PEEKWC capsules prepared by phase inversion technique:

A morphological and dimensional study

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ABSTRACT

A novel type of modified polyetheretherketone (PEEKWC) microcapsules was prepared using a procedure which combines membranes with the sol-gel phase inversion technique. An experimental and theoretical study was carried out to explore the fundamental aspects concerning the production of these polymeric capsules.

By using mono-pore polyethylene (PE) film with pore diameter ranging from 300 to 1400 μm the formation of PEEKWC microcapsules with different morphologies was performed. The capsule morphology, shape, size can easily adjusted changing parameters such as polymer concentration, solvent and non solvent involved phases. The mean diameter of the obtained microcapsules, with different morphology, was ranging from 650 to 2200 μm.

The capsules sizes, obtained experimentally were compared with the droplet diameter derived by a balance force analysis along the pore mouth. The theoretical analysis permitted to understand the droplet detachment mechanism, occurring during this process as function of membrane and process parameters involved.

This study analysed the different morphology and sizes of the capsules and clarified the mechanism by which the capsules are formed as function of the parameters involved in the process.

Keywords

PEEKWC, capsule preparation, phase inversion, porous membrane, microcapsules

INTRODUCTION

Polymeric microcapsules are largely applied in various industrial fields, such as cosmetic, pharmaceutical, chemical, textile and food packaging. Common techniques for producing micro-capsules, having a dense or porous layer, include interfacial polymerisation, and precipitation, in situ polymerisation, etc. [1-6]. However, the micro-capsules preparation with a tailored morphology is still an important challenge.

In this work, polymeric microcapsules using the membrane emulsification concept combined with the phase inversion technique were prepared. This technique can be identify as an integration between the chemical capsule preparation (non-solvent induced phase separation) and the mechanical capsule technique (pressure extrusion) using a mono-pore film [7].

The non-solvent induced phase separation (NIPS) is the most common phase inversion method employed for membrane preparation. This technique has been extensively described in the literature for a large number of polymer/solvent/non-solvent combinations [8-15]. Upon immersion of the casting solution into a coagulation bath, diffusion of a solvent and a non-solvent across the interface between polymer solution and non-solvent induces phase inversion of the polymer solution. Subsequently, solidification of the polymer-rich phase, e.g., by gelation, crystallization, or vitrification, yields the final membrane. The phase inversion process depends on a number of thermodynamic and kinetic factors, which determine the membrane morphology. The exchange rate of solvent and non-solvent in the cast polymeric solution is one of fundamental importance. Depending on the exchange rates, membranes with symmetric or asymmetric structures can be formed.

The use of the NIPS technique for the preparation of microcapsules with different membrane structures has been also reported in literature. These works refer to the preparation of both inorganic and organic capsules [16-17]. G.-J. Wang et al. [18] prepared porous polyethersulfone (PES) microcapsules with straight open pores across the whole membrane thickness by NIPS together with an accompanying process for peeling off the surface dense layer. The polymer solution was gradually dropped into the non-solvent bath through a syringe needle using a syringe pump. The effects of the capsule preparation conditions (polymer concentration, additives in the polymer solution, coagulation bath temperature, dissolution time of the dense layer) on the microstructures of porous microcapsules were deeply investigated. Capsules of about 2000 μm with a well defined pore distribution were prepared. Another interesting study on the preparation and characterisation of polysulfone microcapsules, prepared by NIPS, has been reported by C. Torras et al. [19]. The microcapsules were prepared in two steps: a) polymeric droplet preparation, b) droplet precipitation. Also in this case, the main factors (polymer concentration, solvent/non solvent system, additives in coagulation bath), affecting the capsule morphology, were investigated. Capsules of different size (50-1000μm) and morphology were obtained and characterised.

Another important aspect that has to be considered besides the morphology is the control of the size and shape of the capsules.

Recently, the emulsification processes, that use membranes for emulsion production, have gained attention. With this technique, both size and the size distribution of the droplets may be carefully tailored choosing suitable membranes and some fundamental process parameters. The droplets size depends on: *a)* operating parameters, i.e. transmembrane pressure and disperse phase flow; *b)* membrane parameters, i.e., pore size, active pores, membrane hydrophobicity/hydrophilicity; and *c)* phase parameters, i.e. interfacial tension, viscosity and density of the processed phases. Starting from the mentioned advantages, the membrane

emulsification technique is also employed in capsules preparation. In fact, the capsules are usually produced by membrane emulsification in two steps: *i)* emulsion preparation, pressing the disperse phase through the microporous membrane into the continuous phase *ii)* capsule production, employing a traditional encapsulation technique such as solvent evaporation, coacervation, etc.

Although several authors studied the NIPS process for producing polymeric microcapsules, as already mentioned, the combined use of membrane technique and phase inversion has not been investigated, yet.

In this study, the membrane emulsification and phase inversion were coupled in order to exploit the advantages that both methods present.

The polymer solution was pressed through the porous support. The liquid droplets, formed around pore borders, in the phase 2 (air or liquid), moved to the non-solvent phase in which they immediately coagulated forming the capsules.

The polymer used was the modified polyetheretherekene (PEEKWC) which has excellent chemical, thermal and mechanical properties; moreover it has the advantage, compared to traditional polyetheretherketone, to be soluble in several common organic solvents which facilitates both membrane [20-22] and capsules preparation.

A mono-pore PE film was used as a model for the porous membrane. PEEKWC capsules of different morphology, porosity, size and shell thickness were prepared changing the process parameters and pore dimension of this mono-pore PE film.

The experimental capsule dimension was compared with the droplet diameter obtained by a balance force analysis made along the pore-droplet contact line. This force balance allowed to understand the droplet formation mechanism as function of pore diameter, membrane hydrophobicity, interfacial tension and volume of the polymeric solution used.

2. Experimental

2.1 Materials

PEEKWC was supplied by the Chan Chung Institute of Applied Chemistry, Academia Sinica. N,N-dimethylformamide (DMF) and dimethylacetamide (DMA) was purchased from Merck and used as polymer solvent without further purifications. The solvents (dodecane, iso-octane) were purchased from Sigma-Aldrich and used as oil phase. Alcohols, such as methanol, ethanol and iso-propanol, were mixed with water and employed as non-solvent phase.

2.2 Capsule preparation and characterisation

The polymer, PEEKWC (8, 10 and 15 wt.%) was dissolved in DMF or DMA, at room temperature. The solution was magnetically stirred for at least 1 day to allow a complete dissolution of the polymer.

The polymer solution (*phase 1*) was add to the feed tank of the module in the capsules preparation (Fig. 1). Then, it flowed by means of gravity through the mono-pore film of polyethylene (PE). The droplets formed at PE hole border moved through the dodecane or iso-octane (*phase 2)*, which induce a spherical shape to the latter. These immediately coagulated by phase inversion when in contact with the non-solvent phase, water/alcohol at different concentration (*phase 3*). The capsules obtained were re-immersed and stabilised in the water bath for 24 h, and then recovered using a filter paper. The capsules were then dried over night at room temperature and set in an oven under vacuum for 24h to remove completely the last traces of the solvent.

In table 1, the summary of the main ingredients and process parameters involved in the capsules preparation is reported. The main membrane and process parameters that control the capsule formation summarised below:

- The *Minimum Volume* (V_{min}) is the minimum amount of polymer solution that has to be added into the module in order that its hydrostatic pressure allows the droplet formation at the interface1-2 (polymer solution-oil);
- The *Maximum Volume* (V_{max}) is the maximum amount of polymer solution added into the module in order to make sure that the *formation time* of the droplet is lower than its *permanence time* at the interface 2-3 (oil-coagulation bath). To avoid coalescence phenomena, the Maximum Volume has not to be outmoded exceeded;
- The *Droplet formation Frequency* (*f*) is the number of droplets formed in 1 minute and it is related to the polymer volume and viscosity, pore size and surface tension of phases 1-2;

  The droplet formation frequencies reported in the work are evaluated keeping the polymer volume equal to the maximum volume;
- *Contact angle* of the PE film is defined as shown in Fig. 1b;

The morphology of the dried capsules was determined using a Scanning Electron Microscopy (SEM), Cambridge, Stereoscan 360, at 20kV. The capsules were freeze-fractured in liquid nitrogen for cross-section analysis. All samples were evacuated and then sputter-coated with gold under argon atmosphere before SEM analysis.

The size of the polymer capsules was measured by a digital micrometer (Carl Mahr D 7300 Esslingen a.N.).

RESULTS AND DISCUSSION

In Figure 2 is reported a picture showing the all steps involved in the capsules formation process.

All experiments carried out were repeated several times in order to assess the reproducibility of the results and the variation of the capsules size did not exceed 5%. Experiments were

performed varying either the polymer concentration from 8 to 18 wt% either the polymer solvent (DMF or DMA), phase 1. Spherical capsules were obtained at lower polymer concentrations (8-10wt%).

The phase 3, i.e. coagulation bath, was also modified for tailoring the capsules morphology similarly to the PEEWKC membrane preparation [14]. However, the choice of this phase is crucial since it has to form spherical capsules by phase inversion and it should not be mixed with the phase 2 (dodecane or iso-octane). To achieve a satisfactory formulation of phase 3, both pure water and mixture of water with different concentration of alcohols were tested. The alcohols were added to the water to decrease the surface tension of phase 3 and, then, to reduce the resistance at the interface 2-3. Alcohols with longer chain could not be employed since they easily mixed with phase 2, therefore, alcohols such as methanol, ethanol and iso-propanol were employed. In all experiments, capsules were obtained with a solution of iso-propanol and water at a ratio of 70:30. However, phase 3 with different concentration of alcohols can be also used, the study of several phase 3 is an important aspect of this process.

The experiments were performed in a range of temperature from 15 to 50^{o}C. At a temperature below 25^{o}C, the experiments could be performed for more than 3 days without change of the morphology, shape and size of the capsules. A higher temperature rapidly changed the capsule structure due to the faster mixing of phase 2 with phase 3. For example, at 50°C the experiments could be carried out only for 1 hour.

Once the droplet was in contact with the coagulant, the polymer solvent (phase 1) near to the droplet surface immediately diffused into water. At the same time, the non-solvent solution (phase 3) entered into the forming capsule. At the droplet interface, the PEEKWC polymer concentration rapidly increased and then the dense skin was formed. After the formation of the skin, the exchange rate between the coagulant and the polymer solvent decreases. The skin formation and the consequently reduction of the exchange rate determined a lower PEEKWC

concentration of the polymer solution inside the forming capsule with the formation of a porous structure (asymmetric structure).

The use of oils as phase 2 is due to the fact that the preliminary experiments performed with air and alcohol/water solutions, as phase 2, did not allow to the achieve an optimal capsule formation. In particular, using air it was not possible to tailor accurately the size of the capsules. In fact, the polymeric droplet spread on the surface of the mono-pore PE film and the size of the obtained droplet was not controlled by the pore size. Using, directly as phase 2, the coagulation system the polymer solution solidified at the pore border causing the plugging of the pore-self. On the contrary, using oils as phase 2, the formation of an emulsion O_1/O_2, before the coagulation of the polymeric droplet, was achieved. Capsules with a tailored size and spherical shape were obtained as function of the pore size of the PE film used.
In this work, two oils as phase 2, i.e. *iso-octane* and *dodecane,* were employed.

Phase 2: Iso-octane

Pore size, V_{min}, V_{max}, Droplet formation Frequency and the average capsule diameter measured using iso-octane as phase 2 are summarised in table 2.

As expected, an increase of the pore diameter, from 300 to 1400 μm, determined an increase of the capsules size from 650 to 1500 μm and of the droplet formation frequency.
The minimum volume of polymer solution (V_{min}), need for making the droplets, increase with the decrease of pore diameter.
The experiments were performed at different temperatures. It was observed that at higher temperature (T>30°C) the iso-octane began to mix, fastly, with the non-solvent (phase 3). Thus, capsules "permanence time" increased and the forming capsules attached each other

with a change also of their shape from spherical to oval. The optimal temperature was found to be of 20°C. Therefore, all the experiments were carried out at this temperature.

The SEM pictures of the capsules, obtained with PEEKWC/DMF 10 wt.%, are shown in Fig.3. These capsules were prepared by using a pore diameter of 550 μm and water/iso-propanol (30/70) as non-solvent (phase 3).

The formation of an O_1/O_2 emulsion, made by well defined round droplets of PEEKWC/DMF in iso-octane, was accomplished. The droplets in contact with the phase 3, immediately coagulated and formed the final capsules keeping the spherical shape with a roughness surface (Fig. 3a). The higher affinity of iso-octane with the polymer solution caused a starting of demixing before coagulating at the non-solvent phase 3 with the formation of a roughness and porous surface. Nevertheless, the capsule cross-section (Fig. 3b and c) shows a central cavity and an asymmetric structure, finger type support layer with a porous skin at the shell side.

Phase 2: Dodecane

As in the previous case, an increase of the pore diameter determined either an increase of the capsules size from 1000 to 2200 μm either an increase of the droplet formation frequency as shown in Table 3.

The increase of the capsule dimensions, obtained using dodecane, was significantly higher with respect to iso-octane. On the contrary, the increase of the frequency observed for dodecane was lower than iso-octane. This was probably due to the lower viscosity of dodecane. The V_{max} is strictly connected with the concentration of phase 3 and its increase has to determine an increase of frequency (*f*). Therefore, the concentrations of phase 3 (i.e. water/iso-propanol) determined, in turn, the droplet formation frequency (*f*) values.

The SEM pictures of the capsules, obtained with dodecane, are shown in Fig. 4. These capsules were produced by using the same aforementioned. The capsules have again a

spherical shape but a smooth surface (Fig. 4a). Moreover, the capsule cross-section, as shown in Fig.4b and 4c, present a central cavity and an asymmetric (finger type) structure but with a dense skin layer at the shell side.

These results are in good agreement with various studies on the effect on the morphology of asymmetric membranes of the coagulation medium and conditions. The higher alcohols, i.e. iso-propanol, give membranes with a much thicker dense top layer [14]. These studies indicate that the top layer thickness of the membrane, in general, increases with increasing molar volume of the external nonsolvent species due to their lower diffusion rate which leads to delayed liquid–liquid phase demixing.

Fig. 5 shows the PEEKWC capsules obtained increasing the polymer concentration from **10 wt.%** to **15 wt.%** and keeping the same conditions of phase 2 (dodecane) and phase 3. The increase of the polymer concentration caused a deformation of the spherical symmetry of the capsules. This is, probably, due to a decrease of the interfacial tension of the polymer solution which did not allow to keep the spherical symmetry when the droplets were formed at the pore border and they moved across phase 2 and at the interface 2-3.

In all the experiments, it was verified that the pore size of the membrane did not influence the morphology of the produced capsules. On the contrary, the oil phase can affect the morphology of the final capsules, as in the case of isoocatane, in which its higher affinity towards the polymer solution and its lower surface tension with respect to dodecane determined a change of droplet shape with a lost of their spherical symmetry and control of their dimensions.

Force balance analysis of experimental results.

The experimental data obtained in the previous section were analysed by using a macroscopic force balance to clarify the following question: can the droplet size be predicted by means of a force balance equation?

Formation of the droplets in the gravitational field, generally, occurs by means of neck formation and subsequently closing of this latter, as shown in the Fig. 6. To minimize the surface free energy, the droplet attempts to assume a spherical shape forming a neck, since the sphere has the smaller ratio surface/volume. The neck reduces rapidly until to a mechanic instability "point" which determines the detachment of a droplet fraction (the spherical part, *droplet volume*) whereas the remaining fraction (the grey volume, *attached volume*) is still attached at the hole border. The sum of the *attached* and *droplet volumes* defines the *total volume* V_{tot}. To establish the above mechanic instability, i.e when the complete neck closing occurs, several theoretical models were proposed and are available in literature [23-25]. In this case, conditions based on force balance along the hole border are not applicable to predict the droplet size because the breaking of force balance is not the cause of droplet closing and detachment. The breaking of force balance along the hole border can be considered as a *limit case* of the illustrated mechanism, i.e. when the neck is negligible and the shutting of the droplet is due to *force equilibrium breaking*, Fig 7.

A force balance analysis was performed to establish whether some conditions really exist for droplet detachment by means of the mentioned *limit case.* The main macroscopic forces acting on the droplet fixed to the hole border of diameter D_p, can be summarized as follows [26, 27]:

$$F_w = \frac{1}{4} P_i \pi D_p^2 + \frac{\gamma}{D_{tot.}} \pi D_p^2 + \Delta\rho g V_{tot.} \quad (1)$$

$$F_\gamma = \pi D_p \gamma \, sen\theta \quad (2)$$

The expression of the force F_w used in the following balance equation is different in the two droplet dispositions shown in Fig. 7a and Fig. 7b. Since in this model it was assumed that the droplet equilibrium shape is a sphere, the expression of the F_w was approximated for the case shown in Fig. 7b. This fact, obviously, reduces the predictive reliability of the proposed force balance model. The first term in the right-hand side of Eq. (1) represents the force due to the volume of polymeric solution (ΔV_i) located on the hole plane. The second term represents the Young-Laplace pressure difference needed to overcome the capillarity. The last term is the buoyancy force due to difference of density ($\Delta\rho$) between polymeric solution and phase 2, while g is the gravitational acceleration. D_{tot} and γ represent the droplet diameter corresponding to the *total volume* V_{tot} and the interfacial tension associated to phase 2 and 3, respectively. The total force F_w is a detaching force.

The sum of the interfacial tension differential forces distributed along the pore border yields the force in Eq. (2). This expression is obtained considering the contact angle, θ, shown in Fig.7a invariable along the circular border. The Eq. (2) depends on the border shape and on the contact angle which could not be constant along the pore border as shown in ref. [28]. The F_γ force represents an holding force.

The balance between the considered forces gives a non-linear equation that yields the *total volume* V_{tot} of the droplet fixed at a circular hole subject to the gravitational field:

$$\frac{1}{4}P_i D_p^2 + \frac{\gamma}{D_{tot}}D_p^2 + \frac{1}{6}\Delta\rho g D_{tot.}^3 = D_p \gamma\, sen\theta \qquad (3)$$

Defining P_i as follows:

$$P_i = \frac{F_i}{\Delta S_p} = 4\frac{mg}{\pi D_p^2} = \frac{\rho\pi D_p^2 h(t) g}{\pi D_p^2} = \rho h(t) g \qquad (4)$$

where F_i, ρ and h(t) are the weight, density and height of the polymeric solution while ΔS_i represents the pore surface and introducing Eq (4) in Eq (3), Eq(5) is obtained:

$$\frac{1}{4}\rho h(t) g D_p^2 + \frac{\gamma}{D_{tot}} D_p^2 + \frac{1}{6}\Delta\rho g D_{tot.}^3 = D_p \gamma(t) sen\theta \quad (5)$$

The height h(t) can be derived from the aforementioned volume of polymeric solution ΔV_i as follows:

$$h(t) = h_1 + h_2(t) \quad (6)$$

$$h_2(t) = \frac{4\Delta V_i(t) - \pi D_1^2 h_1}{D_2^2 \pi} \quad (7)$$

in which D_1 (0.014) and D_2 (0.02) represent the lower and upper diameters in the used module (Fig. 8), while h_1 shown in Fig.8 is a constant equal to 0.05 m. It is important to note that the minimum volume of polymeric solution was always larger than $\pi/4\, D_1^2\, h_1$. Using Eqs (5)-(7), D_{tot} can be evaluated for every value of volume of polymeric solution located on the hole plane. The Eqs (5)-(7) show that the *total droplet volume* V_{tot} depends on following parameters:

- dimensions of module;
- size and shape of hole;
- difference of density between polymeric solution and phase 2;
- interfacial tension between polymeric solution and phase 2;
- contact angle , i.e. wetting of the porous support;
- volume of polymeric solution located on the hole plane, ΔV_i (t)

If the droplets detachment occurred by means of a long neck formation then the breaking of force balance is not the cause of its detachment and Eq.(5) is not predictive. Therefore, to understand the reliability of the presented force balance model the relative differences between predicted D_{tot} and the average experimental size of the capsules $D_{\text{exp.}}^{cps.}$ (Table 2 and

Table 3) were evaluated for various pore sizes. The results are shown in Fig. 9. In particular, the (1- $D_{exp.}^{cps.}$ / D_{tot}) values were evaluated for various contact angles and two interfacial tensions corresponding to dodecane and iso-octane (25.35 mN/m, 21.60 mN/m), respectively. It is important to emphasize that during capsule formation at the organic-aqueous interface by means of phase-inversion no significant swelling or reduction of droplet volumes were observed; the influence of organic-aqueous interface on capsules sizes is therefore negligible. The errors of the balance model *decrease* with the *increase* of the pore diameters, Fig. 9a and Fig. 9b. For any phase 2, pore diameters equal to 1400 μm and contact angle equal or larger than 125°, the errors of the model are smaller than 30%. For the same pore size, the force balance error is 10% when dodecane and a contact angle equal 135° is used. Therefore, the force balance yields acceptable errors for contact angles larger than 125° and pore diameter near to 1400 μm. The contact angle in which the balance model gives acceptable results is in agreement with the contact angle of the DMF on a PE surface. The reasons for the errors of the balance model are two-fold. Firstly, the expression of the F_w force used in the Eq. (5). Secondly, the mechanism postulated for the droplet formation is not correct. In fact, in the case of iso-octane, its higher affinity for the polymeric solution coupling to the lower interfacial tension with respect to dodecane determines a more large deformability of the droplet and consequently neck or tail formation. For contact angles and pore diameters lower than 125° and 1400 μm, respectively, the detachment mechanism could occur by means of long neck or tails formation as shown in figure 6. An opposite trend was found when the cross-flow of the continuous phase, flowing parallel to the surface membrane, was applied as reported in literature [28,29].

The Eqs. (5)-(7) show that the D_{tot} values depend on the volume of polymeric solution over the pore, ΔV_i (t). Thus, the behaviour of D_{tot} as function of the maximum volume (V_{max}),

corresponding to ΔV_i (t~0), was studied as well. Independently from phase 2 utilized, the D_{tot} values *decrease* when the V_{max} *increases*. For pore sizes equal to 1400 μm and 800 μm a non-linear behaviour was obtained, whereas for the other pores, 500 and 300 μm, the trend D_{tot} *versus* V_{max} was linear. In particular, for pore size of 500 μm, the slope of linear correlation was equal to –0.23 while for pore size of 300 μm the slope was equal to -0.033. The latter value indicates that for small pore sizes the volume of polymeric solution do not influence the D_{tot}. Large influence of V_{max} on D_{tot} was found for pore size of 1400 μm. It is interesting to note that the non linear behaviour of D_{tot} *versus* V_{max} was found in pores for which the force balance errors are the smallest.

CONCLUSIONS

The fabrication of PEEKWC capsules with different morphologies was successfully developed exploiting the advantages of two well established technologies, such as membrane emulsification and phase inversion. The capsule morphology and dimension can be tailored changing few fundamental processes, ingredients parameters, shape and size of the mono-pore. In all cases, the cross-section of the prepared capsules presented a central cavity and an asymmetric (finger type) structure with a porous or dense skin layer at the shell side depending on the phase 2 employed. These tests also showed that the capsules sizes depend on the film pore diameter. In particular, an increase of the pore diameter from 300 to 1400 μm led to an almost two times higher value of the capsules sizes. The diameters of the obtained microcapsules were ranging from 650 to 2200 μm.

Based on the experimental results, numerical analysis was performed in order to elucidate the mechanism by which the droplets detach. The influence of the membrane and process parameters involved in the capsule formation was, therefore, analysed. The results of the numerical analysis showed that for contact angles larger than 125° and pore diameter of about

1400 μm, droplet formation can occur by breaking of the force balance along the pore border. In these conditions, the model Eq. (5) yielded capsule diameters with relative errors of around 10%. In general, the errors of the force balance model *increased* with the *decrease* of pore diameters; as consequence, for small pore sizes the breaking of the force balance cannot be more considered the cause for droplet formation.

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FIGURE 1

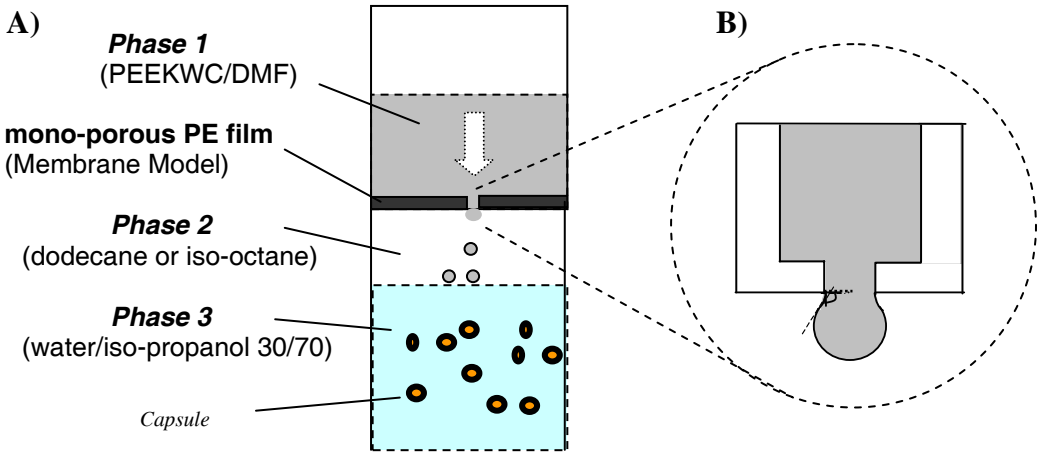


Figure 1. Scheme of the capsule formation process.

FIGURE 2

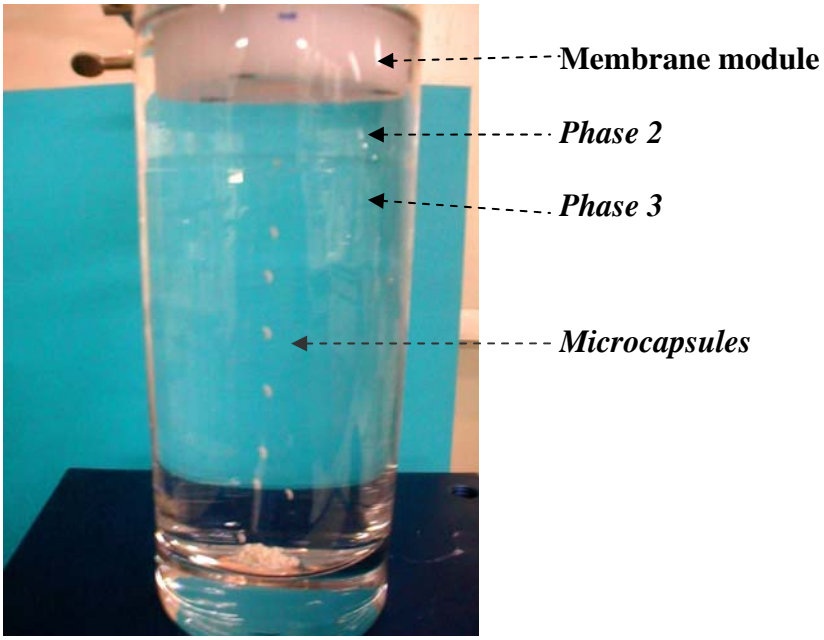


Figure 2. Picture of the PEEKWC capsule preparation.

FIGURE 3

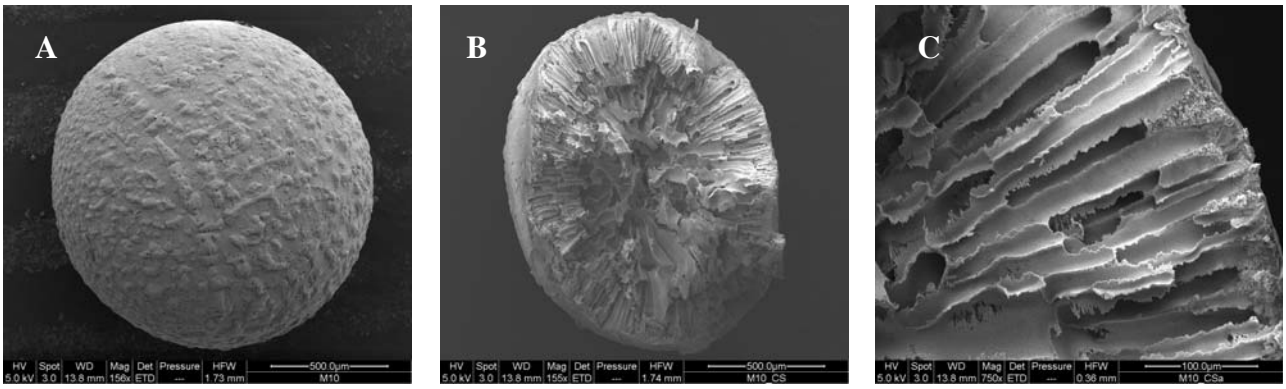


Figure 3. SEM pictures of the *a) Surface* and *b,c) Cross-section* of the capsules prepared using a film with the pore size of 550 μm and **PEEKWC/DMF 10 wt.%,** *phase 1***,** iso-octane, *phase 2*, and water:iso-propanol, *phase 3*.

FIGURE 4

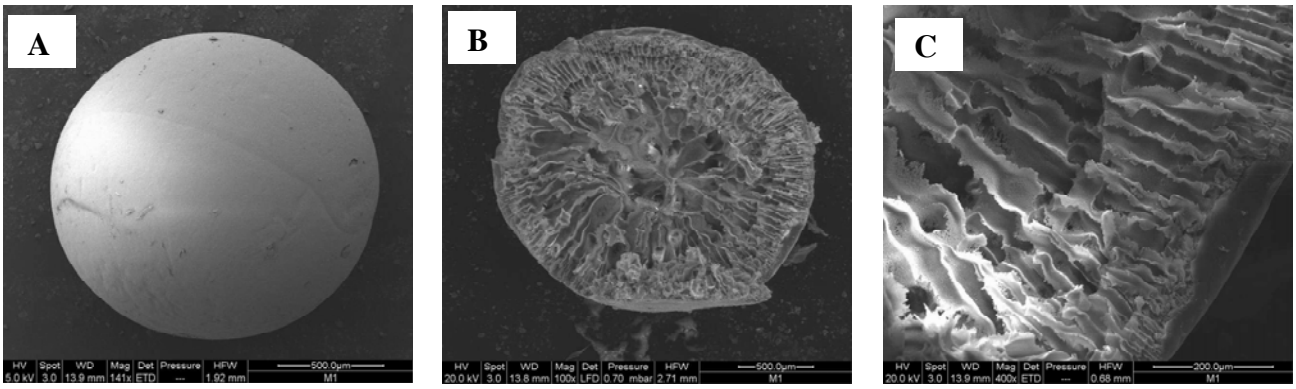


Figure 4. SEM pictures of the *a) Surface* and *b,c) Cross-section* of the capsules prepared using a film with the pore size of 550 μm and **PEEKWC/DMF 10 wt.%,** *phase 1***,** dodecane, *phase 2*, and water:iso-propanol, *phase 3*.

FIGURA 5

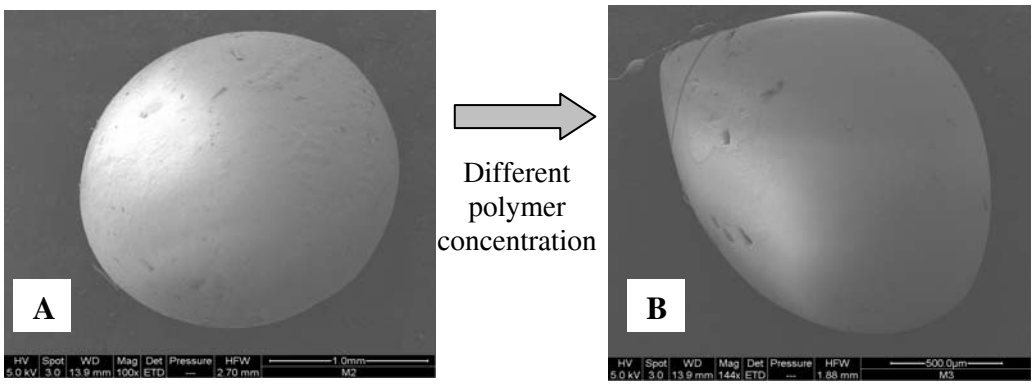


Figure 5. SEM picture of the capsules surface prepared using a film with the pore size of about 500 μm and as *phase 3*, water:iso-propanol, *phase 2*, dodecane and *phase 1*, **PEEKWC/DMF: A*) 10 wt.% and B) 15 wt.%***

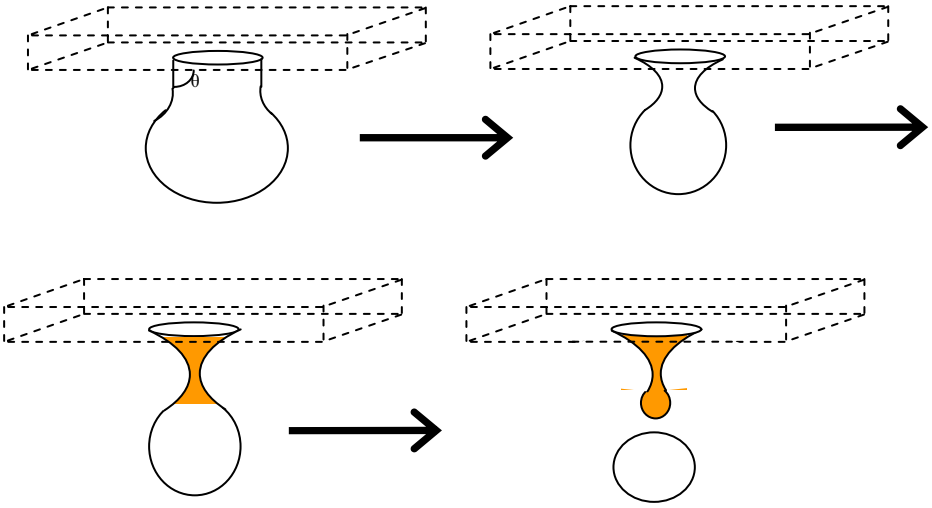


Figure 6. A schematic representation of droplet detachment with neck formation.

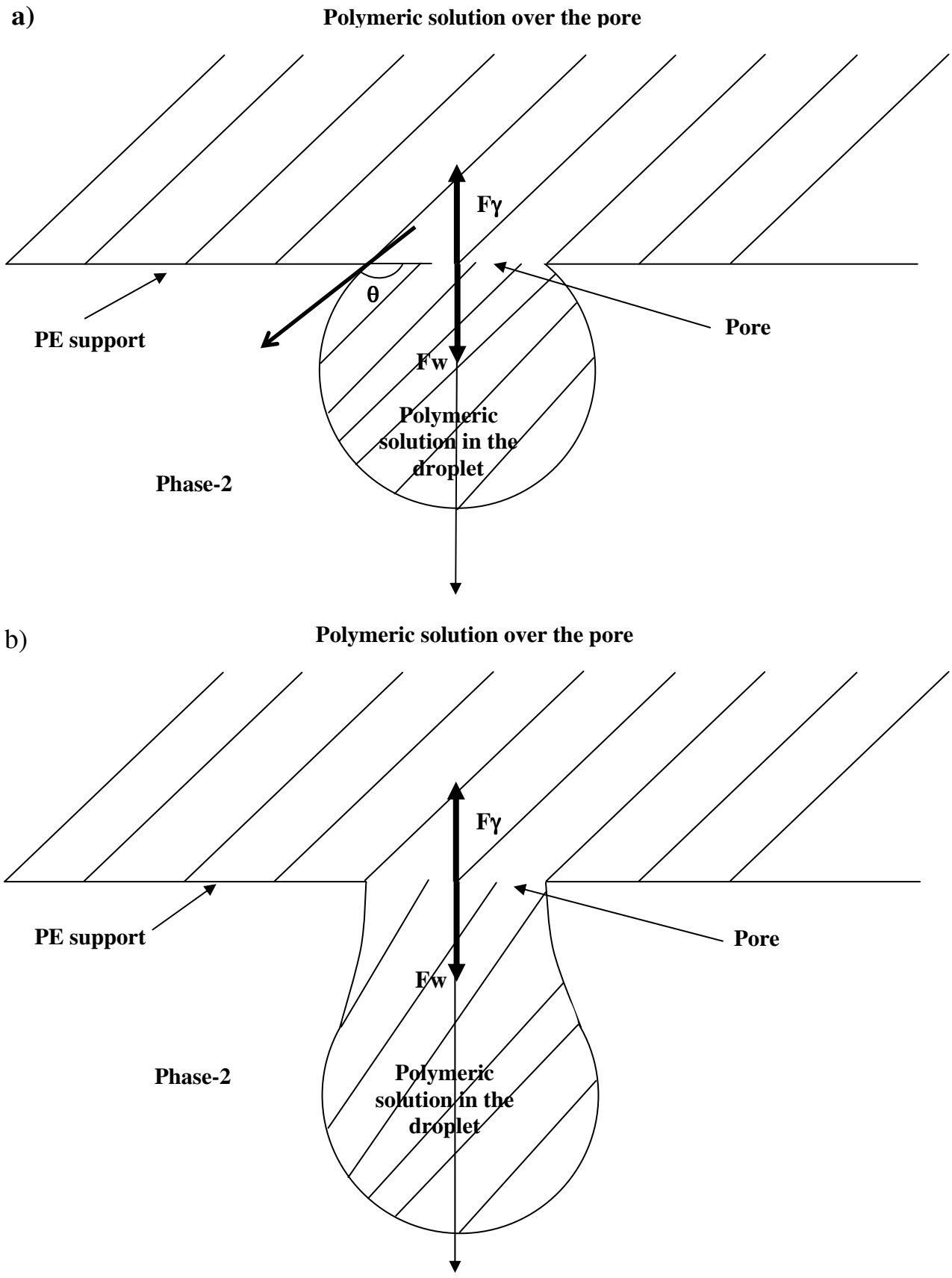


Figure 7. Schematic representations of droplet detachment without neck formation. For (a) picture, the expression of F_w used in the Eq. (5) is correct, for (b) picture the F_w is approximated.

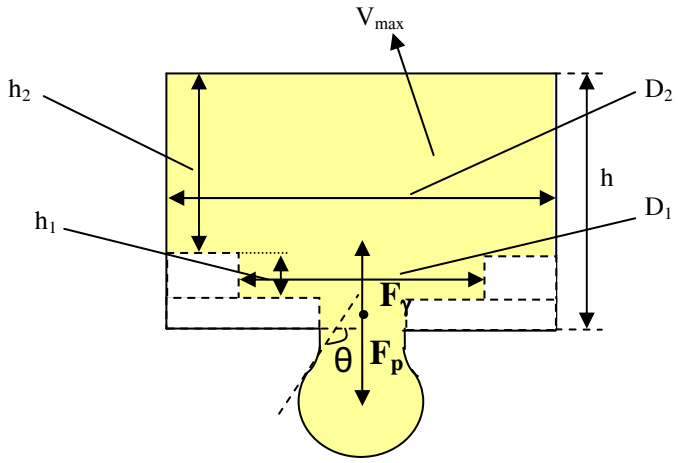
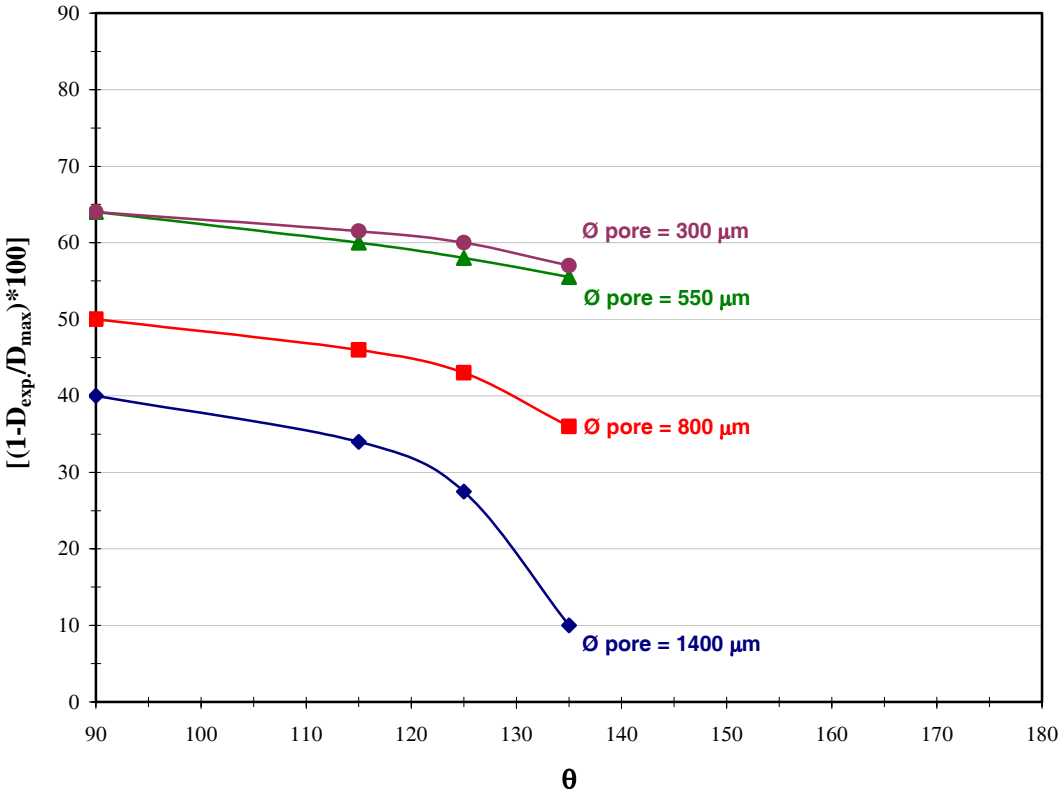


Figure 8. Side section of the module (upper part) used for PEEKWC capsule formation.

Dodecane



Iso-octane

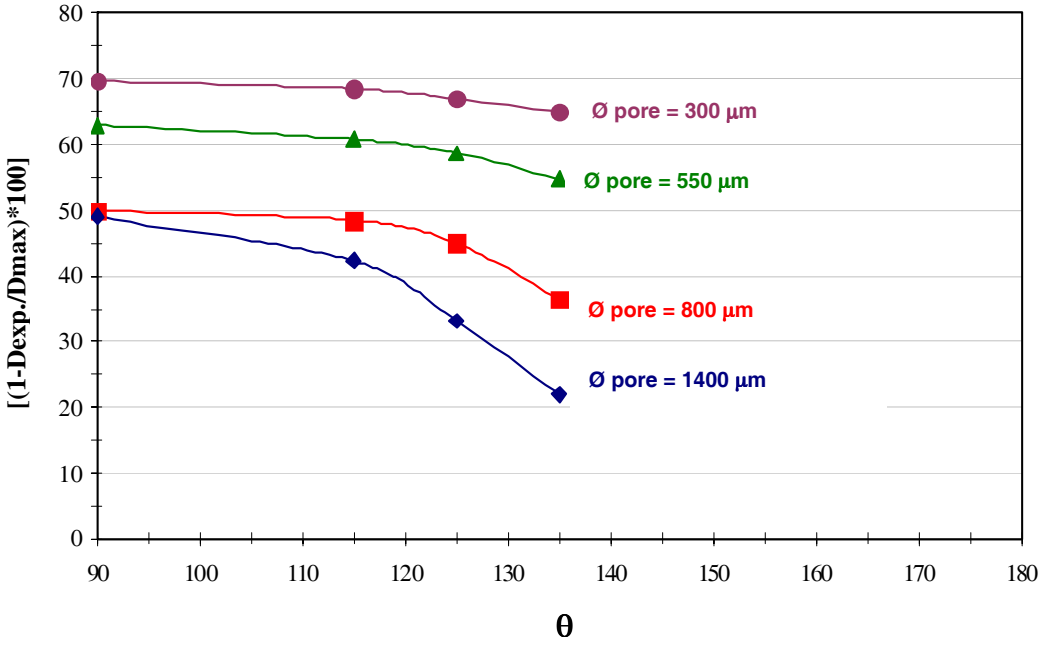


Figure 9. Force balance error (1- $D_{exp.}^{cps.}$ / D_{tot}) *v.s.* droplet contact angle changing *(a)* dodecane and *(b)* iso-octane as phase 2.

Table 1. The main ingredients and process parameters employed in the capsules preparation

Ingredients			**Process parameters**
Phase 1	***Phase 2***	***Phase 3***	Minimum Volume (V_{min}) Maximum Volume (V_{max}) Droplet formation Frequency (f)
PEEKWC/DMF 8wt.%	Dodecane, Iso-octane	Water:iso-propanol (30:70)	
PEEKWC/DMF 10wt.%			
PEEKWC/DMF 15wt.%			

Table 2. PEEKWC capsules prepared using: phase 1: PEEKWC/DMF 10wt.%, phase 2: iso-octane, phase 3: H_2O/iso-propanol (30/70), T=20°C.

Pore Size (μm)	***V_{min} (ml)***	***V_{max} (ml)***	***Droplet formation Frequency* (min^{-1})***	***Average capsule diameter (μm)***
300	0,9	1,2	20	650
550	0,8	1,1	25	1000
800	0,7	1,0	38	1350
1400	0,6	0,7	48	1500

** The frequency has been obtained at the V_{max} of the polymer solution.*

Table 3. PEEKWC capsules prepared using: phase 1: PEEKWC/DMF 10wt.%, phase 2: dodecane, phase 3: H_2O/iso-propanol (30/70), T=20°C.

Pore Size (μm)	***V_{min} (ml)***	***V_{max} (ml)***	***Droplet formation Frequency* (min^{-1})***	***Average capsule diameter (μm)***
300	0,9	1,2	10	1000
550	0,8	1,1	11	1200
800	0,7	0,9	15	1750
1400	0,5	0,6	25	2200

** The frequency has been obtained at a V max of the polymer solution.*

List of Symbols

V_{min} Minimum Volume (ml)
V_{max} Maximum Volume (ml)
f Droplet formation Frequency (min^{-1})
D_p Pore diameter (μm);
D_{tot} Droplet diameter (μm);
D_1, D_2 Inner lower and upper diameters of the module (cm);
$D_{exp.}^{cps.}$ Experimental capsules diameter (μm)
F_w Total detaching force (N);
F_γ Interfacial tension force, Total holding force (N);
F_i Weight force (N);
g Gravitation acceleration (m/s^2);
h Height of the polymeric solution located on the hole plane, (cm);
h_1 Constant height in the module (cm);
P_i Pressure of the polymeric solution located on the hole plane, (Pa);
t time (s);
V_{tot} Droplet volume (ml);

Greek letters
γ Equilibrium interfacial tension (mN /m);
ρ Density of the polymeric solution (kg/m^3);
Δρ Density difference between phase 1 and 2 (kg/m^3);
ΔV_i Volume of polymeric solution located on the hole plane (ml);
ΔS_i Pore surface (μm^2)