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Thermal behaviour of microencapsulated flavours when applied to cellulosic fabrics.

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Abstract.

Microencapsulated products are very common in some fields such as pharmacy and the textile industry has recently incorporated them into their products. Firstly, this research assessed the presence of flavour microcapsules on cotton fabric using different padding applications and evaluated them using Scanning Electronic Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). When the OH stretching region between 3700-3000 cm^{-1} from spectra are examined, we propose some area ratios to quantify the microcapsules presence on the fabric. The ratios proposed show that when the concentration of microcapsules in the padding bath increased their value increased too. Secondly, we analyze the effect that thermal treatment can cause on microcapsules. This was undertake using hot air at 120º C, 140º C and 160º C, or by ironing the fabric impregnated with microcapsules at 110º C, 150º C and 200º C, by ironing 1, 5 and 10 times on the analyzed zone. It was found that when the temperature is higher than 120º C, microcapsules are deflated and damaged. This could be seen using SEM images and checked using FTIR analysis.

KEY WORDS

- Microencapsulation
- Cellulosic fabric
- Infra red
- SEM
- Deconvolution

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Thermal behaviour of microencapsulated fragrances on cotton fabrics.

Abstract.

Firstly, this research assesses the presence of fragrance microcapsules on cotton fabric using different padding applications and evaluates them using Scanning Electronic Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). When the OH stretching region between 3700-3000 cm^{-1} from spectra are examined, we propose some area ratios to quantify the microcapsules presence on the fabric. The ratios proposed show that when the concentration of microcapsules in the padding bath increases their value increases too. Secondly, we analyze the effect that thermal treatment can have on microcapsules. This was undertaken using hot air at 120º C, 140º C and 160º C, or by ironing the fabric impregnated with microcapsules at 110º C, 150º C and 200º C, and by ironing 1, 5 and 10 times on the analyzed zone. It was found that when the temperature is higher than 120º C, microcapsules are deflated and damaged. This could be seen using SEM images and checked using FTIR analysis.

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1.- Introduction.

Nowadays textiles are required to have extra properties, they should offer active functionality, and in recent years some textiles have come to be known as smart textiles. It is very common to think that smart textiles contain electronic devices, but this is not necessarily so. The term smart textile refers to textiles that are able to react when an external effect is present. Consequently textiles impregnated with microcapsules have been developed in the last few years which now are giving rise to industrial interest.

Microencapsulated products are very common in some fields such as pharmacy and the textile industry has recently incorporated them into their products. Some papers have been published on fragrance microcapsules [1-6], in which these were studied bearing in mind their final use on textile or other materials, and their effect.

The pharmaceutical industry uses microencapsulated products quite regularly and they have been studied in depth, however, they are relatively new to the textile industry, and we do not know how to quantify their presence on the surface of textiles.

The composition of microencapsulated products can be very different because they are made of different shell materials and diverse core materials. The core material will define the use, i.e. medicine, food, etc. The cosmetic industry uses fragrances in liquid cores, and although they can be used in aromatherapy they are not as important as in medicine. They are less expensive and this is why we used them in our study. Odour is measured in many industries, such as in the chemical, food, oil, and motor industries, and in the textile industry some measuring apparatus have been presented. [7]

Moreover, some instrumental techniques such us X-ray analysis, infrared spectroscopy, Scanning Electron Microscopy (SEM), particle size distribution and average diameter, HPLC chromatography, have been applied for physico-chemical analysis and characterization of microcapsules, as witnessed in many papers [1,6,8-11]. With reference to textiles, however, SEM is widely used for qualitative studies, although non-quantitative analyses have been published.

A procedure for impregnating textile fibres with microcapsules was studied to increase their yield [12]. It was not possible to determine microencapsulated concentrations in fabrics. Thus, the authors prepared different fabrics with microcapsule concentrations which were studied and compared.

Moreover, textiles are submitted to different thermal treatments such as washing, drying, or ironing. Consequently, a procedure was established to determine the effect of thermal treatment on microencapsulated products.

It is very common for fabrics to undergo thermal treatment, either during manufacture (dried, fixed, dyed, etc.) or when used (washed, dried, ironed, etc.)

The influence of thermal treatments on cellulose fibres is well known, but in this respect we are going to study the effect of temperature on microcapsules. Hence we are going to study two effects:

- Thermal conditions for polymerizing the resin. Thermoset coatings based on the reaction of melamine/formaldehyde resins with hydroxyl functional polymers or others have long been used in the coatings industry [11]. Microencapsulated products usually do not react with fibres, so resins should be used, in order to join microcapsule to textile fibre. These products need thermal treatment in order to develop the polymerization process which allows microcapsule retention.
- Thermal conditions for ironing the fabric. This kind of treatment can be done at different temperatures.

The aim of this paper is to evaluate different concentrations of microcapsules on textiles when different concentrations are applied using padding to demonstrate procedure can evaluate microcapsules presence. Because of thermal damage observed, we also tried to evaluate how curing temperature, or ironing could affect microcapsules, as we think it is important to know what kind of damages microcapsules can suffer while garments are used.

Some techniques will be used in order to study microcapsule presence on fabrics. A procedure based on FTIR spectroscopy is also proposed to quantify the presence of the microcapsules in the fabrics. Scanning Electron Microscopy (SEM) will be used in order to observe their presence and their shape which will corroborate FTIR conclusions. Differential Calorimetric Scan (DSC) will allow characterization commercial products and their thermal behaviour at the temperatures range we worked with.

2.- EXPERIMENTAL

2.1.-Materials

Microcapsules (CENTER FINISH 164/01 MT) were supplied by COLOR CENTER (Tarrasa, Spain). Microcapsule specifications are given below. The wall material was melamine formalin, and the microcapsules contained peppermint, and apple fragrance. The mean size distribution of the microcapsules was around 5–10 μm, which was checked using SEM. No further information was supplied by the provider, as companies disclose as little information as possible. In order to bond the microcapsules to the fabric, an acrylic resin (CENTER FINISH BC) was applied, also supplied by Color Center.

As the microcapsules were dispersed in the water phase, in order to determine the average quantity of microcapsules, samples were introduced in a WTC BINDER 030, at a temperature between 100º C and 105º C, where they remained until weight remained constant. Table 1.

The fabric used was a 100% cotton twill which had been chemically bleached with peroxide in an industrial process. Fabric characterization was carried out applying standard UNE 40.600-5:1996 to evaluate yarn count, and UNE EN 12127:1998, for evaluation of mass per unit area using small samples. Fabrics were a satin of cotton 100% and 200 g/m^2. Yarn density was 35 warp/cm or 20 weft/cm, and they were either in warp or weft 25.2c tex. Every sample was 20 cm wide in the weft and the minimum length required for foulard treatment.

2.2.- Microcapsule application on fabric.

Commercial microcapsules were applied to the surface of the fabric. In the finishing process a resin was used as a binder. For this reason thermal treatment in the form of hot air was applied to cure the resin.

To study the effect that changes in microcapsule concentration produces on the fabric, some samples were prepared with different known concentrations.

Subsequently, different thermal treatments took place, either by heating or by ironing the fabric.

Fragrances were added to fabrics either by impregnation or by bath exhaustion. For impregnation, samples were obtained using a 2608 TEPA foulard of 1 kW. The bath treatment for impregnation comprised of different microencapsulated concentrations, and 15 g/l of acrylic resin in all baths. Foulard work was performed at a speed of 2 m/min and cylinder pressure of 1.5 kg/cm in order to obtain a pick-up of around 89–90%. Samples were thermally fixed in a scale pin stenter at different temperatures for 10 min in WTC BINDER 030.

2.3.- Calorimetric study. DSC. TGA.

To determine thermal influence on microencapsulated product, calorimetric curves were obtained. The microencapsulated products used as samples were like those provided by the supplier. These samples were prepared as required by the equipment. DSC curves were obtained using a Mettler-Toledo 821 DSC (Mettler-Toledo Inc., Schwerzenbach, Switzerland) at 10 °C min^{-1} heating rate in a nitrogen atmosphere (60 ml min^{-1}). The pan type used are standard Aluminium crucibles with a 40 µl volume with capacity of sealed to avoid losses of material. The weight of samples was approximately 3 mg.

TGA was carried out using a Mettler-Toledo TGA/SDTA 851 (Mettler-Toledo Inc., Schwerzenbach, Switzerland) with initial temperature 25 °C and final temperature 450 °C using a 20 °C min^{-1} heating rate, in a nitrogen atmosphere (20 ml min^{-1}). Aluminium oxide crucibles were of 70 µl volume. The samples used weighed 3 mg approximately.

Calorimetric curves were obtained for each commercial sample and these were compared with the calorimetric curve obtained when samples were dried and crushed. The reason for crushing was to break the microcapsules to enable the fragrance to evaporate and thus only the thermal behaviour of the microcapsule membrane was analyzed.

2.4 .- FTIR

The infrared experiments were performed in a Nicolet Magna 550 spectrometer equipped with a DTGS detector and a Spectra Tech transmission accessory. Spectra were collected with a resolution of 8 cm^{-1} and given as the ratio of 200 single beam scans to the same number of background scans in pure KBr (IR grade supplied by Aldrich). KBr was ground to a fine powder and mixed with fibre samples (2% w/w). KBr blended with fibres were dried on a thermogravimetric scale and poured onto the transmission sample holder before IR spectrum acquisition.

To explain the broadening of different bands in the region between 3700 – 300 cm-1, deconvolution was applied to reveal overlapping spectral features that can not be resolved by collecting data at a higher resolution setting. Deconvolution was undertaken by Microcal Origin, and Gaussian curves were the ones that fitted experimental spectra. Bandwidth is an estimate of the widths of the overlapped bands and enhancement is a measure of the degree to which features are revealed. The deconvolution is applied in this study with a bandwidth at 8 and an enhancement factor at 1.6.

2.5.- SEM

For surface observation, a SCANNING MICROSCOPE JEOL JSM-6300 scanning electron microscope (SEM) was used. Each sample was fixed on a standard sample holder and sputter coated with gold. It was then examined with a SEM with suitable acceleration voltage (10 kV) and magnification.

2.6.- Thermal heating.

2.6.1.- Thermal heating by air

It is known that microcapsules can be damaged by heat [12], but it has not been studied in relation to fabrics.

To study this we worked with the fabric that was prepared with Peppermint 3 and with the 60 g/L concentration. When the microcapsules had been padded, they were heated in order to polymerize the resin to fix the microcapsules. Studies were undertaken at three different temperatures - 120º C, 140º C and 160º C. They were all treated for 10 minutes, and later on studied using Scanning Electron Microscopy (SEM) and FTIR, these were used to identify the effect heat can cause. We know that fragrances can be detected on fabrics, and artificial noses

can be employed to analyze the fabric [12], but we tried to establish an analytical method for studying fabrics impregnated with microcapsules.

2.6.2.- Thermal heating by Ironing.

For ironing samples an iron with metallic surface was used, which was heated by electrical power. Different temperatures were tested, as standard ISO 3758:2005 indicate, so we tested at 110ºC, 150º C, and 200º C.

As it is possible to pass the iron over the fabric several times, we tested the fabrics when it was treated, 1 time, 5 times and 10 times.

3.- Results and Discussion.

3.1.- Microcapsules . Dry weight.

From commercial samples a dried extract was obtained, which was white, and weight results are shown in table 1. Dried samples were used to prepare samples in the thermal study.

Insert TABLE 1 about here]

All of them are from the same supplier. Moreover we have analyzed two peppermint microcapsules from the same supplier and they showed differences. It can be observed that the dried extract weight is very different between samples, thus we used reference Center finish 164/02 (Peppermint 3) throughout the study.

3.2.- Behaviour of microcapsules to DSC heating.

To begin with, we show in figure 1 the behaviour that calorimetric curves show when the dried product CENTER FINISH 164/02 was analyzed. This product contains fragrances in the microcapsule, and we obtained samples for Peppermint 1 and Peppermint 3.

[Insert Figure 1a and 1b about here]

Figure 1 shows a graphical representation of calorimetric curves for peppermint, black is the commercial sample after drying. The red line shows thermal behaviour when the same sample has been dried and crushed.

It can be observed that at about 100º C, a minimum is visible, which may be attributable to moisture loss. Another minimum point could be observed at about 350º C, which may be caused by polymer membrane degradation. Melamine formalin discomposes at about 320-430º C[13,14]

Figure 2 shows calorimetric curves for samples in which the encapsulated fragrance was apple. Either apple or peppermint 1 show when crushed, a minimum point at higher temperatures than when the sample has not been crushed.

[Insert figure 2 about here]

When the calorimetric study for peppermint 1 and peppermint 3 are compared, see figure 3, we can observe that they are similar.

[Insert figure 3 about here]

We stated that the minimum observed at about 100º C may be due to the loss of moisture on dried samples, but when mass variations are studied, as shown in figure 4, we see that the effect does not stop between 105º C- 110º C, but remains until it reaches more or less 150º C. From 150º C to 300º C it is more or less constant, but when treated at 300º C another minimum point appears. Nevertheless Mint 3 does not show, that minimum what shows another product has been used for shell and not melamine.

[Insert figure 4a about here]

[Insert figure 4b about here]

As mass decreases at temperatures above 110º C, the commercial emulsion in which the samples were provided is affected by temperatures in excess of 100ºC. It is well known that fragrances are volatile products with temperatures, thus we assign the loss of mass at that point either to water evaporation or to fragrance. The second peak is assigned to membrane polymer degradation.

This can be confirmed when crushed samples were studied, because fragrance should evaporate before the sample is tested and inflection because of fragrance should not be observed. This can be seen in figure 4b, in which inflection at about 100º C is not appreciated, and it allows us to confirm that changes at about 100º C can be assigned not only because of water but to fragrance too.

Figure 4 shows behaviour for Peppermint 1, nevertheless, similar behaviours were obtained for other samples studied. Thus, we are able to confirm that thermal treatment when temperatures are higher than 100º C can produce changes on the active substances inside the shell. We cannot confirm if moisture is on the wall or inside the microcapsule but we know that when crushed it disappears.

Because of thermal response of the microcapsules product we decided to analyze what happens on thermal treatment of textiles with microcapsules. The thermal changes occur in the range of temperatures that are frequently reached in cotton fabrics so we investigated what happens either in production or while they are used as garments.

3.3.- Application procedure.

Padding was the procedure that obtained the best results when compared with bath exhaustion, [15]. We can see in figure 5 evidence on the different quantity of microcapsules on different fabrics studied. Thus, we applied our microcapsules by padding in our study. Four padding baths were prepared with different microcapsule concentrations 10, 30, 40, 60 g/L and with 15 g/L of resin. Thus we obtained four fabrics, which can be seen in figure 6.

Insert figure 5 about here

[Insert figure 6 about here]

We can see from figure 6 that some differences were detected in bath concentrations, but it is not possible to quantify microcapsule presence using this method.

3.4.- Microcapsule concentration on fabrics. Infrared spectroscopy.

As the concentration of microcapsules is increased in the bath, there should be more microcapsules on the fabric, this could be seen in images from the fabric by Scanning Electron Microscopy in figure 6

We obtained and represented some infrared spectra of the fabrics attained at different concentrations. As the fabric was made of cotton, the infrared spectra showed variation in the cellulose for each sample. In this paper changes in the OH stretching region will be studied. But we do not analyze microcapsules because it is not the aim of this work, and it was partially shown in other works [15].

When figure 7 is observed, it is noticeable that the spectra are very similar; this is because all the fabrics are made of cellulose fibres, and the difference is due to the quantity of microcapsules that have been applied. The quantity of microcapsules is not too high when compared to the quantity of fibre, and this is why the spectra are very similar.

[Insert figure 7 about here]

The study of the OH stretching region was made by deconvoluting the band that the spectra present in this region. The experimental result was reproduced by deconvoluting it in three Gaussian curves, with maximum peaks centred at wave number 3500 cm^{-1} for band I, 3450 cm^{-1} for band II and 3300 cm^{-1} for band III. The cotton fabric sample is not present in band II which could be assigned to the microcapsule presence. This band could be assigned to the amine group [11, 15-17]. Deconvolution results for representative spectra from figure 7 are shown in table 2. A very good match between the experimental vibration envelope (dotted line) and the fitting curve (solid line) is observed, calculated by convoluting the three individual contributions (dashed line). The presence of band II and its evolution shows it is sensitive to the presence of microcapsules.

[Insert Figure 8a up to figure 8e about here]

The combined intensity of the three deconvoluted bands is also tabulated in Table 2 for the different samples. It can be observed that when cotton is not treated, the area values or the ratios between areas are 0 because of the absence of band II. When cotton fabric is impregnated with microcapsules, the area values increase if compared to the area obtained for original cotton fabric. When the concentration in the padding bath was higher, the ratio also increased. A trend can be clearly observed.

Area II / Area I ratio tendency is more proportional to concentration than when Area II / Area III is studied. We suggest that this is because overlapping curves for band II and band III are higher than between band II and band I.

3.5.- Thermal variations.

Given the results at this point, we studied the influence of ironing because it could be undertaken up to temperatures about 200º C, and we thought it could produce changes in the microcapsules.

3.5.1.-Thermal heating by air. FTIR

As mentioned earlier, thermal treatments were applied to fabrics. The temperatures studied were 120º C, 140º C and 160º C.

When concentration effect was analyzed we were able to ascertain that all the spectra were very similar, because of the presence of cellulose. In this study a similar occurrence may be observed. A spectrum of the cotton fabric containing 60g/L of microcapsules and 15 g/L of resin was studied. In figure 9, differences in the OH stretching region between 3700 and 3000 cm^{-1} were observed. These changes on the spectra may be attributed to thermal degradation of the microcapsules.

[Insert figure 9 about here]

This region was studied by deconvoluting the band in the region, in a similar way as before, when concentration effect was studied.

[Insert Figure10.a up to figure 10.e about here]

When figure 10 is scrutinized, the presence of three bands can be appreciated, as we explained before when discussing concentrations. The central band (band II, centered at 3450 cm^{-1}) is due to the presence of microcapsules in the fabrics produced by the presence of an amine group, found in microcapsules but not in cotton fibre.

If we study the three bands exhaustively, some changes were observed when the temperature treatment changes. The middle band goes down when the thermal treatment is applied at higher temperatures. This effect can be observed in the area of the band, which decreases when temperature is increased. This suggests to us that some modifications occur on microcapsules because of thermal treatment. To confirm this behaviour, the areas of the three bands were studied, and results are shown in table 3.

Insert TABLE 3 about here]

Due to the fluctuation of the signal from one spectrum to another, we have calculated the ratios between areas of each band. When ratios are analyzed band behaviour can be observed.

Analysis of these ratios give us a clear idea of how the bands behave.

There are no noticeable differences between the fabric impregnated with microcapsules and the same fabric when treated at 120º C. Nevertheless when the temperature of the treatment is increased, the ratio decreases because the middle band's area (assigned to the presence of microcapsules) decreases too and because the area of the other two bands increases. It means that these ratios are capable of measuring the loss of microcapsules after hot air treatment. It is possible that hot air allows the resin to lose some microcapsules This will be verified by SEM.

3.5.2. Thermal heating by air. Scanning Electronic Microscopy (SEM).

The fabric treated by air at 120º C was observed using Scanning Electronic Microscopy (SEM), and the presence of apparently unaltered microcapsules could be seen on the fabric. These images can be seen in figures 11.1. and 11.2.

Figures 11.3 and 11.4 show two micrographs of the same fabric when heated at 140º C. Some deflated microcapsules are visible, as the spectrum predicted. Figures 11.5 and 11.6 show the fabric heated to 160º C in which the swelling has been reduced considerably in each microcapsule. Those figures show that microcapsules remain on the fibre, but the fragrance has gone out partially. Because of this, we can conclude that FTIR can show not only microcapsules shells but active products too. It is likely that microcapsules presence can be determined by FTIR ratios studied in this project.

[Insert Figure 11.1 up to figure 11.6 about here]

We attempted to evaluate the quantity of microcapsule presence on the fabric when heated by air, at 120º C, 140º C and 160º C. We use tendency as calculated in table 4 we show ratio values.

As a consequence of the data in Table 2 and 3, we calculated the theoretical concentration of microcapsules that the fabric contained when heated to 140º C or 160º C. As a result, we show the values in figure 12, and at these temperatures we can observe that the quantity is lower than the one obtained when the fabric was treated using a padding bath with 10 g/L of microcapsule product.

[Insert figure 12 about here]

In the light of this study we have concluded that temperature can give rise to changes in microcapsules and we saw the need to study the effect of ironing.

3. 5.3.-Thermal heating by ironing. SEM.

Due to results obtained when the effect of hot air on microcapsules was studied, it was thought that microcapsules could be damaged after ironing an impregnated fabric at the temperature recommended for each kind of fibre.

At this point we are going to examine the effect of ironing.

[Insert Figure 13.1 up to figure 13.9 about here]

Figure 14 shows the SEM images obtained from the same fabric when ironed at different temperatures (120º C, 150º C and 200º C), and with varying numbers of applications of the iron at each one.

It can be observed that when temperature increases or the number of applications is higher, the microcapsules become deflated. Analysis of SEM images gives us an idea of the effect of ironing, but this was verified using FTIR to confirm the tendency detected. Moreover this will confirm that the result observed by hot air effect is the same than when fabrics are ironed.

3. 5.4.-Thermal heating by ironing. FTIR.

Figure 14 shows spectra of the microcapsule-impregnated fabric before and after ironing for comparison, in order to examine the effect of temperature and number of applications of the iron. Spectra of the same fabric were examined when the bath padding contains 60 g/L of Center finish 164/02 microcapsules, referred to as Peppermint 3 and ironed once, five times and ten times at 110º C, compared to the not ironed fabric.

[Insert figure 14 about here]

Figure 15 shows the OH stretching zone between 3700 cm^{-1} and 3000 cm^{-1} at 150º C. Figure 16 shows the same as figure 15, but when it has been ironed at 200º C. It is noticeable that when it has been ironed more times the maximum peak moves towards higher wavenumbers.

[Insert figure 15.and 16 about here]

We have deconvoluted the band in three peaks as described before, and the results can be seen in figure 17. Values have been analyzed and are shown in table 4. It can be observed that the area ratios studied and assigned to the presence of microcapsules on the fabric surface (**A II** / **A I)**, decreases.

[Insert Figure 17.a up to figure 17.d about here]

Insert TABLE 4 about here]

Values from table 4 are shown in figure 18 and indicate that both ratios for **Areas II / I** and **Areas II / III** present a decreasing linear tendency in which the lower value is assigned to the sample that is subjected to the most ironing

The same analysis has been applied to fabrics when ironed at 150º C and 200º C, as figure 19 and 20 show, and we studied spectra from those fabrics. Deconvolutions for OH stretching

region described before (3000-3700 cm^{-1}), have been carried out. Table 4 shows the values for the area ratio studied when ironed once, five and ten times at 150º C.

Insert figure 19 and 20 here.

We can see that the more the fabric is ironed, the area ratio studied decreases, this means that the microcapsule effect is lower the more the fabric is ironed, and thus confirm what we had observed on SEM images, and that ironing fabrics with microcapsules can produce a similar effect to hot air.

When the ironing temperature is 200º C and not 150º C, the same effect occurs. Nevertheless behaviour at 200º C presents more or less the same downward tendency. When the ratio between the areas was examined, it was ascertained in all cases that between Area I / Area II, the ratio was more linear than the one between Area II/ Area III. Because of the FTIR, we can determine the temperature increase influence, but SEM analysis shows that microcapsules are not lost, it is the presence of fragrance on fabric that changes.

4.- CONCLUSIONS

As a result of the FTIR study and SEM analysis, for each fabric subjected to different treatments we can conclude the following points.

We can confirm that when different concentrations of microcapsules are used in the padding bath, the quantity of microcapsules that remain on the fabric is different. SEM is a good technique for qualitative analysis and indicates this behaviour, but when FTIR is used, a process is proposed to quantify their presence in the fabric.

When microcapsules are on the fabric at different concentrations, FTIR spectra shows some variations We have demonsrated that all of these variations are focused on a band assigned to amine group from microcapsules and that is named band II. To obtain this band the region of OH stretching between 3700 and 3000 cm^{-1},has been deconvoluted on three Gaussian peaks, with maximums at wavenumber 3500 cm^{-1} for band I, 3450 cm^{-1} for band II and 3300 cm^{-1} for band III.

The ratio between area II/ area I presents a linear correlation with the concentration bath padding, and the one between area II/area III presents the same tendency although it is not such a linear correlation because of overlapping curves in that zone. This ratio allows us to quantify the presence of microcapsules in the fabrics, and although we can not determine the exact amount, it is possible to express it in relation to the initial microcapsule bath concentration. It has been checked that FTIR analysis proposed is sensitive enough to detect variations on fragrance concentration, so we can analyze the microcapsules concentration and if they are full or partially empty.

The microcapsules were analyzed in order to determine the thermal effect when temperatures exceed 120º C. This behaviour has been studied using Differential Scanning Calorimetry (DSC) study and thermogravimetric analysis (TG). It was found that fragrance loss from microcapsules occurs at temperatures between 90º C and 150º C, and that membrane polymer is degraded at about 300º C.

The SEM study shows that when hot air or any treatment at these temperatures is applied to fabrics, it can give rise to deflation of microcapsules and this can be quantified by FTIR in the OH stretching region described above (3700 – 3000 cm^{-1}). The ratios between area II/ area I or area II/area III, present a way of measuring changes in microcapsule presence, in relation to the results obtained in the padding concentration study.

Results show that micorcapsules cannot withstand temperatures higher than 120º C, so it means that if fabric is dried with hot air at temperatures higher than this, the microcapsules

become deflated, and this is manifested in results at 140º C and 160º C, as SEM or FTIR ratio shows.

As a consequence of this effect, we investigated the ironing process in which fabrics were ironed at 110º C, 150º C or 200º C, depending on the kind of fibre. In this case, the fabric was cotton so it could be ironed at 200º C. Experience shows that thermal treatment of microcapsule-impregnated cotton fabric causes damage to the microcapsules when the temperature exceeds 120º C, but it is clear that the number of times the iron is applied also affects them. We demonstrated, by FTIR analysis of ratios between area I / area II, and between area II/ area III that the higher the temperature the greater the damage caused. It was also found that the more times the fabric is ironed, the more microcapsules are damaged.

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FIGURE CAPTIONS

Figure 1.- Calorimetric curves of CENTER FINISH 164/02 a) Perppermint 1 and b) Peppermint 2. Black = emulsion product. Red= dried and powdered product.

Figure 2.- Calorimetric curves of CENTER FINISH 164/02 Apple. Red= dried and powdered product.

Figure 3.- Calorimetric curve comparison between CENTER FINISH 164/02 Perppermint 1 and Perppermint 3

Figure 4.- Weight loss related to temperature. a) Perppermint 1. b) Powdered Perppermint 1

Figure 5. Cotton fabric with microcapsules by bath exhaustion. Magnification x500.

Figure 6. Cotton fabric padded at diferent concentrations.Magnification x1000.
*Figure 6.1 fabric C31 = **10** g/l Perppermint 3 (CETERFINISH 164/02) and 15 g/L Center BC resin.*
*Figure 6.2 fabric C33 = **30** g/l Perppermint 3 (CETERFINISH 164/02) and 15 g/L Center BC resin.*
*Figure 6.3 fabric C34 = **40** g/l Perppermint 3 (CETERFINISH 164/02) and15 g/L Center BC resin.*
*Figure 6.4 fabric C36 = **60** g/l Perppermint 3 (CETERFINISH 164/02) and15 g/L Center BC resin.*

Figure. 7..- Infra Red Spectra of microencapsulated fabrics at different padding concentrations with Perppermint 3. T0 = Cotton fabric without microcapsules; C31= Cotton fabric with microcapsules 10 g/L.; C33= Cotton fabric with microcapsules 30 g/L; C34= Cotton fabric with microcapsules 40 g/L; C36= Cotton fabric with microcapsules 60 g/L

Figure 8. OH stretching region deconvoluted from figure 6 spectra.
Figure 8.a = Cotton fabric;
Figure 8.b = Cotton fabric with 10 g/L of Perppermint 3;
Figure 8.c = Cotton fabric with 30 g/L of Perppermint 3;
Figure 8.d = Cotton fabric with 40 g/L of Perppermint 3;
Figure 8.e = Cotton fabric with 60 g/L of Perppermint 3;

Figure 9.- Infra Red Spectra of cotton fabrics with 60 g/L of microcapsules when treated by hot air. C36STF = Cotton fabric with 60g/l of microcapsules and without air treatment; C36120 = Cotton fabric with 60g/l of microcapsules and dried at 120º C; C36140 = Cotton fabric with 60g/l of microcapsules and dried at 140º C; C36160 = Cotton fabric with 60g/l of microcapsules and dried at 160º C.

Figure 10.- OH stretching region deconvoluted from figure 9 spectra
10.a = Fabric without treatment;
10.b= Fabric dried at 120º C;
10.c= Fabric dried at140º C;
10.d= Fabric dried at 160º C:

Figure 11..- Cotton fabric with 60g/L CENTER FINISH 164/02 Perppermint 3 heated at different temperatures.
Figure 11.1 Fabric C36 500x magnification dried at 120º C.
Figure 11.2 Fabric C36 2000x magnification dried at 120º C.
Figure 11.3 Fabric C36 500x magnification dried at 140ºC.
Figure 11.4. Fabric C36 2000x magnification dried at 140ºC
Figure 11.5.Fabric C36 500x magnification dried at 160ºC.
Figure 11.6. Fabric C36 2000x magnification dried at 160ºC

Figure 12.- Areas ratios, from dried fabrics, related to initial padding bath concentration.

Figure 13- SEM images for cotton with 60 g/L of microcapsules ironed fabrics at different temperatures and some iron cycles. Magnification x1000.
13.1. Fabric ironed at 110º C and 1 pressing.
13.2. Fabric ironed at 110º C and 5 pressing
13.3. Fabric ironed at 110º C and 10 pressing
13.4. Fabric ironed at 150º C and 1 pressing.
13.5. Fabric ironed at 150º C and 5 pressing.
13.6. Fabric ironed at 150º C and 10 pressing.
13.7. Fabric ironed at 200º C and 1 pressing
13.8. Fabric ironed at 200º C and 5 pressing.
13.9. Fabric ironed at 200º C and 10 pressing.

Figure 14.- OH stretching region spectra of fabrics with 60 g/L of microcapsules and ironed at 110º C, 0 times, 1 time, 5 times and 10 times.

Figure 15.- OH stretching region spectra of fabrics with 60 g/L of microcapsules and ironed at 150º C 0 times, 1 time, 5 times and 10 times

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Figure 16.- OH stretching region spectra of fabrics with 60 g/L of microcapsules and ironed at 200º C. at 0 times, 1 time, 5 times and 10 times.

Figure 17.- OH stretching region deconvolution from fabric with 60 g/L of microcapsules ironed at 110º C.
a = without pressing,
b= 1 pressing;
c= 5 pressing;
d= 10 pressing

Figure 18. - Areas ratios values from deconvoluted spectra of cotton fabric with 60 g/L of microcapsules ironed at 110º C. 1 pressing, 5 pressing, and 10 pressing.

Figure 19. - Area ratio values from deconvoluted spectra of cotton fabric with 60 g/L of microcapsules ironed at 150º C. 1 pressing, 5 pressing, and 10 pressing.

Figure 20.- Area ratio values from deconvoluted spectra of cotton fabric with 60 g/L of microcapsules ironed at 200º C. 1 pressing, 5 pressing, and 10 pressing.

Table 1. Dried extract weight for microcapsules weight	
PRODUCT	% DRY WEIGHT
Center Finish 164/02 (Peppermint nº 1)	47%
Center Finish 164/02 (Apple)	43%
Center Finish 164/02 (Peppermint nº 3)	27%
Resina Center BC (Acrylic dispersion)	39%

Table 2.- Variation of ratio band areas when concentration of microcapsules is modified.

Padding bath	BAND I	BAND II	BAND III	Ratio Band Areas	
	3500 cm^{-1}	3300 cm^{-1}	3200 cm^{-1}		
	Area Units			II/ I	II / III
T0 W.T.	2.27	0.00	5.57	**0.00**	**0.00**
10 g/L	3.30	3.47	6.85	**1.05**	**0.51**
30 g/L	1.87	2.72	3.86	**1.46**	**0.71**
40 g/L	1.56	2.35	2.18	**1.51**	**1.08**
60 g/L	3.63	7.82	1.78	**2.15**	**4.39**

Table 3.- Variation of ratio band areas when fabric (padding 60g/L) is heated at different temperatures.				**RATIO**	
	BAND I 3500	BAND II 3300	BAND III 3200	**II / I**	**II / III**
W. T	1.76	6.28	1.50	**3.57**	**4.20**
120º C	3.63	7.82	1.78	**2.15**	**4.39**
140º C	6.11	4.09	3.06	**0.67**	**1.34**
160º C	9.07	3.46	4.15	**0.38**	**0.83**

Table 4.- Variation of ratios band areas when fabric is ironed at 110º C					
	BAND I	BAND II	BAND III	Ratio Areas	
	3500	3300	3200	II / I	II / III
No Iron	3.63	7.82	1.78	**2.15**	**4.39**
Iron 110ºC .1 app.	1.27	2.41	0.70	**1.90**	**3.43**
Iron 110ºC . 5 app.	2.24	2.64	2.40	**1.18**	**1.10**
Iron 110ºC 10 app.	3.84	1.23	1.06	**0.32**	**1.16**