

Coagulation bath composition and desiccation environment as tuning parameters to prepare skinless membranes via diffusion induced phase separation

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ABSTRACT: Diffusion Induced Phase Separation (DIPS) is a currently used technique to produce porous membranes for a large variety of applications. A strong limitation is represented by the occurrence of a dense skin, which is formed during the process, highly reducing the membrane permeability. To overcome this issue, two modifications of the standard DIPS protocol were investigated: the use of coagulation baths composed by a solvent/nonsolvent mixture and the desiccation in a controlled environment, by modulating the partial pressure of nonsolvent vapor. An appropriate choice of coagulation bath composition, together with an appropriate desiccation protocol (i.e., the use of a nonsolvent vapor), will produce a skinless membrane, and offers the chance to control the morphology of both membrane surfaces. These results underline the importance of post-treatment stage in membrane preparation via phase separation, thus suggesting that membrane washing/drying stage will affect the final morphology. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42151.

KEYWORDS: morphology; membranes; phase behavior; porous materials

Received 13 October 2014; accepted 25 February 2015

DOI: 10.1002/app.42151

INTRODUCTION

The production of polymeric membranes via Diffusion Induced Phase Separation (DIPS) has been widely studied and applied for a number of model systems. The main steps of membrane formation through DIPS protocol are: (i) casting of a polymer solution on a support and (ii) immersion into a coagulation bath, usually composed by a nonsolvent. The mutual exchange of solvent and nonsolvent will modify the casted solution composition, inducing phase separation when the equilibrium curve is crossed (see Figure 1). The liquid–liquid phase separation is responsible for the formation of a porous membrane, and it can occur via nucleation and growth and/or spinodal decomposition mechanisms.

As DIPS technique allows the preparation of a porous membrane with a rather simple procedure, it has converged a great and increasing interest during last 40 years, as witnessed by numerous scientific publications focused on this topic.¹ Researchers tried to modulate every possible processing parameter, such as casting and coagulation bath composition, temperature, and system components. The net effect of all parameters is the modification of outward/inward flux of solvent/nonsolvent,

thus influencing concentration distributions inside the casted film. Local composition, in its turn, determines the demixing mechanism and the amounts of separated phases, according to its location in phase diagram. As a general rule, the immersion in a coagulation bath composed only by nonsolvent will produce a porous membrane, but with a dense skin: this was related to a rapid increase of polymer concentration at the interface, owing to a fast outward solvent diffusion, which induces crystallization. This fact has been inferred by mass transfer modeling, providing an estimate of concentration profiles inside the polymeric film.^{2–4}

As regards to the polymer employed in this study (poly-L-lactide, PLLA), Van de Witte *et al.*^{5,6} studied the influence of solid–liquid demixing, liquid–liquid demixing and vitrification on PLLA membrane morphology obtained via immersion precipitation. Chloroform and methanol were used as solvent and nonsolvent, respectively. In a different study, the same research group applied the relations between phase diagram and membrane morphology for the ternary PLLA-chloroform-methanol system to PLLA-dioxane-methanol, PLLA-dioxane-water, and other ternary systems.⁷ Further experimental studies regarding to the formation

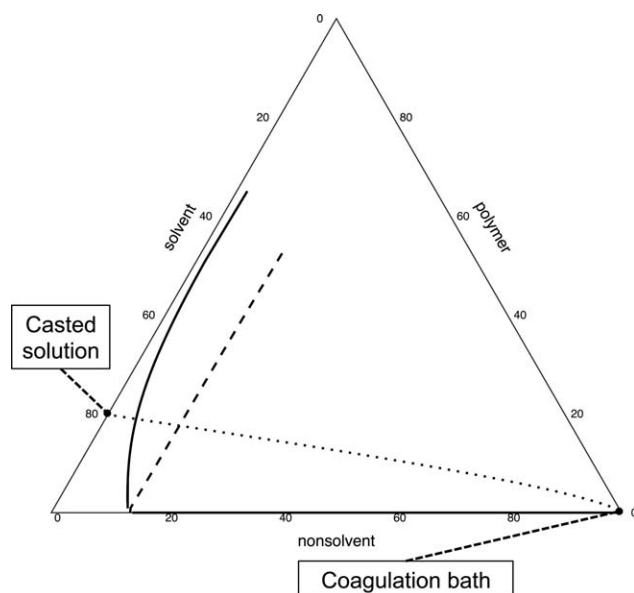


Figure 1. Schematic of DIPS process. Bold line is binodal curve, dashed line is spinodal curve, dotted line represents a reasonable composition path.

of PLLA membranes by immersion precipitation have been reported in literature,^{8–11} where the effect of different solvents and nonsolvents, casting and coagulation bath concentration, and temperature, were investigated to control the membrane morphology. By varying those processing parameters, a vast latitude of membrane morphologies, in terms of pore size and distribution, shape and interconnection can be produced.

Undoubtedly, these studies present a satisfactory picture of main features involved in DIPS process. However, some points, related to the external surface morphology and the influence of drying step, need to be further investigated and clarified. As a matter of fact, membranes prepared via DIPS ordinarily show a completely closed and nonporous external surface, owing to a local polymer concentration increase.¹² This fact reduces sensibly the overall membrane permeability, thus affecting the choice of potential applications. A number of solutions to this limitation were investigated, e.g., employing a coagulation bath composed of both nonsolvent and solvent,^{13,14} or multiple coagulation baths,^{15–17} adopting a sacrificial layer approach^{18,19} or wetting both surfaces with a modified spinneret.²⁰ In this article, the use of a binary coagulation bath and/or multiple coagulation baths were explored, showing the influences of composition and immersion time on resulting surface microstructure. Moreover, the experimental campaign presented in this work is aimed to demonstrate the influence of desiccation step, i.e., of solvent removal on the morphology of external surface. In typical DIPS practice, the membrane is washed or dried immediately after the immersion step: however, researchers often neglect the effects of this last operation on the membrane microstructure. As a matter of fact, during solvent removal the system composition will vary: thus, an influence on membrane morphology can be reasonably expected. For example, by washing the membrane with a nonsolvent, a further mass transfer will occur, with a related composition modification. On the other hand, if the membrane is exposed to a gaseous phase to

promote drying, the presence of nonsolvent vapor in desiccation environment will influence the driving force for mass transfer, i.e., its direction and rate. Therefore, the solvent removal rate can be modulated by tuning the partial pressure of nonsolvent in desiccation environment. A further option provided by this phenomenology is the induction of phase separation by diffusion of nonsolvent vapor into the liquid phase.²¹ Following this latter rationale, polyethersulfone²² and poly(vinylidene fluoride)²³ membranes with a porous external surface were produced, by exposing the casted solution to a vapor phase containing nonsolvent (Vapor Induced Phase Separation, VIPS).

To sum up, the objective of this work is the understanding of the effects of double immersion and desiccation conditions on the morphology of membrane surfaces, in order to take advantage of these features to prepare skinless membranes.

EXPERIMENTAL

Materials

The polymer examined in this study was the PLLA RESOMER[®] L 209 S, purchased from Boehringer-Ingelheim (inherent viscosity 3 dL/g). The solvents employed were deionized water and 1–4 dioxane (Sigma-Aldrich, used without further purifications).

Membrane Preparation and Characterization

The membrane preparation protocol can be subdivided into three steps:

1. dip-coating
2. immersion into one (or more) coagulation bath(s)
3. desiccation

The dip-coating consists in a slow pulling-out of a glass slide (15 × 50 mm, thickness 2 mm) immersed in a PLLA-dioxane solution (see Figure 2). In this way, the slab surface gets coated with a layer of polymer solution. The as-obtained layer thickness depends on pull-out velocity, solution concentration and temperature, as widely shown in literature.²⁴ In this work, these parameters were taken constant in all experiments: the pull-out velocity was 3 cm/min, the polymer concentration was 8 wt % and the temperature was set to 30°C.

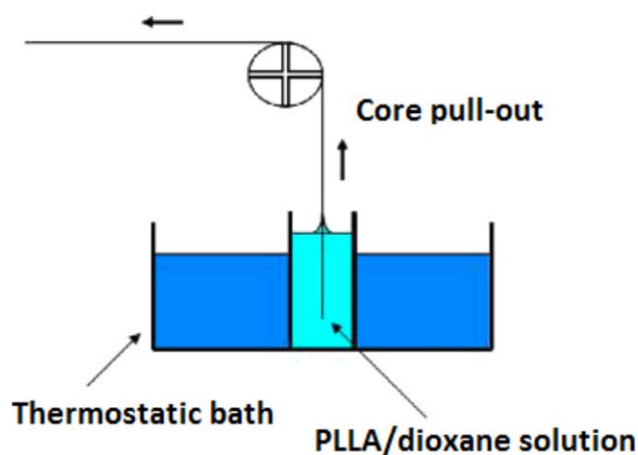


Figure 2. Schematic of dip-coating process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

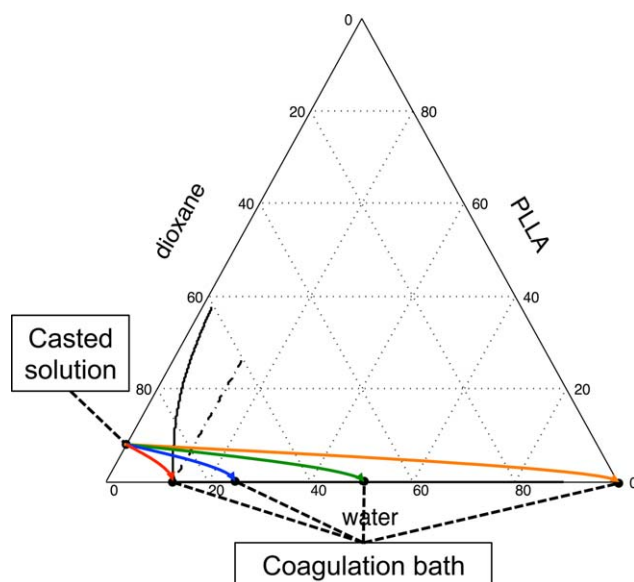


Figure 3. Phase diagram of PLLA-dioxane-water system calculated via Sanchez-Lacombe model, with reasonable composition paths encountered in DIPS experiments performed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The typical DIPS operation is accomplished via pool immersion of the coated slab into a coagulation bath, for a certain time interval. During this step, the diffusion of solvents from and to the casted solution changes its composition, inducing liquid–liquid phase separation and/or polymer crystallization. A schematic of this stage is presented in Figure 3, showing a calculated phase diagram of PLLA-dioxane-water. The model adopted was based on Sanchez-Lacombe with specific interactions,^{25,26} with the interaction parameters slightly modified to achieve a better fit on cloud point data (details on measurement and results are reported in Refs. [27 and 28]). In this work, membranes were prepared via immersion into one or two (subsequent) coagulation bath(s) (see Figure 4), in order to investigate the influence of bath concentration and immersion time on the resulting microstructure. The investigated compositions of first coagulation bath were 87/13, 75/25, and 50/50 (dioxane/water wt/wt). The (optional) second coagulation bath was constituted of pure water. The baths temperatures were maintained at 30°C. As showed in Figure 3, by modulating the water concentration in coagulation bath, the composition path will accordingly vary, entering the miscibility gap at different points and times, thus influencing phase separation.

After the DIPS process, the as-obtained samples were desiccated in an environment with controlled humidity for 24 h. Two kinds of desiccating environments were tested: dry (nitrogen atmosphere) and humid (around 70% relative humidity) ambient.

To analyze the effect of bath composition and immersion time on the resulting microstructure, both inner and outer surfaces of the as-produced samples were observed via Scanning Electron Microscopy (SEM), utilizing a Philips SEM quanta FEI, at 10 kV.

The crystallinity of PLLA membranes was investigated through Differential Scanning Calorimetry (DSC), employing a DSC131 EVO (Setaram). Membrane samples were heated at 10°C/min in the range 50–200°C.

RESULTS AND DISCUSSION

Direct Drying and Immersion in a Water Bath

When desiccating the casted binary solution in a dry environment, without performing a DIPS step, a dense membrane is obtained, with both closed internal and external surfaces [see Figure 5(a)]. This result can be ascribed to the evaporation of dioxane, which does not induces any phase separation, except for polymer crystallization, thus not producing any porosity. On the other hand, if the solution is desiccated in a wet environment, the resulting external surface gets porous [see Figure 5(b)], owing to the water diffusion into the casted polymeric film which induces phase separation. However, in both cases, the internal surface remains closed: this suggests that, in humid environment, water penetration does not involve the whole film thickness.

Conversely, immersion in a water bath gives out a porous membrane, as the nonsolvent diffusion induces phase separation in the whole casted solution. However, the external surface does not exhibit any pore: this fact is related to the rapid polymer crystallization at the interface with the coagulation bath, induced by the fast outer diffusion of dioxane that locally increases polymer concentration, as reported in several works.^{2–4}

These results suggest that to obtain a porous membrane without a dense skin, a different protocol must be adopted. In the following sections, membranes prepared with a binary coagulation bath are presented.

Single Immersion: Influence of Coagulation Bath Composition and Desiccation

When the binary polymer solution is immersed in a dioxane/water bath for 5 min, and then desiccated, the resulting morphology depends on both coagulation bath composition and desiccation environment (humid vs. dry ambient).

If desiccation is performed in a dry ambient, a closed external surface was obtained for both 87/13 and 75/25 coagulation

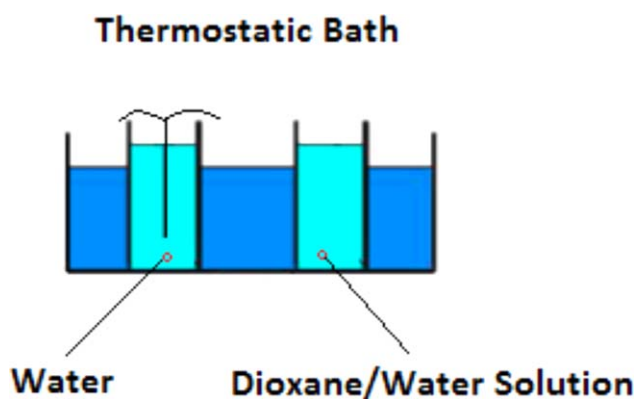


Figure 4. Schematic of DIPS baths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

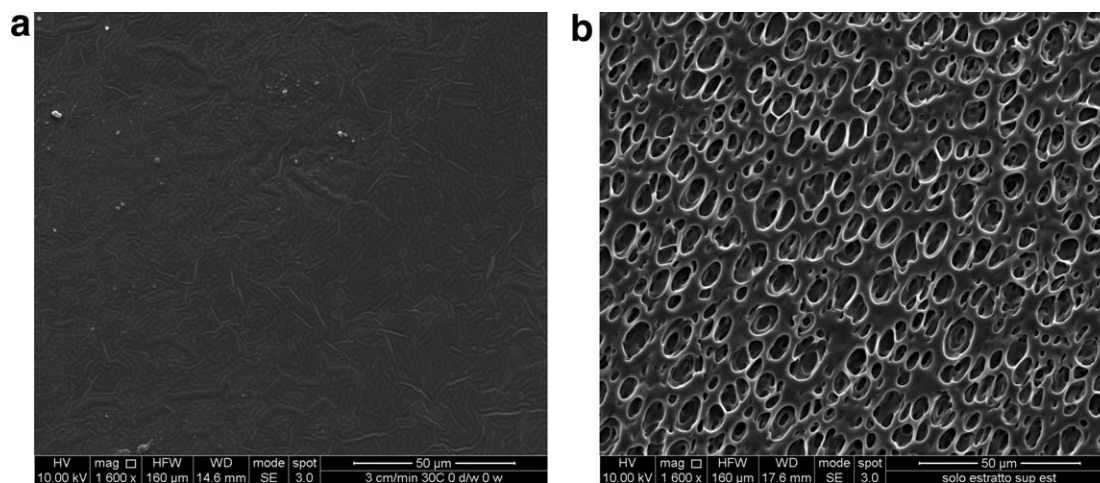


Figure 5. Morphology of membrane external surfaces obtained without immersion in a coagulation bath, i.e., direct desiccation. (a) Dry. (b) Humid.

baths (see Figure 6). The dioxane/water system shows a minimum azeotrope, for which the liquid phase enriches of dioxane if its concentration is higher than 83 wt %.²⁹ As the system focused in this study has a third component, which is nonvolatile, a variation in azeotropic concentration is expected. Although no vapor–liquid equilibrium data for this ternary

system are available, the azeotropic concentration should be reasonably located close to two mixed bath compositions tested in this work, i.e., 87/13 and 75/25. Therefore, nonideal vapor–liquid equilibrium behavior can affect membranes prepared with the aforementioned baths. As a matter of fact, as the external surface may decrease its water content by evaporation, an

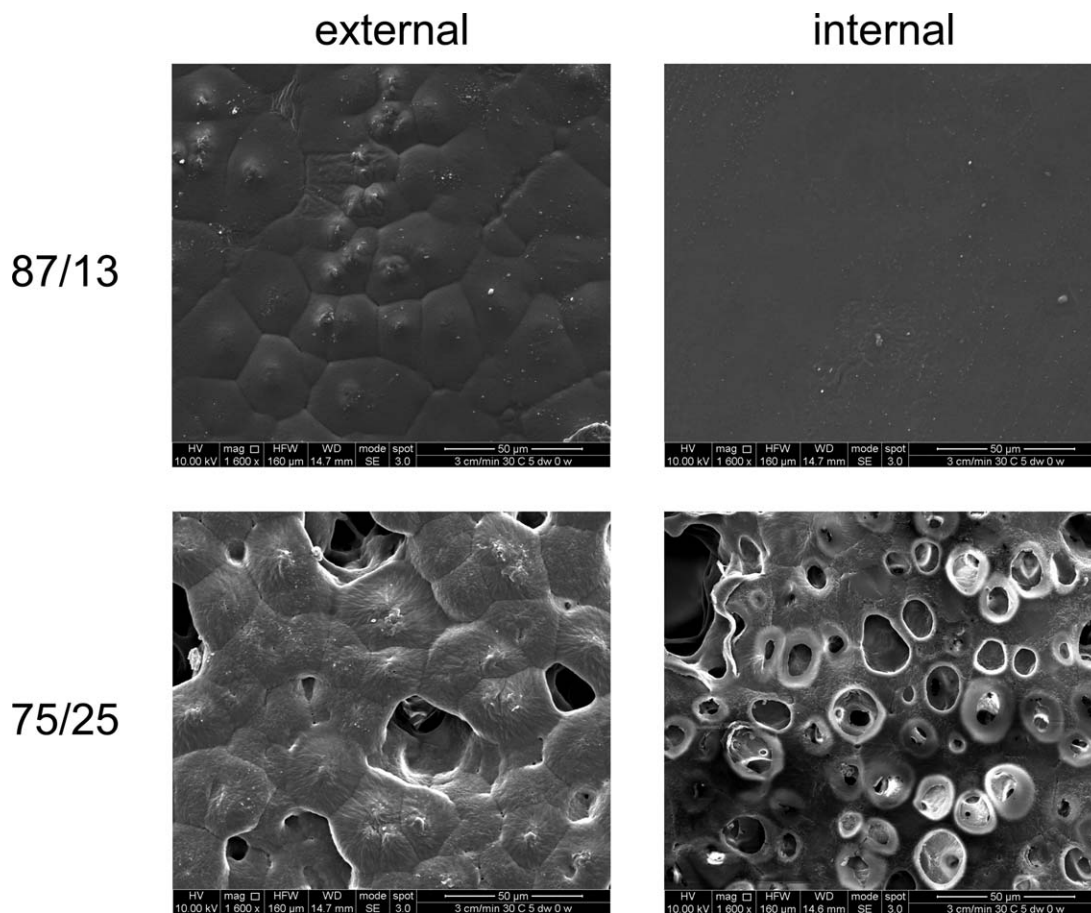


Figure 6. Morphology of membrane surfaces obtained with a single immersion in a dioxane/water bath for 5 min and desiccated in dry environment.

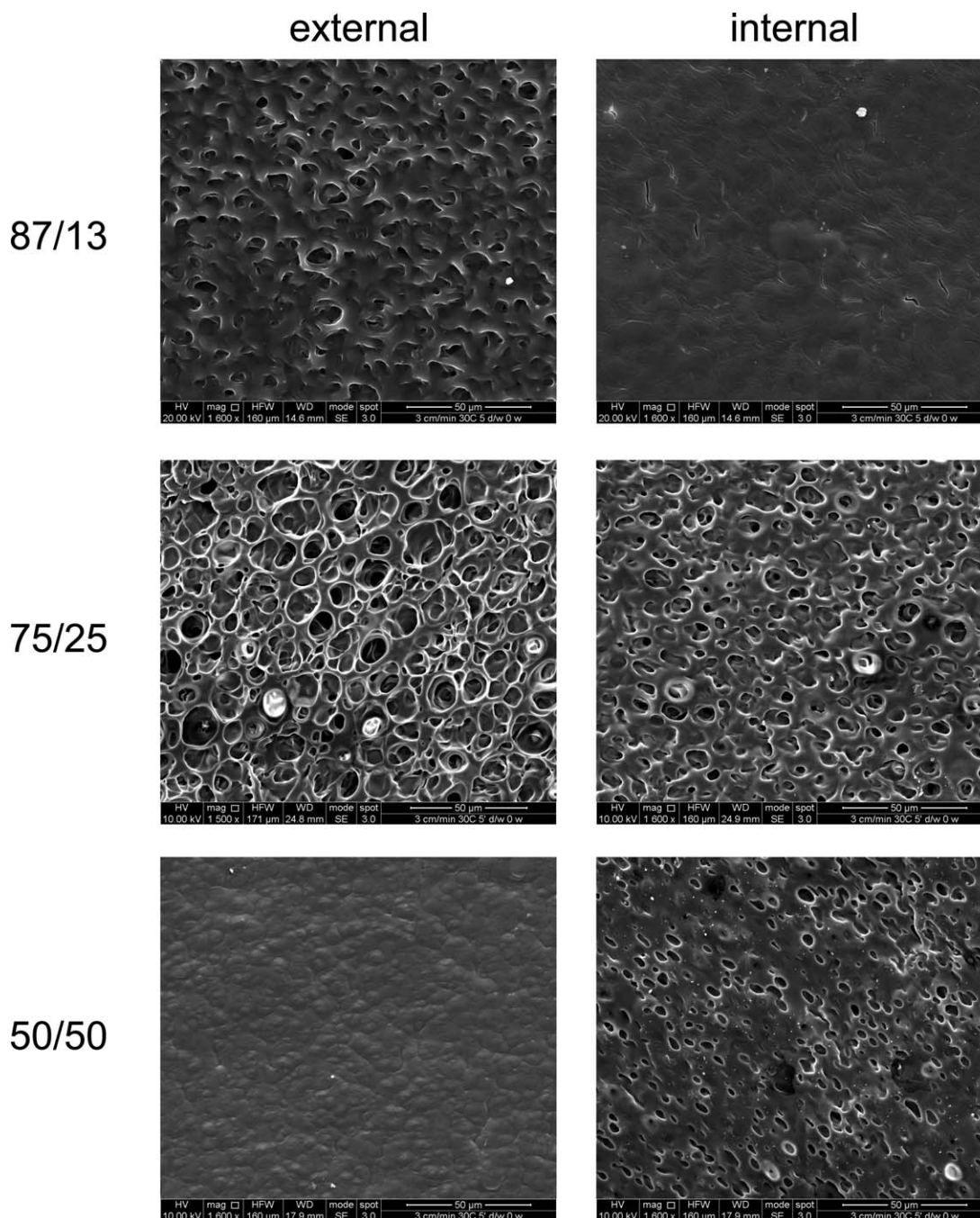


Figure 7. Morphology of membrane surfaces obtained with a single immersion in a dioxane/water bath for 5 min and desiccated in humid environment.

increased dioxane concentration could be able to reestablish a single-phase condition, thus giving out a crystalline morphology of polymer after solvent evaporation. This fact is more noticeable in membranes prepared with the 87/13 bath: in this case, both inner and outer surfaces result closed and crystalline. On the other hand, with the 75/25 bath, the internal surface resulted open, whereas the external one is crystalline (closed). Even if voids are noticeable on the external surface, they are not the result of a liquid–liquid phase separation: it is more likely the occurrence of a local fracture due to shrinkage induced by crystallization. As for the internal surface, the

pore morphology suggests a separation mechanism by nucleation and growth, thus prompting that water has reached the support in a sufficient amount to cross the binodal curve, but not the spinodal one, owing to the relative short immersion time.

If samples are desiccated in a humid ambient, external surfaces will be more likely porous (see Figure 7). As a matter of fact, membranes obtained with the 75/25 bath are porous on both surfaces. On the other hand, membranes prepared with the 87/13 bath show a open porosity on the external surface, whereas

Table I. Membranes Surfaces (Internal/External, C, Closed, O, Open) Obtained by Varying Coagulation Bath Concentration (Rows) and Immersion Times (Columns, Reported in Minutes)

d/w	Dry			Humid		
	5'+0'	5'+5'	10'+5'	5'+0'	5'+5'	10'+5'
87/13	C/C	O/O	O/O	C/O	O/O	O/O
75/25	O/C	O/C	O/C	O/O	O/O	O/O
50/50	–	–	–	O/C	O/C	O/C

The first number refers to immersion time in the d/w bath, the second number refers to immersion time in pure water.

the inner one is closed. A third case is offered by the 50/50 bath, which showed no pores on the outer surface, whereas the inner one has few and small pores. The morphology obtained in the latter case is comparable with that recorded when using a coagulation bath constituted of pure water (as shown previously). As a matter of fact, when a polymer–solvent solution is immersed in a nonsolvent bath, the solvent is able to diffuse rapidly from casted film to the bath, increasing the polymer concentration at the interface, and then inducing the crystallization on that surface. Obtaining similar results with a 50/50 bath could mean that this condition is characterized by a relatively low content of solvent, which does not sufficiently reduce the driving force to outward dioxane flux. On the other hand, higher dioxane concentrations will reduce the outer diffusion of solvent from membrane, thus inhibiting the surface crystallization and giving out an open-pore morphology on the external surface. However, the internal surface of 87/13 sample appears closed, as few nonsolvent can reach that section and then inducing liquid–liquid demixing. As showed in previous section, the humid/dry environment has a direct effect on the external surface, whereas the internal one is determined by the coagulation bath. Therefore, the resulting morphology of internal surface does not depend on the desiccation environment, but only on the coagulation bath concentration. A midway situation is represented by the 75/25 bath: in this case, the water concentration is high enough to reach the inner surface and induce demixing, and low enough to avoid a rapid crystallization of the polymer at the outer surface.

Influence of the Second Immersion Step

As seen previously, with the immersion in a water bath, the inner surface can experience liquid–liquid demixing, and then shows an open-pore morphology. On the other hand, the outer surface results closed, owing to the polymer crystallization induced by an increase in its concentration. As a matter of fact, when immersing a binary solution in a nonsolvent bath, a rapid outflow of solvent will increase the polymer concentration at the surface. Simulated values are around 20–30%.⁴ To limit the solvent outflow (and simultaneously control the nonsolvent inflow), a double immersion into two different coagulation baths was investigated. The first one is a dioxane/water mixture (with the same concentrations explored previously), whereas the second one is constituted of pure water. The net effect of the first immersion step is an enrichment in water of the proto-membrane, without losing a consistent amount of dioxane, as

its outflow is reduced, owing to a small driving force. The second immersion will enhance mass transfer, promoting solvent/nonsolvent exchange between casted film and coagulation bath. However, the water contained in the casted film, due to the first immersion, will reduce the driving force to nonsolvent inflow with respect to the direct immersion of casted film in a water bath, thus providing an intermediate condition between binary and pure water coagulation baths. A summary of as-obtained membrane surfaces morphology is reported in Table I.

If samples are desiccated in a dry environment, different morphologies are noticed, on the basis of coagulation bath composition. For example, 75/25 bath produces an essentially closed external surface, with few and very small pores (see Figure 8). Increasing the first immersion time, the surface becomes completely closed. These results are in line with those showed previously, as the first immersion step is responsible for the formation of a dense skin layer on the external surface. On the other hand, when using a 87/13 bath, the external surface results open. The second immersion in water gave out a nonsolvent intake which allowed the cross of azeotropic concentration: therefore, as liquid phase will lose more dioxane than water by evaporation, the return to a single phase system is avoided. As a further effect of this increased inward water flux, internal surface become porous, with a shape recalling nucleation and growth kinetics.

When drying in a humid environment, membranes obtained with both 87/13 and 75/25 coagulation baths showed an open external surface, with the internal one showing also an open structure (see Figure 9). This fact suggests that a slower water removal extends the time for phase separation, thus giving out pore sizes higher than those obtained by desiccation in dry environment. Moreover, as the desiccation process takes place in a longer time interval, a mass diffusion within the polymer film, which locally modifies concentrations with respect to those established after the immersion, may occur.

However, the morphology of external surfaces depends on the first coagulation bath composition. At higher dioxane concentration, the outer surface exhibits a higher porosity and pore size than the inner one. On the other hand, when lowering the dioxane content in coagulation bath, the external surface appears similar to the internal one, with circular pores and similar porosity value.

Increasing the immersion time in the dioxane/water bath does not influence appreciably the membrane morphology. This could be due to the relatively small variation in sample composition during the first immersion step. As a matter of fact, the sample should absorb a small amount of water.

These results show that even a short immersion time (5 min) in water produces a significant modification of membrane morphology. Therefore, the common used washing step after DIPS, consisting in a long lasting immersion in a water bath, will strongly influence the final membrane morphology. This fact suggests that, in immersion precipitation, the membrane post-treatment step for solvents removal should be taken into account when discussing the relations between processing parameters and resulting morphologies.

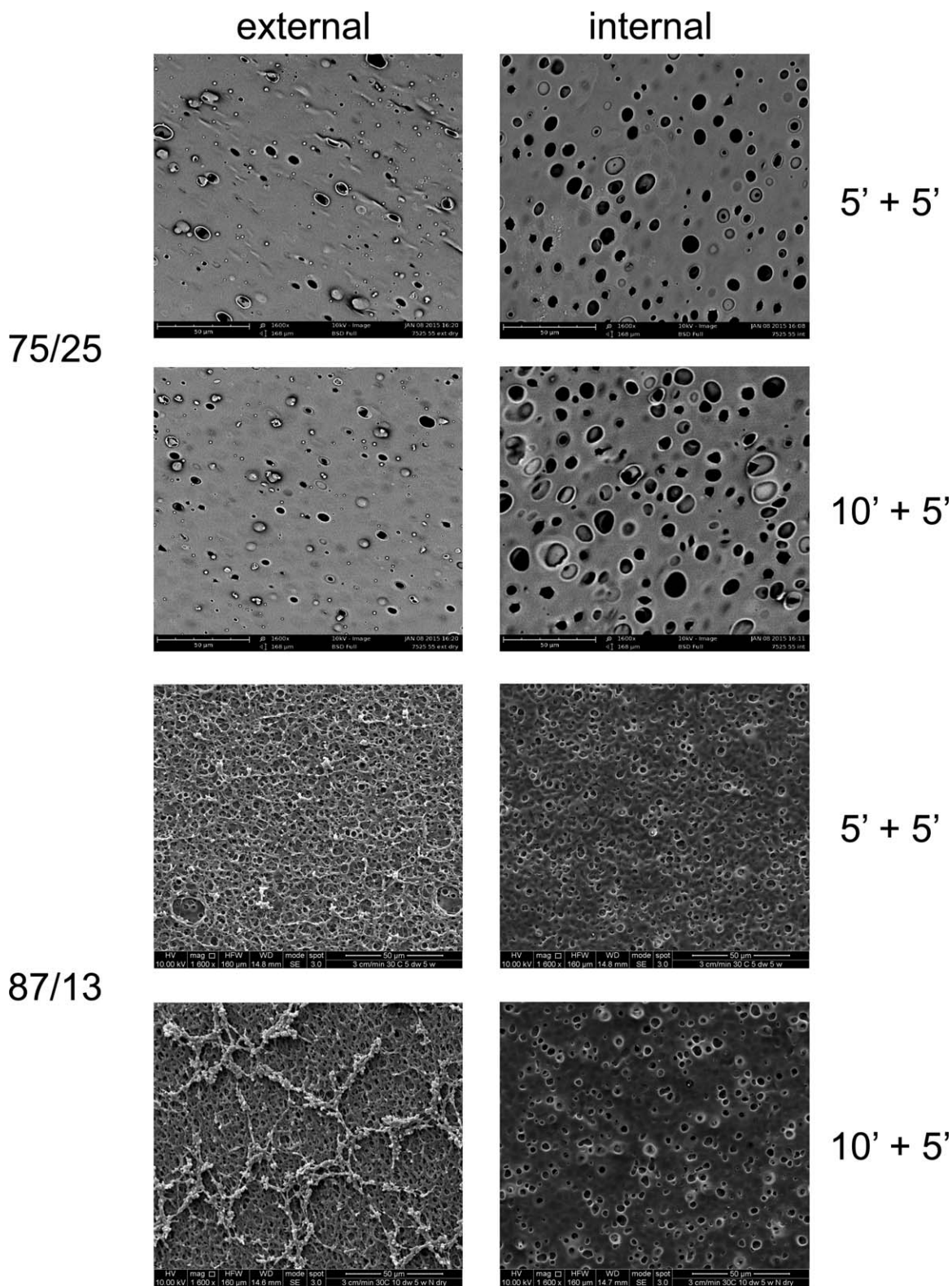


Figure 8. Morphology of membrane surfaces obtained with a double immersion, first in a dioxane/water bath, then in pure water, and desiccated in dry environment.

When reducing the dioxane/water ratio in the coagulation bath to 50/50, results were similar to those obtained with a single immersion. External surface remains closed, whereas the

internal one is porous, with a pore size higher than that obtained with a single immersion. This result is in line with those obtained with a single immersion: as discussed in the

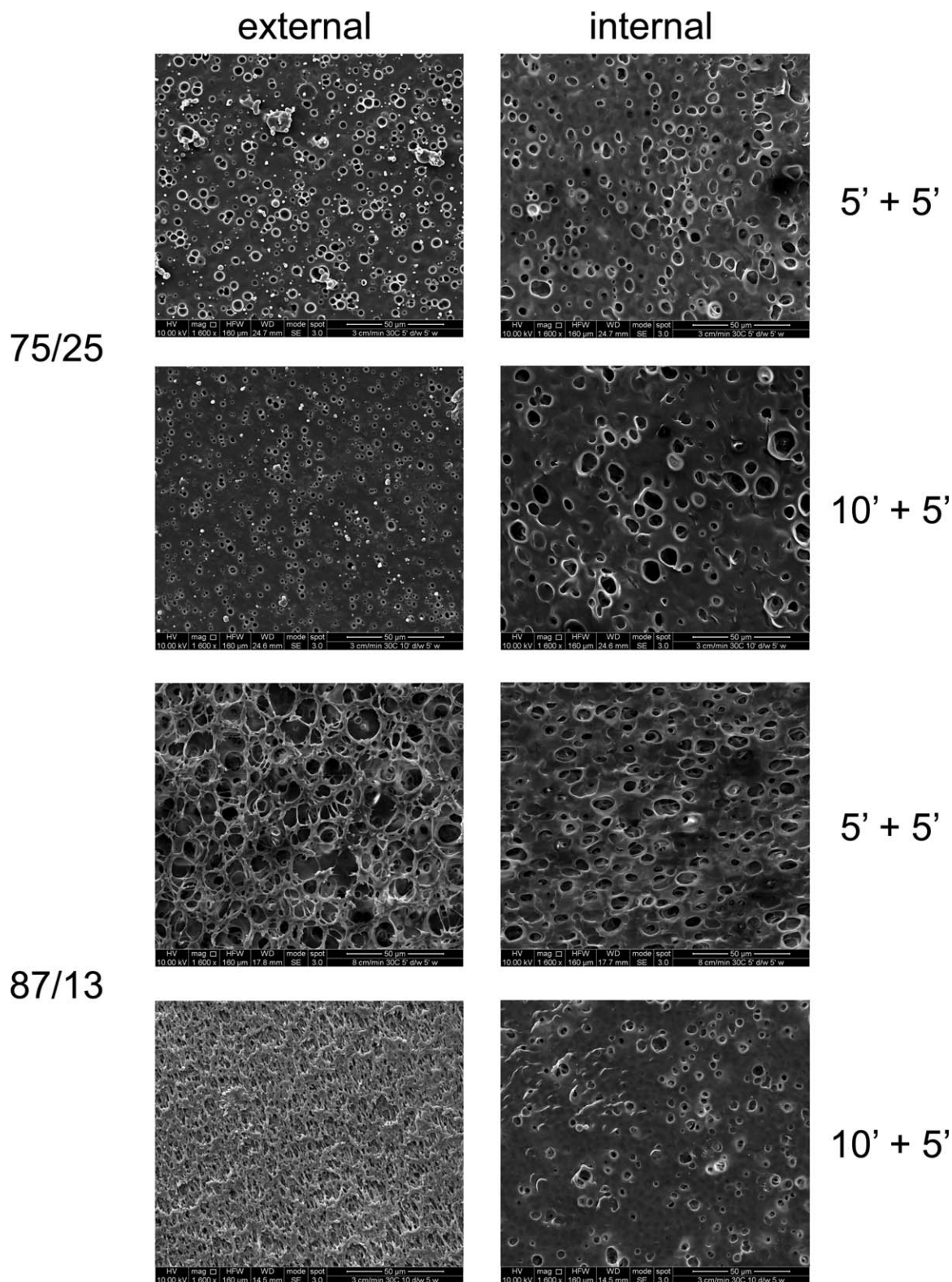


Figure 9. Morphology of membrane surfaces obtained with a double immersion, first in a dioxane/water bath, then in pure water, and desiccated in humid environment.

previous section, the water concentration in the coagulation bath is high enough to give out result similar to a pure water bath, thus a second immersion step does not introduce any substantial difference in concentrations and morphologies.

DSC

A further characterization of membranes was performed via DSC measurements. The heating curves of membranes prepared with a 87/13 coagulation bath (single and double immersion)

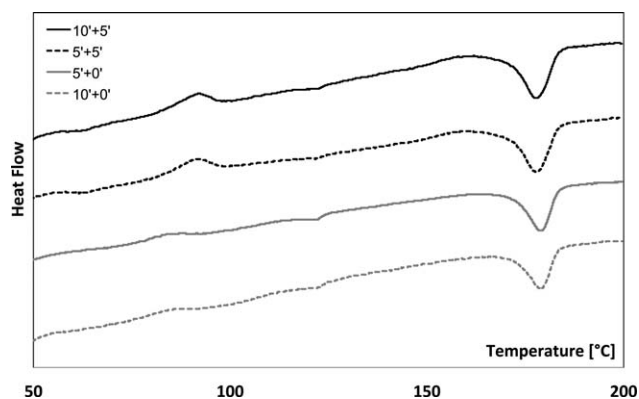


Figure 10. DSC heating curves of membranes prepared at various immersion times (reported in minutes) in 87/13 coagulation bath and desiccated in a dry environment.

and desiccated in dry environment are depicted in Figure 10. The heat flow data were normalized with the total sample weight: thus, the area of melting peaks is related to the melting enthalpy of the crystalline fraction. The melting peak is about 178°C for all investigated samples. The small endothermic peaks located around 120°C are ascribable to water desorption, therefore are not related to physical properties of membranes. A summary of collected data (melting and cold crystallization enthalpy) is reported in Table II.

The melting enthalpy (ΔH_m) does not vary significantly by changing the experimental conditions, falling in the 30–50 J/g range. For d/w ratio 87/13, for both the humidity conditions tested, the immersion time in d/w bath does not influence sensibly ΔH_m , whereas it was increased at high humidity. An opposite trend was recorded for 75/25 samples, where high humidity gave out membranes with a lower ΔH_m , and the immersion time in d/w bath positively influenced the melting enthalpy.

A remarkable difference may be noticed when looking at cold crystallization. As a matter of fact, membranes prepared with 87/13 coagulation bath showed the cold crystallization phenomenon in all explored cases (see the exothermic peaks at around 80–90°C in Figures 10 and 11), but it gets more evident in samples obtained via double immersion; conversely, membranes prepared via single immersion in pure water do not show cold crystallization. Moreover, the desiccation environment did not influence sensibly this behavior. Similar results were obtained with 75/25 and 50/50 coagulation baths: however, in those cases, the cold crystallization was detected only in samples prepared via double immersion. Membranes prepared via double immersion are then characterized by an amorphous phase with a higher mobility, i.e., they are more prone to crystallize from the amorphous state, than those prepared with a single step. This is probably due to the practically instantaneous demixing induced by the immersion in water, which rapidly generates a polymer rich phase; owing to the dioxane diffusion to water bath, the polymeric phase loses mobility and the crystallization process is slowed down. As already pointed out by other authors, phase separation onset is almost instantaneous for samples pre-immersed in a mixed solvent, whereas a direct immersion in a pure nonsolvent bath will delay the demixing process.¹³

Table II. Enthalpy of Melting (ΔH_m) and Cold Crystallization (ΔH_{cc}) Measured via DSC

d/w	Humidity	t_{DW} (min)	t_W (min)	ΔH_m (J/g)	ΔH_{cc} (J/g)
87/13	L	5	0	32.25	3.98
87/13	L	10	0	31.50	5.22
87/13	L	5	5	40.65	11.80
87/13	L	10	5	40.58	11.87
87/13	H	5	0	34.40	3.01
87/13	H	10	0	37.79	8.84
87/13	H	5	5	41.60	14.14
87/13	H	10	5	41.46	18.89
75/25	L	5	0	45.99	0.00
75/25	L	10	0	47.01	0.00
75/25	L	5	5	35.67	2.73
75/25	L	10	5	44.48	12.87
75/25	H	5	0	32.14	0.00
75/25	H	10	0	40.33	0.00
75/25	H	5	5	34.49	3.85
75/25	H	10	5	40.26	5.80

The cold crystallization enthalpy (ΔH_{cc}) of 75/25 and 50/50 membranes is lower than 87/13 samples. Thus, ΔH_{cc} increases with dioxane content in coagulation bath.

When desiccating in a dry environment, membrane crystallinity, melting temperature and cold crystallization were substantially identical to those obtained with humid desiccation, except for 75/25 single immersion.

Thereby, it can be concluded that crystallinity and morphology of PLLA membranes can be controlled by tuning residence time, coagulation bath composition, and single/double immersion protocol.

CONCLUSIONS

The effects of coagulation bath composition and desiccation environment on surface morphology of membranes prepared

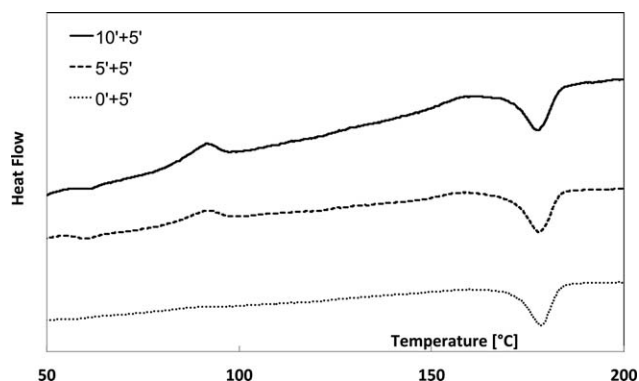


Figure 11. DSC heating curves of membranes prepared at various immersion times (reported in minutes) in 87/13 coagulation bath and desiccated in a humid environment.

via DIPS were explored and discussed. The composition of coagulation bath determines the morphology of internal surface, corresponding with the casted solution in contact with the support, whereas desiccation environment affects the external surface, i.e., the zone directly exposed to the coagulation bath. When adopting a desiccation in humid environment, external surface was more likely open. This fact can be related to the slower water removal, which extends the time available for the growth of phase separated domains. Otherwise, when desiccating in a dry environment, the external membrane surface is more likely closed, as a faster water removal could reestablish a single-phase condition, thus favoring polymer crystallization.

The double bath technique promotes the formation of an open external membrane surface. As a matter of fact, the immersion in a pure nonsolvent will produce a dense skin, owing to the polymer concentration increase at the interface between casted solution and coagulation bath. Skinless membranes were produced with a double immersion, first in a dioxane/water bath, and then in a pure water bath. The compositions of first baths were 87/13 and 75/25 wt/wt.

A final consideration regards the role of membrane post-treatment after the immersion stage. Results showed that controlling the desiccation conditions, i.e., nonsolvent partial pressure, could modify membrane morphology. This evidence provides a way to control surface morphology, and underlines the importance of post-treatment stages on final membrane properties. Therefore, to fully understand the mechanisms involved in membrane production via phase separation and to achieve better control on membrane morphologies, all steps after immersion must be taken into account.

ACKNOWLEDGMENTS

This study has been supported by the Italian Ministry of University and Research (PRIN 2010–2011 - prot. 20109PLMH2_008). The authors kindly acknowledge the precious help of master student Livia Rodonò, for her contribution in carrying out membrane preparation experiments.

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