

# Continuous Production of Melamine-Formaldehyde Microcapsules Using a Mesostructured Reactor

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Cite This: *Ind. Eng. Chem. Res.* 2020, 59, 18510–18519

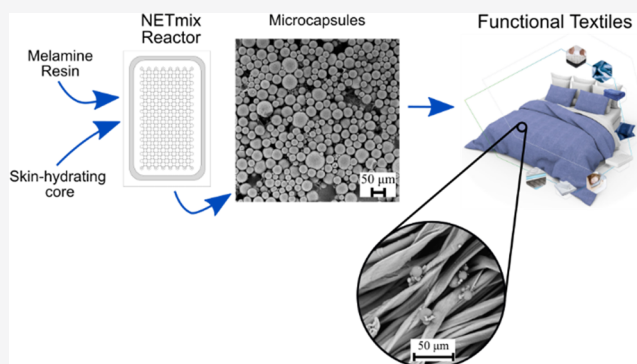
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**ABSTRACT:** A mesostructured NETmix reactor was adapted to develop a continuous process to produce microcapsules, focusing on the steps commonly used in batch formulation: the emulsion and cure. Microcapsules were formed through a polycondensation process by coating Miglyol, a skin-hydrating emollient, with melamine-formaldehyde, which is a resistant shell material with surface smoothness. Different recirculation times were tested for the cure step. Microcapsules show a spherical shape and smooth membrane. Efficiencies of encapsulation of 75%, core contents of 70%, and diameters around 20  $\mu\text{m}$ , ideal range for textile impregnation, were obtained. Scanning electron microscopy shows the integrity of microcapsules on textiles after impregnation and their flexible behavior. The thermogravimetric analysis confirmed the thermal stability of microcapsules up to 210  $^{\circ}\text{C}$ . With the NETmix reactor, it is possible to reduce the cure time of traditional batch formulation in 80%, producing microcapsules with similar characteristics in a continuous process.



## 1. INTRODUCTION

Microencapsulation involves coating of an active ingredient by a membrane of another material.<sup>1</sup> The core of microcapsules is the active principle, which is responsible for its functionalization and, depending on its characteristics, the respective application. The external material, the shell, covers the core, providing protection against external factors and stability of the active principle and masking unwanted properties such as odor or taste.<sup>2</sup> These properties can be a great advantage and benefit depending on the final application. Food,<sup>3,4</sup> medicine,<sup>5,6</sup> agriculture,<sup>7</sup> cosmetics,<sup>8,9</sup> or textile industries<sup>10–14</sup> are some examples of areas of interest. The textile industry is an important area of interest for microencapsulation since functionalized textiles promote comfort and protection. According to Devan Chemicals, fabrics can be divided into four markets, bed and bath, home, clothing, and mobility,<sup>15</sup> and in all cases, the functionalized fabrics must have the same characteristics as a nontreated fabric, for example, a soft touch or the visual effect of the fabric. The encapsulated active principle is chosen based on the characteristics that are responsible for the fabrics' functionalization. Antibacterial materials such as vitamins<sup>16,17</sup> are encapsulated to avoid the growth of microorganisms and fungi in bed clothes or ligatures.<sup>18</sup> Carrier oils such as triglycerides are non-irritating skin emollients<sup>19</sup> with excellent skin absorption<sup>20</sup> and are encapsulated due to their skin-hydrating properties. These

active principles are marketed in fabrics, which can be used for long contact periods with skin, such as cosmetic textiles.<sup>21</sup>

There are several methods of microencapsulation, but in most cases, with common steps such as preparation of aqueous and organic solutions,<sup>10,22,23</sup> emulsification,<sup>1,11,22,24–26</sup> curing,<sup>10,27</sup> and/or solidification/hardening of microcapsules.<sup>1,11,24,25</sup>

Emulsification, with the formation of a stable emulsion, is the key step in microencapsulation since the diameter of oily droplets defines the diameter of the microcapsules.<sup>28</sup> A good emulsion promotes the stability of droplets during the entire process.

Droplet size control is particularly difficult when the emulsification process is scaled from laboratory to industrial scale, commonly polydisperse origination emulsions.<sup>28–30</sup> Furthermore, in batch processes, care must be taken to obtain a homogeneous and stable emulsion to produce microcapsules with consistent properties in terms of morphology, diameter, and encapsulation efficiency.<sup>31</sup> Different types of stirring

Received: May 28, 2020

Revised: September 14, 2020

Accepted: September 16, 2020

Published: September 16, 2020

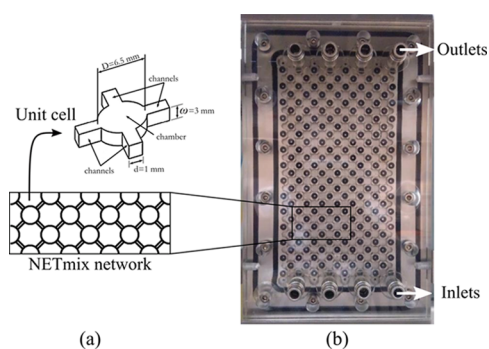


systems are often used at laboratory scale, such as mechanical stirrers, ultrasonic mixers, and homogenizers. To obtain a good mixture, various types of stirring systems can be used, and it must be ensured that conditions such as the power of the stirrer, the stirrer velocity, or its positioning promote mixing through the whole volume of the vessel.<sup>28,32</sup>

Interfacial polycondensation and in situ polymerization are some of the chemical methods used to produce microcapsules with melamine resin as a wall material. These procedures require a step of prepolymer formation, where monomers are added in a solution, and then a cure of prepolymer around the oily droplets is taken by increasing the temperature.<sup>32</sup> Usually, traditional batch methods to produce melamine-based microcapsules present the main disadvantage of long (around 4 h) duration procedures, where the cure step takes 2 to 3 h.<sup>22,33–35</sup>

In the past few years, nonconventional techniques, such as microfluidic devices, have gained attention to produce emulsions and microcapsules in continuous mode. Different geometries of microfluidic capillaries such as coflow,<sup>36,37</sup> flow-focusing,<sup>37,38</sup> and T-junction and their variants (cross section or V-junction)<sup>39,40</sup> have been used. Some advantages of this technique are the combinations of different geometries in the different steps of the microencapsulation process<sup>41,42</sup> and the production of droplets of high control of internal morphology.<sup>43</sup> However, this technique is mostly used at laboratory scale and due to the high cost for manufacturing of the microfluidic devices. These high costs are due to the complex fabrication of miniaturized units, requiring special operation procedures and specially trained researchers.<sup>44</sup> Additionally, one of the most used materials to fabricate the microfluidic capillaries (polydimethylsiloxane) has limitations, such as working at high temperatures and chemical incompatibility with organic solvents.<sup>44,45</sup>

The main goal of this work was to produce microcapsules in continuous mode using a NETmix technology, creating a stable oil-in-water emulsion and reducing the operation time of the cure step. The mesostructured reactor NETmix is a patented technology<sup>46</sup> developed at LSRE-LCM, and it consists of a network of interconnected chambers and channels (Figure 1a), where chambers operate as mixing zones and



**Figure 1.** (a) Schemes of NETmix network and unit cell and (b) prototype of Lab-scale NETmix 2D.

channels behave as a plug flow. Above a critical Reynolds number of 150, this system evolves to a self-sustained oscillatory laminar flow regime, inducing local strong laminar mixing.<sup>47–49</sup> This technology applied to microencapsulation allows an effective reactant distribution promoting a good emulsification step, controlling the reactant flow, and decreasing the time of procedure.<sup>48</sup> Another advantage of

NETmix is that different injection schemes may be used by feeding the reactants to different inlet channels. A continuous process for the production of highly pure, synthetic nanocrystalline hydroxyapatite using NETmix was developed and implemented at the industrial level (<https://www.fluidinova.com/>).<sup>50,51</sup> Other applications using NETmix include the production of nanohydroxyapatite/chitosan dispersions and photocatalysis processes.<sup>52,53</sup>

A NETmix prototype, the Lab-scale NETmix 2D (Figure 1b) with geometry and characteristics described by Fonte et al.,<sup>54</sup> was used to produce a stable oil-in-water emulsion and to cure the membrane of the microcapsules. This NETmix reactor consists of a network of 29 rows and 8 columns of cylindrical chambers with a diameter ( $D$ ) of 6.5 mm and depth ( $w$ ) of 3 mm. The prismatic channels have a width ( $d$ ) of 1 mm and the total volume of the reactor is 23 mL.

Commercial melamine-formaldehyde capsules were chosen as a case study for a project in collaboration with Devan Chemicals, who provided the reactants and batch formulation. Melamine-formaldehyde is used as a shell material due to several advantages such as good resistance against water and heat, protecting the core, high hardness and mechanical robustness, and surface smoothness, which is a benefit for textile applications.<sup>22,27,55</sup> According to Devan Chemicals, in these capsules, a methylated melamine resin, with a low level of formaldehyde, is used, as well as formaldehyde quenchers, resulting in microcapsule slurries with 200–300 ppm formaldehyde. When this type of product is applied in fabrics, the levels of formaldehyde are below 75 ppm, which enables its use in underwear clothing fabrics, and, in many cases, below 16 ppm, suitable for use in fabrics for babywear.

Miglyol, a carrier oil, was used as a core material due to its characteristics of skin-hydrating agents and proper skin absorption.<sup>20</sup> Furthermore, this caprylic/capric triglyceride has an excellent emollience and is a good carrier material for encapsulated substances that require oxidative and physical stability, such as vitamins.<sup>20,56</sup> Oily droplets were encapsulated by melamine-formaldehyde through an interfacial polycondensation process. The produced microcapsules were impregnated by the padding process for the purpose of obtaining functionalized textiles. Microcapsules were characterized by optical microscopy (OM) and scanning electronic microscopy (SEM) to evaluate morphology and size. Particle size distribution, solid and core content, encapsulation efficiencies, and shell thickness were also evaluated. Thermal stability was accessed by thermogravimetric analysis. Microcapsules impregnated in textiles were observed with SEM.

## 2. MATERIALS AND METHODS

**2.1. Materials.** A melamine-formaldehyde prepolymer and Miglyol 812 were used respectively as the membrane material and active principle. An aqueous solution of urea (37.5 wt %, Sigma-Aldrich) was used as the coating agent. For pH control, an aqueous solution of sodium hydroxide (25 wt %, Fisher Chemicals) was used. Isopropyl alcohol (VWR Chemicals) was used to wash the microcapsule solution and acetone (Fisher Chemicals) was used as a solvent for Soxhlet extraction.

**2.2. Microencapsulation Process.** Microcapsules were prepared by a polycondensation method for which the original batch formulation of melamine-formaldehyde microcapsules was provided by Devan Chemicals and comprises the following steps: emulsification of melamine-formaldehyde prepolymer and Miglyol by moderate homogenization for 4 min; cure of

microcapsules' membrane in a batch reactor by heating the solution from room temperature to 80 °C by a ramp-up of 0.6 °C/min and extending for more 60 min at a constant temperature; coating by addition of a urea solution and adjusting the microcapsule solution to neutral pH; addition of a few drops of a stabilizer to ensure that phase separation does not occur.

An emulsion of melamine-formaldehyde prepolymer (MFPP) and Miglyol was obtained in the experimental setup shown in Figure 2a using the NETmix reactor at room temperature in two modes: using just one single (first) pass or using recirculation of 4 min (the emulsification time in the batch formulation) after the first pass. In Figure 2b, black filled arrows represent the first emulsion circuit and white filled arrows represent the emulsion recirculation circuit. At the initial feeding of MFPP and Miglyol streams for the emulsion step, the three-way valve is opened toward the waste stream to flush out any water that may remain in the reactor, ensuring that the whole system is filled with reactants only. Afterward, the three-way valve is turned to the product vessel (icon 3 of Figure 2b) to collect the produced emulsion.

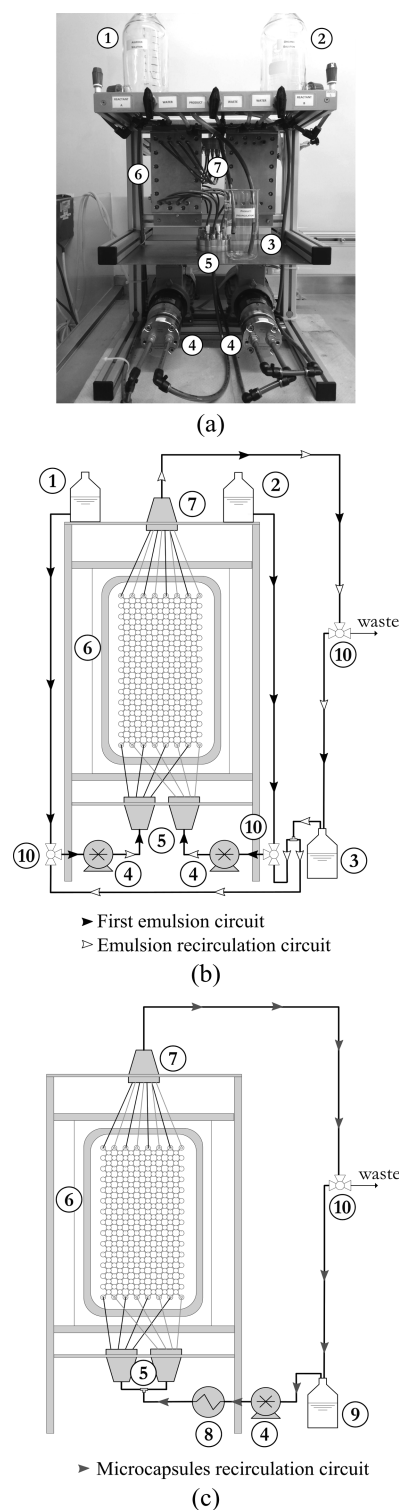
The emulsion then undergoes a cure step where the temperature is increased to 80 °C, enabling the formation of the microcapsule shell. This cure step was done by recirculating the emulsion in the NETmix reactor, as shown with gray filled arrows in Figure 2c. Two different cure times were tested in NETmix: 120 min, similar to batch mode, and a shorter period of 30 min.  $Re \approx 200$ , above the critical Reynolds number, was set for the emulsion and cure steps.

After the recirculation, the NETmix system is drained and the solution of cured microcapsules is discharged in the product vessel (icon 9 in Figure 2c). Then, the solution is transferred to the batch reactor for the final coating step, which is done by adding an aqueous solution of urea and adjusting the solution pH to neutral with a sodium hydroxide solution. Finally, a few drops (circa 1 drop per 50 mL of solution) of a stabilizer are added to the solution to prevent particle coalescence and sedimentation.

**2.3. Impregnation of Textile Substrates.** The functionalization of cotton fabrics was made by padding, a traditional process of impregnation, using methodologies patented by Devan Chemicals.<sup>57,58</sup> A nonreactive system, i.e., an impregnation bath with the microcapsule solution and water, was prepared. Fabrics were submerged in this bath and then passed through rollers under a pressure of 4 bar to promote the microcapsule adhesion. The used quantity of dried microcapsule solution was 12 g/m<sup>2</sup> per textile substrate. Fabrics were then dried at 80 °C for 10 min to fix the microcapsules.

**2.4. Characterization Techniques.** **2.4.1. Optical Microscopy (OM).** The emulsion and cured and final microcapsules were observed by optical microscopy using a Leica DM 2000 apparatus with different resolutions (100× and 200×). Sampling of the emulsion and cured microcapsules was done by pipetting through a plastic Pasteur pipette circa 1.5 mL from the respective product vessel (icons 3 and 9 in Figure 2). These measurements were used to evaluate the behavior of oily droplets and produced microcapsules in terms of size, morphology, and agglomerates.

**2.4.2. Scanning Electronic Microscopy (SEM).** A desktop scanning electron microscope (Phenom ProX) was used to verify the shell wall integrity, aggregation, morphology, and size of microcapsules. Some droplets of a diluted final solution are placed under a carbon tape. Pins with samples were dried at



**Figure 2.** (a) Experimental setup of Lab-scale NETmix; installation schemes for (b) emulsification step and (c) cure step. Legends: 1, MFPP vessel; 2, Miglyol vessel; 3, product vessel (emulsion); 4, pumps; 5, distributor; 6, LabNETmix reactor; 7, collector; 8, inline heater; 9, product vessel (microcapsules); 10, three-way valve.

room temperature for 24 h. SEM was also used to check the microcapsules' impregnation in textiles and verify the dispersion of microcapsules and their behavior after the padding process.



**2.4.3. Laser Diffraction Size Distributions.** Size distributions of emulsion droplets and cured and final microcapsules were obtained using a laser diffraction particle size analyzer LS 230 (Beckman Coulter). Sampling was described in Section 2.4.1. The mean values of distributions in volume were determined. The size distributions allow us to infer the range of obtained diameters and the presence of agglomerates of droplets or microcapsules.

Volume size distributions were determined from two measurements of each sample of emulsion droplets and cured and final microcapsules. From each distribution, a value of the mean diameter was obtained. For each sample, an average of mean diameters was calculated as well as its standard deviation, considering two observations of mean diameters.

**2.4.4. Shell Thickness Estimative.** The membrane thickness,  $d_s$ , is usually estimated by an equation reported by Sliwka for spherical microcapsules of core-shell type<sup>59</sup> and it was used in this work with a few modifications: different densities of core,  $\rho_c$  and shell,  $\rho_s$ , and the actual encapsulated active principle mass,  $w_c$ , were assumed, rather than assuming 100% encapsulation efficiency. The following relationship was obtained

$$d_s = (r_m - r_c) = \left[ \left( \frac{w_s \rho_c}{w_s \rho_s} + 1 \right)^{1/3} - 1 \right] r_c \quad (1)$$

where  $r_m$  is the mean outer radius of the microcapsule,  $r_c$  is the radius of the inner core, and  $w_s$  is the wall material mass. The densities are  $\rho_c = 950 \text{ kg/m}^3$  and  $\rho_s = 1220 \text{ kg/m}^3$ .

**2.4.5. Solid Content.** Solid content estimates the percentage of the mass of microcapsules (shell material and encapsulated oil) in the total mass of the final solution (containing microcapsules, water, and some nonencapsulated oil). The determination of solid content was based on the European norm 827 (British Standards Institution, 2005).<sup>60</sup> This method allows us to obtain the solid content percentage by the difference in the initial mass of microcapsule solution and the final mass after evaporation of water. A mass of microcapsule solution,  $m_i$ , is weighed and placed in an oven at 100 °C. After 30 min, the sample is removed from the oven and placed in a desiccator for 15 min. The residual mass is weighed, and the sample is placed again in the oven for 30 min. The process is repeated until the difference of followed weights of residual mass does not exceed 2 mg; that is, the residual mass,  $m_f$ , is stable. The solid content percentage is obtained by

$$\text{SC (\%)} = \frac{m_f}{m_i} \times 100 \quad (2)$$

**2.4.6. Core Content and Encapsulation Efficiency.** Core content is the mass percentage of the active principle, which constitutes the microcapsule core. Soxhlet extraction and Buckner filtration were used to obtain the core content and encapsulation efficiency of the active principle. A known mass of microcapsule solution is filtrated and washed with isopropyl alcohol to remove the nonencapsulated oil dispersed in the solution. The filter cake of microcapsules is then dried in an oven at 100 °C for 24 h.

For core content quantification, a given mass of dried microcapsules,  $m_{\text{mcp}}$ , is transferred to a thimble, which is then placed inside a Soxhlet apparatus setup with acetone as the solvent. Extraction occurs for 16 h with 5 min cycles.

Afterward, the thimble is removed and dried in the oven at 100 °C for 24 h to evaporate the residual solvent. The remaining material in the thimble corresponds to the microcapsule shell and the respective mass,  $m_s$ , is obtained. The core content is determined by

$$\text{CC (\%)} = \frac{m_{\text{mcp}} - m_s}{m_{\text{mcp}}} \times 100 \quad (3)$$

where  $m_{\text{oil, enc}} = m_{\text{mcp}} - m_s$  is the mass of the encapsulated oil.

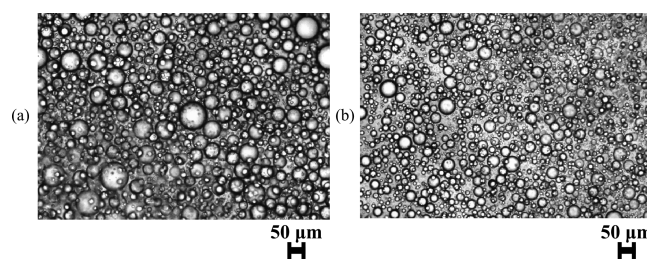
To obtain an estimated value of encapsulation efficiency, the filtrate resulting from the washing step is dried in a 100 °C oven. From the filtrate, the water is evaporated, and the mass of the free, nonencapsulated oil,  $m_{\text{oil, free}}$ , is obtained. The encapsulation efficiency is then given by

$$\text{EE (\%)} = \frac{m_{\text{oil, enc}}}{m_{\text{oil, free}} + m_{\text{oil, enc}}} \times 100 \quad (4)$$

**2.4.7. Thermogravimetric Analysis.** Thermogravimetric (TG) analysis was performed on a TG 209 F3 Tarsus by NETZCH. Samples of about 7–8 mg each were put on aluminum pans and heated at a rate of 10 °C/min from room temperature to 600 °C under a constant N<sub>2</sub> flow rate of 50 mL/min. TG enables the evaluation of the stability of microcapsules by heating through loss mass measurements.

### 3. RESULTS AND DISCUSSION

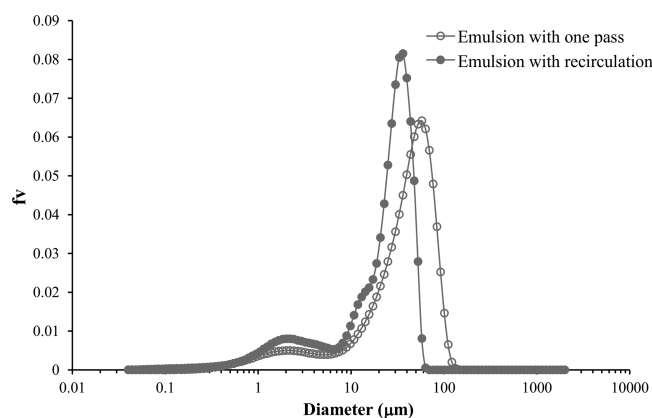
**3.1. Production of Microcapsules.** **3.1.1. The Emulsion Step.** In the first set of experiments, the emulsions were obtained using a single pass in the NETmix reactor, mixing MFPP and Miglyol, at  $Re \approx 200$ . The flow rate was measured at 5 L/min using a simple bucket and stopwatch method. To evaluate the effect of emulsion recirculation, the second set of experiments was done by placing the resulting emulsion through a recirculation process in the NETmix for a period of 4 min; for this value of  $Re$ , the passage time in the reactor system is equal to 3.5 s, and thus, this recirculation time corresponds to approximately 70 passes. Figure 3 shows optical microscopy images of the emulsion obtained with a single pass and with recirculation, and Figure 4 shows the respective droplet size distributions.



**Figure 3.** Optical microscopy images of produced emulsion with (a) a single pass and (b) recirculation. Magnification of 100 $\times$ .

An emulsion containing well-defined spherical droplets with no agglomerates is observed in Figure 3a. A wide range of droplet sizes is observed including large droplets with diameters of circa and above 40  $\mu\text{m}$ . These diameters are in accordance with the droplet size distributions obtained by laser diffraction (Figure 4). The mean diameter is  $44.4 \pm 0.2 \mu\text{m}$ , and a bimodal distribution in volume is observed, with a higher intensity peak between 10 and 100  $\mu\text{m}$ . Even though large diameters are observed, these emulsions remain stable.





**Figure 4.** Droplet size distribution of emulsion with a single pass and recirculation.

Figure 3b shows the emulsion obtained after recirculation, where again well-defined droplets with uniform and spherical shape and the absence of agglomerates are observed. These emulsions are also stable. However, a decrease in the droplet size is clearly observed, which is confirmed in Figure 4 showing the volume droplet size distributions for selected trials with and without recirculation. The mean droplet diameter here is circa  $26.3 \pm 0.2 \mu\text{m}$  and the main peak of the bimodal distribution has a higher intensity and is observed between 20 and  $50 \mu\text{m}$ .

For all trials, after 4 min of recirculation, the emulsion identity point has been reached with similar droplet size distributions for all experiments (data not shown) and mean droplet diameters ranging from  $23.8 \pm 0.2$  to  $32.3 \pm 0.7 \mu\text{m}$ , resulting in a mean droplet diameter for all emulsion trials of  $27 \pm 3 \mu\text{m}$ .

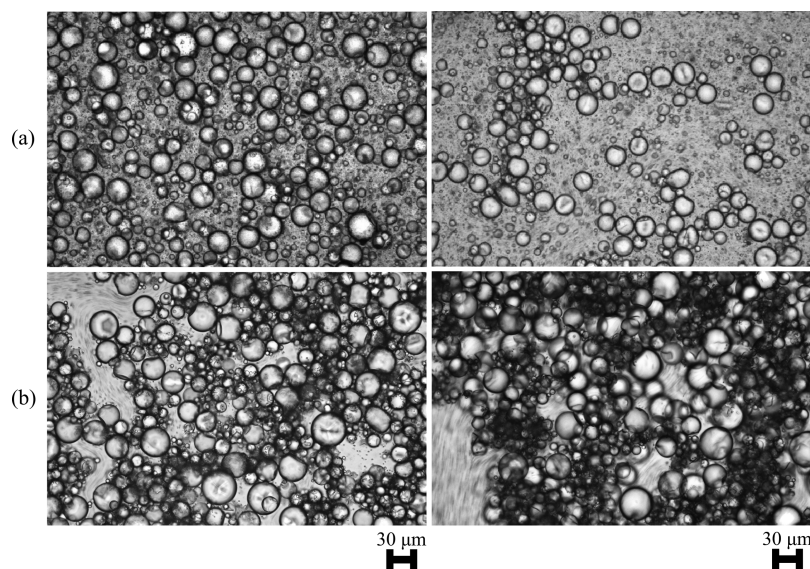
Droplet size is a key parameter in microcapsule textile applications. On the one hand, small microcapsules are easier to fix in fabrics.<sup>11,61</sup> However, microcapsules with sizes under  $10 \mu\text{m}$  will not break easily since they can be entrapped between the fabric fibers, and thus, the active principle release and diffusion process are hindered and the respective

performance becomes limited.<sup>33</sup> On the other hand, microcapsules with sizes above  $30\text{--}40 \mu\text{m}$  are too fragile and have higher probability of rupture on textiles, releasing the active principle or even breaking during the impregnation process. Also, the larger microcapsules can leave the fabrics after a few washing cycles.<sup>11,61</sup> Thus, it is generally assumed that the preferred microcapsule sizes for textile applications are between 10 and  $40 \mu\text{m}$ ,<sup>33</sup> the range obtained in the experiments with recirculation in the NETmix. Therefore, in the following experiments for the cure step, all emulsions were obtained with 4 min recirculation.

**3.1.2. The Cure Step.** After the emulsion step, the cure step was carried out by recirculating the mixture in the NETmix reactor while increasing the temperature to  $80 \text{ }^\circ\text{C}$ . Figure 5 shows optical images of the microcapsules in solution after each cure step (left-hand side images). The rise in temperature was done in two different ways. Figure 5a shows microcapsules produced with a continuous temperature increase of  $0.75 \text{ }^\circ\text{C}/\text{min}$  to  $80 \text{ }^\circ\text{C}$  (circa 1 h and 20 min) and then kept constant for another 40 min for a total period of 2 h. In Figure 5b, a temperature increase of  $4 \text{ }^\circ\text{C}/\text{min}$  was set, with circa 15 min to reach  $80 \text{ }^\circ\text{C}$  and a further 15 min at constant temperature for a total of 30 min.

In terms of morphology, all cured microcapsules have the same characteristics. A well-defined spherical shape and the absence of agglomerates were observed. Some cured microcapsules are flat, characteristic of this type of membrane.<sup>33,35</sup> Microcapsules cured for just 30 min present similar morphology characteristics as those cured for 120 min. This indicates that the cure time can be reduced using the NETmix reactor, which is noteworthy when compared with a typical cure time of around 150 min in the traditional batch process.

After curing, the microcapsules undergo the final coating process as described in Section 2.2. These microcapsules, as shown in Figure 5 (right-hand side images), are stable, do not disintegrate, and maintain the same morphology after the cure step until the end of the production process.



**Figure 5.** Optical microscopy images of microcapsules after the cure step in NETmix (left) and final solution (right) for a total recirculation period of (a) 2 h and (b) 30 min. Resolution of  $200\times$ .

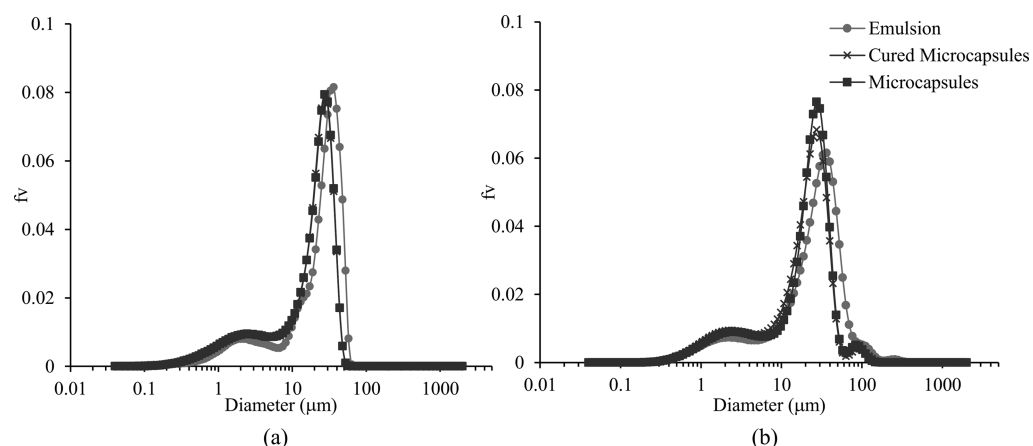


Figure 6. Volume size distribution for a total recirculation period of (a) 2 h and (b) 30 min.

Table 1. Measured Mean Volume Diameters, Shell Thickness, Solid and Core Content, and Encapsulation Efficiency<sup>a</sup>

circulation	mean diameter ( $\mu\text{m}$ )			shell thickness ( $\mu\text{m}$ )	solid content (%)	core content (%)	encapsulation efficiency (%)
	emulsion	cured microcapsules	microcapsules				
120 min	27	21	20	1.3	25	75	75
30 min	32	23	24	1.6	25	73	75

<sup>a</sup>Note that all data correspond to the mean value of two measurements.

Figure 6 shows the measured size volume distributions for the emulsion droplets, the cured microcapsules (just after the cure step), and the final microcapsules for selected trials.

The bimodal distribution observed for the emulsion is maintained after the cure and final steps. Distributions of cured and final microcapsules match perfectly, confirming the stability of microcapsules until the end of the process; that is, there is no disintegration or agglomeration. However, the distributions show a slight decrease in size for the cured microcapsules when compared with the emulsion droplet sizes. This is confirmed by the mean volume diameters in Table 1; mean diameters range from  $21.1 \pm 0.6$  to  $23.2 \pm 0.3 \mu\text{m}$ , resulting in a mean droplet diameter for all trials of  $22 \pm 1 \mu\text{m}$  for the cured microcapsules and from  $20.4 \pm 0.1$  to  $24.4 \pm 0.2 \mu\text{m}$ , resulting in a mean droplet diameter for all trials of  $22 \pm 2 \mu\text{m}$  for the final microcapsules.

The decrease in size observed between the emulsion droplets and cured microcapsules is slightly lower for the 30 min curing trial. At the beginning of the cure step, the temperature is not high enough to cure the shell. The microcapsule surface only starts to consolidate at a temperature around  $50 \text{ }^\circ\text{C}$ , at which point the membrane is easily detected by OM (no data are presented). Thus, in the first minutes of recirculation in the cure step, the droplet diameters decrease slightly until the  $50 \text{ }^\circ\text{C}$  temperature is reached. As previously mentioned, microcapsules obtained with 120 and 30 min curing times were performed at different rates of temperature rise. This means that a temperature of  $50 \text{ }^\circ\text{C}$  is reached after circa 40 and 8 min for microcapsules cured for 120 and 30 min, respectively, leading to slightly higher diameters for the 30 min curing time.

**3.1.2.1. Solid Content, Core Content, and Encapsulation Efficiency.** Table 1 shows the solid content, core content, and encapsulation efficiency values determined for the different recirculation periods. Similar values were obtained in both cases with maximum uncertainty within 0.2, 10, and 2% for

solid content, core content, and encapsulation efficiency, respectively.

Core content values show that microcapsules are composed of more than 70% of the oily active principle and the remaining percentage corresponds to the shell material. These values are expected for melamine-formaldehyde-based microcapsules produced by methods similar to polycondensation. The literature reported values of core content around 50–80%.<sup>62–64</sup> The high value for the encapsulation efficiency indicates that only a small percentage of oil was not encapsulated.

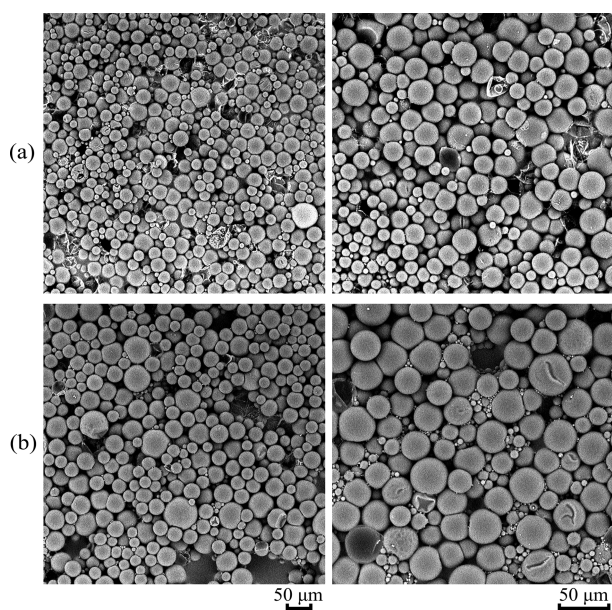
Table 1 also shows the estimated shell thickness, which is above  $1 \mu\text{m}$  for both cases. Microcapsules with 120 min of circulation show a smaller shell thickness ( $1.3 \mu\text{m}$ ) compared with microcapsules with 30 min ( $1.6 \mu\text{m}$ ) of circulation, which is expected due to its higher core content (75% versus 73%).

Finally, robustness and stability after washing were confirmed by submitting the dried microcapsules to a new cycle of washing and filtration and verifying that there was no oil in the filtrate.

**3.1.2.2. Scanning Electron Microscopy.** Figure 7 shows SEM images of the final microcapsules obtained for the two different recirculation periods. Some microcapsule deformation and a few broken microcapsules are observed, but no membrane fragments that could result from the disintegration of microcapsules are detected. In both cases, microcapsules show the same characteristics in terms of morphology: intact microcapsules with spherical shape and smooth membrane. This type of morphology was also reported in previous works for melamine resin microcapsules containing a fragrance for textile impregnation.<sup>22,65</sup> The sizes of microcapsules match the range of size distributions in volume. Two ranges of diameters are observed: some microcapsules with a size around  $5 \mu\text{m}$  and, in a larger percentage, microcapsules with a size around  $20 \mu\text{m}$ .

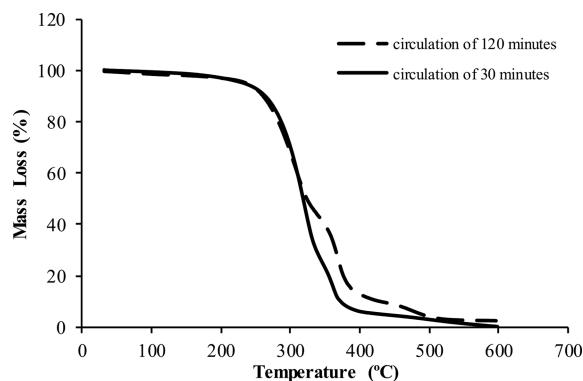
**3.1.2.3. Thermogravimetric Analysis.** TG thermograms of produced microcapsules obtained with different circulation





**Figure 7.** SEM images of microcapsules for a total recirculation period of (a) 2 h and (b) 30 min. Resolutions of 500 $\times$  (left) and 1000 $\times$  (right).

times are shown in Figure 8. In both samples, no substantial water is observed since, until 100 °C, the percentage of weight

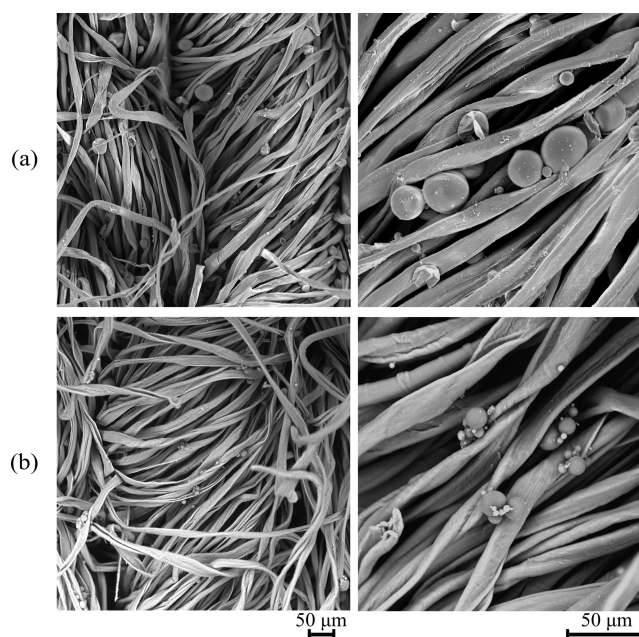


**Figure 8.** TG thermograms of melamine-formaldehyde microcapsules with curing recirculation of 120 and 30 min.

loss is circa 1%. Melamine resin microcapsules present thermal stability until around 210 °C. This value is in agreement with previously reported data for melamine-formaldehyde microcapsules containing a flame retardant, where the thermal stability was set at around 225 °C.<sup>66</sup> Studies of production of nanocapsules of melamine-urea-formaldehyde containing paraffin also show thermal stability around 200 °C.<sup>67</sup> From 210 to 340 °C, the first stage of considerable weight loss is observed in both samples, resulting from the degradation of melamine-formaldehyde with mass losses of 53 and 71% for samples with recirculation of 120 and 30 min, respectively. These differences can be attributed to the slightly higher core content obtained in the 120 min circulation samples, which is lower shell content and thus lower weight loss due to melamine-formaldehyde degradation. Above 340 °C, a second stage of the mass loss is observed due to the continuous structural decomposition of melamine-formaldehyde. For the sample with recirculation of 120 min, the second stage is

observed in the range of 340–440 °C, with a mass loss of 34%, while for the sample with recirculation of 30 min, it is in the range up to 400 °C with a mass loss of 19%. Similar behavior of structural decomposition of melamine-formaldehyde around 340–370 °C has been reported for microcapsules of melamine-formaldehyde containing fragrances and flame retardants.<sup>22,66,68</sup> Moreover, a study of the thermal behavior of melamine-formaldehyde resin has reported that one of the stages of decomposition occurs in the range of 350–400 °C.<sup>27</sup>

**3.2. Application of Microcapsules to Textiles.** The produced microcapsules were impregnated in cotton fabrics at a pressure of 4 bar. After the impregnation process, a piece of fabric was analyzed by SEM to evaluate the integrity of microcapsules after impregnation and adhesion in textiles (Figure 9).



**Figure 9.** SEM images of impregnated microcapsules in cotton for a total recirculation period of (a) 2 h and (b) 30 min. Resolutions of 500 $\times$  (left) and 1000 $\times$  (right).

In all cases, the abundance of microcapsules well fixed on the surface of the fibers is apparent. The integrity and shape of the microcapsules were maintained, and the presence of broken microcapsules and membrane fragments is rare.

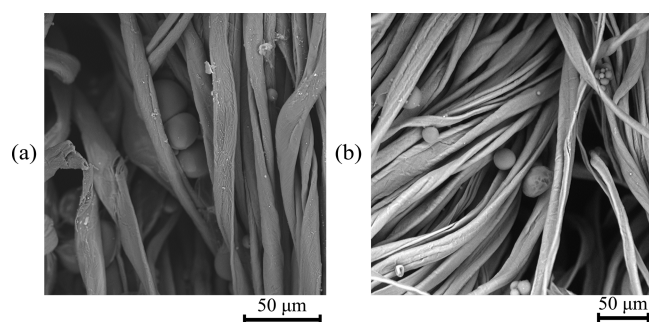
One known characteristic of this type of melamine-formaldehyde microcapsule is the flexible behavior of the shell, which can be observed in Figure 10.

This characteristic is due to viscoelastic behavior at a small deformation, as reported in the literature.<sup>22</sup> During microcapsule impregnation, the used pressure on roller padding forces some microcapsules to adapt to the fibers and thus prevents the rupture of the membrane. The largest microcapsules (above 30  $\mu\text{m}$ ) are located among the fibers instead of at their surface. This is an advantage for textile application since entrapped microcapsules are better protected.

#### 4. CONCLUSIONS

In this work, microcapsules of melamine-formaldehyde with an oily active principle, Miglyol, were produced in a continuous mode using the NETmix technology. The emulsion step was





**Figure 10.** SEM images of impregnated microcapsules in cotton for a total recirculation period of (a) 2 h and (b) 30 min. Resolutions of 1500 $\times$  (a) and 1000 $\times$ .

performed with a single pass and with recirculation. Both processes produce stable oil-in-water emulsions, which remain stable until the end of the production process. However, recirculation promotes the decrease in the droplet size, from circa 40 to 20  $\mu\text{m}$ , which is the ideal size range for application on fabrics. The cure step was performed in the NETmix using different recirculation times; in both cases, spherical, resistant, smooth-faced microcapsules, with similar morphology and sizes, were produced. Microcapsules show efficiencies of encapsulation of 75% and core contents above 60%. Both microcapsules showed thermal stability up to 210  $^{\circ}\text{C}$ . Thus, by performing the cure step in the NETmix, a time reduction from more than 2 h to 30 min was achieved. Concerning textile impregnation applications, microcapsules were well fixed to the fibers and present a viscoelastic behavior. Breakability during impregnation was not observed. Thus, the use of the NETmix technology results in stable emulsion production, microcapsules with the desired characteristics, and the reduction of cure time (80%) compared to the traditional batch formulation.

This work provides a proof of concept for the capability of NETmix to replace batch processes for microencapsulation. Further work will focus on a different NETmix setup, namely, with smaller chamber and channel sizes and incorporated heat exchanger for easier operation, and on other types of microencapsulation processes. Future work on melamine-formaldehyde will focus on process optimization, namely, the effect of recirculation times and Reynolds number on the microcapsule size distributions (uni- or bimodal) and mean diameter. Encapsulation of other active principles, such as vitamin E carried by Miglyol since it is an excellent vehicle for vitamins, and its quantification on textiles will also be carried out.

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## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by Associate Laboratory LSRE-LCM UID/EQU/S0020/2019 funded by national funds through FCT/MCTES (PIDDAC) and Project TexBioPro, POCI-01-0247-FEDER-003472, funded by FEDER, through COMPETE 2020, under PT2020.

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