Polysulfone Microcapsules with Different Wall Morphology

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ABSTRACT: For the production of polysulfone microcapsules, a process was proposed, which allowed the obtaining of capsules with different wall morphology. A polysulfone solution was projected to a precipitation bath. Three solvents were assessed: N,N-dimethylformamide, N,N-dimethylacetamide, and N-methyl-2-pyrrolidone. Precipitation baths were composed by water, pure or mixed with solvent. Surfaces and cross–sections of different preparations were observed by Scanning Electron Microscopy. The study was focused on capsules of 30 ± 10 μm of diameter. Microcapsules surfaces were porous and two different structures were distinguished in the cross-section: macrovoids and sponge-like structures. High concentration of solvent in the precipitation bath reduced the porosity of the surface and the macrovoids of the wall, thus favoring sponge-like structures. The present work set some bases for a better control of polysulfone microcapsules morphology. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1625–1636, 2013

INTRODUCTION

Microencapsulation is an emerging technology, which its applications are found in different fields[1] such as in medicine,[2,3] in pharmaceutics to control drug delivery,[4–6] in the food industry,[7] cosmetics, hygiene, and agriculture.[8] There is also a growing interest in the textile industry[9,10] and in construction.[11] In the latter cases, encapsulation leads to improved thermo regulating properties of materials and textiles. The products of this technology are microcapsules; capsules which their diameters are ranging between 1 and 1000 μm. The internal material is the encapsulated one: the core. Surrounding the core there is a polymeric membrane, which is named wall.[7] The wall is intended to isolate, protect and/or control the release of the core material.[1] Thus, adequate wall properties are a key factor for the performance of the final product. Properties of a polymeric membrane are not only strongly determined by the polymer, but also by the membrane morphology, which is related to the preparation conditions. For this reason, an interest in determining relations between preparation conditions and final morphology is manifested in many works. Concretely, the effects of diverse process variables on the structure of microcapsules were investigated for capsules prepared by polymerization[12–15] and phase inversion by solvent removal,[16,17] among others.[18–20]

The present work was focused on the production and characterization of polysulfone microcapsules. Polysulfone is one of the most used polymers for preparing membranes and microcapsules because of its good mechanical, thermal, and chemical properties.[21,22] The production method was based on phase inversion by immersion precipitation, which is a commonly used technique for the preparation of polysulfone capsules.[21,23–28] Our aim was to investigate some of the preparation conditions that affect the membrane formation process, thus having a clear influence on the final wall morphology. Elucidation of the variables that determine wall morphology is a first step toward the preparation of tailored polysulfone capsules. For that purpose, phase inversion by immersion precipitation was studied. Fundamentals of the technique involve the interaction among at least three compounds: the chosen polymer, a solvent, and a non-solvent of the polymer. When a polymeric solution is immersed into a precipitation bath, which contains the non-solvent, a diffusion process takes place. In the polymeric solution the concentration of solvent decreases meanwhile the concentration of non-solvent increases and, at certain moment, the solution reaches a thermodynamically unstable region. The instability forces a splitting up of the solution into two different phases, which are immiscible between them; one phase is rich in polymer whereas the other phase is poor in it. The separation of these phases is known as liquid–liquid demixing. The nuclei of the poor-in-polymer phase are responsible for pore formation, whereas the polymer in the rich-in-polymer phase solidifies, thus leading to the obtaining of the membrane. The liquid–liquid demixing rate affects the pore formation process (thus, the final morphology of the membrane)[29] and it is determined by thermodynamics and mass transfer kinetics. Thermodynamic characteristics depend on the

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system (non-solvent/solvent/polymer), whereas mass transfer kinetics can be modified, typically by the addition of solvent to the precipitation bath.[29–40]

The influence on wall morphology of both the polymer and some additives concentration were reported.[24,25,41-45] However, this work aimed to provide new knowledge in that field, by addressing the problem from two different approaches: (a) thermodynamics changes by using different solvents; and (b) modification of mass transfer kinetics by addition of solvent to the precipitation bath. Thus, several experiments were performed by using different solvents and precipitation baths. Polymer concentration in the polymeric solution and the non-solvent used, pure water, were constant in all the preparations. The solvents for polysulfone were selected among the most effective ones, on the basis of a ranking published elsewhere[46] and being the miscibility between solvent and non-solvent a requirement for the selection. The selected solvents were: N,N-dimethylformamide, N-methyl-2-pyrrolidone, and N,N-dimethylacetamide. In addition, there was another variable that needed to be controlled, which was the size of the capsules. It was suspected that the diameter of the capsules could influence on their morphology. Reported images of polysulfone macrocapsules (around 1 mm)[47] and microcapsules (around 20 μm) prepared in the same conditions[23] showed different cross-section characteristics. Our products showed a wide size distribution, thus, in order to determine the effect of solvents and precipitation baths in the morphology, the possible effects due to size differences should be discarded. Although possible improvement in size distribution could be achieved by using flow focusing techniques,[48,49] it was not possible to narrow it with the available equipment; moreover, it was not in the scope of the research. Thus, to address the need to eliminate size variability, we focused the analysis of the results exclusively on capsules of 30 $\pm$ 10 μm of diameter. These capsules were the most interesting for us, due to the most common applications we deal with.

Surfaces and cross-sections of the different preparations were observed by Scanning Electron Microscopy (SEM) in order to elucidate the main differences among them.[50] Moreover, a description of the different structures obtained, together with a proposed explanation of the reasons that lead to these differences, was stated.

The main finding of the work was that when the precipitation bath was pure water, macrovoids appeared in the wall structure, whereas if solvent was added to the precipitation bath (in a 60 wt % or higher concentration), morphology could be turned into a sponge-like structure. About the surface features, all the preparations showed pores in their outer layer, but the addition of solvent to the precipitation bath reduced surface porosity.

EXPERIMENTAL METHODS

Material
Polysulfone (PSf, Sigma–Aldrich, Spain, transparent pellets of M_w = 16,000) was used as polymer. Three solvents were assessed; N,N-dimethylformamide (DMF, Scharlab, reagent grade ACS-ISO), N,N-dimethylacetamide (DMAc, Scharlab, synthesis grade), and N-methyl-2-pyrrolidone (NMP, Scharlab, 99 +% A.C.S. reagent). The non-solvent used was distilled water.

Methods
An air atomizing nozzle (nozzle diameter = 0.8 mm) was installed over a beaker containing the precipitation bath. Air pressure was set to 2.5 bar and the air flow at this pressure was 250 L/h. Figure 1 shows the schematic diagram of the setup.

The polymeric solutions were prepared 24 hours before microcapsules production and they were kept in a closed bottle in order to avoid their contact with humid atmospheric air, which could cause polymer precipitation. The polymeric solution microdroplets were projected into the precipitation bath, producing immediately the microcapsules. Finally, the product was collected by filtration and kept into a desiccator.

Several experiments were performed using various solvents and precipitation baths, as it is shown in Table I. For minimizing the increase of solvent concentration in the precipitation bath, only 5 mL of polymeric solution were atomized over 100 mL of bath. Each experiment was repeated at least three times.

Characterization of the different preparations was performed by SEM, by using a Jeol JSM-6400 Scanning Microscopy, working with a voltage between 15 and 20 kV. The analysis of the results was focused on capsules with a diameter of 30 $\pm$ 10 μm. Microcapsules samples were sputtered with gold, at 30 mA for 180 s, and afterward, their surface features were investigated. Moreover, with the aim to elucidate the main differences in the wall structure, samples were cut by cryogenic breaking[50] and their cross-sections were also sputtered with gold at the conditions aforementioned and observed by SEM. Cryogenic breaking is an easy and simple technique, the procedure followed for the obtaining of the samples is described below. The first step was to mix the microcapsules with a freezing medium (Jung Tissue Freezing Medium, Leica Instrumental) and to immerse the mixture into a liquid nitrogen bath, in order to freeze it. The medium froze fast, forming a matrix where the capsules were embedded and supported for sectioning. Afterward, frozen samples were located into a cryochamber (Leica CM1850) which was set to a temperature of –22 °C and they were cut with a blade, using thickness intervals of 15 μm (in previous observations we had concluded that this was the most adequate thickness for our samples). The obtained slides were deposited over a glass, which was ready to be sputtered with gold and examined by SEM.

Several images of each preparation were obtained, both from the surface and from the wall cross-section. In the case of surface characterization, several micrographs could be obtained without difficulty, because there were hundreds of capsules in the samples. The surface micrographs presented in the results were obtained at 17,000 magnifications. This value was selected in order to provide images showing about the 5% of the observable surface of a capsule of 30 μm diameter (due to the spherical geometry of the capsules, the observable area of a capsule with a determined diameter was the area of a circle of the same diameter). On the other hand, when cross-sections were observed, the number of capsules in the cryomicrotomed samples was lower, because they were dispersed in the freezing medium. In addition, not all the capsules were cut, and not all the cut capsules allowed a detailed observation of the wall structure. Due to this added difficulty, our analysis was based on 10 capsules of each preparation, which were selected at random.
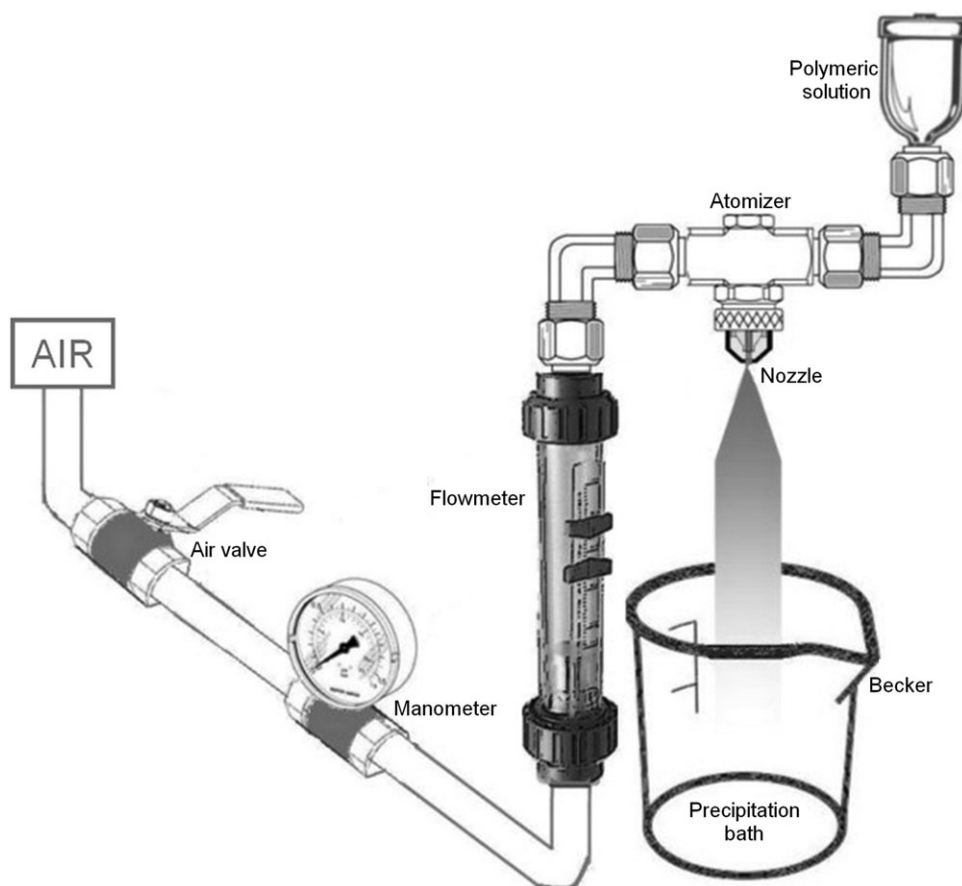
Figure 1. Schematic diagram of the atomization setup.

Table I. Summary of Experiments Performed for the Preparation of Microcapsules

| Polymeric solution | Precipitation bath | | Sample ID |
	Solvent (S)	Water	
15 wt % PSf in DMF	0 wt % DMF	100 wt %	1.1
	15 wt % DMF	85 wt %	1.2
	50 wt % DMF	50 wt %	1.3
	60 wt % DMF	40 wt %	1.4
	75 wt % DMF	25 wt %	1.5
15 wt % PSf in NMP	0 wt % NMP	100 wt %	2.1
	15 wt % NMP	85 wt %	2.2
	50 wt % NMP	50 wt %	2.3
	60 wt % NMP	40 wt %	2.4
	75 wt % NMP	25 wt %	2.5
15 wt % PSf in DMAc	0 wt % DMAc	100 wt %	3.1
	15 wt % DMAc	85 wt %	3.2
	50 wt % DMAc	50 wt %	3.3
	60 wt % DMAc	40 wt %	3.4
	75 wt % DMAc	25 wt %	3.5

RESULTS AND DISCUSSION

Surface Features of Microcapsules Samples

Microcapsules were successfully obtained and their shape was spherical in all the assessed preparations. Figure 2 shows, as an
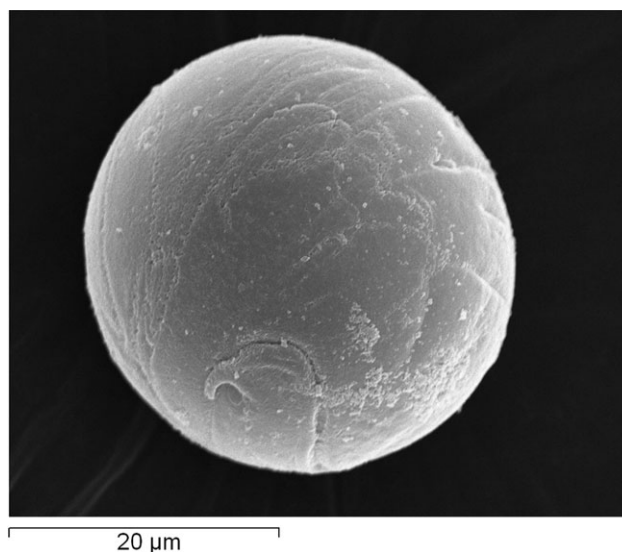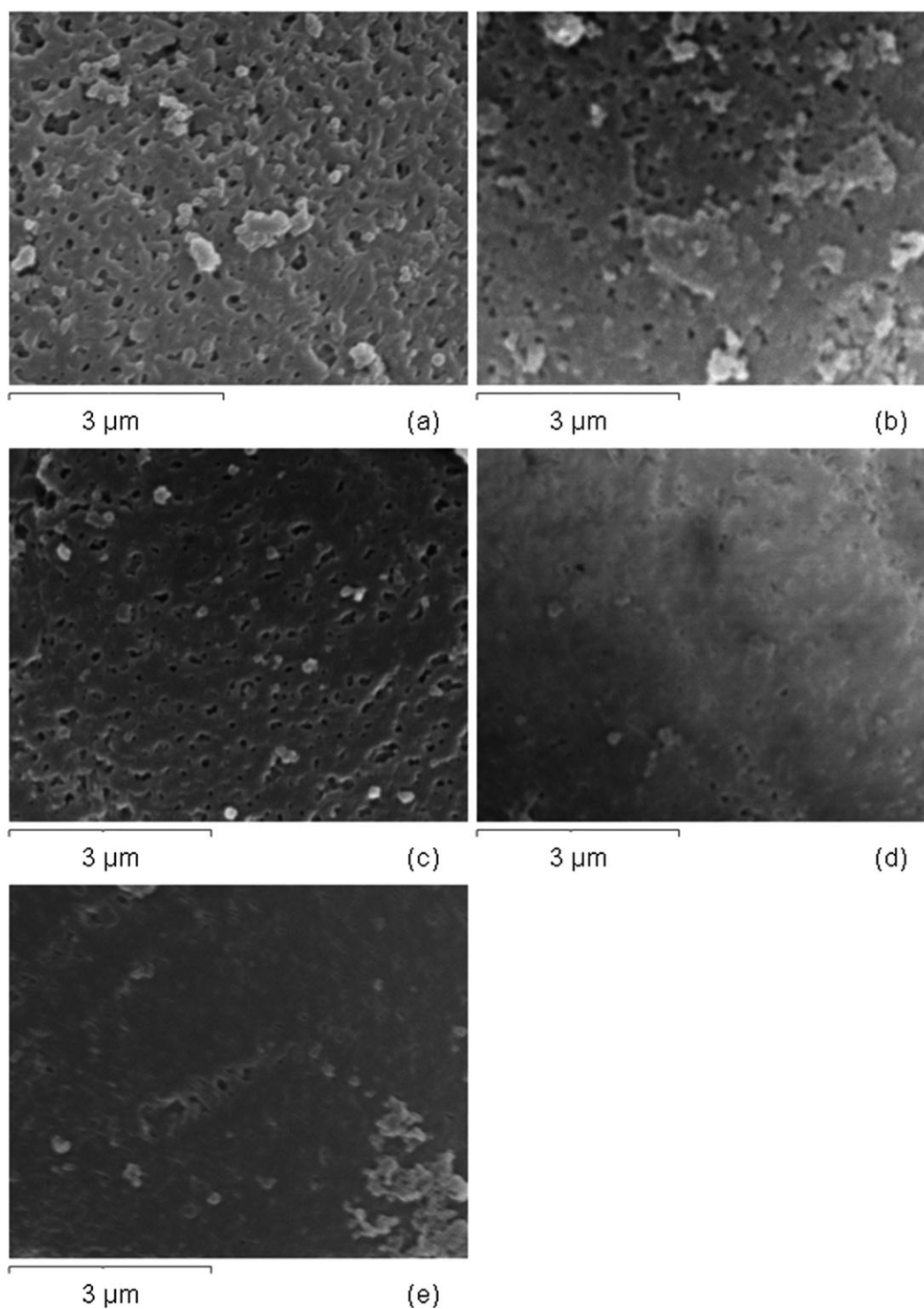

Figure 2. SEM image of a capsule prepared by using 15 wt % PSf in DMF as polymeric solution and 60 wt % DMF in distilled water as precipitation bath.
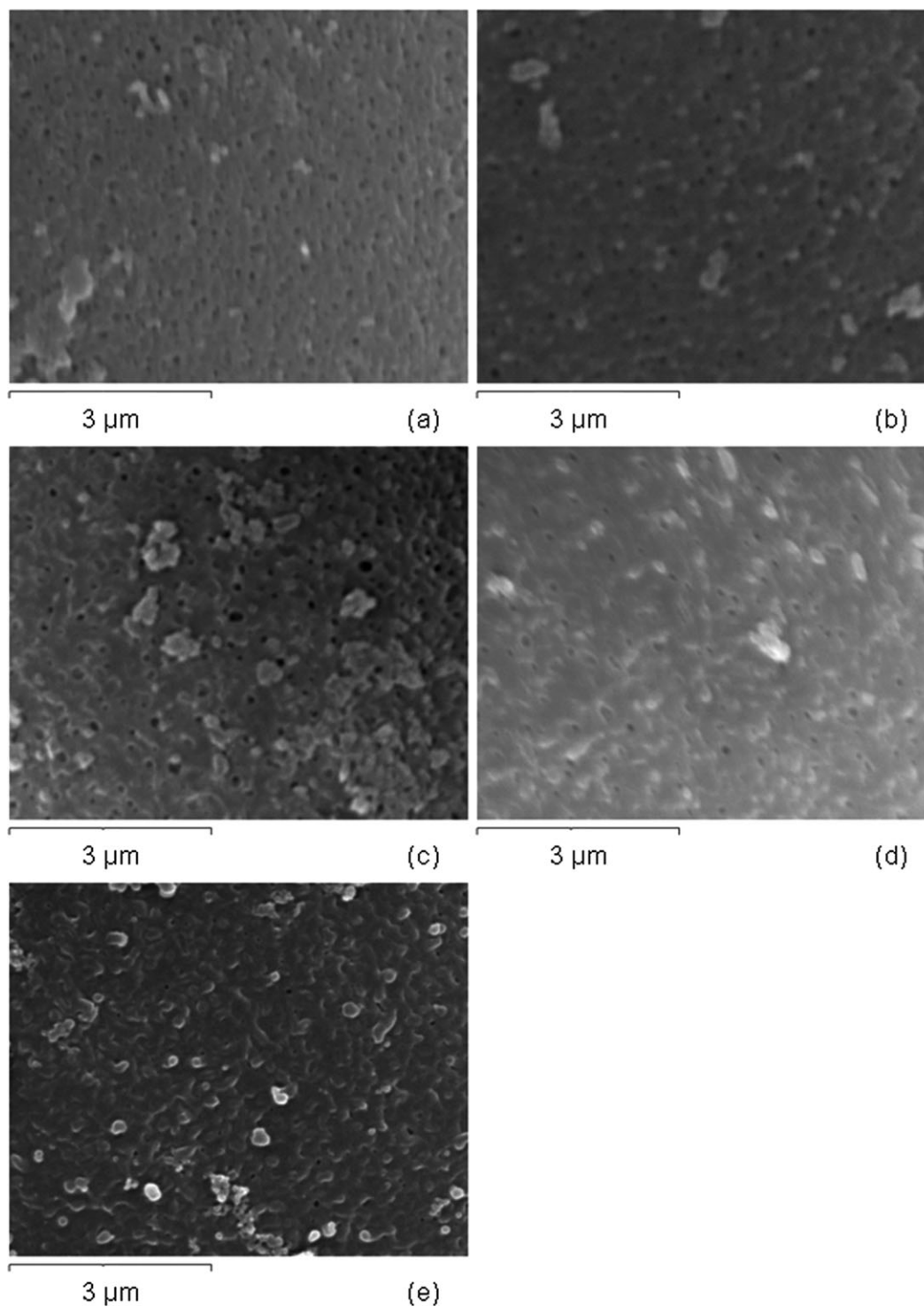
Figure 3. Surface micrographs of microcapsules prepared by using 15 wt % PSf in DMF as polymeric solution. The precipitation bath was composed by: (a) distilled water; (b) 15 wt % DMF in distilled water; (c) 50 wt % DMF in distilled water; (d) 60 wt % DMF in distilled water; (e) 75 wt % DMF in distilled water.

example, a capsule prepared by using 15 wt % PSf in DMF as polymeric solution and 60 wt % DMF in distilled water as precipitation bath.

The SEM images corresponding to capsules surfaces are shown in Figures 3, 4 and 5. Additional surface micrographies are included as supporting information. As can be seen, all the preparations showed pores on their surface. However, it can be observed that the number of pores tended to decrease with the addition of solvent to the precipitation bath. In the case of capsules prepared using DMF as solvent, this observation was in agreement with the existing literature on polysulfone flat membranes. It was reported that the addition of DMF to the
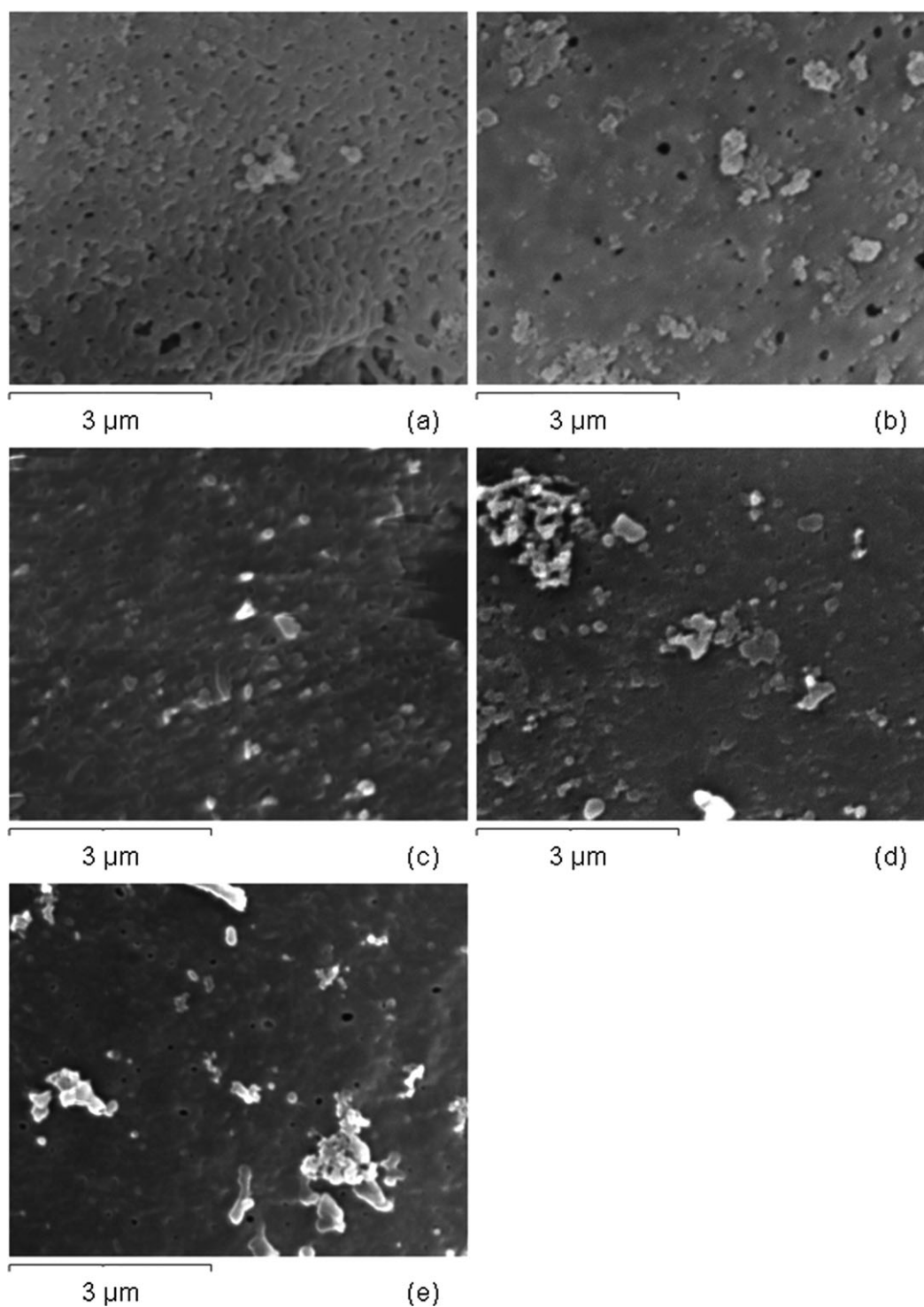
Figure 4. Surfaces micrographs of microcapsules prepared by using 15 wt % PSf in NMP as polymeric solution. The precipitation bath was composed by: (a) distilled water; (b) 15 wt % NMP in distilled water; (c) 50 wt % NMP in distilled water; (d) 60 wt % NMP in distilled water; (e) 75 wt % NMP in distilled water.

precipitation bath reduced the porosity of the surface layer.[30] The same trend may be valid in the case of capsules. Moreover, capsules prepared using NMP showed similar behavior. In the case of DMAc less amount of solvent was required to cause an important decrease on porosity.

Effect of Solvent and Precipitation Bath Composition on Microcapsules Inner Structure

The SEM images corresponding to capsules wall morphology are shown in Figures 6, 7 and 8. Additional cross-section micrographies are included as supporting information. As it can
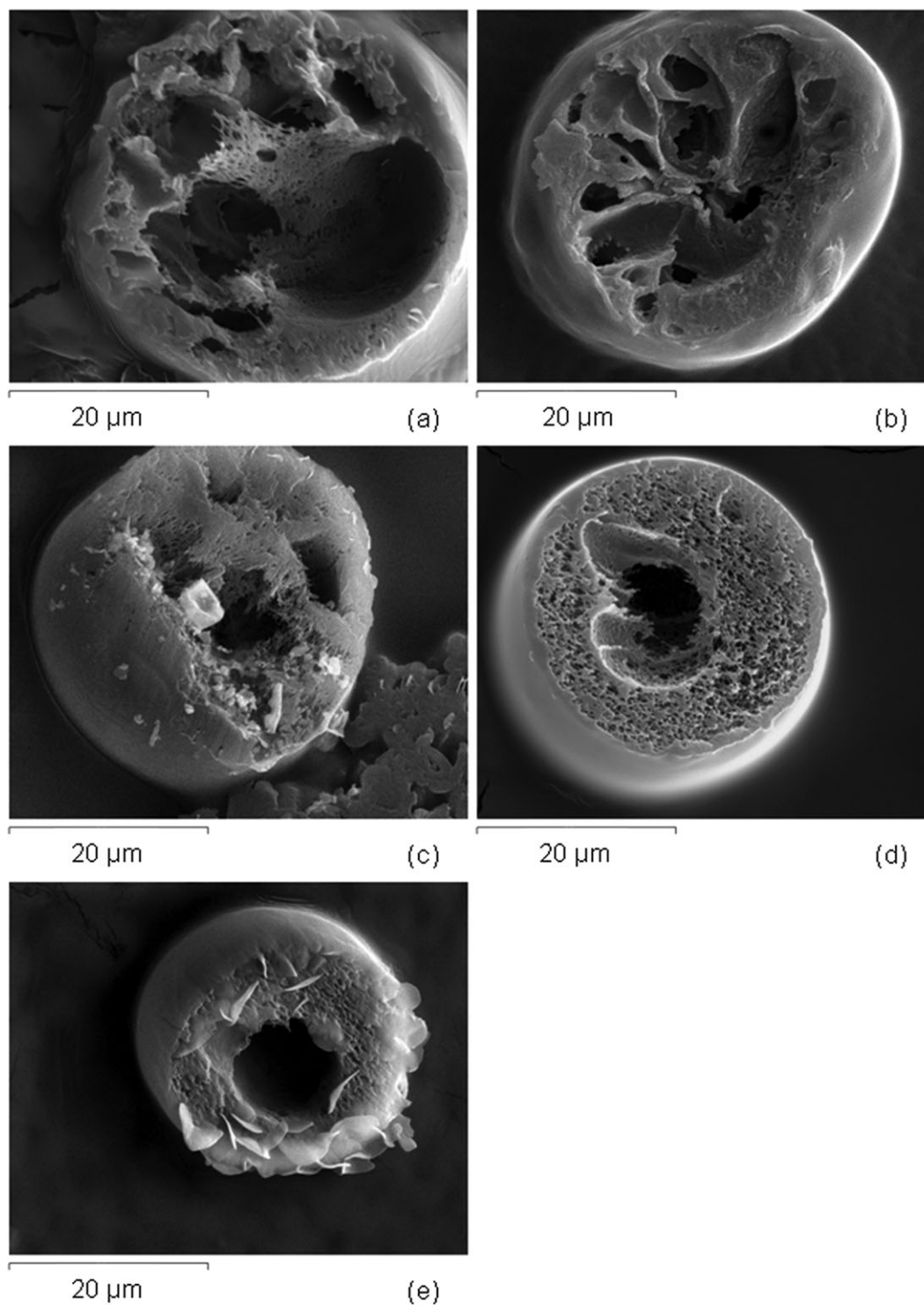
Figure 5. Surfaces micrographs of microcapsules prepared by using 15 wt % PSf in DMAc as polymeric solution. The precipitation bath was composed by: (a) distilled water; (b) 15 wt % DMAc in distilled water; (c) 50 wt % DMAc in distilled water; (d) 60 wt % DMAc in distilled water; (e) 75 wt % DMAc in distilled water.

be seen, two clearly different wall structures were obtained: wall structures with large elongated pores (macrovoids) and sponge-like structures.

Significant differences on morphology caused by the use of different solvents were not encountered. On the other hand, precipitation bath had a clear effect on the morphologies. The results were in agreement with the literature about phase separation processes in polymer solutions, which has been widely studied for flat polymeric membranes.[29,39,40]
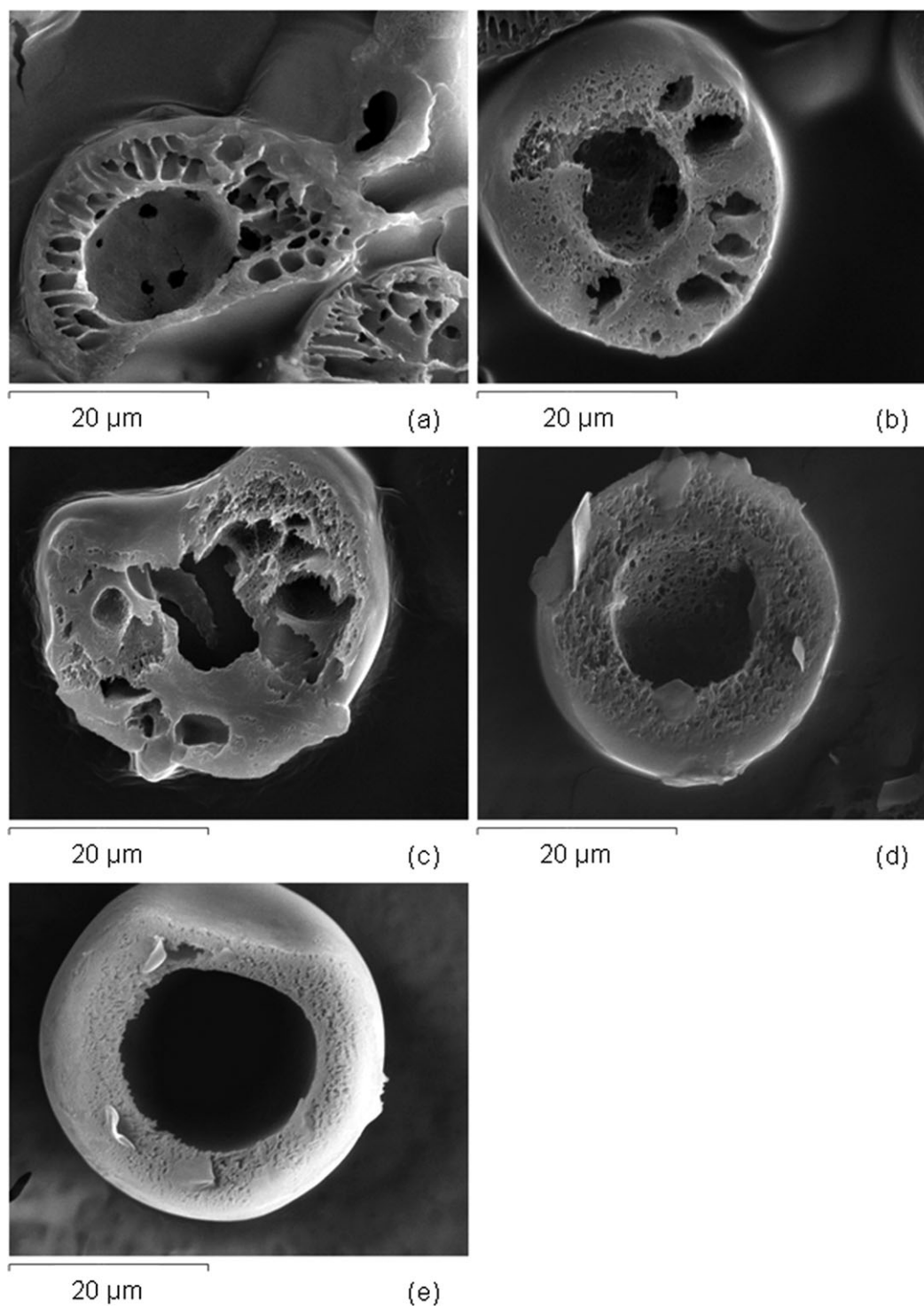
Figure 6. Cross-section micrographs of microcapsules prepared by using 15 wt % PSf in DMF as polymeric solution. The precipitation bath was composed by: (a) distilled water; (b) 15 wt % DMF in distilled water; (c) 50 wt % DMF in distilled water; (d) 60 wt % DMF in distilled water; (e) 75 wt % DMF in distilled water.

It is accepted that membrane morphology is determined during the liquid–liquid demixing process,[29] which is ruled by thermodynamics and mass transfer kinetics.

Firstly, the influence of the thermodynamic parameters of the studied systems is discussed. These parameters are determined by the compounds in the system [non-solvent (1)/solvent (2)/polymer (3)]. Interaction among them is a key factor determining the demixing rate and it can be expressed by the Flory–Huggins interaction parameter (χ) or by the Relative Energy Density (RED) calculation, which is a measure to express the affinity of a polymer for a solvent, based on the distance
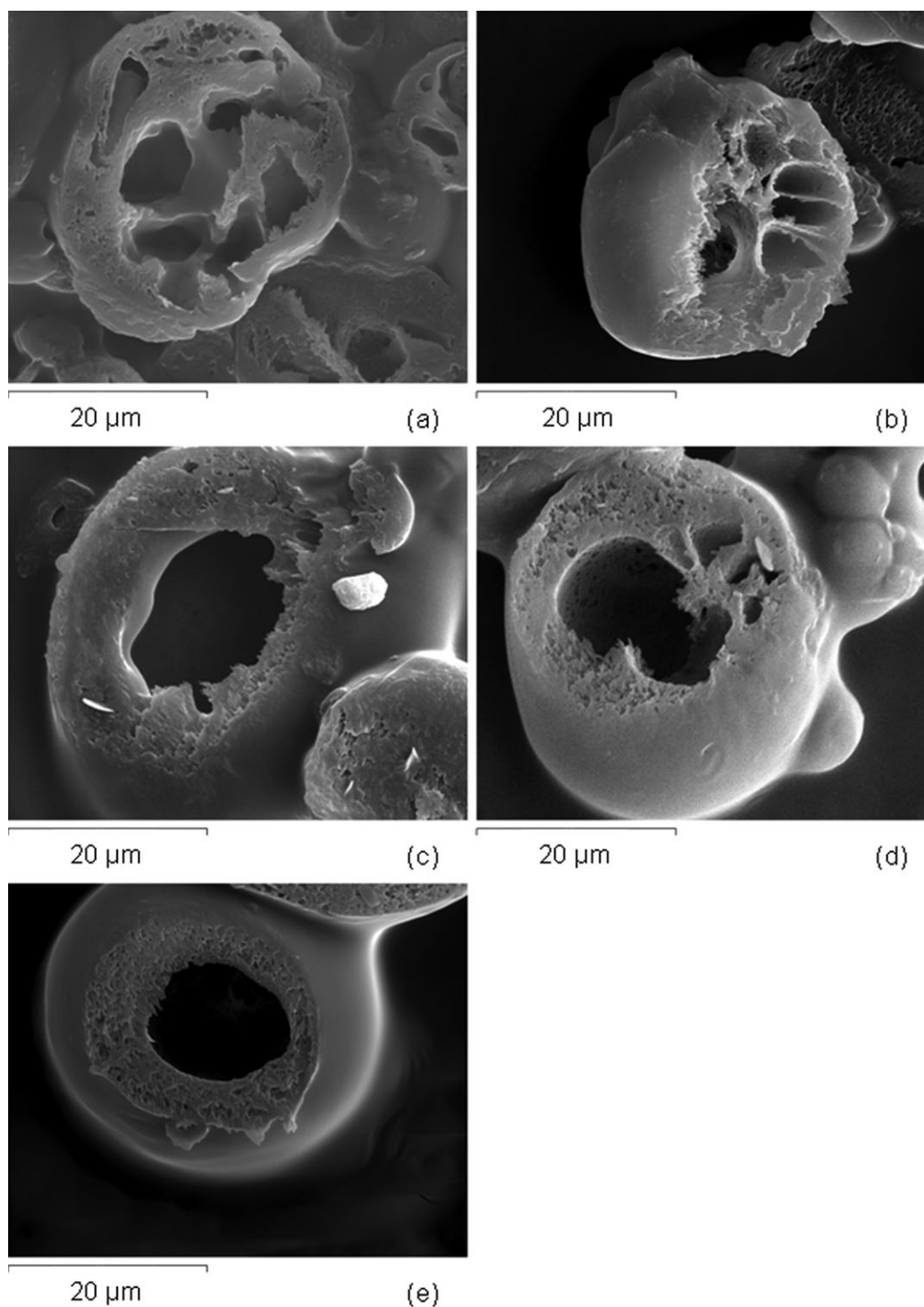
Figure 7. Cross-section micrographs of microcapsules prepared by using 15 wt % PSf in NMP as polymeric solution. The precipitation bath was composed by: (a) distilled water; (b) 15 wt % NMP in distilled water; (c) 50 wt % NMP in distilled water; (d) 60 wt % NMP in distilled water; (e) 75 wt % NMP in distilled water.

between their Hansen Solubility Parameters.[22] The higher is the Flory–Huggins interaction parameter, the lower is the affinity between the compounds.

In our system, affinity of polysulfone for the three assessed solvents was similar. Table II shows the Relative Energy Density Calculation for Selected Solvents and Polysulfone.[22] Solubility of a polymer in a solvent increases as RED approaches 0. If RED > 1 the polymer is not soluble in that solvent. According to Table II, Polysulfone shows higher affinity for NMP, followed by DMAc and, finally, the solvent which shows less affinity for the polymer is DMF.

Figure 8. Cross-section micrographs of microcapsules prepared by using 15 wt % PSf in DMAc as polymeric solution. The precipitation bath was composed by: (a) distilled water; (b) 15 wt % DMAc in distilled water; (c) 50 wt % DMAc in distilled water; (d) 60 wt % DMAc in distilled water; (e) 75 wt % DMAc in distilled water.

On the other hand, RED for water and polysulfone is 4.49, which express very low affinity of the polymer for water. This is in agreement with the high Flory Huggins interaction parameter reported for the pair polysulfone-water ($\chi_{13} = 3.7$[33]). Fast demixing is expected to happen in systems with low affinity between polymer and non-solvent, because it is required a low concentration of non-solvent in the solution to start the demixing.[33]

As χ_{13} was constant and affinities of the polymer for the different solvents were similar, the main variable determining

Table II. Relative Energy Density Calculation for Selected Solvents and Polysulfone

Solvent	RED
NMP	0.68
DMAc	0.86
DMF	0.96

differences in thermodynamics behavior was the affinity between solvent and non-solvent, which can be expressed by a concentration dependent interaction parameter (g_{12}). Figure 9 shows the concentration dependent interaction parameter (g_{12}) for the selected solvents and water (DMF,[51] NMP,[33] and DMAc).[35] Tetrahydrofuran (THF) was added to the figure only for comparison, because it is generally accepted as a solvent with very low affinity for water,[29] thus, it can be seen that g_{12} for THF is quite higher than for the other solvents.[33] Although it would have been very interesting to prepare polysulfone microcapsules by using this solvent, experimentation could not be performed with the available equipment for safety reasons. The way in which affinity between solvent and non-solvent affects the demixing process is discussed below.

During demixing, pores are formed from the nuclei of the poor in polymer phase. Once a nucleus is initiated, it attracts solvent to diffuse inward in order to reach the thermodynamic equilibrium of the phase. If the affinity between solvent and non-solvent is low the driving force is also low and growth of the pores is restrained. On the other hand, if that affinity is high, pores grow fast and they continue growing as long as: (a) solvent is available or (b) the polymer concentration in the rich-in-polymer phase is high enough to cause polymer precipitation. Nevertheless, if many nuclei are growing at the same time less solvent is available, because all of them are consuming it. Thus, pore growth is limited by competition for the solvent and physical space availability. When affinity between solvent and non-solvent is high, solvent diffuses rapidly to the precipitation bath and a polymer concentrated top layer is formed, which restrains diffusion flow in the sublayer. Then, few nuclei are initiated under the top layer, but little amount of non-solvent in a nucleus is enough to induce solvent diffusion inwards to maintain the equilibrium of the poor-in-polymer phase. Thus, few nuclei are formed, but their growth is fast and, in addition, there is more solvent available for each one. These conditions are expected to favor macrovoids formation.

The three solvents assessed showed high affinity to water.[51] Even from Figure 9 it is observed that the affinity between NMP and water is lower than for DMF and DMAc, this difference was not high enough to cause any significant effect in the morphology. As the affinity between non-solvent and the solvents was high (low g_{12}), and in addition, the interaction parameter χ_{13} was very high, these two characteristics favored fast demixing and for this reason macrovoids were observed in Figures 6(a–c), 7(a–c), and 8(a,b).

Nevertheless, it was observed that the addition of solvent to the coagulation bath decreased macrovoids formation. By using

DMF and NMP as solvents, when the precipitation bath contained a 60 wt % of solvent, macrovoids were not observed and a sponge-like structure formed by small pores was obtained instead [Figures 6(d,e) and 7(d,e)]. In the case of DMAc, the addition of 45 wt % of the solvent into the precipitation bath was enough to prevent macrovoids formation. See Figure 8(c,d,e). Non-occurrence of macrovoids may be explained by a reduction of the diffusion rate, because the addition of solvent lowered the chemical potential gradients. Reduction of diffusion rate caused a delay in the liquid–liquid demixing rate. When phase separation began, certain amount of non-solvent had diffused, not only in the top layer but in the whole transversal section and, consequently, many nuclei were initiated at the same time. Those nuclei growth was slow because of the driving force reduction. In addition, growth of each pore was limited by the surrounding pores, because all of them were consuming solvent. In those conditions macrovoids formation was not possible. In the case of DMAc, less solvent was required, which was not justifiable on the basis of affinity between solvent and non-solvent. However, a possible explanation based on the gelation process was given in a previous work with polyethersulfone.[35]

CONCLUSIONS

A process for the production of polysulfone microcapsules was proposed. The process was based on a well-known technique, phase inversion by immersion precipitation. In addition it was performed by using a very simple atomization setup, which allowed the fast obtaining of capsules.

Knowledge of the fundamentals of the precipitation technique set the basis for our experimental design. Several experiments were performed in order to elucidate the influence on the final morphology of two factors: (a) the solvent used in the polymeric solution, and (b) the precipitation bath composition.

On one hand, morphology was not affected by the solvent used as the three solvents studied have similar affinity with the non-solvent and also with the polymer.

On the other hand, the addition of solvent to the precipitation bath was identified as a factor causing great differences in wall morphology. Concretely, when the precipitation bath was pure water, macrovoids appeared in the wall structure. On the other hand, if solvent was added to the precipitation bath,
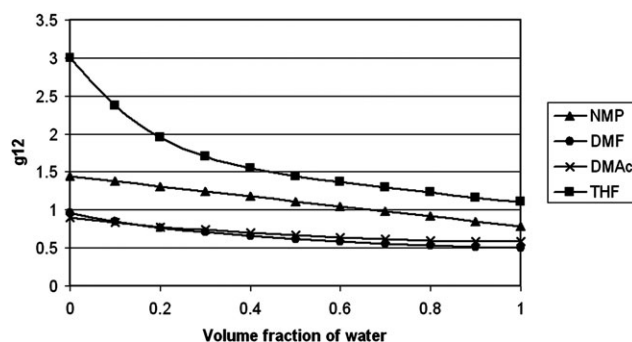
Figure 9. Concentration dependent interaction parameters (g_{12}) for the selected solvents with water (DMF,[51] NMP,[33] DMAc[35], and THF[33]).

morphology could be turned into a sponge-like structure. However, the concentration of solvent in the precipitation bath was required to be over 60 wt %, lower concentrations did not show clear effect on macrovoids reduction, except in the case of preparations by using DMAc as solvent.

The present work provides additional knowledge about parameters affecting polysulfone microcapsules wall morphology. A better control of capsules morphology is the first step toward the preparation of tailored microcapsules in which wall membrane could be designed in order to fit possible applications, as it is already known and widely published for flat polymeric membranes.

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