

A fundamental study of Morphology Prediction for Nano and Microstructure of PVDF for Membrane Fabrication and Film Formation Applications

Saeed Ashtiani, Mehdi Khoshnamvand, Anna Shaliutina-Kolešová

Abstract: *This study examine the indispensable science of fabricating poly (vinylidene fluoride) (PVDF) as a hydrophobic polymer which can produced via the phase inversion method for membranes and film formation well as a strategy to fabricate a nano and micro size of PVDF films for further applications . A series of isothermal ternary phase diagrams of PVDF/solvents/nonsolvent systems were prepared. The binodal curves were gained by testing each point three times via simple titration method. Evidence of SEM imaging and AFM topology of membranes indicate different nano and micro structure on the surfaces and bulk of PVDF membrane. Based on this research which can be used as a fundamental research for any film and membrane applications; predicting the desire morphology membranes and films with specific amount of polymer and type of non-solvent is feasible.*

Index Terms: PVDF, Nano and Micro Structure, Film Formation, Membrane Applications

I. INTRODUCTION

The fostering of polymeric membranes has been developed for many industrial applications. Poly (vinylidene fluoride) (PVDF) which recently got a immense attention as a unique polymer because of its outstanding properties like high chemical and thermal resistances is used in vast area for different applications like medical usage [1] membrane technology [2-5], lithium battery [6, 7]. The attention of a polymeric membrane shows the distinguishing of membrane like microfiltration and ultrafiltration which are indebted for gas separating and bio-filtering. Based on utilizing the membrane the variety of different systems exists, as hollow fibers, tubular and flat sheets. There are several ways to prepare these membrane like thermally induced phase separation (TIPS), non-solvent induced phase separation (NIPS) [8], vapor induced phase separation (VIPS) [9] and so on. But the main and common method for attaining a polymeric membrane is non solvent induced phase separation. The phase inversion technique which is known as the Loeb-Sourirajan technique [10] was applied to fabricate the first cellulose acetate membrane for water treatment

applications. According to this method, at first a solution of polymer with a solvent was prepared at high temperature and then the solution was cast on the plate which exposed to the air with the certain thickness by means of an applicator or simple blade. Then, there are two ways to put the casted film in the colligation bath with low temperature which is encompasses non-solvent for phase separating. In the first method is giving a few minutes to membrane for pre-evaporation of solvent and then put it into non-solvent bath. The other way is to submerging the casted film immediately into non-solvent bath for doing phase separation process. The diversity of these two methods directly affected on the morphology of membrane. NIPS, as an important method for preparing polymeric membrane, has a great potential to discuss its thermodynamics and kinetics. For instance Wang and Juin [11] studied the recent advances in the fundamentals of NIPS for the development of breath figure, phase separation micro-molding and a technique based on the combination of NIPS and self-assembly of block copolymers as three novel techniques for controlling morphology. Fabrication a microporous PVDF membranes was studied [12] via NIPS-TIPS by lee et al. They showed that the membrane morphology and the mechanical properties, pore size distribution, and flux of the prepared membranes can be tailored by different factors like colligation bath temperature or solvent concentration. Initially there is only one phase that consists of solvent and polymer (lean phase) which are homogenous (stable region). By exchanging solvent and non-solvent the previous solution becomes two phases (unstable region). Additionally during this phase inversion there is also a middle region called metastable region which is located between two important binodal and spinodal curves. Feijen et al. studied the further physical and theoretical research of polymeric phase inversion [13]. Eventually, advocating to concept of these is vital for preparing ternary phase diagram that is the best approach to understand the composition changing and find the optimum amount of polymer, solvent and non-solvent concentration and how to choosing solvent and non-solvent for a specific polymer with other significant information that one could be adapted from these diagrams. Here in, we report the straight forward method to prepare ternary phase diagram for PVDF with different of all appropriate solvents and non-solvents which can be generalized for preparation of other polymeric membranes than can be used for membrane and film formation applications.

Revised Version Manuscript Received on April 05, 2018.

Saeed Ashtiani, Sahand university of Technology, Tabriz, Iran, E-mail: S.jamali@sut.ac.ir

Mehdi Khoshnamvand, State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China. University of Chinese Academy of Sciences, Beijing 100049, China) Email: mehdi.khoshnam@yahoo.com

Anna Shaliutina-Kolešová, CAS Key Laboratory of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, P.R. China, E-mail: kolesova@frov.jcu.cz

II. EXPERIMENTAL

A. Materials

Poly (vinylidene fluoride) (PVDF) was purchased from Hylar® 460. N-Methyl-2-pyrrolidone, Dimethyl sulfoxide, N, N-Dimethylformamide, Acetone and 2-Propanol all were obtained from Ningbo Fuhao Chemical Co and distilled water was used in the experiment. Also a shaker was used for preparing a homogenous solution and a pipette to measured volume of non-solvent. All the mentioned chemicals used without further purifications.

B. Plotting Isothermal Ternary Phase Diagram

The binodal curve or coexistence curve illustrates the region of temperature and composition in ternary phase diagram which a transition occurs from miscibility of the components to conditions where single-phase mixtures are metastable or unstable [13].

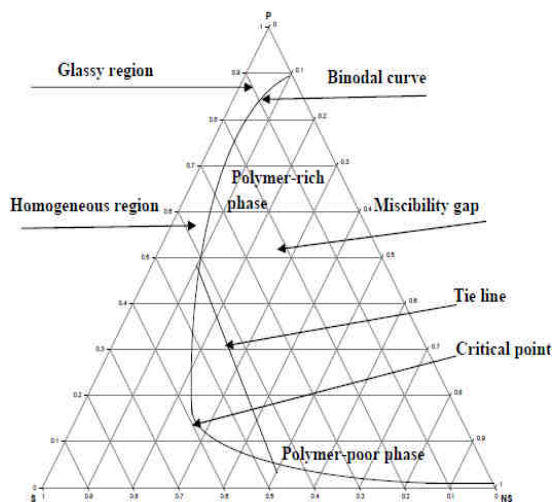


Figure 1. Ternary Phase Diagram of Polymer, Solvent and Non Solvent. [13].

To clarify this statement it should note that the boundary of liquid-liquid demixing gap is also called bimodal [14] but for some polymers the term “cloud pint curve” is more convenient. In this study we measured cloud point data by titration method [14] with focusing on the emerging of cloud point. According to this method series of PVDF with different weight percent and different solvent used to make a homogenous solution. The solution immersed in hot oil bath with the temperature between 70- 80°C and a mechanical stirrer run to makes PVDF solution homogenous. Via a digital pipette with accuracy of 1µm, the non-solvent was to the PVDF solution dropwisely and gradually. All in all, the droplets of non-solvent added until the solution toke opaque or milky color that was easily to see. Then by calculating the amount of non-solvent which was added with polymer and solvent in weight percent, one point in ternary phase diagram has already achieved. Before the ternary diagram of Polymer-solvent and non-solvent sketched the data should be normalized to fit based on the diagram’s scale.

C. PVDF Film Fabrication

In the different 100 ml glassy vessels the certain amount of PVDF was dissolved in different amount of solvent and stirred homogenously for at least 24 h, the obtaining solution

was kept in the vacuum oven without stirring in order to degas the polymer solution until no possible air bubbles were found. The solution was cast on a simple glass plate and left in the coagulation bath for 24h, and then aged 24h at 80oC to remove all the exist solvent.

III. RESULTS AND DISCUSSION

In this study based on our best experience, among the possible solvents for PVDF, which play the key role in both phase separation and membrane morphology, N, N-Dimethyl formamide was chosen and the others solvent PVDF phase diagram are reported in references [5, 6]. The experimental data was obtained at temperature 70-80°C which is called isothermal phase diagram. Each point in the ternary phase diagram indicates a phase which present in any amalgamation of a particular solvent, polymer and non-solvent consecration at a specific temperature. This array of these points would help in predicting the phases, morphology and their amounts and compositions at a certain temperature. As it is shown in Figure 1.a. the first diagram with the components of PVDF, DMF and mixture of acetone with 2-propanol (2/3 wt. %) which the apex of diagram inclined to the top and it means reaching to phase separation between the single phase of polymer-solvent to two phases that encompass of reach and lean phase of polymer, occurs faster than the situation which the water is used as a non-solvent. Furthermore, the amount of non-solvent decrease as the weight percent of polymer increases. According to the Table 1[7], as it mentioned before the solvent has a key role for phase separation it must be compatible with the polymer and this is because of there are three important solubility parameters as δ_d , δ_p , and δ_h that indicate the dispersion, polar and hydrogen bonding parameters, respectively. For instance the δ_h relates to the hydrogen bonding that demonstrates the affinity of one part to the other one. In this case the δ_h of 2-propanol is more close to DMF than water and this provide the situations in colligation bath to phase separating more quickly because the migration of solvent from the phase one to the pure non-solvent depends on the affinity of polymer and solvent to exchange the solvent with non-solvent.

Table 1 The Solubility Parameters of DMAC, Water, PVDF, DMF, DMSO and NMP

Component <i>s</i>	$\delta_d/MPa^{1/2}$	$\delta_p/MPa^{1/2}$	$\delta_h/MPa^{1/2}$	$\delta/MPa^{1/2}$
DMAC	16.8	11.5	10.2	22.771
water	15.5	16.0	42.3	47.8
PVDF	17.1	12.6	10.6	23.2
DMF	17.4	13.7	11.3	24.86
DMSO	18.4	16.4	10.2	26.7
NMP	18	12.3	7.2	22.96
Acetone	15.5	10.4	7	19.9
Isopropano l	15.8	6.1	16.4	23.5



By changing the non-solvent from 2- propanol (Fig.2.b) to the mixed of Acetone and water (Fig.2.a) with the ratio of 2/3 the second diagram obtained that the two phases region enlarged which is mean the possibility of phase separation increases because at this temperature in each concentration of polymer if we move from the one phase region to the bottom of the diagram definitely we will encounter to two phase region. The more interesting result was happened when we used two non-solvents with the ration 2/3 acetone/2-propanol, Fig.2.c that the apex of the curve shifted above compared to single non-solvent as shown in Figure 2.b and the domed shape of the previous diagrams converted to curve form which is indicated that at the high concentration of polymer in solution, the behavior of phase separation from one phase to two distinct phases does not change significantly and also the amount of non-solvent decreases and the rate of exchanging solvent with non-solvent increases.

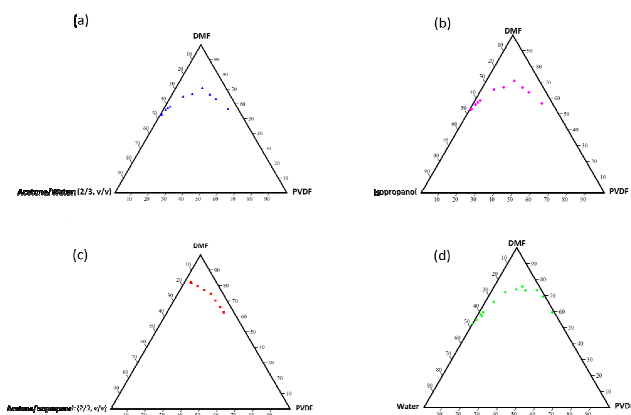


Figure 2. Ternary phase diagram of PVDF, DMF and (a) Acetone/water, (b) isopropanol, (c) Acetone/isopropanol with volume ratio 2/3 and water.

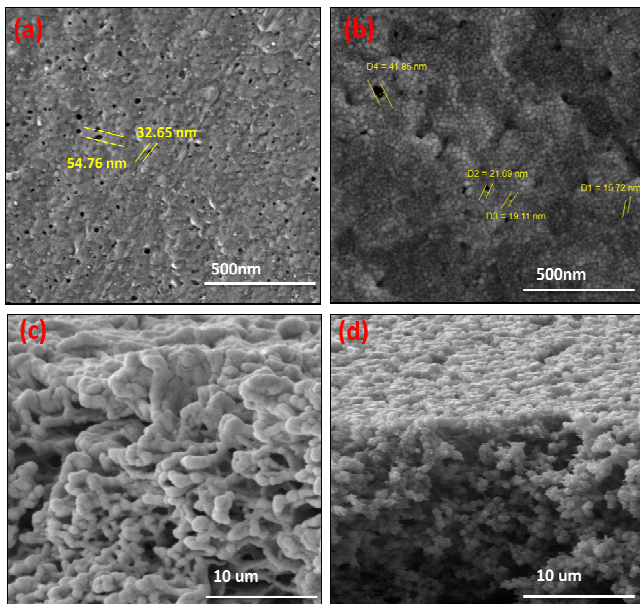


Figure 3. The SEM image of prepared PVDF with different non solvent and (a) Acetone/water, (b) isopropanol, (c) Acetone/isopropanol with volume ratio 2/3 and water.

Scanning electron micrographs (SEM) were taken in secondary electron contrast at an acceleration voltage of

10kV using a VEGA TESCAN emission instrument. For the cross-section view was taken by breaking the samples under liquid nitrogen and coated with Ag. Two different SEM and AFM were used to illustrate the surface and cross-section morphology and topology of fabricated films. As shown in Fig3. a and Fig4.a, the surface of PVDF which fabricated via acetone/water as non-solvent are more uniform with the pores size is less than 50 nm and the roughness 73nm with 2 nm deviation. In contrast for the membranes which contain Isopropanol the surface was so brittle with roughness around 180 nm Fig.4(c) and (d) and micro voids was found in SEM images Fig 3(c) and (d).

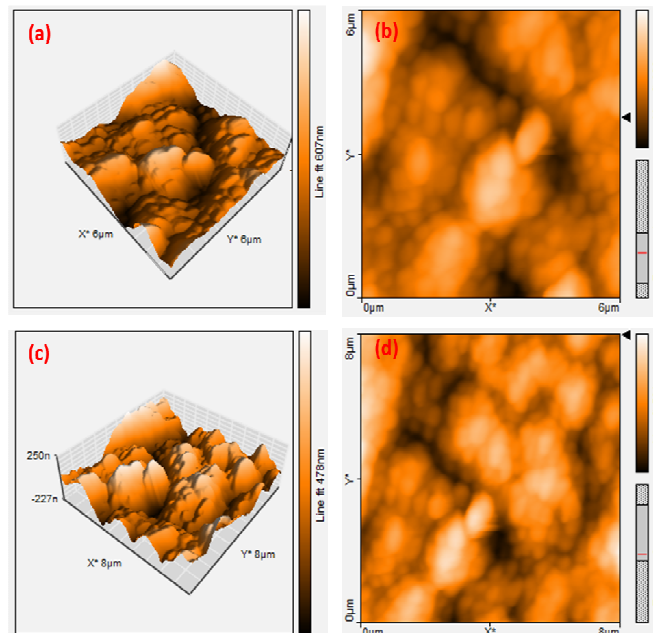


Figure4. 3D and 2D AFM images of (a) and (b), acetone/water (2/3 V/V %) and c and d acetone/ Isopropanol (2/3 v/v %), the operation procedures applied in contact mode. The Ra differs from 180.1 to 73 nm.

IV. CONCLUSIONS

Ternary phase diagram of PVDF with DMF as key solvent and different kind of non-solvents plotted. Based on thermodynamics reasons that discussed which indicate that more useful non-solvent for DMF can be ranked in the order of Acetone/ water > Acetone/ 2-propanol > 2-propanol. Remembering that because of wide difference between Hydrogen bonding parameter; some solvents are not compatible with some non-solvent like NMP as solvent with 2-propanol those system did not. Based on the achieved data the morphology of PVDF film can be forecasted in case of nano pores to micro pores for variety of membrane and film formation applications. Plus, using these diagrams the limitation of using common non-solvent, water, omitted and also based on these diagram ones can decided at which concentration of polymer-solvent and non-solvent could be worked to reached the best region in two phases region definitely.

A fundamental study of Morphology Prediction for Nano and Microstructure of PVDF for Membrane Fabrication and Film Formation Applications

REFERENCES

1. Danielle L Graham, Scott Edwards, Ryan K Bachtell, Ralph J DiLeone, Maribel Rios & David W Self, Dynamic BDNF activity in nucleus accumbens with cocaine use increases self-administration and relapse, *Nature Neuroscience* 10, 2007, 1029–1037.
2. Guo-dong Kang, Yi-ming Cao, Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review, *Journal of Membrane Science*, Volume 463, 2014, 145-165.
3. Mimi Tao, Lixin Xue, Fu Liu, Lei Jiang, An Intelligent Superwetting PVDF Membrane Showing Switchable Transport Performance for Oil/Water Separation, *advanced materials*, 26, 2014, 2943–2948.
4. Chenggui Sun, Xianshe Feng, Enhancing the performance of PVDF membranes by hydrophilic surface modification via amine treatment, *Separation and Purification Technology*, 185, 2017, 94-102.
5. Fengtao Chen, Xingxing Shi, Xiaobing Chen, Wenxing Chen, Preparation and characterization of amphiphilic copolymer PVDF-g-PMABS and its application in improving hydrophilicity and protein fouling resistance of PVDF membrane, *Applied Surface Science*, 427, 2018, 787-797.
6. P. Tamilselvi, M. Hema, Conductivity studies of LiCF₃SO₃ doped PVA: PVDF blend polymer electrolyte, *Physica B: Condensed Matter*, 437, 2014, Pages 53-57.
7. A. Bottino, G. Capannelli, S. Munari, A. Turturro, Solubility parameters of poly(vinylidene fluoride), *J. Polym. Sci., Part B: Polym. Phys.* 26, 1989, 785–794.
8. M. Yeow, Y. Liu, K. Li, Morphological study of poly(vinylidene fluoride) asymmetric membranes: effects of the solvent, additive, and dope temperature, *J. Appl. Polym. Sci.* 92(2004)1782–1789.
9. Antoine Venault, Melibeth Rose B. Ballard, Yu-Tzu Huang, Yi-Hung Liua, Chi-Han Kaob, Yung Chang, Antifouling PVDF membrane prepared by VIPs for microalgae harvesting, *Chemical Engineering Science*, 142, 2016, 97-111.
10. H. Strathmann, P. Scheible, R. W. Baker, A rationale for the preparation of Loeb-Sourirajan-type cellulose acetate membranes, *Applied Polymer*, 15, 1971 Pages 811–828.
11. Da-Ming Wang, Jun-Yih Lai, Recent advances in preparation and morphology control of polymeric membranes formed by nonsolvent induced phase separation, *Current Opinion in Chemical Engineering*, 2, 2013, 229-237.
12. Ju Tae Jung, Jeong F. Kim, Ho Hyun Wang, Emanuele di Nicolo, Enrico Driol, Young Moo Lee, Understanding the non-solvent induced phase separation (NIPS) effect during the fabrication of microporous PVDF membranes via thermally induced phase separation (TIPS), *Journal of Membrane Science*, 514, 2016, 250-263.
13. Ayman Taha Abd El-aziem El-gendi, Phase Diagram and Membrane Desalination, chapter 3, PP.2003, 37-77.