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Selection Criteria for Solvent and Coagulation Medium to Modulate the Structure of Polymethylmethacrylate Prepared by Wet Phase Inversion

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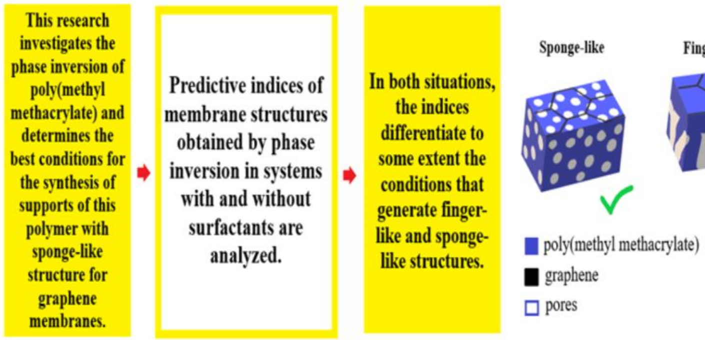
Polymethylmethacrylate, PMMA, with sponge or finger pores are interesting depending on the application. Our goal was to investigate parameters (Φ and Φ') to foresee the morphology of PMMA prepared by phase inversion based on chemical composition (amount and type of solvent, non-solvent and surfactant). A literature survey was conducted with different chemical composition and analyzed by statistical tools. Sponge-like structures were obtained in systems whose Φ value is less than 0.22 or the Φ' value is more than 0.55. Both indexes can differentiate to some extent systems that generate finger-like structures from those that generate sponge-like ones.

Graphical abstract



This research investigates the phase inversion of poly(methyl methacrylate) and determines the best conditions for the synthesis of supports of this polymer with sponge-like structure for graphene membranes.

Predictive indices of membrane structures obtained by phase inversion in systems with and without surfactants are analyzed.

In both situations, the indices differentiate to some extent the conditions that generate finger-like and sponge-like structures.

Keywords

Phase inversion
Polymethylmethacrylate supports
Statistical analysis
Thermodynamic parameter

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1. Introduction

Reverse osmosis is the major desalination process, accounting for 65% of installations [1]. It is more efficient than thermal desalination techniques [2]. Increasing the energy efficiency of reverse osmosis plants involves the development of new membranes with increased permeability, selective rejection of specific compounds, oxidation resistance, hydrophilicity and scale resistance without harming saline rejection [1-6]. New materials such as zeolites, carbon nanotubes or graphene can improve membrane performances [4, 6, 7].

It is necessary to promote sufficient mechanical strength to enable the handling of reverse osmosis membrane and its exposure to high pressures [8]. The polymer structure obtained by phase inversion can be symmetric, with uniform pore size distribution throughout their entire length, or asymmetric, with different pore sizes distributed in their

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structure [9,10]. The asymmetric structure has a dense film of 0.1 to 2 μm thick, formed at the interface between the non-solvent and the polymer solution, in addition to a porous layer that has finger-like pores [9,10]. Structures with large, finger-like pores are attractive for many specialized applications [11]. However, large pores are a problem for membranes intended for high pressure applications such as reverse osmosis and gas separation since the voids of this morphology cause low mechanical strength [9,10]. Therefore, the sponge-like structure is the most suitable for making supports in desalination membranes.

The demand for supports with a specific type of porosity motivated the study of factors that affect the morphology of a polymer obtained by phase inversion. The kinetics of the process, for example, influence the porosity of the material, and, normally, low separation rates produce membranes with sponge-like structures, while instantaneous separations cause the formation of finger-like structures [9]. Furthermore, combinations of different pairs of solvents and non-solvents also interfere in the characteristics of the polymeric support [9]. In this case, there is a general tendency that when the miscibility between the solvent and the non-solvent is high, the generated structure has large finger-like pores, because the non-solvent can easily cross the interface and penetrate the polymer solution, leaving large empty spaces when expelled [9]. The use of additives such as surfactants may also modify the morphology of supports upon decreasing the interfacial tension between the polymeric solution and the non-solvent [12].

Ruaan and coauthors [13] studied the phase inversion of PMMA and created a parameter, Φ, that enables the prediction of the structure of membranes obtained from this polymer. The main result found by the authors indicated that obtaining sponge-like structures occurs when the Φ index is more than 0.25 [13]. However, such parameter is not widely used in membrane preparation. The objective of this work was to extend Φ index by means of statistical tools with a larger volume of experimental data reported in the literature about phase inversion of polymethylmethacrylate. Furthermore, the best synthesis conditions of PMMA supports with sponge-like structure suitable for application in reverse osmosis membranes were determined. We also proposed for the first time a modified index Φ' to predict the structure generated by the phase inversion of PMMA in systems with surfactants.

2. Material and Methods

2.1 Ruaan parameter (Φ)

The cohesive energy of a substance in a condensed state is defined as the increase in its internal energy that would be generated if all its intermolecular forces were eliminated [14], according to **Equation 1**.

$$E_{coh} = \Delta U \qquad (1)$$

where E_{coh} is the cohesive energy in J and U is the internal energy in J [14]. Cohesive energy density, in turn, is defined as the cohesive energy per volume unit [14], according to **Equation 2**.

$$e_{coh} = \frac{E_{coh}}{V} \qquad (2)$$

where e_{coh} is the cohesive energy density in $J.m^{-3}$ or Pa and V is the volume in m^3 [14]. The solubility parameter, a value widely used to correlate polymer and solvent interactions, is defined as the square root of the cohesive energy density in the amorphous state at room temperature, according to **Equation 3** [14].

$$\delta = \sqrt{e_{coh}} \qquad (3)$$

where δ is the solubility parameter in $Pa^{0.5}$ [14]. This parameter can be decomposed into three quantities that represent dispersion forces, polar forces and hydrogen bonds, according to **Equation 4** [14].

$$\delta^2 = {\delta_D}^2 + {\delta_P}^2 + {\delta_H}^2 \qquad (4)$$

where δ_D is the solubility parameter related to dispersion forces in $Pa^{0.5}$, δ_P is the solubility parameter related to polar forces in $Pa^{0.5}$ and δ_H is the solubility parameter related to hydrogen bonds in $Pa^{0.5}$ [14]. For the determination of each component (δ_D, δ_P and δ_H) of the solubility parameter, there are theoretical estimation methods that are based on the contribution of groups to the molecular structure, such as the Hoy's Method [14]. The thermodynamic criterion determines that two substances are miscible if the free energy of mixing, determined by **Equation 5**, is negative [14].

$$\Delta G_M = \Delta H_M - T\Delta S_M \qquad (5)$$

where ΔG_M is the free energy of mixing in J, ΔH_M is the enthalpy of mixing in J, T is the temperature in K, ΔS_M is the entropy of mixing in $J.K^{-1}$ [14]. As the mixing entropy is normally positive, according to Equation 5, there is a maximum limit for the mixing enthalpy value so that the free energy of mixing is negative [14]. The enthalpy of mixture can be calculated by **Equation 6** [14].

$$\Delta H_M = \varphi_1\varphi_2 V\left[\left(\delta_{D,i} - \delta_{D,j}\right)^2 + \left(\delta_{P,i} - \delta_{P,j}\right)^2 + \left(\delta_{H,i} - \delta_{H,j}\right)^2\right] \qquad (6)$$

where φ is the volume fraction and the letters i and j denote the two components of a binary mixture [14]. If the square root of the term in square brackets in Equation 6 is calculated, a quantity known as the difference between the solubility parameters is reached, according to **Equation 7** [14].

$$\Delta\delta_{i-j} = \sqrt{\left[\left(\delta_{D,i} - \delta_{D,j}\right)^2 + \left(\delta_{P,i} - \delta_{P,j}\right)^2 + \left(\delta_{H,i} - \delta_{H,j}\right)^2\right]} \quad 7)$$

where $\Delta\delta_{i-j}$ is the difference between the solubility parameters in $Pa^{0.5}$ [14]. From the observation of Equations 6 and 7, it is clear that as the enthalpy of mixing has a maximum limit value, therefore, the difference between the solubility coefficients also has a maximum limit for the dissolution of a polymer in a solvent to occur, around 5 $MPa^{0.5}$ [14]. Therefore, a polymer is normally soluble in solvents that have a chemical structure similar to its own and, consequently, values of solubility parameter components close to its own [14].

Ruaan and coauthors [13] used the concepts of solubility parameter (Equation 3) and difference between solubility parameters (Equation 7) to propose a parameter, which can be used in predicting the structure of a membrane, defined by **Equation 8**.

$$\Phi = \frac{\Delta\delta_{p-s}\Delta\delta_{p-ns}}{\delta_{p}\Delta\delta_{s-ns}} \tag{8}$$

where Φ is the dimensionless parameter created by Ruaan and coauthors [13], and p, s and ns denote, respectively, the polymer, the solvent and the non-solvent of a phase inversion. The result found by the authors shows that high values of Φ are associated with systems that generate finger-like structures, while low values of Φ are found in systems that generate sponge-like structures [13]. For PMMA solutions with concentrations close to 15% and film thicknesses close to 300 μm, for example, the authors suggested the selection of solvents and non-solvents that result in a value of Φ less than 0.25 to obtain sponge-like structures [13]. This conclusion was obtained from the analysis of experimental data reported by Cheng and coauthors [9]. Ruaan and coauthors [13] used the Hoy's Method to determine the solubility parameter of PMMA and its components and used values available in the literature for the solvent parameters.

2.2 Modified Ruaan parameter (Φ')

Surfactants are substances whose molecules have both polar and non-polar groups and one of the characteristics usually used in their choice is the HLB or Hydrophilic-Lipophilic Balance, that is calculated from the relationship between the size and importance of these groups in the structure [12,15]. Surfactants with HLB > 11 generate products with aqueous characteristics and surfactants with HLB < 9 generate products with oily characteristics [15]. Therefore, it is possible to use its addition in the polymeric solution before the phase inversion to control the properties of the supports [12]. Considering that the work of Ruaan and coauthors [13] did not address this type of system and given its importance, we proposed a new parameter to predict the structure of PMMA membranes generated by phase inversion of mixtures with surfactants.

Lin and coauthors [12] reported that systems that generate sponge-like structures have their behavior inverted and start to generate finger-like pores by adding surfactants to the polymer solution in concentrations from 1.8% v/v. Furthermore, the increase in the concentration of these compounds causes an intensification of this phenomenon [12]. It is worth mentioning that surfactants with a high HLB index tend to cause structure change when water is used as a non-solvent and surfactants with a low HLB form finger-like pores when n-hexane is used as a non-solvent [12]. According to Wang and coauthors [11], the opposite effect is also valid. For a support synthesis system that can generate a finger-like porous structure, adding to the polymer solution a surfactant with low affinity to the non-solvent can suppress this formation [11]. This can be summarized into four statements:

- if a surfactant with a high HLB is added to a solution that normally generates a sponge-like structure when immersed in a hydrophilic non-solvent, then this system starts to generate finger-like structures;
- if a surfactant with a low HLB is added to a solution that normally generates a sponge-like structure when immersed in a hydrophobic non-solvent, this system starts to generate finger-like structures;
- if a surfactant with a low HLB is added to a solution that normally generates a finger-like structure when immersed in a hydrophilic non-solvent, then this system starts to generate sponge-like structures;
- if a surfactant with a high HLB is added to a solution that normally generates a finger-like structure when immersed in a hydrophobic non-solvent, this system starts to generate spongy structures.

Keeping some degree of similarity with the Ruaan parameter [13], we proposed for the first time here a modified parameter (Φ'), to be used as an indicator of non-solvent hydrophilicity the average of the components of its parameter of solubility related to polar forces (δ_P, non-solvent) and hydrogen bonds (δ_H, non-solvent). Thus, a surfactant with high HLB combined with high values of δ_P, non-solvent or δ_H, non-solvent generates finger-like structures, the same occurring for a surfactant with low HLB combined with low values of δ_P, non-solvent and δ_H,non-solvent. Sponge-like structures are obtained when a surfactant with high HLB is combined with low values of δ_P, non-solvent and δ_H, non-solvent, or when a surfactant with low HLB is combined with high values of δ_P, non-solvent or δ_H, non-solvent. Therefore, the greater the relative difference in modulus between the HLB value and the mean value between δ_P, non-solvent and δ_H, non-solvent, the greater the probability of obtaining a sponge-like structure. Based on this finding, **Equation 9** was proposed, where the numbers 16.9, 22.8 MPa$^{0.5}$ and 40.4 MPa$^{0.5}$ were chosen so that both the term referring to the HLB and the term referring to the mean of the solubility parameters varied between 0 and 1 in the range of data analyzed in this work. The modified parameter (Φ') is empirical, as in the case of HLB.

$$\Phi' = \left| \frac{HLB}{16.9} - \frac{\left(\frac{\delta_{P,non-solvent}}{22.8MPa^{1/2}} + \frac{\delta_{H,non-solvent}}{40.4MPa^{1/2}} \right)}{2} \right| \tag{9}$$

2.3 Statistical analysis

In order to statistically assess the applicability of the Ruaan parameter to a larger volume of data, firstly, published works that reported obtaining polymeric membranes with sponge-like or finger-like structure from phase inversion by immersion-precipitation of pure PMMA were searched in the literature. It is worth mentioning that there were few papers in which PMMA was used, probably due to the fact that such biodegradable material is devoted to hemodialysis membranes and sensor materials.

From these works, conditions for the synthesis of polymethylmethacrylate membranes (solvent and non-solvent used) were obtained, which were divided into four groups:

- Conditions that lead to the formation of sponge-like structures without the addition of surfactant;
- Conditions that lead to the formation of finger-like structures without the addition of surfactant;
- Conditions that lead to the formation of sponge-like structures with the addition of surfactant;
- Conditions that lead to the formation of finger-like structures with the addition of surfactant.

Data from the first two groups were used in Equation 8 to calculate the Ruaan parameter (Φ) for each solvent/non-solvent pair that resulted in a membrane with a sponge-like or finger-like structure [13]. Therefore, Hoy's method was used to calculate the solubility parameter of PMMA and its components.

In addition, components of the solubility parameters of solvents calculated by the Hoy method available in the literature [16] were used and components of the solubility parameters of solvent mixtures were calculated using the weighted average where the weights were the volume fractions of the constituents of these mixtures.

The Φ values for the first two groups were submitted to normality tests using Minitab software. The means and standard deviations of the Φ values, plus the 95% confidence intervals for the population mean of the Φ values for both groups were calculated using Minitab software. These results, in addition to the result of the hypothesis test that statistically determined whether the population means of the Φ values of the first and second group could be equal to the 95% confidence level, were analyzed. The analysis allowed to assess whether, when statistically tested with a larger volume of data, the Φ parameter maintained its ability to indicate the structure of the membranes.

For the last two groups, the same steps described for the first two were followed, using the modified Ruaan parameter proposed in this work (Φ'), more suitable for these systems.

3. Results and Discussion

The solubility parameter of PMMA and its components were determined by the Hoy's Method and the values obtained were as follows: $\delta = 19.40$ MPa$^{0.5}$; $\delta_D = 13.60$ MPa$^{0.5}$; $\delta_P = 9.26$ MPa$^{0.5}$; $\delta_H = 10.28$ MPa$^{0.5}$ [14]. The components of the solubility parameters of the solvents that were studied in this research are available in **Table S1 (Supporting information)** and were obtained from the literature [16]. The components of the solubility parameters of the solvent mixtures calculated from these data were also included in this table.

3.1 Ruaan parameter

The conditions reported in the literature for obtaining sponge-like and finger-like structures from phase inversion by immersion-precipitation of PMMA without the addition of surfactants are presented, respectively, in **Tables 1 and 2**. The tables also present the Φ values calculated for each of the conditions and the values found by the authors themselves. The indices calculated in this work were equal to the values calculated by Ruaan and coauthors [13] for most conditions, except for the 1,4-Dioxane/water and acetone/N-hexane systems. It is not possible to understand exactly the reason for the difference for these systems, because the exact values of the solubility parameters used by Ruaan and coauthors [13] in calculating the parameters were not available. Furthermore, Ruaan and coauthors [13] did not calculate the parameter for a number of conditions analyzed in that work (identified with x in Tables 1 and 2), so that comparison was not allowed. Thus, it is possible that the difference between the two conditions mentioned above may originate, for example, in the source used to obtain the solubility parameters of the solvents shown in Table S1 (Supporting information).

Table 1. Conditions for obtaining polymethylmethacrylate membranes with a sponge-like structure without the addition of surfactants. Source: Authors

Solvent (% v/v)	Non-solvent (% v/v)	References	Φ - Calculated in this work	Φ - Ruaan and coauthors [17]
Acetone	Ethanol	[17]	0.06	x
Acetone	Methanol	[13]	0.06	0.07
Acetone	N-hexane	[9]	0.05	0.23
Acetone	Water	[9,12,18]	0.06	0.06
Butanone	N-hexane	[9]	0.05	0.05
Butyl acetate	N-hexane	[9]	0.27	0.27
Cyclohexanone	N-hexane	[9]	0.11	x
Chlorobenzene	Ethanol	[6]	0.27	x
1,4-Dioxane	Butanol	[19]	0.13	x
1,4-Dioxane	Ethanol	[19]	0.15	x
1,4-Dioxane	Methanol	[19]	0.16	x
1,4-Dioxane	Propanol	[19,20]	0.14	x
Ethyl acetate	N-hexane	[9]	0.09	0.09
N-methylpirrolidone	N-hexane	[10,13]	0.19	0.19
N-methylpirrolidone	Water	[21, 22]	0.26	0.25
Tetrahydrofuran	N-hexane	[9]	0.22	0.22
Tetrahydrofuran	Water	[13]	0.19	0.19
1,4-Dioxane	Methanol (50); Water (50)	[9]	0.17	x
Ethyl acetate	Acetone (20); N-hexane (80)	[9]	0.05	x
Ethyl acetate	Ethyl acetate (20); N-hexane (80)	[9]	0.09	x
Acetone (82); Ethanol (18)	Water	[12]	0.14	x
Acetone (77); N-heptane (23)	N-hexane	[9]	0.20	x
Acetone (77); N-hexane (23)	N-hexane	[9]	0.20	x
Acetone (77); N-octane (23)	N-hexane	[9]	0.20	x

Table 2.. Conditions for obtaining polymethylmethacrylate membranes with a finger-like structure without the addition of surfactants. Source: Authors

Solvent (% v/v)	Non-solvent (% v/v)	References	Φ – Calculated in this work	Φ – Ruaan and coauthors 17
Acetone	Water	[23]	0.06	0.06
Butyl acetate	N-hexane	[9,11]	0.27	0.27
Cyclohexanol	Water	[24]	0.30	x
1,4-Dioxane	Water	[13]	0.18	0.41
N-methylpirrolidone	Water	[9-11,25]	0.26	0.25
N-methylpirrolidone (95); Water (5)	Water	[25]	0.33	x
N-methylpirrolidone (92); Water (8)	Water	[25]	0.39	x
N-methylpirrolidone (89); Water (11)	Water	[25]	0.45	x

In the work by Ruaan and coauthors [13] only data originating from the work by Cheng and coauthors [9] collected under the same experimental conditions for polymethylmethacrylate membranes were analyzed. Visual inspection of the data in Tables 1 and 2 allows to state that, when the analysis is expanded to a larger number of works and experimental conditions, without fixing the synthesis procedures, such as the thickness of the polymeric film, for example, it was impossible determine a numerical index that depends only on the properties of PMMA, solvent and non-solvent and fully differentiate sponge-like from finger-like structures. This is because changes in parameters such as the thickness of the polymeric solution film and the temperature at which the experiments were carried out alter the kinetics of the process of diffusion of the non-solvent into the polymeric solution and of dissolution of the solvent in the non-solvent, that directly influences the structure generated by the phase inversion.

This finding comes from the observation that some solvent/non-solvent pairs can generate both finger-like and sponge-like structures, depending on the experimental conditions, such as butyl acetate/N-hexane, acetone/water, N-methylpyrrolidone/water. As there was little data obtained for these solvent/non-solvent pairs, it was not possible to draw conclusions about how other properties caused formation of one or another structure. More detailed experimental data for each of these conditions (and all others in Tables 1 and 2) can be found in **Table S2 and S3 (Supporting information)**.

Although it was not possible to make a distinction between sponge-like and finger-like structures using only the parameter proposed by Ruaan and coauthors [13], it differentiates these structures to some degree. A statistical analysis of Φ values calculated in this work was performed and to assess the quality of our data.

3.1.1 Statistical analysis

The first step of the statistical analysis was the assessment of the normality of Φ values calculated in this work (Tables 1 and 2) whose results are shown in **Figure 1**. As both p-values calculated by the Anderson-Darling normality test were more than 0.05, it was not possible to reject the hypothesis of normality of populations from which both samples were taken at the 95% confidence level. As the sample sizes are small, it is possible that the normality test does not rule out the normality of a considerably non-normal distribution. However, populations were assumed to be normal so they could be analyzed using statistical tools such as calculating confidence intervals for means and performing hypothesis tests.

A statistical hypothesis test was performed to assess whether, at the 95% confidence level, the mean Φ value for sponge-like structures could be equal to the mean Φ value for finger-like structure. The test presented a p-value of 0.02264 (less than 0.05) that leads to the rejection of the null hypothesis. That is, at the 95% confidence level, it can be said that the means of Φ for sponge-like and finger-like structures are different.

With the mean and standard deviation values shown in Figure 1, confidence intervals were calculated for the mean at the 95% confidence level. As expected by the hypothesis test result, the intervals do not overlap. The intervals obtained were as follows:

- Population mean of Φ (μ_Φ) for sponge-like structures: $0.11562 \leq \mu_\Phi \leq 0.17621$
- Population mean of Φ (μ_Φ) for finger-like structures: $0.17668 \leq \mu_\Phi \leq 0.38271$

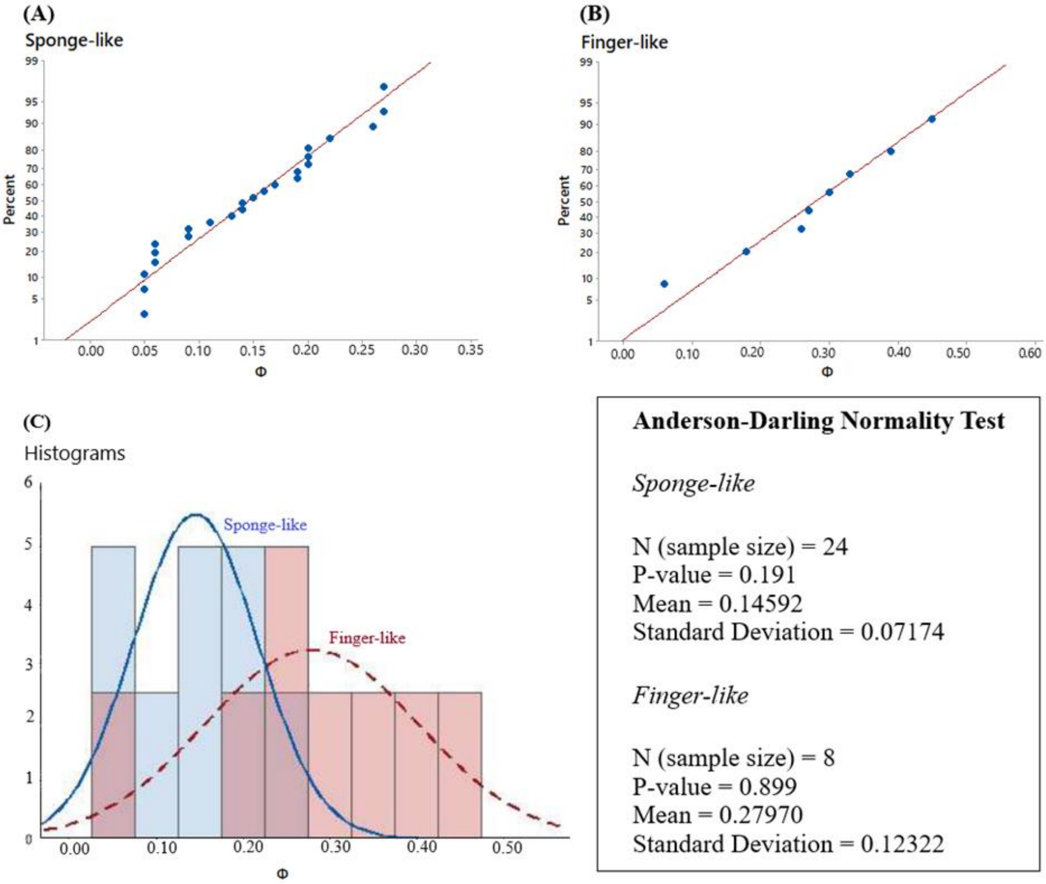
The structure of a membrane depends on both kinetic and thermodynamic factors. However, although the Φ value does not take into account kinetic factors, the results found are consistent with what happens in practice. A low value of $\Delta\delta_{s-ns}$ indicates high affinity between solvent and non-solvent, as well as leads to a high value of the index Φ, since δ_{s-ns} is in the denominator (Equation 8). Therefore, the fact that high values of Φ generate finger-like structures is in agreement with the fact that high affinity between solvent and non-solvent generates finger-like structures. Similarly, a high value of $\Delta\delta_{p-s}$ indicates low affinity between polymer and solvent, as well as leading to a high value of the index Φ, since $\Delta\delta_{p-s}$ is in the numerator (Equation 8). Therefore, the fact that high values of Φ generate finger-like structures is also in agreement with the fact that low affinity between polymer and solvent generates finger-like structures.

Observing the overlapping of the histograms in Figure 1, it can be seen that, for the samples analyzed, the probability of obtaining sponge-like structures is greater when Φ is between 0 and 0.22 and the probability of obtaining finger-like structures is greater when Φ is more than 0.22. It is important to mention that, as shown in the literature review, 0.25 was the limit set by Ruaan and coauthors [13] for the transition between sponge-like and finger-like structures in systems with polymer solution concentration close to 15% v/v and film thickness close to 300 μm. Therefore, the result was similar to that reported by the researchers.

For a more likely successful choice of the solvent/non-solvent pair, other factors that are not described by the solubility parameters but affect transport during membrane formation need to be taken into account. Decreasing the concentration of the polymeric solution, for example, tends to increase the probability of formation of finger-like structures and, therefore, very dilute solutions need a very low value of Φ to generate sponge-like pores [13]. Similarly, increasing the thickness of the polymer solution film tends to increase the probability of formation of finger-like pores, so films with large thickness require a very low value of Φ to generate sponge-like structures [13].

3.2 Modified Ruaan parameter (Φ’)

The conditions reported in the literature for obtaining sponge-like and finger-like structures from phase inversion by immersion-precipitation of polymethylmethacrylate with the addition of surfactants are presented, respectively, in **Tables 3 and 4**. Tables 3 and 4 also show the Φ' values for each of these conditions, calculated from the surfactant HLB data presented in **Table S4** and the solvent solubility parameters (non-solvents, in this case) presented in the Table S1.



Anderson-Darling Normality Test

Sponge-like

N (sample size) = 24
P-value = 0.191
Mean = 0.14592
Standard Deviation = 0.07174

Finger-like

N (sample size) = 8
P-value = 0.899
Mean = 0.27970
Standard Deviation = 0.12322

Fig. 1. Normality test of the index proposed by Ruaan and coauthors [13] for sponge-like **(A)** and finger-like **(B)** structures, in addition to histograms for both structures **(C)**. Source: Authors

Table 3. Conditions for obtaining polymethylmethacrylate membranes with sponge-like structure with the addition of surfactants. Source: Author.

Surfactant	Non-solvent (% v/v)	References	Φ’
Brij 35	N-hexane	[12]	1.00
Span 20	Water	[12]	0.49
Span 40	Water	[12]	0.62
Span 80	Water	[12]	0.75
Span 85	Water	[12]	0.89
Tween 20	N-hexane	[11,12]	0.99
Tween 80	N-hexane	[10-12]	0.89
Tween 85	N-hexane	[12]	0.65

Table 4: Conditions for obtaining polymethylmethacrylate membranes with finger-like structure with the addition of surfactants. Source: Author.

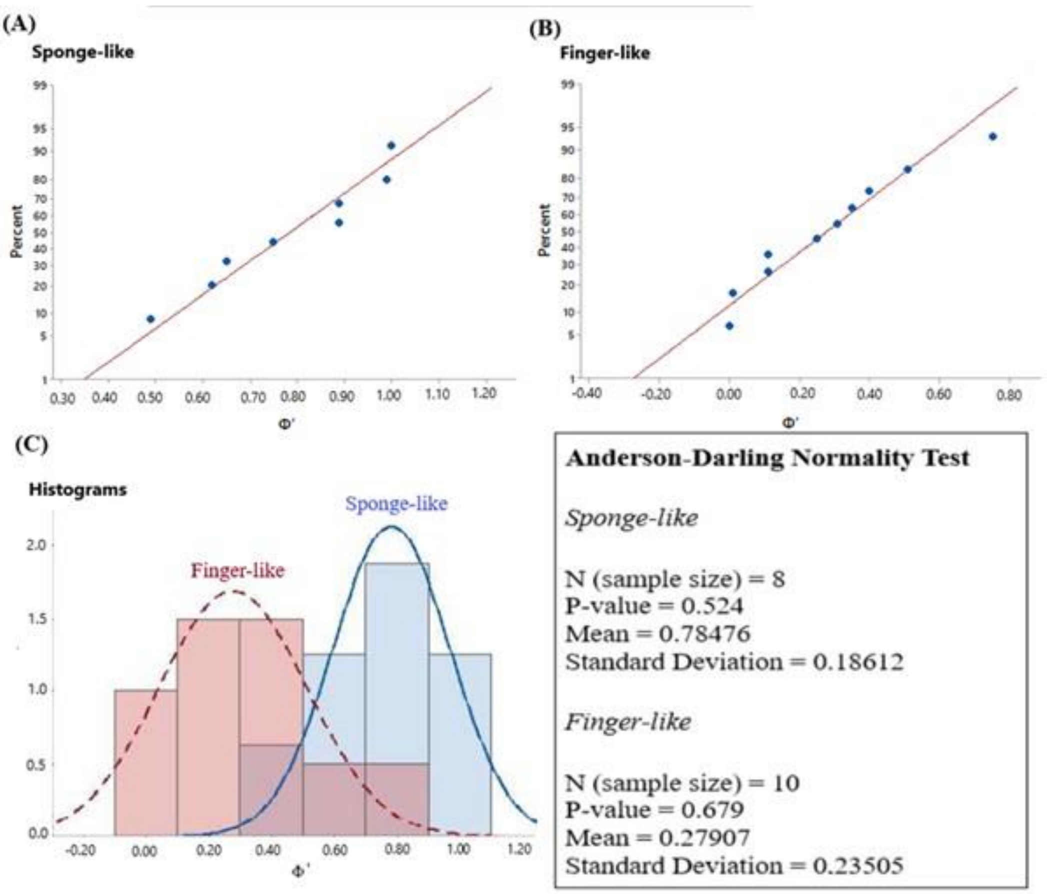
Surfactant	Non-solvent (% v/v)	References	Φ'
Brij 35	Water	[12]	0
Span 20	N-hexane	[12]	0.51
Span 40	N-hexane	[10-12]	0.40
Span 80	N-hexane	[12]	0.25
Span 80	Water	[12]	0.75
Span 85	N-hexane	[12]	0.11
Tween 20	Water	[12]	0.01
Tween 80	Methanol	[11]	0.31
Tween 80	Water	[10-12]	0.11
Tween 85	Water	[12]	0.35

Visual inspection of the data in Tables 3 and 4 allows to state that, without fixing the synthesis procedures, such as the surfactant concentration, for example, it is impossible to determine a numerical index that depends only on the properties of the surfactant and of the non-solvent and fully differentiate sponge-like from finger-like structures. For instance, Span 80/water pair can generate both finger-like and sponge-like structures depending on the experimental conditions. As only one pair with this characteristic was obtained, it was not possible to establish conclusions about what other properties led to the formation of one or another structure. More detailed experimental data for each of these conditions (and all others in Tables 3 and 4) can be found in **Tables S5 and S6** (Supporting information).

Although it is not possible to make a distinction between sponge-like and finger-like structures using only the Φ' value, it differentiates these structures to some degree and to assess the quality of this differentiation the statistical analysis of the Φ' values was also performed.

3.2.1 Statistical analysis

The first step of the statistical analysis was the assessment of the normality of the calculated Φ' indices (Tables 3 and 4) whose results are shown in **Figure 2**.



Anderson-Darling Normality Test

Sponge-like

N (sample size) = 8
P-value = 0.524
Mean = 0.78476
Standard Deviation = 0.18612

Finger-like

N (sample size) = 10
P-value = 0.679
Mean = 0.27907
Standard Deviation = 0.23505

Fig. 2. Normality test of the index proposed in this work for sponge-like **(A)** and finger-like **(B)** structures, in addition to histograms for both structures **(C)**. Source: Authors

An important information that can be obtained from Figure 2 is that, as both p-values calculated by the Anderson-Darling normality test were more than 0.05, it is not possible to reject the hypothesis of normality of the populations from which both samples were taken, at the 95% confidence level. As the sample sizes are small, it is possible that the normality test does not rule out the normality of a considerably non-normal distribution. However, populations were assumed to be normal so they could be analyzed using statistical tools such as calculating confidence intervals for means and performing hypothesis tests.

A statistical hypothesis test was performed to assess whether, at the 95% confidence level, the mean Φ' value for sponge-like structures could be equal to the mean Φ' value for finger-like structure. The test presented a p-value of 0.001408 (much less than 0.05) that leads to the rejection of the null hypothesis. That is, at the 95% confidence level, it can be said that the means of Φ' for sponge-like and finger-like structures are different.

With the mean and standard deviation values shown in Figure 2, confidence intervals were also calculated for the mean at the 95% confidence level. The intervals obtained were as follows:

- Population mean of Φ' ($\mu_{\Phi'}$) for sponge-like structures: $0.62916 \leq \mu_{\Phi'} \leq 0.94037$
- Population mean of Φ' ($\mu_{\Phi'}$) for finger-like structures: $0.11092 \leq \mu_{\Phi'} \leq 0.44721$

As can be seen, for the Φ' value the intervals do not overlap either, which is evidence that sponge-like structures and finger-like structures on average have different values of Φ'.

The results found are consistent with what happens in practice. A high value of the Φ' means that there is a large difference between the hydrophilicity of the surfactant and the hydrophilicity of the non-solvent, that makes it difficult for the non-solvent to enter the polymer solution and, therefore, generates sponge-like structures.

Observing the overlapping of the histograms in Figure 2, it can be seen that, for the samples analyzed, the probability of obtaining sponge-like structures is greater when Φ' is between 0.55 and 1 and the probability of obtaining finger-like structures is greater when Φ' is between 0 and 0.55.

It is important to emphasize that the results found for Φ cannot be compared with the results found for Φ' because the parameters were created to be applied in different systems. While Φ is only used to analyze systems without surfactants, Φ' is only used to analyze systems with surfactants.

4. Conclusions

The parameters presented in this work (Φ and Φ') are complementary. The results reported here contribute to the scientific knowledge about the phase inversion of polymethylmethacrylate by demonstrating for the first time the application of a numerical index that allows predicting the structure generated by the phase inversion of the polymer in systems with surfactants (Φ'). Although the systems are subjected to the kinetics of diffusion during wet phase inversion of the membranes, it was possible to have a rule for membrane morphology based on solubilities parameters with help of a statistic tool. The best conditions for carrying out the phase inversion of polymethylmethacrylate in order to obtain sponge-like supports were determined: systems whose Φ index is less than 0.22 or the Φ' index is between 0.55 and 1.00.

Supporting Information

Tables S1, S2, S3, S4, S5, and S6.

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Author Contributions

Gustavo Barcelos: Conceptualization; formal analysis; investigation; methodology; writing – original draft; visualization. André Ferlauto: Supervision. Kátia Figueiredo: Funding acquisition; project administration; writing – review & editing.

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