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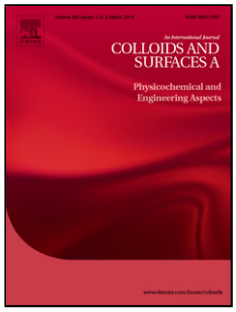

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MICROENCAPSULATION OF EPOXY RESINS: OPTIMIZATION OF SYNTHESIS CONDITIONS

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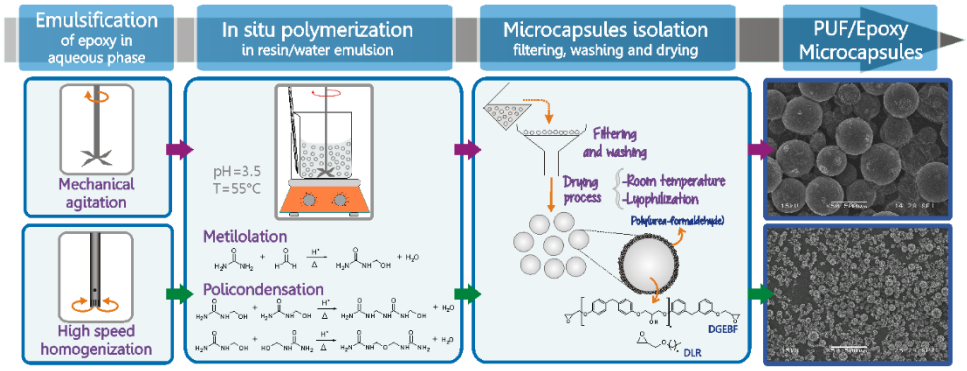
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Epoxy resin was microencapsulated by in situ polymerization in oil-in-water emulsion.
- Poly(urea-formaldehyde) was selected as shell material.
- Several reaction conditions were analyzed.
- Lyophilized microcapsules resulted in stable free flowing powders.
- Microcapsules were strong enough to bear the manufacturing of a composite material.

ABSTRACT

In this work, a series of microcapsules were prepared by in situ polymerization in oil-in-water emulsion with poly(urea-formaldehyde) as shell material and diglycidyl ether of bisphenol F as core substance. Different reaction parameters were analyzed: emulsification conditions (time, agitation method and rate), the viscosity of the core phase, stirring speed during synthesis, core/shell mass ratio and drying process. Morphology, chemical structure, mean size, size distribution and thermal properties of the resulting microcapsules were studied by Scanning Electron Microscopy (SEM) and Optical Microscopy (OM), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC).

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Several spherical microcapsules with different sizes and distributions were obtained by the adjustment of reaction parameters. Lyophilized microcapsules resulted in free flowing powders, which remained stable under more than 1 year at ambient laboratory conditions. From preliminary testing results, it was demonstrated that microcapsules fabricated under optimized reaction conditions had a satisfactory size and shell structure and were strong enough to bear the manufacturing of an epoxy-based composite material. Thus, results obtained in this work show that these microcapsules are potential candidates for the development of self-healing composites.

Keywords: Microcapsules, synthesis, epoxy, poly(urea-formaldehyde); self-healing.

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1. INTRODUCTION

Microencapsulation is the process in which tiny particles or droplets of liquids or gasses are enclosed in an inert shell or embedded in a homogeneous or heterogeneous matrix, with the aim of isolating and protecting them from an external medium [1-2]. In the last years, with the advances in materials science and microencapsulation technology, several new applications of microcapsules in advanced fields of smart and functional materials have been developed [3]. Recently, microcapsules have been applied in the growing field of self-healing polymeric composites and coatings. The introduction of microcapsules filled with a liquid healing agent within a polymeric matrix is one of the most successful and versatile approaches for the development of self-healing materials [4]. When the propagating crack triggers the rupture of a number of the embedded microcapsules, the healing agent is released into the crack plane through capillary action. Subsequently, it undergoes a chemical reaction (typically polymerization) or a physico-chemical process to reestablish the structural integrity of the material [5]. Based on this concept, novel self-healing concepts and chemistries have been developed to solve different challenges [6].

Epoxy resins are important core materials for healing chemistries because they can react with a wide variety of curing agents or hardeners at different temperatures [7]. So they may be used as healing agents for the fabrication of self-healing composites [6, 8]. The microencapsulation of epoxy resins has increasingly attracted researchers' interest due to the fact that miscibility between the healing agent and the epoxy based composites is guaranteed. Moreover, high thermal decomposition of epoxy resins may endow microcapsules with higher thermal stability.

The microcapsule synthesis and design is one of the vital features for the effectiveness of the healing system. Microencapsulated healing agents that possess adequate size, strength and optimal bonding to the host matrix are required for these materials. Besides, the release properties of the microcapsules depend on the wall materials, but also on the microencapsulation technique, on the physico-chemical parameters of the process, the mean particle size and shell thickness [9]. A precise controllable microencapsulation process is essential to obtain microcapsules with the appropriate

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features which can ensure their final performance. Thus, the selection of the best experimental conditions of microencapsulation is critical [10-11].

Emulsion based *in situ* encapsulation techniques are commonly used for compartmentalizing hydrophobic core materials in a polymeric shell. Amino resins are most commonly used as shell materials in view of their reasonable cost, adequate strength and long shelf-life [12]. ~~Specifically,~~ P~~p~~oly(urea-formaldehyde) (PUF) and poly(melamine-formaldehyde) (PMF) resins are ~~one of~~ the most used materials for encapsulation of chemically active substances [11, 13-15]. Specifically, ~~A~~as shell materials, PUF resins are strong enough to remain intact during mixing and manufacturing of polymer composites, but also brittle enough to rupture and release the core materials upon a propagating crack when required.

The usual *in situ* PUF polymerization starts with a primary emulsion preparation in which liquid core reagents are first dispersed in an aqueous phase. Initially, urea and formaldehyde react in water phase to form a colloidal low-molecular-weight pre-polymer, which grows with time and deposits on the core material-water interface. Polycondensation of urea and formaldehyde at this stage leads to the formation of a solid and non-permeable capsule shell wall around the dispersed phase [12, 16]. Polymerization of urea-formaldehyde can be both acid- or base-catalyzed [17]. Most of the studies that apply the technique of in situ polymerization of urea and formaldehyde for encapsulating epoxy resins are based on a two stage method in which the UF prepolymer is firstly synthesized in basic medium and then polycondensation occurs in the acidified emulsion. In 2006, Yuan et al. [15] reported the first microencapsulation of DGEBA resin (with 20 wt% of butylglycidyl ether as a diluent) with this method. Based on this work, Yuan et al, as well as other authors, reported variations of this method, using different experimental conditions [10, 18-20]. Alternatively, PUF microcapsules can be prepared with single-step method, in which urea and formaldehyde react in acidic conditions, without preparing a precondensate [17]. This method was developed by Brown [11] for encapsulation of dicyclopentadiene and was employed by Cosco et al. [14, 21] with slight modifications to encapsulate a DGEBF resin. Furthermore, this technique was used by Caruso et al. [22], and was later modified by Blaiszik et al. [13], for encapsulating mixtures of an epoxy resin with organic solvents with low polarity and high boiling point. However, these mixtures contained low percentages of epoxy

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resin (up to 20 wt.%). Based on the work of Blaiszik and coworkers, Jin et al. [23] encapsulated a commercial mixture of DGEBA resin with 13.6 wt. % of reactive diluent. Besides PUF, PMF has also been successfully applied as shell material to prepare epoxy-loaded microcapsules [24-26].

The aim of this research was to elucidate the optimal conditions for preparing microcapsules containing epoxy resins. In this context, a series of epoxy-loaded microcapsules were prepared by one-stage *in situ* polymerization of urea-formaldehyde in an oil-in-water emulsion. Different parameters were analyzed: viscosity of the core material, core/wall forming materials mass ratio, homogenization mode, time and speed, as well as the final drying procedure of the microcapsules. The morphology, chemical structure, mean particle size and thermal properties of the microcapsules were studied and discussed in detail. The motivation for the study of the encapsulation of epoxy resins was based on the potential application of these containers in polymer matrices, both in bulk materials or in coatings, for the development of systems with self-healing capabilities by different chemical strategies. Thus, finally, a preliminary study was performed in order to evaluate the feasibility dispersing a series of microcapsules within epoxy matrices.

2. EXPERIMENTAL

2.1. Materials

A diglycidyl ether of bisphenol F epoxy resin (DGEBF, Distraltec RBF170), with an epoxy equivalent weight of 182.8 g eq^{-1}), was used as core material. A reactive diluent, alkylglicidyl ether C12-C14 (DLR, Distraltec), was used to decrease the viscosity of the epoxy resin. All reagents of the shell forming polymers, urea (Anhedra), resorcinol (Biopack) and formaldehyde (40 wt% solution, Biopack), as well as ammonium chloride (Timper) and 1-octanol (Sigma Aldrich) were used as received. Poly(ethylene-*alt*-maleic) anhydride powder with Mw=400,000 (EMA, Sigma Aldrich) was selected as surfactant.

DGEBF resin cured with triethylenetetramine, TETA (Dicure 351), was chosen as the polymer matrix.

2.2. Preparation of the microcapsules

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Microcapsules were prepared by in situ polymerization of urea and formaldehyde in an oil-in-water emulsion, adapting the procedure reported by Brown et al. [11]. First, 100 ml of an aqueous solution of 0.5 wt.% EMA was prepared in a 250 ml beaker. Then, 2 g urea, 0.2 g resorcinol and 0.2 g ammonium chloride were dissolved and the pH value of the solution was raised to 3.5 by adding a few drops of NaOH solution. The baker was immersed in a temperature-controlled glycerin bath placed on a programmable hotplate with external temperature probe (Dragon Lab, model MS-H-Pro). After that, the epoxy resin was added to form an emulsion and different methods of emulsification were evaluated: with a digital mixer (Dragon Lab, model OS 40-Pro) equipped with a four-bladed, 50 mm diameter, mixing propeller or with a high speed homogenizer (Ultraturrax, model T25). After stabilization, 4.75 ml of 37 wt.% formalin solution was added. The emulsion was covered with aluminium foil and heated to 55 ºC under the selected agitation rate. After 4 h of reaction time, PUF formed a solid shell around the epoxy droplets and the microcapsules were then cooled to ambient temperature, filtered and rinsed with distilled water. Four drying methods of the isolated microcapsules were evaluated: air drying for 48 h at room temperature; lyophilization (72 h at -45 °C and 100 mTorr). The yield of microcapsules was calculated relative to the mass of starting materials.

The experimental parameters analyzed in each of the syntheses are summarized in **Table 1**. Samples D1 to D7 were emulsified at room temperature with mechanical stirring at varying speeds for 30 minutes. In samples D8 to D17 the emulsification process of the resin was performed using a high speed homogenizer. Furthermore, the effect of adding 20 wt.% of DLR to the resin in order to reduce its viscosity was studied (the mixture was designated as DGEBF+DLR).

2.3. Preparation of microcapsule-loaded epoxy samples

Microcapsules were incorporated into the DGEBF resin by hand and the mixture was degassed for 30 min at 60 °C to remove entrapped air. Then, a stoichiometric amount of TETA was added at room temperature and the suspension was degassed again for 30 min at 40 °C. The mixture was poured in an aluminum mold with a rubber o-ring of 10 x 10 x 0.2 cm. The curing cycle consisted on 30 min at 50 °C, followed by 1 h at 80 °C and 2 h at 120 °C. The unfilled epoxy specimens were prepared in the same way through mixing stoichiometric amounts of DGEBF resin and TETA.

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2.4. Characterization techniques

The encapsulation reactions were monitored with a Leica DMLB Optical Microscope equipped with a video camera Leica DC 100.

The morphology of microcapsules was observed by Scanning Electron Microscopy (SEM, JEOL JSM 6460 LV). The microcapsules were previously mounted on adhesive tape and sputter coated by a thin layer of gold/palladium. Mean diameter and standard deviation were determined from at least 200 measurements. SEM microscopy was also used to investigate fracture surface of broken epoxy/microcapsule specimens.

The core content of the microcapsules was determined by extraction method. Using acetone as extraction solvent, the microcapsules were treated in a Soxhlet apparatus for 24 h to remove the epoxy resin from the core. Three specimens were analyzed for each sample.

The thermal stability of the capsules was assessed by thermogravimetric analysis (TGA) in a TA Q200/TGA Q50 thermal analyzer. The microcapsules were heated from 25 to 600 ºC at a rate of 10 ºC/min, under nitrogen atmosphere.

The chemical structure of microcapsules was studied by Fourier Transform Infrared Spectroscopy (FTIR) in a Nicolet 6700 Thermoscientific Spectrometer equipped with a diamond ATR probe, from 400 to 4000 cm^{-1} wavenumber region, with a resolution of 4 cm^{-1}.

Differential Scanning Calorimetry (DSC) thermograms were recorded using a TA-Q2000 calorimeter. The tests were performed at a scan rate of 10 ºC/min from room temperature to 250 ºC in aluminum pans with sample amounts of about 5 mg.

3. RESULTS AND DISCUSSION

3.1. Emulsification with mechanical stirring

First, the feasibility of using mechanical agitation during the dispersion of the DGEBF resin and the encapsulation reaction was evaluated. In sample D1, emulsification was developed at 500 rpm for 30 minutes at room temperature. During this process, it was noted that in the first minutes of

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stirring, the breakdown of droplets to form a dispersion of smaller drops of DGEBF was difficult. The product of this synthesis was a waxy solid composed of large, collapsed and agglomerated capsules.

According to the recommendations of Nesterova et al. [27], in samples D2 and D3, the DGEBF to wall forming materials mass ratio was reduced. In the case of sample D2, the encapsulation process was improved and the product was filtered without problems. However, many capsules were broken during the washing process. This could be attributed to the fact that the PUF wall of these capsules was not robust enough. Again, after drying, most capsules collapsed and after one week an agglomerated waxy solid was obtained. **Figure 1a** shows the SEM micrographs of the capsules resulting from this synthesis and it can be noticed the presence of free DGEBF resin adhered on the surface of the large capsules (mean diameter = 381 μm ± 84 μm). In the case of sample D3, the initial resin/wall mass ratio was reduced to 2.5 and large capsules were originated as well. Also, very small PUF particles, which were not deposited on the surface of the capsules and remained in suspension, were formed, hindering the filtering and washing processes.

In the synthesis of sample D4, the effect of increasing the stirring rate to 650 rpm was evaluated, while keeping the mass ratio between the resin and the wall forming materials at 3.6. The increment in the shear forces by the slightly improved vigorous emulsification process of the resin resulted in smaller drops. Consequently, smaller capsules (mean diameter = 230 μm ± 44 μm) were obtained [28]. In **Figure 1b**, it can be noted that while a large amount of spherical microcapsules were obtained, a fraction of them collapsed after drying. Thus, part of the encapsulated resin was released and acted as an adhesive between the rest of the capsules. This could be attributed to the fact that PUF wall did not have the adequate strength to maintain its integrity [27].

Optical micrographs in **Figure 2** show the evolution of the encapsulation process over time in sample D4. It can be noted that, unlike the encapsulation process DCPD [11], the wall surface of the capsules is very smooth with dents and defects from the early hours of reaction, probably due to the collisions between the capsules during agitation and to their fragile walls [27]. The smoothness of the capsules compared to PUF/DCPD can be attributed to the fact that the viscosity of the emulsion was higher, because DGEBF resin is much more viscous than DCPD. Consequently, diffusion of PUF

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particles formed in the aqueous phase to the interface of the droplets is more difficult and this results in a significant reduction of the surface roughness of the wall.

In the case of samples D5, D6 and D7, analogous to D2, D3 and D4 respectively, DGEBF resin was replaced by a mixture of DGEBF with 20 wt.% DLR. In general, it was observed that the reduction in the viscosity of the core fluid favored the emulsification process in the aqueous medium [29]. Comparing samples D5 (**Figure 1c**) and D2, it could be deduced that by reducing the viscosity of the resin, an increment in the surface roughness of the capsules occurred. This is consistent with what was reported in the previous paragraph. Also, sample D5 had an aspect of a free flowing powder, without agglomerates or residual resin on the surface of the capsules. However, small PUF particles were also observed. The synthesis of sample D6, presented similar results to the ones registered for sample D3. The excessive amount of PUF particles in suspension, probably due to the lower initial resin/wall mass, hindered the process of washing and filtering, leading to the rupture of a large number of capsules. SEM micrographs of sample D7 are observed in **Figure 1d**. Again, it can be noted that the increment in the stirring speed, compared to sample D5, produced a reduction in the average size of the capsules. However, the amount of PUF aggregates also increased.

Regarding the size distributions, samples obtained at 500 rpm (D2 and D5), evidenced the presence of two populations of different sized microcapsules. This was attributed to the method of agitation during emulsification and synthesis of the capsules. While larger microcapsules were generated in the periphery of the beaker, the population of smaller capsules was generated in the vicinity of the agitator blades where the flow is turbulent and there is more energy transfer [28]. Also, sample D5, containing the less viscous resin mixture, had a smaller average size of both populations of capsules and narrower size distribution. This is consistent with the information reported in literature. It is known that the efficiency of rupture of drops in the formation of emulsions with turbulent mixing systems depends on the intensity of the shear forces, the type and concentration of surfactant and the ratio of the viscosities of the dispersed phase and the continuous phase [30]. In this case, the emulsions formed in samples D2 and D5 differ only on the viscosity of the dispersed phase. Therefore, by increasing the viscosity of the dispersed phase in the continuous phase, there is greater resistance to breakage of the drops against the shear forces by turbulent mixing [31], resulting in larger drops

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compared to dispersed phases with lower viscosity (and thus microcapsules of similar size). Also, it has been reported that the increase in viscosity of the dispersed phase produces emulsions with wider size distribution of drops [32].

In the samples obtained at 650 rpm (D4 and D7), the mixing process was more uniform and two populations of microcapsules were no longer obtained; however, a normal size distribution was not observed. Moreover, there were practically no differences between the samples with and without diluent, which could be attributed to increased shear stress due to a more vigorous agitation.

Regarding the drying method, it was noted that regardless of the type of sample, drying at room temperature produced collapsed capsules, resulting in agglutinated products by the resin released from the broken capsules. The lyophilization process markedly favored the appearance of the products only for samples D5 and D7, in which a free flowing powder was obtained.

The yield of the reactions D5 and D7 was relatively high, as shown in **Table 2**. The core content was higher in the case of sample D7, which could be attributed to the greater stability of the emulsion obtained with a higher agitation speed.

It is important to verify that the encapsulation process did not affect the reactivity of the epoxy groups of the resin. In the aqueous phase there are numerous chemical species that could potentially react with the epoxy resin or catalyze the curing process (such as urea, EMA or acidic protons). However, the conditions of acidity and temperature of the reaction system are not sufficient for this to occur appreciably [15, 33]. Therefore, the reactivity of the encapsulated resin in the presence of TETA was confirmed by DSC tests. For reference, the reaction of a stoichiometric mixture of DGEBF with TETA was tested and an exothermic peak was registered at 98.7 °C with a heat of reaction (ΔHr) of -562.6 J/g, corresponding to the epoxy-amine polycondensation [10]. Then a small portion of the dried capsules was mixed with a few drops of TETA and ground to ensure the rupture and release of the resin. $|\Delta Hr|$ values shown in Table 2 were elevated in both cases being higher in the case of sample D7, which is in accordance with the higher content of encapsulated epoxy resin.

3.2. Emulsification with high speed homogenization.

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In this section, the emulsification process of the epoxy resin was performed in more energetic conditions, with agitation speeds between 5000 and 15000 rpm using a high speed homogenizer. In view of the results of the previous section, lyophilization was selected as the drying method of all samples. The main results are reported in **Table 3**. It is important to mention that only the samples which did not agglutinate after the lyophilization were further analyzed.

The effect of each of the reaction variables on the final properties of the capsules were evaluated separately and are discussed in the following sub-sections.

3.2.1. Effect of changing the emulsification method

For samples D1 to D4 it was not possible to encapsulate the DGEBF resin because its high viscosity did not allow a proper emulsification with the applied shear stress. Thus, the feasibility of DGEBF encapsulation was evaluated using emulsification conditions with higher shear stresses. For sample D8, with the same formulation as in sample D2, emulsification was performed for 5 minutes at 11000 rpm, as shown in Table 1. This remarkable increase in the shear forces helped to improve the process of breaking large drops into smaller ones. **Figure 3** comparatively shows SEM micrographs of samples D2 (a) and D8 (b), with their respective size distribution curve. It can be noted that in the case of the sample D8, significantly smaller capsules with rougher walls were obtained. After drying, the microcapsules had the aspect of a free flowing powder, which is consistent with the SEM micrographs since no free resin adhered on the surface of the capsules was observed. From Table 3, it is clear that the core content in the capsules was high and not excessive losses were generated during synthesis and filtering, since the yield was close to 76 %.

3.2.2. Effect of the initial mass ratio between epoxy resin and wall forming materials

PUF/DGEBF+DLR microcapsules were synthesized with different initial resin/wall forming materials in order to identify the value that maximizes the content of encapsulated resin without impairing the final properties of the microcapsules.

In the case of sample D9, the same formulation and processing method as in sample D8 were used, except for the lower viscosity of the encapsulated resin. An optical micrograph of the

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microcapsules in suspension after 4 hours of reaction is shown in **Figure 4**. It can be noticed the presence of large capsules with diameters greater than 100 μm, and aggregates of small capsules (marked with circles). In the SEM micrograph, these aggregates of capsules are displayed as irregular structures of different sizes and shapes. Although Table 3 reports a yield close to 80 %, with high content of encapsulated resin, it is clear that a fraction of smaller capsules agglomerated during the encapsulation process.

Figure 5 shows a SEM image of a section of a broken microcapsule from sample D9. It can be seen that the inner surface of the capsule wall is smooth, while the outer part is rough. This shell morphology has been attributed to the mechanism of PUF formation in the core/water interface with EMA as emulsifier [17]. It has been reported that surface roughness enhances mechanical adhesion of the microcapsules when embedded in a polymer matrix and contributes to improve the performance in self-healing applications [13].

Figure 6 shows SEM micrographs of the microcapsules synthesized with resin/wall mass ratio values between 3.0 and 1.9. Table 3 evidences that the reaction yields slightly decreased by reducing the amount of incorporated resin into the emulsion. This can be attributed to the fact that by increasing the proportion of PUF, especially in sample D12, small PUF particles were formed in the aqueous phase and hindered the filtering process. Moreover, the core content decreased by lowering the resin/ wall mass ratio. This is consistent with the observations of other authors [10, 15]. Figure 6 also evidences that samples D10, D11 and D12 presented wide and bimodal size distribution curves. Independently of the resin/wall mass ratio, all samples contained a high proportion of small capsules, with sizes below 150 - 200 μm and a minor proportion of large capsules with less resistant walls with dimensions between 200 and 500 μm. Such size distribution has been observed in the emulsification process of viscous oil droplets in aqueous phases [32, 34]. Another fact that contributes to the bimodal size distribution is the process of coalescence of the drops that occurs at the end of the vigorous emulsification step, which continues with mechanical agitation at a remarkably slower rate, prior to the addition of formaldehyde to the emulsion [35]. It can also be observed that the reduction of

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the initial resin/wall mass ratio only produced a slight decrease in the average size of both populations of capsules.

3.2.3. Effect of emulsification time

SEM micrographs of samples prepared with various emulsification times are displayed in **Figure 7**, with an epoxy resin/wall mass ratio fixed at 3. In the samples D10, D13 and D14 the emulsification was performed at 11000 rpm for 5, 10 and 20 minutes respectively.

By comparing the images of **Figures 7** b and c it may be noted that while the population of large capsules dropped, it could not be completely eliminated by increasing the time of emulsification. This can be attributed to the viscous nature of the DGEBF+DLR resin compared to water. It is also important to note that the process of filtering and washing sample D14 was hindered by the presence of small PUF particles that remained in suspension. This led to a detriment in the yield of the reaction (less than 60%) and to the breakage of the larger capsules which caused partial agglomeration of the product after drying. It can also be observed that the increment in emulsification time produced a refinement in the size distribution of capsules, as observed in other high shear emulsification processes reported in literature [36-37]. However, although the amount of large capsules was reduced, it was not possible to completely eliminate them. From these results, it can be deduced that it is not beneficial to perform the emulsification process for more than 5 or 10 minutes. While increasing the emulsification time the capsule size decreases, excessive emulsification time does not improve the final appearance of the capsules but, on the contrary, it deteriorates it due to the formation of small PUF particles hindering filtering and washing of the product.

3.2.4. Effect of shear stresses during emulsification process

In order to reduce the process of resin droplet coalescence in the transition in the mode of stirring after emulsification in the synthesis of samples D15, D16 and D17, the addition of formaldehyde was performed during the course of the emulsification process, unlike all previous syntheses in which formaldehyde was added as soon as mechanical agitation at 500 rpm began, that is, after the dispersion of the resin. With this slight change in the process, three samples with epoxy

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resin/wall forming materials mass ratio fixed at 3.6 and 5 minutes of emulsification at different speeds between 5000 and 15000 rpm were synthesized.

In **Figure 8** SEM micrographs of samples D15, D16 and D17 with different magnifications are compared. Comparing Figures 8 a and b, it can be noted that the increase in emulsification speed caused a reduction in the size of the capsules. This can be visualized in the size distribution curves and in the average diameter values reported in Table 3. This effect is attributed to the increase in the stirring speed during the dispersion of the resin in the aqueous phase that results in higher shear forces which favor the rupture of the droplets, creating a finer emulsion and therefore, smaller capsules. It is also evident that the addition of formaldehyde during the emulsification process reduced the coalescence of droplets, significantly improving the dispersion of sizes of the resulting capsules. Both reactions had a high yield, greater than 85%. It can also be noted that the epoxy content was high in both cases, being slightly greater in the sample D17, which presented larger microcapsules.

In the case of the sample D15, the emulsification step was performed at 15000 rpm. Instead of getting smaller capsules, as expected, large irregular aggregates of particles were formed. This effect has been reported by Hwang et al. [38], who attributed this phenomenon to the instability of the emulsion caused by excessive stirring speed. Therefore, the drops of the dispersed phase collapsed due to the destabilization of the emulsion, resulting in irregular particles observed in SEM images. It is noteworthy that although the product does not present an adequate morphology, the reaction yield was greater than 80% and the resin content was high (85 wt.%), so it can be deduced that the large aggregates are formed by the agglomeration of small microcapsules (as was observed in sample D9).

3.3. Chemical characterization and reactivity of the core material of the microcapsules

To confirm DGEBF encapsulation and ensure its reactivity inside the capsules, DSC tests were performed as previously mentioned. The presence of the characteristic exothermic peak of the epoxy-amine polymerization reaction was detected in all the samples. This implies that the encapsulation process did not affect the reactivity of the epoxy groups.

Figure 9 shows the FTIR spectrum of sample D16 as an example, in comparison with the spectra of DGEBF+DLR mixture and neat PUF, whereas **Table 4** summarizes the main peak

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assignments [39-40]. In the FTIR spectrum of sample D16 the presence of the epoxy resin can be corroborated, mainly by the absorbance peak located at 915 cm^{-1} (marked with *) associated with the epoxide ring [41]. This peak was identified in the spectra of all the samples that are listed in Table 3.

3.4. Thermal stability of the microcapsules

The thermal stability of the microcapsules is important for future applications in polymer based composite materials that require thermal curing cycles [42]. Curves of mass loss as a function of temperature were recorded for sample D16, DGEBF+DLR mixture and neat PUF. The resulting thermograms are plotted in **Figure 10.** It is evident that capsules' thermal decomposition started at approximately 160 °C and proceeded in two stages [19]: the first weight loss was observed between 160 and 250 °C, attributed to the rupture of the capsule wall that caused the diffusion of the resin; the second mass loss between 300 and 450 °C was due to decomposition of the PUF and resin. This is consistent with the data reported in literature [43].

3.5. Incorporation of epoxy-loaded microcapsules into an epoxy matrix

In this section, preliminary tests were performed to assess the effect of incorporation of microcapsules in an epoxy matrix. Plaques loaded with 5 wt.% of microcapsules corresponding to samples D7 and D16 were prepared. In both cases, the resulting materials were free of bubbles with a macroscopically uniform distribution of microcapsules.

The incorporation of microcapsules did not modify the *Tg* of the polymer matrix, which was 138 °C. A SEM micrograph of the cracked surface of neat epoxy resin (not shown) evidences a smooth surface, without traces of plastic deformation, which is a typical feature of brittle thermosetting polymers [44]. SEM images of fractured surfaces of specimens with 5 wt.% of samples D7 and D16 are shown in **Figure 11** a and b, respectively. In the first case with larger capsules, the surface inspection mainly reveals the presence of areas with plastic deformation of the matrix. It is also important to note that few capsules were observed in the studied area. This could indicate that a portion of the microcapsules broke during the manufacturing process, possibly by having PUF walls with low resistance. An inset magnification of the interface between the wall of a broken capsule and

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the polymeric matrix, evidences good adhesion between them, with no signals of debonding. Furthermore, the fracture surface of the material with 5 wt.% of sample D16 (Figure 11 b) evidences a uniform distribution of capsules without clusters or bubbles. It is important to note that in this case, the microcapsules maintained their integrity during the manufacturing of the material. In addition, a good adhesion with the epoxy matrix was observed. It has been reported that when the capsules are incorporated into the matrix, a three-part interphase region is formed, comprised of the smooth inner shell wall, the rough exterior shell wall infiltrated by epoxy resin and the epoxy matrix [13]. This mechanical bonding to the surrounding polymer material increases the probability of capsule fracture upon a propagating crack and, therefore, favors the healing process.

4. CONCLUSIONS

In this work, different strategies of microencapsulation of epoxy resins by the one-stage *in situ* polymerization of urea and formaldehyde in an oil-in-water emulsion technique were investigated.

The emulsification procedure of the resin in the aqueous phase (emulsification time, mode and stirring rate) was a critical step in the microencapsulation process since it determined the quality, size and morphology of the resulting capsules, as well as the encapsulation efficiency. In the cases in which mechanical agitation was applied for the emulsification of the resin, only diluted mixtures of DGEBF with 20% of DLR (DGEBF+DLR) could be encapsulated after having adjusted the core/shell mass ratio and the agitation speed. In the case of pure DGEBF resin, large spherical capsules with wide size distribution (in the range of 100 and 600 μm) were obtained and collapsed after drying because of the high viscosity of the core substance and the low strength of PUF wall.

The emulsification process of DGEBF and DGEBF+DLR mixture in high shear conditions caused a significant reduction on the average diameter of the microcapsules and a notorious increment in the reaction yields. After optimizing several reaction parameters such us the core/shell mass ratio, homogenization time and speed, and protocol of addition of formaldehyde into the emulsion, it was possible to reduce the size and size distribution of the capsules below 150 μm.

Regarding the drying process, lyophilization avoided the agglomeration of the microcapsules, allowing obtaining products in the form of free flowing powders.

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DSC and FTIR analysis evidenced the presence of epoxy resin inside the capsules. Furthermore, reactivity of the epoxy groups of the encapsulated resin was confirmed. This indicates that the encapsulation process did not compromise the reactivity of the core substance. Moreover, the microcapsules presented good thermal properties which is advantageous for the practical use in thermally cured composite materials.

Two types of PUF/DGEBF+DLR microcapsules with different average sizes were successfully incorporated into epoxy matrices. On the one hand, larger microcapsules (200 μm) were partially ruptured during the manufacturing process on the composite material due to the fact that few microcapsules were observed in the surface of fractured specimens. On the other hand, the mixing process and thermal curing of the composite materials did not deteriorate the morphology of the smaller microcapsules (synthesized with high speed homogenization). Furthermore, good dispersion, compatibility and adhesion between the wall of the capsules and the matrix was observed. Fracture surfaces of the systems evidenced the rupture of the capsules by the propagating cracks.

The microcapsules synthesized in this work are promising for the development of self-healing materials. Work in progress is in this direction. Moreover, the optimized encapsulation methods are extensible to other core materials and applications.

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Figure 1. SEM micrographs of PUF/DGEBF and PUF/DGEBF+DLR microcapsules, with their corresponding magnifications at the right and size distribution at the center, of samples D2 (a), D4 (b), D5 (c) and D7 (d).

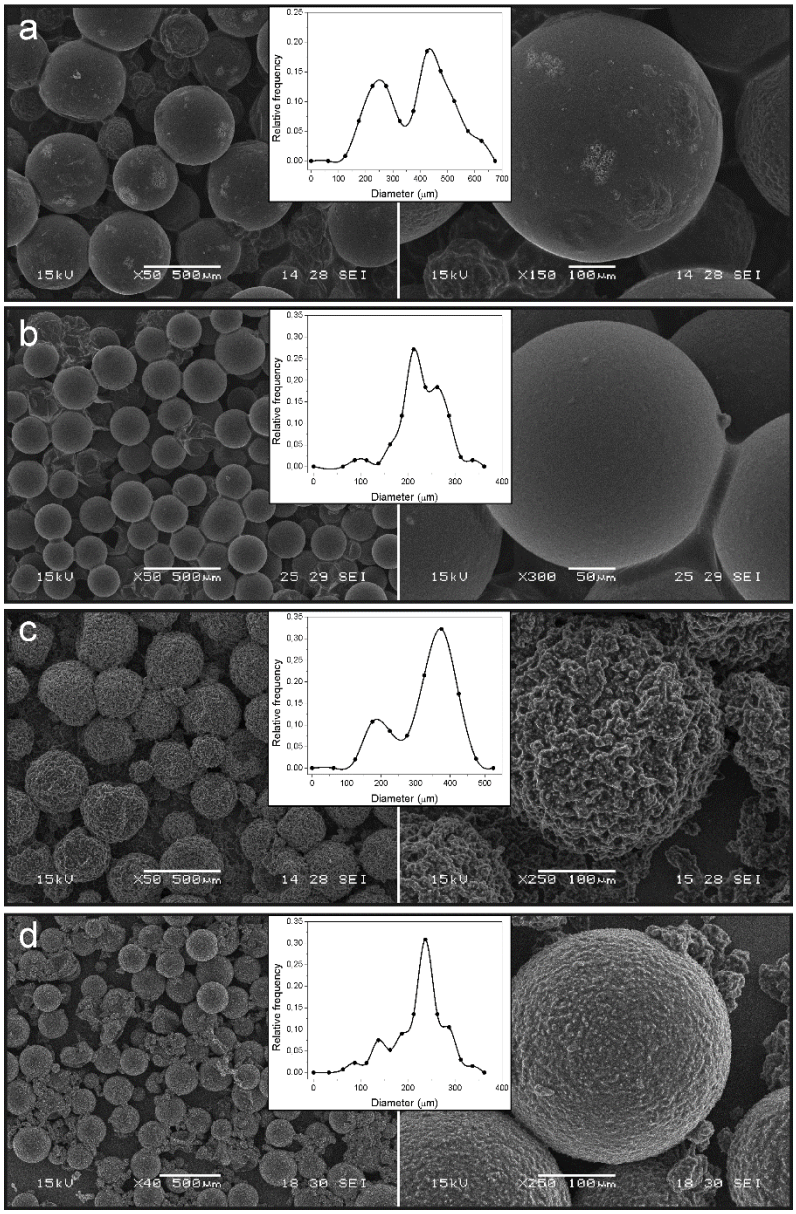

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Figure 2. Optical microscopy images of the evolution of the encapsulation process of sample D4 over time.

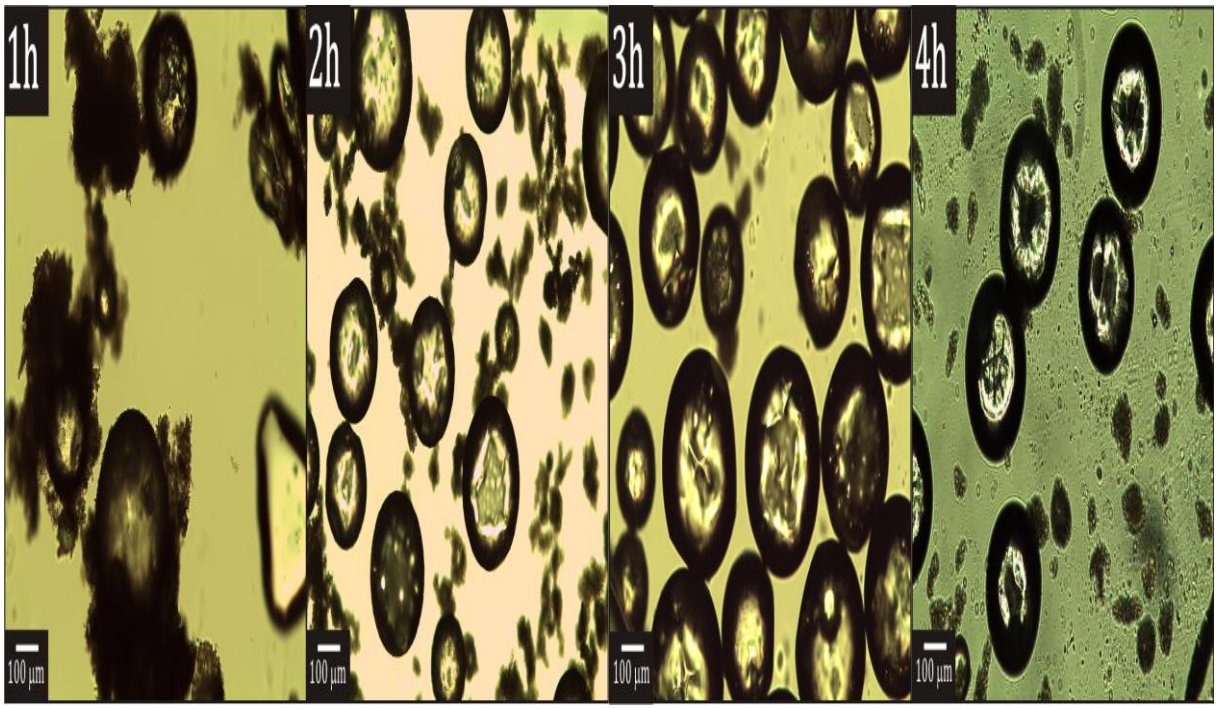

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Figure 3. SEM micrographs of PUF/DGEBF microcapsules obtained with different emulsification processes: 30 min at 500 rpm (Sample D2); b) 5 min at 11000 rpm (Sample D8).

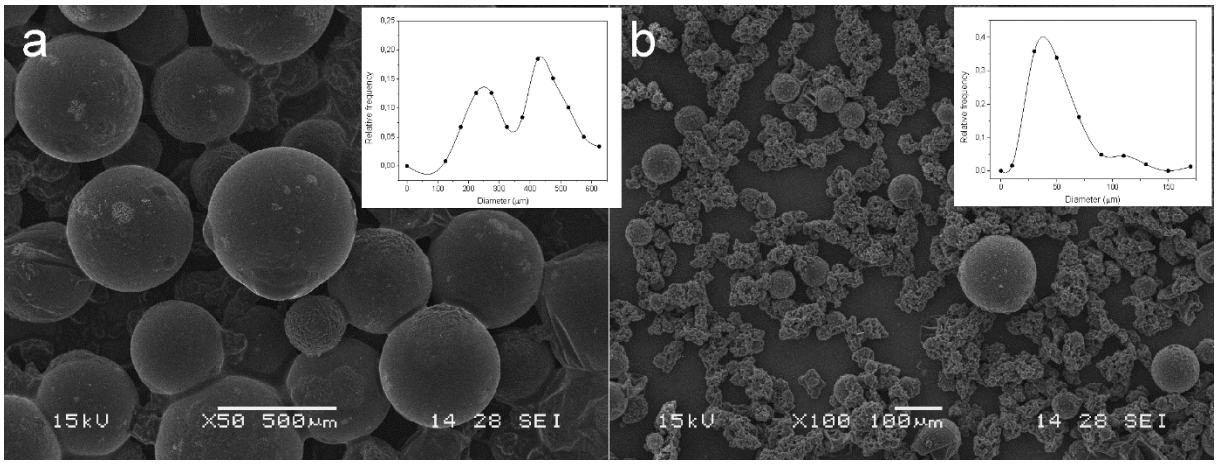

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Figure 4. Optical (left) and SEM (right) micrographs of sample D9.

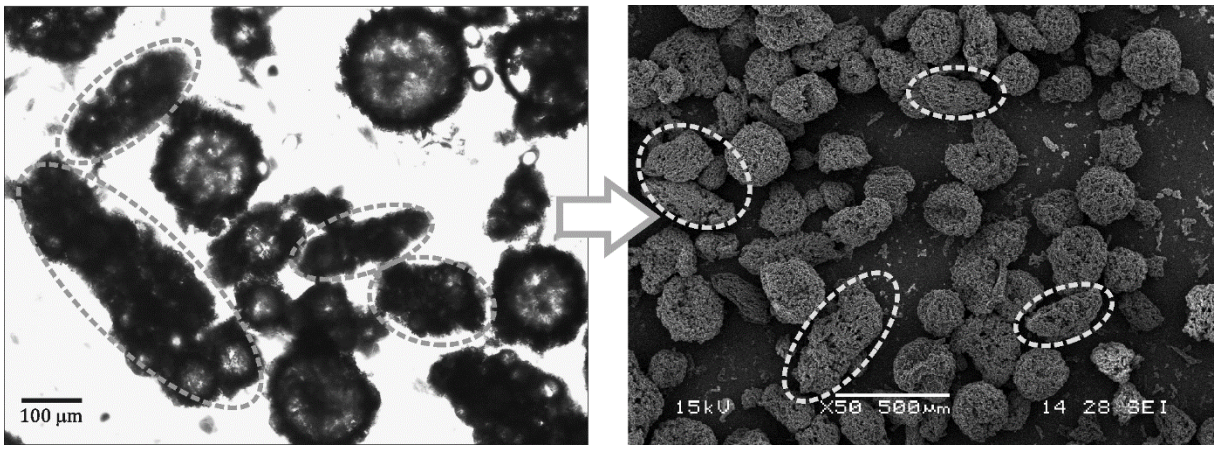

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Figure 5. SEM micrograph of a broken capsule of sample D9.

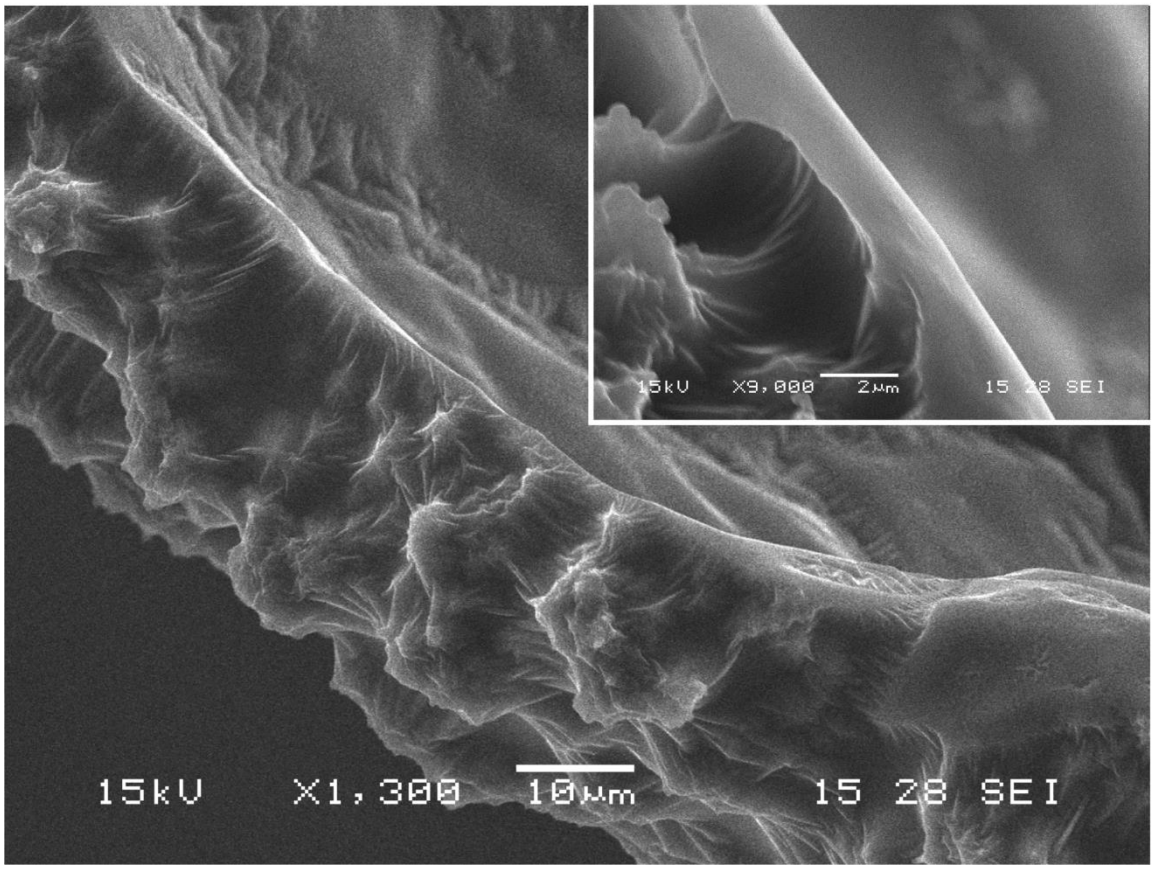

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Figure 6. SEM micrographs of PUF/DGEBF microcapsules, with their corresponding magnifications at the right, obtained with different resin/wall mass ratios: sample D10 (a), D11 (b) and D12 (c).

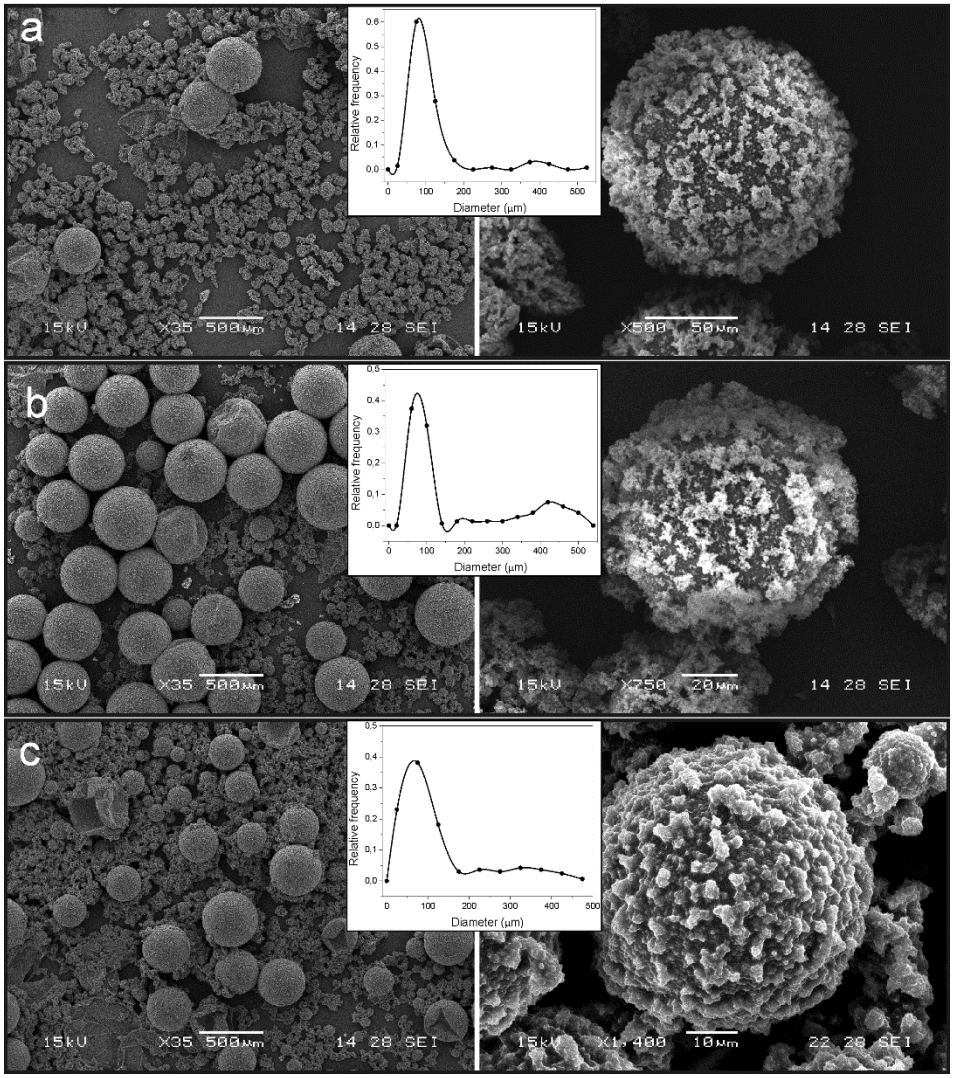

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Figure 7. SEM micrographs of PUF/DGEBF+DLR microcapsules, with their corresponding magnifications at the right, obtained with different emulsification times: sample D10 (a), D13 (b), D14 (c).

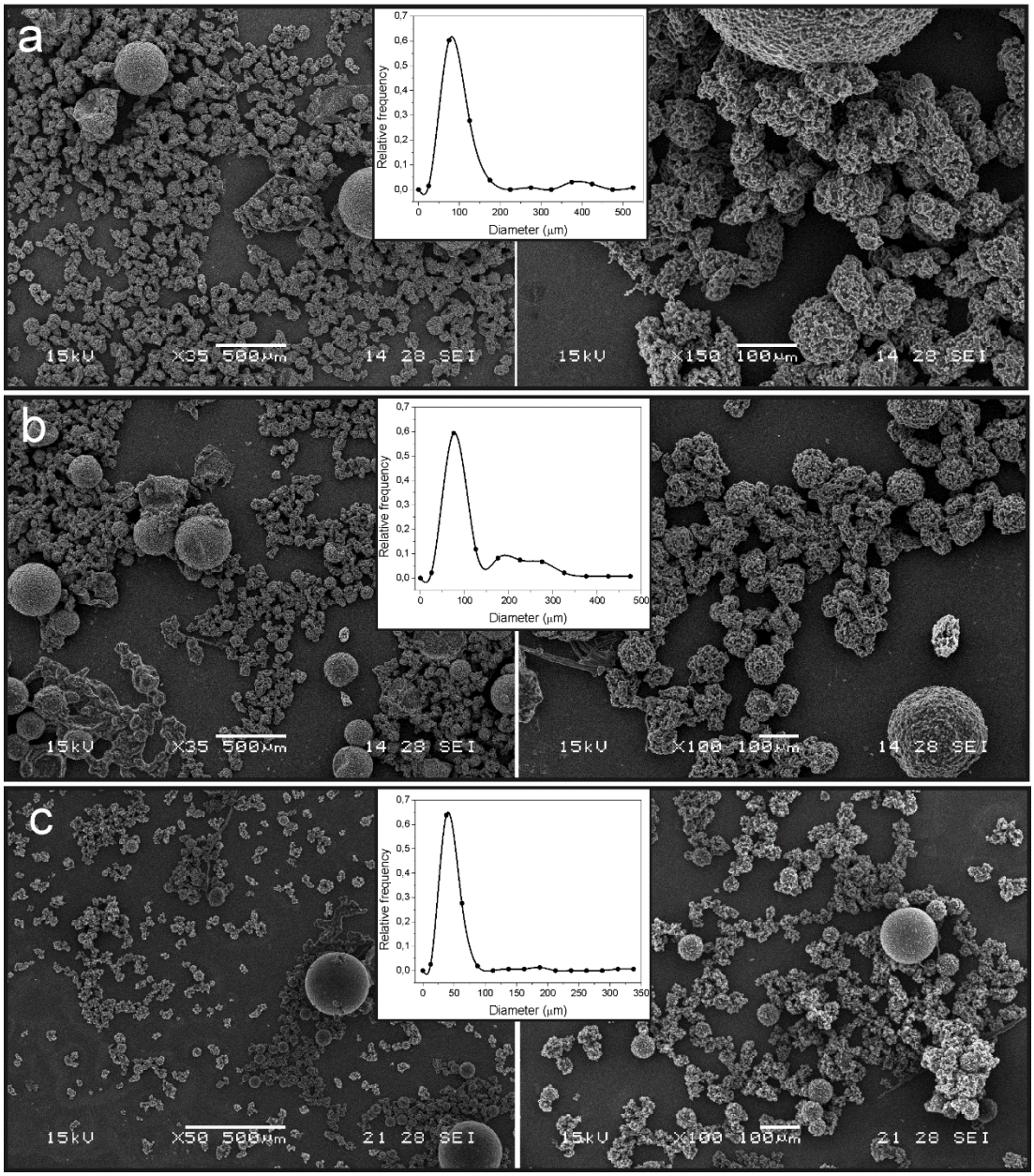

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Figure 8. SEM micrographs of PUF/DGEBF+DLR microcapsules, with their corresponding magnifications at the right, obtained with different emulsification speeds: sample D17 (a), D16 (b), D15 (c).

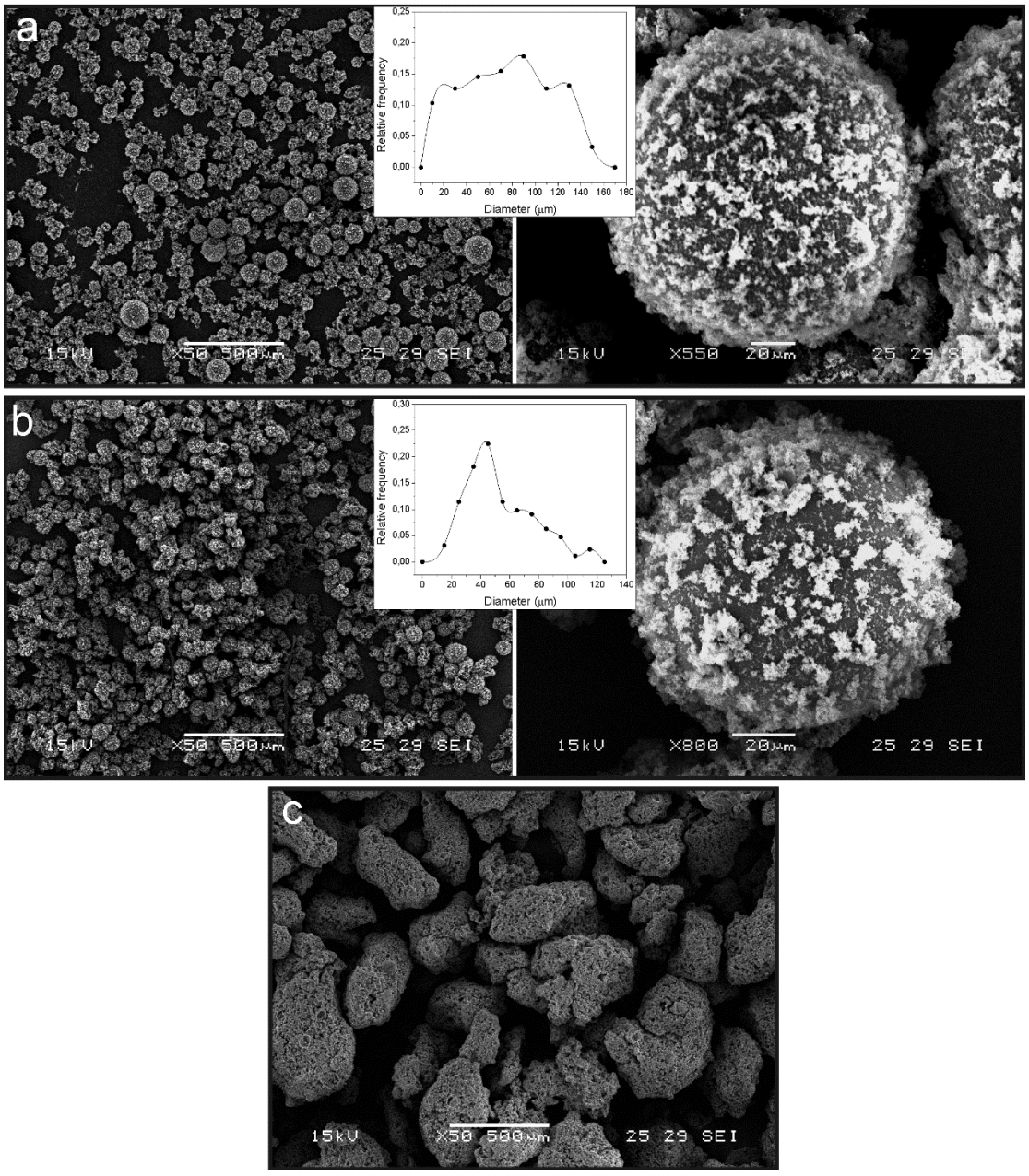

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Figure 9. FTIR Spectra of sample D16, compared to *DGEBF+DLR and PUF*.

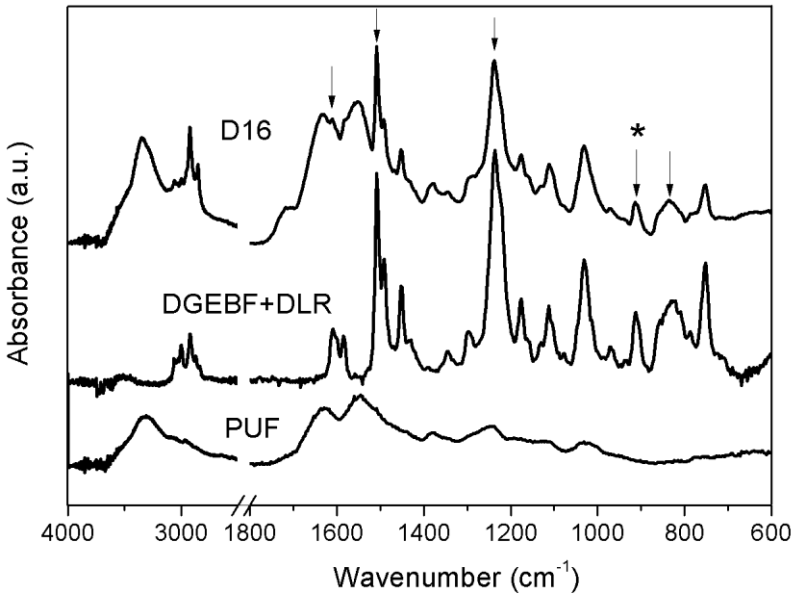

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Figure 10. Representative TGA curves for microcapsules of sample D16 and separated core and shell materials.

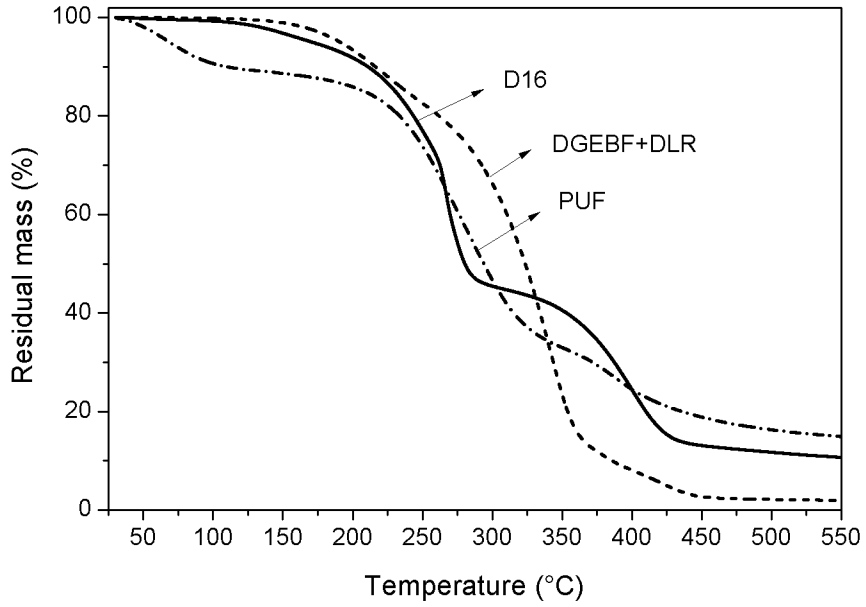

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Figure 11. SEM images of fracture surface of epoxy specimens loaded with 5 wt.% of samples D7 (a) and D16 (b).

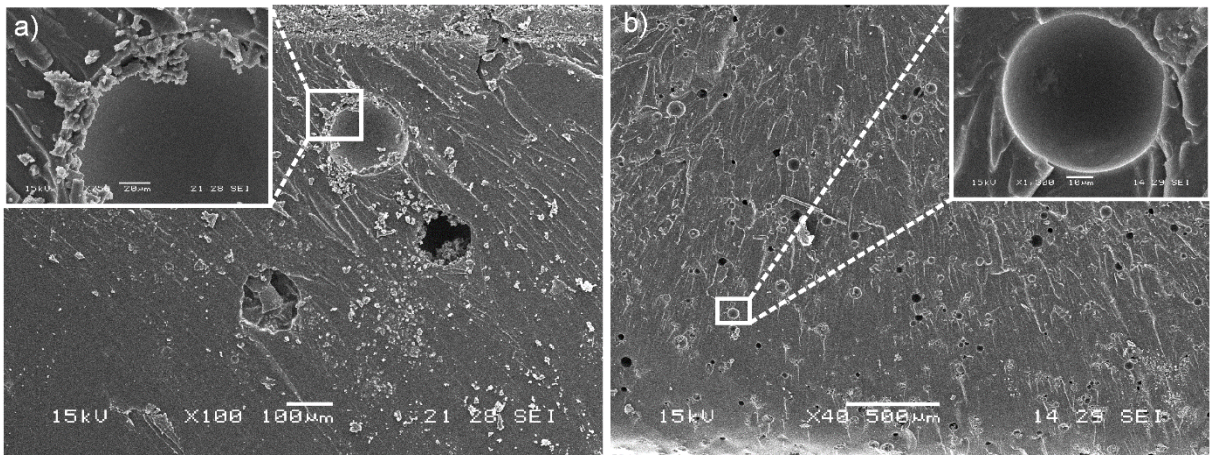

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Table 1. Experimental parameters studied in the synthesis of epoxy-loaded microcapsules.

Sample	Core phase	Core/Wall mass ratio	Emulsification conditions			Agitation rate during synthesis (rpm)
			Homogenization device	Time (min)	Agitation rate (rpm)	
D1	DGEBF	5.4	Mechanical stirrer	30	500	500
D2	DGEBF	3.6	Mechanical stirrer	30	500	500
D3	DGEBF	2.5	Mechanical stirrer	30	500	500
D4	DGEBF	3.6	Mechanical stirrer	30	650	650
D5	DGEBF+DLR	3.6	Mechanical stirrer	30	500	500
D6	DGEBF+DLR	2.5	Mechanical stirrer	30	500	500
D7	DGEBF+DLR	3.6	Mechanical stirrer	30	650	650
D8	DGEBF	3.6	High speed homogenizer	5	11000	500
D9	DGEBF+DLR	3.6	High speed homogenizer	5	11000	500
D10	DGEBF+DLR	3.0	High speed homogenizer	5	11000	500
D11	DGEBF+DLR	2.4	High speed homogenizer	5	11000	500
D12	DGEBF+DLR	1.9	High speed homogenizer	5	11000	500
D13	DGEBF+DLR	3.0	High speed homogenizer	10	11000	500
D14	DGEBF+DLR	3.0	High speed homogenizer	20	11000	500
D15*	DGEBF+DLR	3.6	High speed homogenizer	5	15000	500
D16*	DGEBF+DLR	3.6	High speed homogenizer	5	8000	500
D17*	DGEBF+DLR	3.6	High speed homogenizer	5	5000	500

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Table 2. Yield, core content, *ΔHr* values and mean diameter of PUF/DGEBF+DLR microcapsules obtained with mechanical agitation.

Sample	Yield (%)	Mean diameter (μm)	Core content (wt.%)	ΔH_r (J/g)
D5	84.7	332 ± 78	50.9 ± 2.5	-227.0
D7	84.8	222 ± 54	82.4 ± 3.7	-250.6

Table 3. Yield, core content and mean diameter of PUF/DGEBF and PUF/DGEBF+DLR microcapsules obtained with high speed homogenization.

Sample	Yield (%)	Core content (wt.%)	Mean diameter (μm)
D8	75.8	85.7 ± 3.4	53 ± 16
D9	78.3	80.9 ± 1.2	190 ± 64
D10	85.8	81.4 ± 0.9	92 ± 24 & 397 ± 72
D11	73.7	72.3 ± 2.5	78 ±12 & 389 ± 94
D12	72.7	73.0 ± 3.1	72 ± 35 & 300 ± 85
D13	92.0	85.4 ± 1.7	84 ± 18 & 245 ± 72
D15	91.1	85.5 ± 0.1	53 ± 23
D16	85.6	87.9 ± 0.5	74 ± 39

Table 4. FTIR wavenumbers and assignments of the principal functional groups in DGEBF resin and neat PUF.

DGEBF resin		**Neat PUF**	
Wavenumber (cm^{-1})	**Peak assignment**	**Wavenumber (cm^{-1})**	**Peak assignment**
3056	C-H (epoxy ring)	3329	-N-H and -O-H
3030	=C-H (aromatic ring)	2962	-C-H
1505; 1607	-C=C- (aromatic ring)	1631	-C=O
1247	=C-O-	1553	-C-N
1036	-C-O-		
915	CH_2-O-CH (epoxy ring)		
830	*Para*-disubstituted aromatic ring		