 57: 2-18

33. El Asbahani A, Miladi K, Badri W, Sala M, Aït Addi EH, Casabianca H, El Mousadik A, Hartmann D, Jilale A, Renaud FNR, Elaissari A (2015) Essential oils: from extraction to encapsulation. Int J Pharm 483: 220–243

34. Prajapati V, Tripathi AK, Aggarwal KK, Khanuja SPS (2005) Insecticidal, repellent and oviposition-deterrent activity of selected essential oils against Anopheles stephensi, Aedes aegypti and Culex quinquefasciatus 96: 1749-1757

35. Solomon B, Sahle FF, Gebre-Mariam T, Asres K, Neubert RHH (2012) Microencapsulation of citronela oil for mosquito-repellent application: formulation and *in vitro* permeation studies. Eur J Pharm Biopharm 80: 61–66

36. Specos MMM, Garcia JJ, Tornesello J, Marino P, Della Vecchia M, Defain Tesoriero MV, Hermida LG (2010) Microencapsulated citronela oil for mosquito repelente finishing of cotton textiles. T Roy Soc Trop Med H 104: 653–658

37. Hsieh W, Chang C, Gao Y (2006) Controlled release properties of chitosan encapsulated volatile citronella oil microcapsules by thermal tratments. Colloid Surface B 53: 209–214

38. Higuchi T (1963) Mechanism of sustained-action medication. Theoretical analysis of rate of release of solid drugs dispersed in solid matrices. J Pharm Sci 52: 1145– 1149

39. Korsmeyer RW, Gurny R. Doelker E, Buri P, Peppas NA (1985) Mechanisms of solute release from porous hydrophilic polymers. Int J Pharm 15: 25–35

40. Shukla P, Rajagoplan N, Sivaram S (1993) Starch urea – formaldehyde matrix encapsulation iv. influence of solubility and physical state of encapsulant on rate and mechanism of release. J Appl Polym Sci 7: 1209–1222

41. Shimokawa K, Saegusa K, Wada Y, Ishii F (2013) Physicochemical properties and controlled drug release of microcapsules prepared by simple coacervation. Colloids and Surfaces B: Biointerfaces 104: 1-4

42. Lv Y, Zhang X, Zhang H, Abbas S. Karangwa E (2013) The study of ph-dependent complexation between gelatin and gum arabic by morphology evolution and conformational transition. Food Hydrocolloid 30: 323–332

43. Krishnan S, Kshirsagar AC and Singhal RS. The use of gum arabic and modified starch in the microencapsulation of a food flavoring agent. *Carbohydrate Polymers* 2005; 62: 309–315.

44. Otálora MC, Carriazo JG, Iturriaga L, Nazareno MA, Osorio C (2015) Microencapsulation of betalains obtained from cactos fruit (*Opuntia ficus-indica*) by spray drying using cactus cladode mucilage and maltodextrin as encapsulating agents. Food Chem 187: 174–181

45. Torini L, Argillier JF, Zydowicz N (2005) Interfacial polycondensation encapsulation in miniemulsion. Macromolecules 38: 3225–3236

46. Fei X, Zhao H, Zhang B, Cao L, Yu M, Zhou J, Yu L (2015) Microencapsulation mechanism and size control of fragrance microcapsules with melamine resin shell. Colloid Surface A 49: 300– 306

47. Al-Shannaq R, Farid M, Al-Muhtaseb S, Kurdi J (2015) Emulsion stability and cross-linking of pmma microcapsules containing phase change materials. Sol Ener Mat Sol C 132: 311– 318

48. Prata AS, Grosso CRF (2015) Production of microparticles with gelatina and chitosan. Carbohyd Polym 116: 292–299

49. Silvestrin RM, Alecastro RB (2007) Identificação espectrométrica de compostos orgânico. Rio de Janeiro: Livros Técnicos e Científicos, 429 P., 2007

50. Rocha-Selmi GA, Bozza FT, Thomazini M, Bolini HMA, Fávaro-Trindade CS (2013) Microencapsulation of aspartame by double emulsion followed by complex coacervation to provide protection and prolong sweetness. Food Chem 139: 72–78

51. Carreras N, Acuna V, Martí M, Lis MJ (2013) Drug release system of ibuprofen in pcl-microspheres. Colloid Polym Sci 291: 157– 165

52. Lopes WA, Fascio M (2004) Esquema para interpretação de espectros de substâncias orgâmicas na região do infravermelho. Quím Nov 27: 670–673

53. Lee PI (1985) Kinetics of drug release from hydrogel matrices. Journal of Controlled Release 2: 277-288

456 54. Dash S, Murthy PN, Nath L, Chowdhury P (2010) Kinetic modeling on drug release from controlled drug
457 delivery systems. Acta Poloniae Pharm 67: 217– 223
458 55. Fité FJC (1995) dying polyester at low temperatures: kinetics of dying with disperse dyes. Text Res J 65:
459 362–268
460 56. Sóti PL, Nagy ZK, Serneels G, Vajna B, Farkas A, Gucht FV, Fekete P, Vigh T, Wagner I, Balogh A,
461 Pataki H, Mezö G, Marosi G (2015) Preparation and comparison of spray dried and electrospun bioresorbable drug
462 delivery systems. Eur Polym J 68: 671–679
463
464

Fig. 1a Optical microscopy of the micro-capsules formed by complex coacervation magnitude x1.000

Fig. 2a Thermogravimetric curves TGA from citronella, gelatin, gum arabic and micro-encapsule

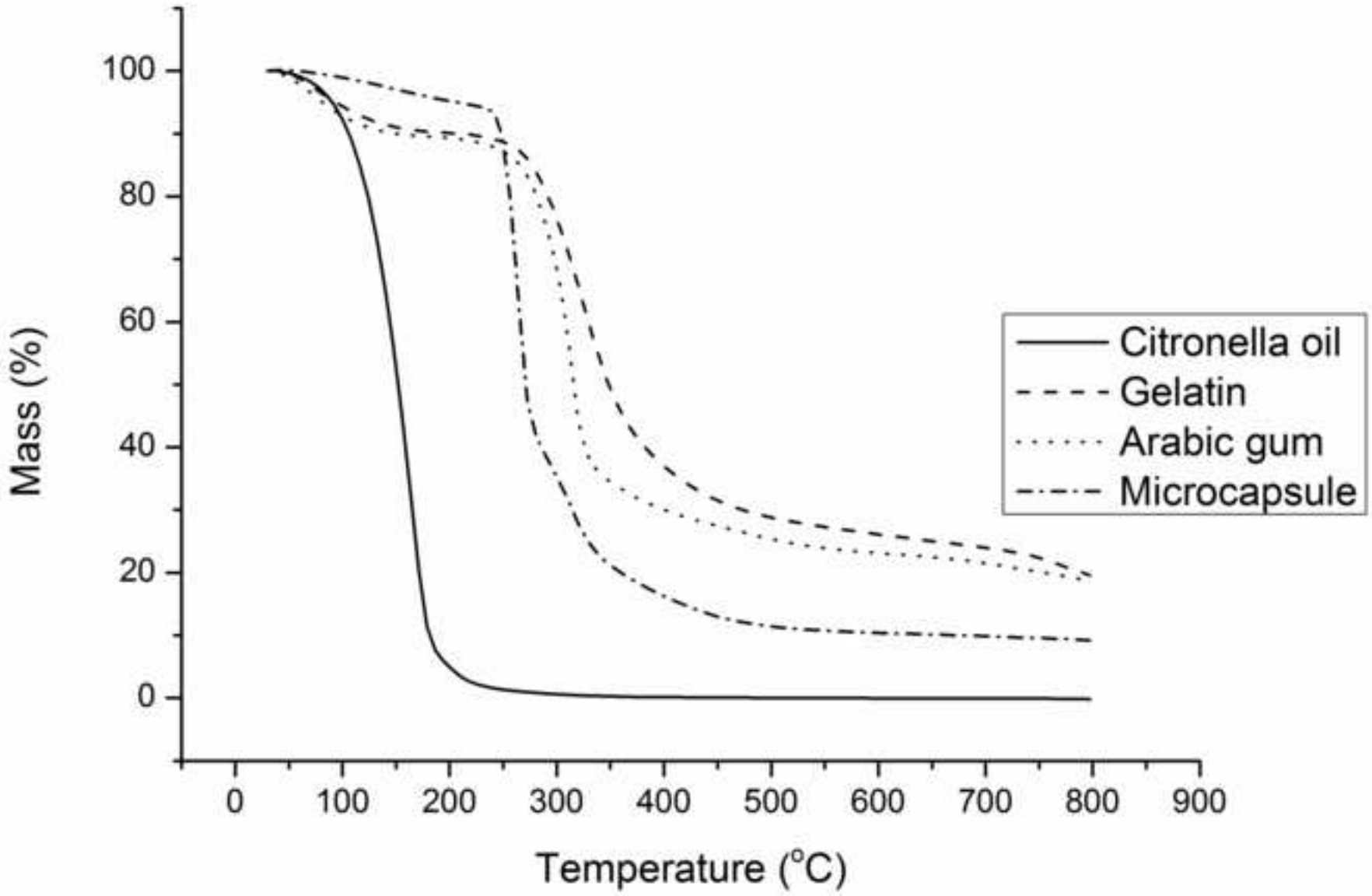

Fig. 2b Thermogravimetric curves dTGA from citronella, gelatin, gum arabic, and micro-capsule

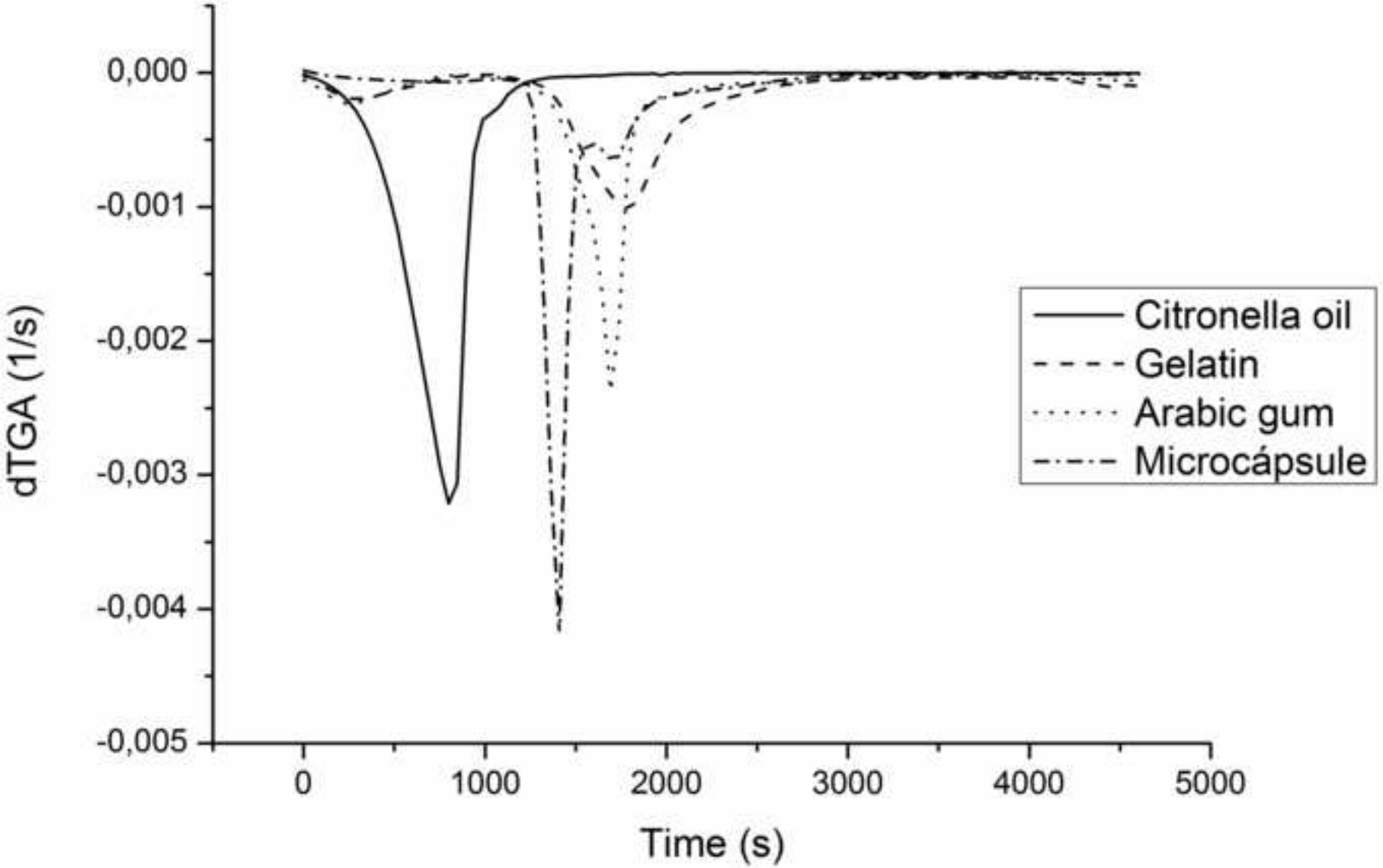

Fig. 3 Histogram of the size distribution of the micro-capsules of the citronella essential oil and the accumulation of the distribution

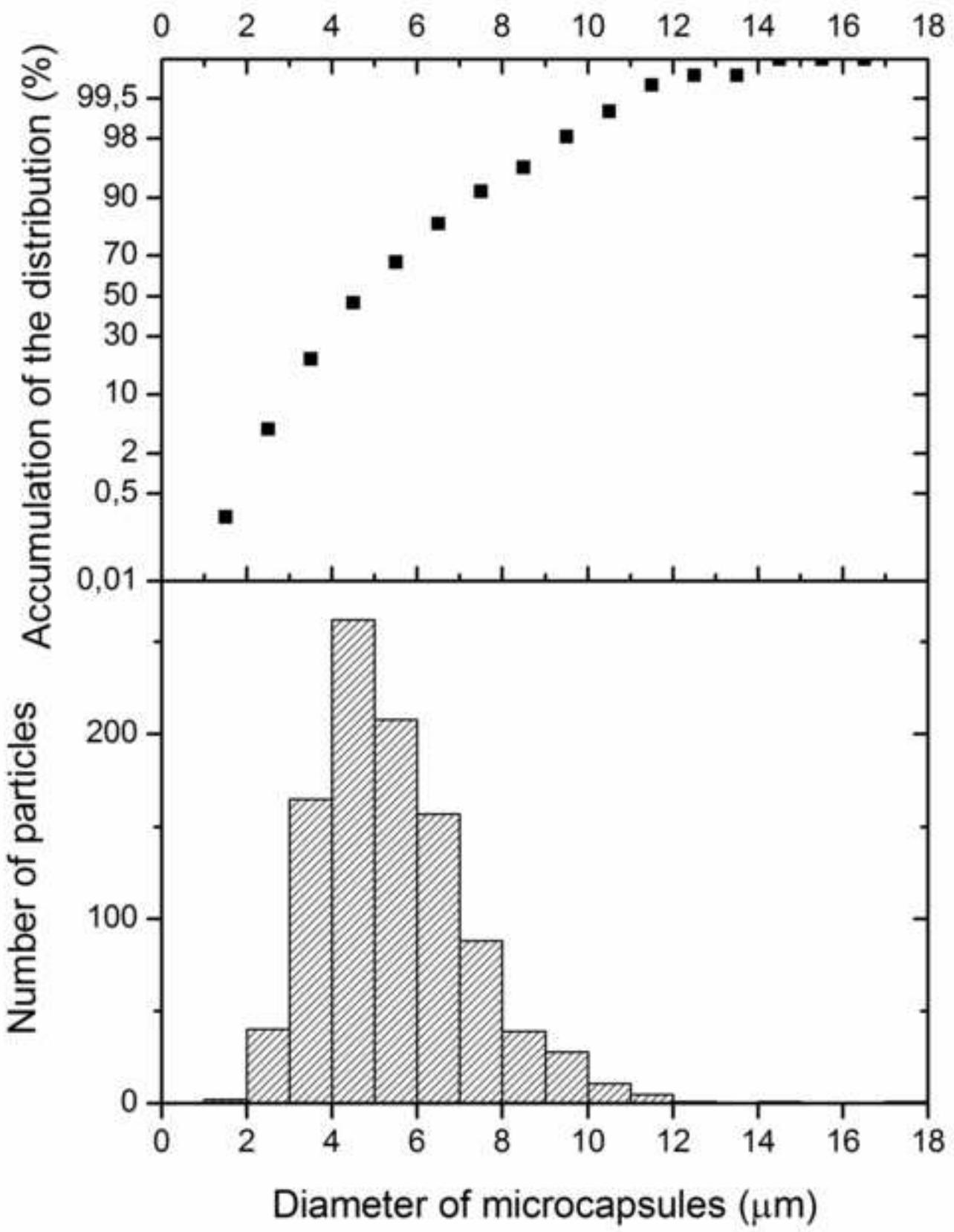

Fig. 4 Spectroscopy in the region of the attenuated infrared (FTIR-ATR) of the textile substrate 100% CO with micro-capsule finish:

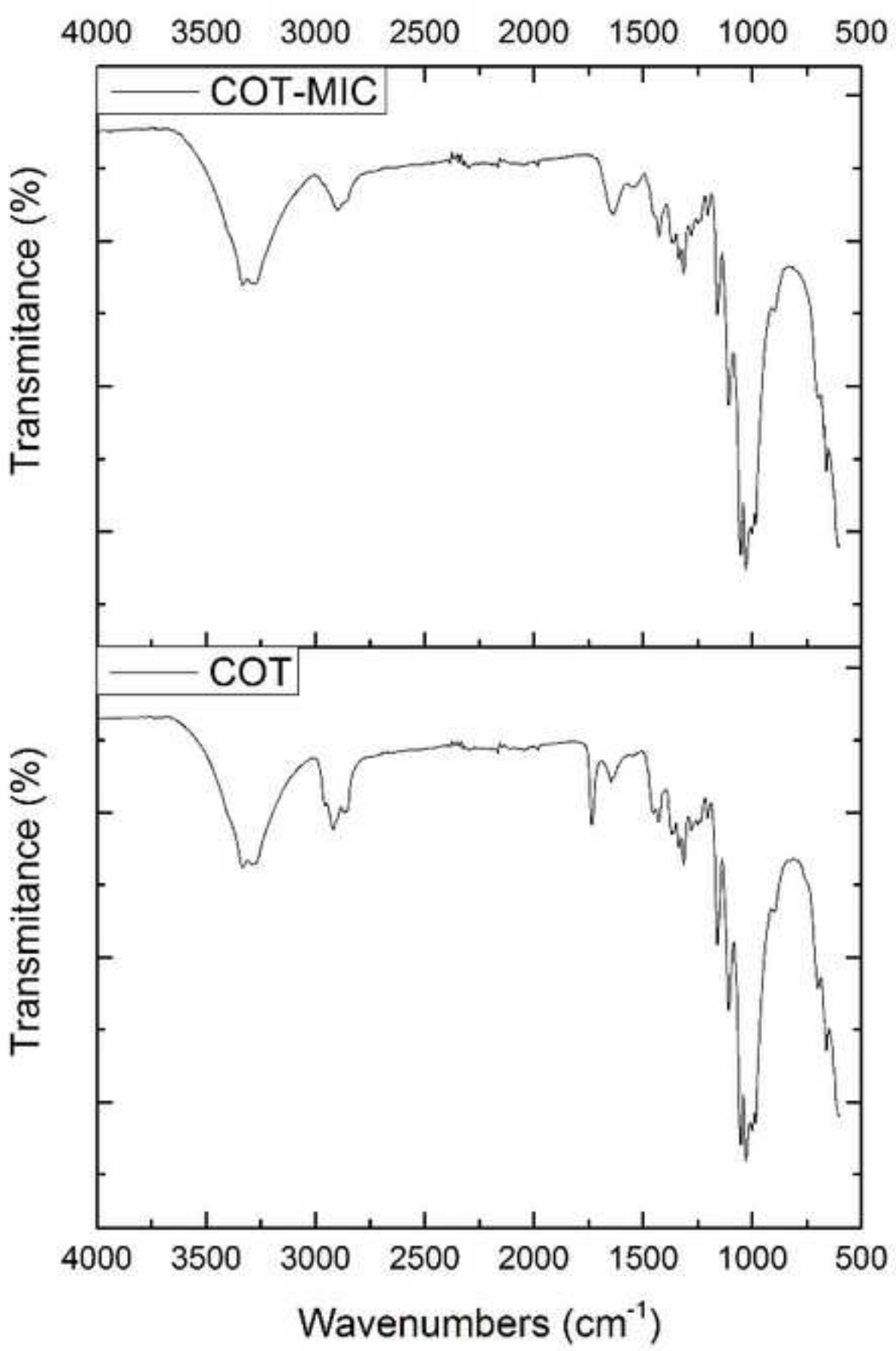

Fig. 5 Spectroscopy in the region of attenuated infrared (FTIR-ATR) of the textile substrate 100% PES with the micro-capsule

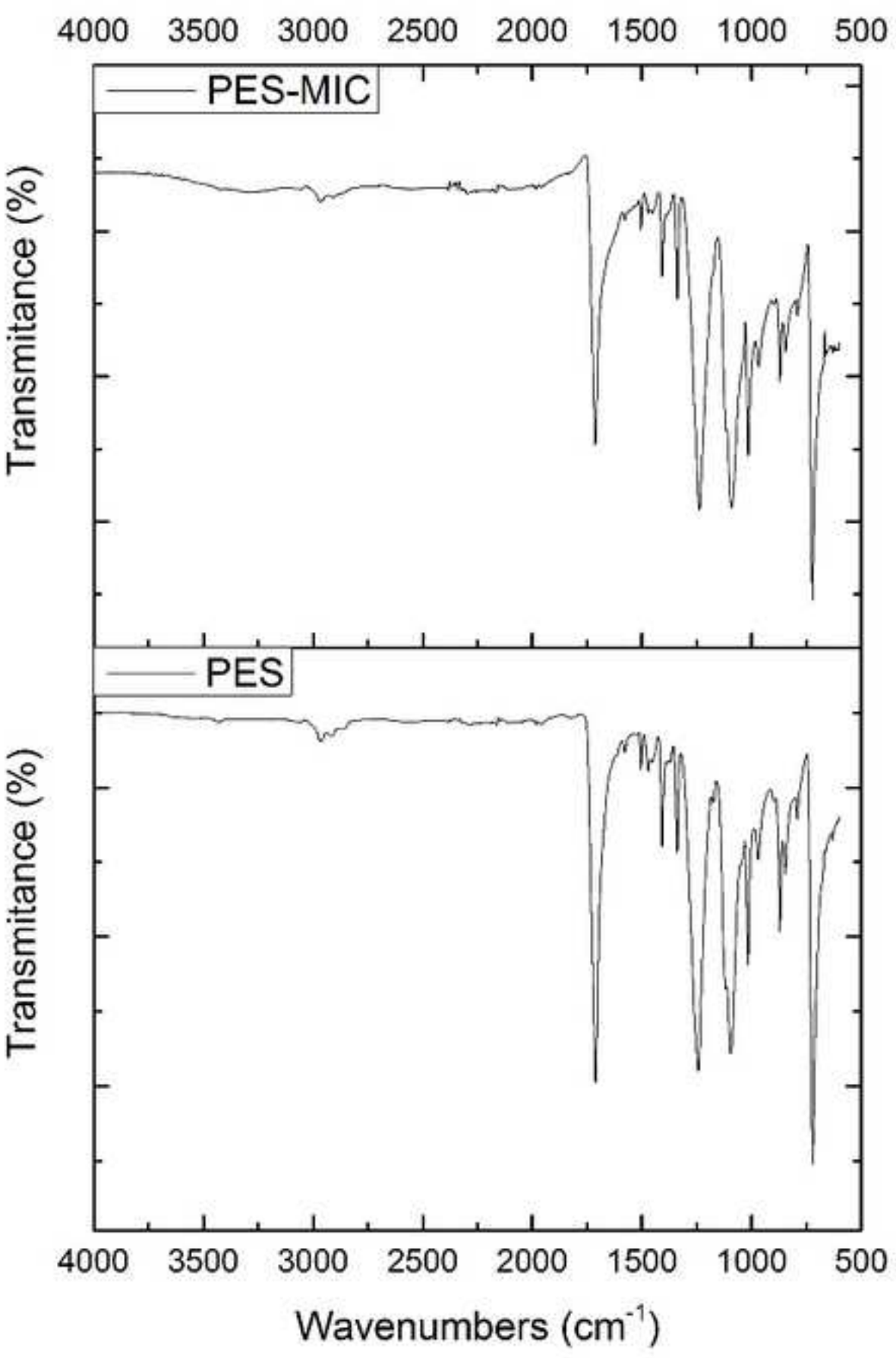

Fig. 6a Controlled in vitro release profiles of the citronella essential oil micro-encapsulated and free in water, at 37 ºC applied in cotton

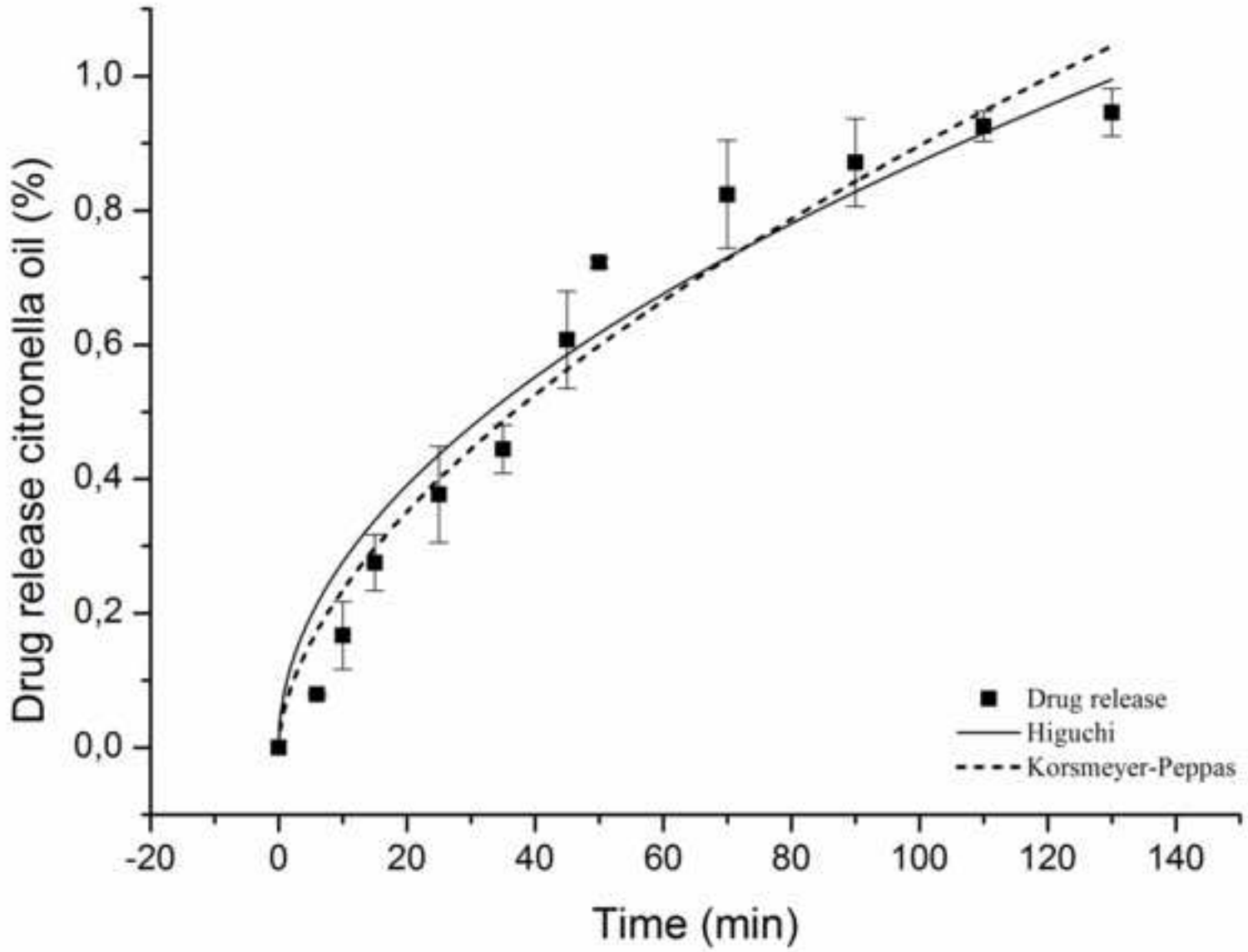

Fig. 6b Controlled in vitro release profiles of the citronella essential oil micro-encapsulated and free in water, at 37 ºC applied in polyester

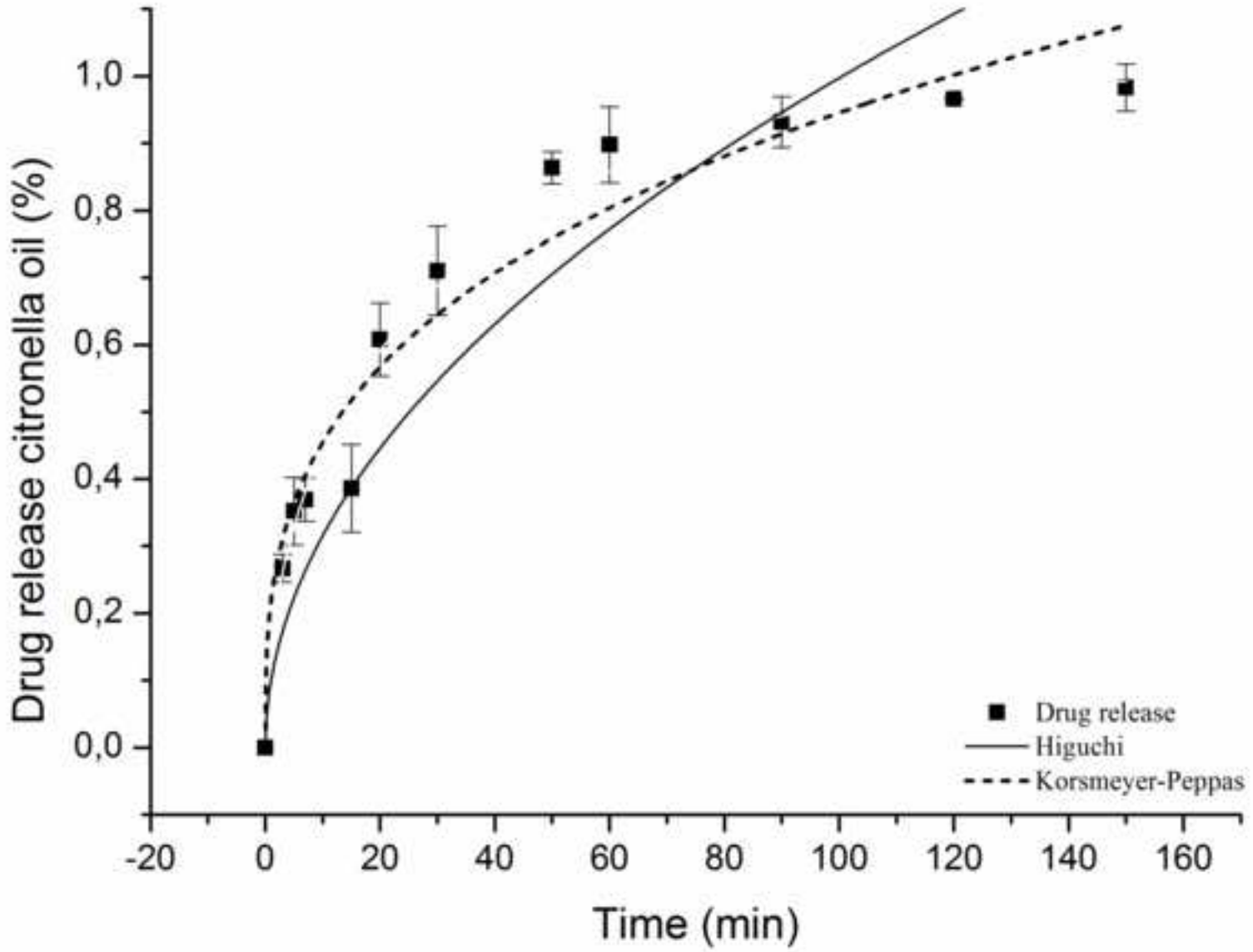

Fig. 1b Scanning electron micrographs of microcapsules with citronella oil (×1,820).

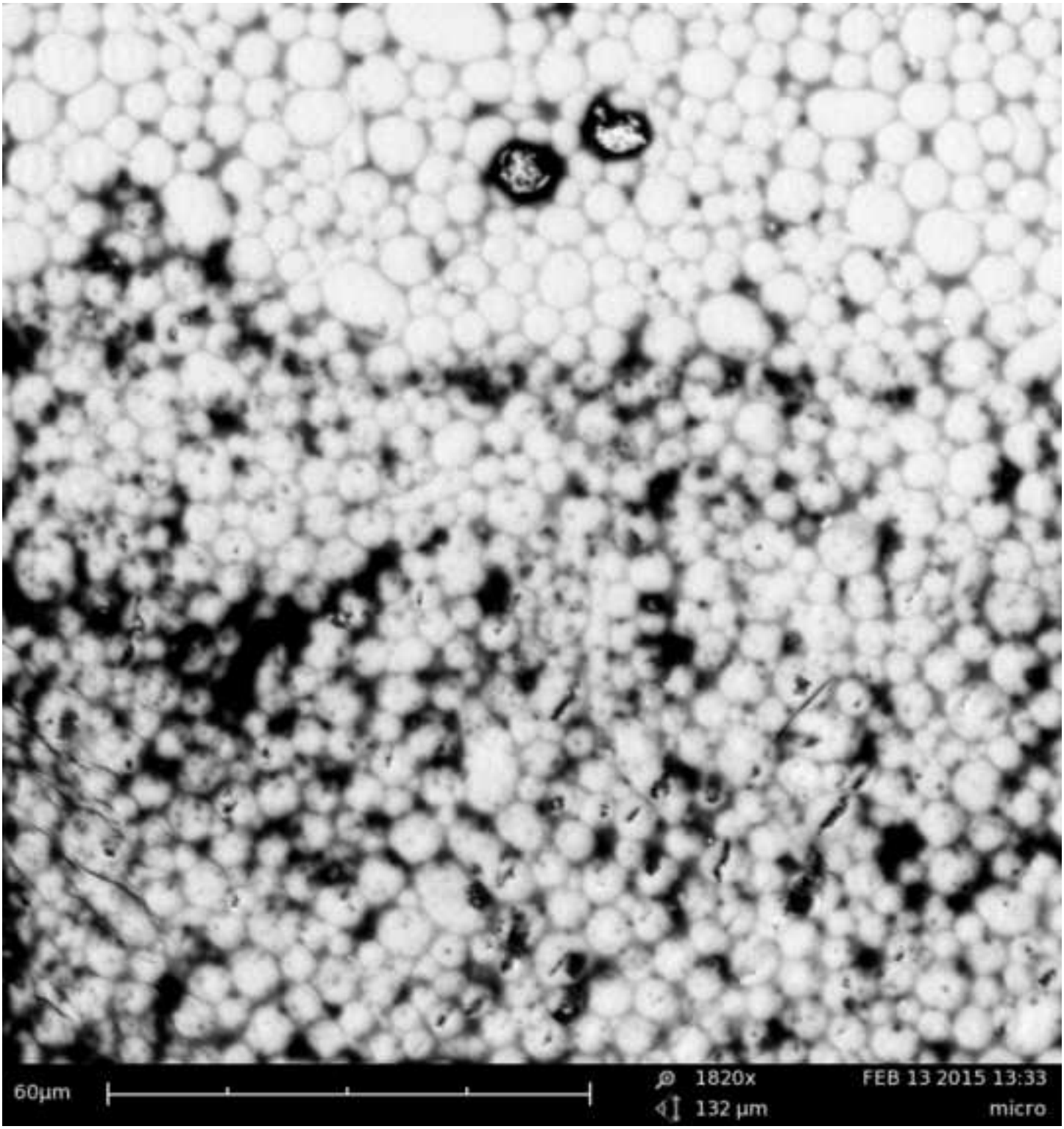

Table 1 Thermogravimetric data from the samples of citronella essential oil, gelatin, gum arabic and microcapsules

Table 1 Thermogravimetric data from the samples of citronella essential oil, gelatin, gum arabic and microcapsules

		CITRONELLA	**GELATIN**	**ARABIC GUM**	**MICROCAPSULE**
Stage 1	ΔT_{dec}*	30 – 192.5 ºC	30 – 124 ºC	30 – 116.2 ºC	30 – 131.8 ºC
	T_{max}	192.5 ºC	92.7 ºC	92.7 ºC	124 ºC
	% $_{loss\ mass}$	97.8 %	7.7 %	8.5 %	2.4 %
Stage 2	ΔT_{dec}	-	241 – 460 ºC	233 – 398 ºC	233 – 272 ºC
	T_{max}	-	296 ºC	280 ºC	260 ºC
	% $_{loss\ mass}$	-	61.7 %	61.4 %	53.1 %
Stage 3	ΔT_{dec}	-	-	-	280 – 429 ºC
	T_{max}	-	-	-	288.5 ºC
	% $_{loss\ mass}$	-	-	-	32.8 %
Residual		0 %	19.6 %	18.7 %	9.2 %

ΔT_{dec}* decomposition temperature

Table 2 Statistic data concerning the diameter of the formed microcapsules

Table 2 Statistic data concerning the diameter of the formed microcapsules

Total microcapsules	**Mean (µm)**	**Standard deviation**	**Minor diameter (µm)**	**Major diameter (µm)**
1.008	5.435	1.784	1.566	17.247

Table 3 Modelling parameters for the controlled release of the citronella essential oil applied to textile substrates

Table 3 Modelling parameters for the controlled release of the citronella essential oil applied to textile substrates

MODEL	PARAMETERS	COTTON	POLYESTER
Higuchi	**R^2**	0.9476	0.8291
	K	0.0873±0.0032	0.0997±0.0058
	$D_f(10^{-2})$*	0.1496±0.0110	0.1952±0.0227
Korsmeyer-Peppas	**R^2**	0.9540	0.9477
	K	0.0611±0.0015	0.2189±0.0304
	N	0.5833±0.0573	0.3177±0.0329

D_f* diffusion coeficiente (min^{-1})