Construction of Ternary Phase Diagram and Membrane Morphology Evaluation for Polyamide/Formic acid/Water System

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Abstract: In this article, the ternary phase diagram in polyamide-6 (PA6)/Formic acid (FA)/Water system was constructed by experimental measurement. The determination of binodal curve was measured according to titration of the PA6 polymer solution with water as a non-solvent until the onset of turbidity. Also, the phase separation process of the prepared membranes structures system was investigated. The morphology of PA6 membrane has been formed during phase separation, which is dependent on the phase inversion, and the equilibrium ternary phase diagram system, that is a good tool for understanding and controlling the morphology of the membrane structure. According to the constructed ternary phase diagram of PA6/FA//Water system, a large amount of water (26-39 wt% water) was needed to achieve liquid–liquid phase separation in that ternary system.

Key words: ternary phase diagram; membrane morphology; binodal curve; polyamide-6/Formic acid//Water

INTRODUCTION

The phase inversion process is the most important technique for membrane preparation, which is used in the preparation of polymeric symmetric, asymmetric and composite membranes, to be used in different membrane processes and applications.

The equilibrium thermodynamic properties of the ternary system polymer/solvent/non-solvent play an important role in the description of membrane preparation process [Yip ; McHugh,2006; Zhenyu *etal.*, 2012]. Thus, depending on the choice of the ternary system there are three possible results can occur during the membrane formation process, which are [Frommer and Lancet**, 1972**; Altena and Smolders,1982**]; (i) Non-porous film (symmetrical dense membrane), (ii) Porous film (symmetrical porous membrane), (iii) Asymmetric membrane which has a thin dense top layer on a porous supporting layer.

From a thermodynamic point of view, study of polymer–solvent– nonsolvent system can be well depicted in a ternary phase diagram. The Flory-Huggins theory [Wijmans and Smolders, 1986] was found to be a convenient and useful framework for thermodynamic analysis of component mixing in a membrane preparation system. The ternary phase diagram of polymer /solvent/ nonsolvent systems can be constructed by theoretical calculations based on the Flory–Huggins theory for three-component systems [Rautenbach and Albrecht, 1989]. For thermodynamic evaluations of a membrane-forming system, the Flory-Huggins theory of polymer solutions [Flory1953], which has been extended to a ternary system containing nonsolvent/solvent/polymer systems were studied firstly by Tompa 1956.

The systems which include mixture of ternary components: a polymer, a solvent and a third component (such as non-solvent). This ternary system is completely miscible over a certain composition range, but a miscibility gap has appeared at composition over this certain composition range, as shown in Fig.1, which indicates an isothermal phase diagram of the ternary components. The pure components are represented at the corners of the triangle while boundary lines between any two corners of triangle represent mixtures of two components, and any point inside the triangle diagram represents a mixture of all three components. The main elements of ternary-phase diagram are: binodal and spinodal curves, a critical point, tie lines, and a glassy region shown in Fig.1. For the studied ternary system, the evaluation of interaction parameters for the binary mixture has allowed a remarkably accurate prediction of the ternary phase diagram.

The main input parameters of the Flory-Huggins relation are constructed from the binary interaction parameters of polymer/solvent, polymer/ nonsolvent, and nonsolvent/ solvent. The magnitude and concentration dependency of these interaction parameters have a large effect on the binodal curve, spinodal curve, and critical point positions of a phase ternary diagram. Some of researchers developed the effects of these parameters on the ternary phase diagram of a membrane-forming system of various ternary systems [Frank etal., 1982 Wijmans eta., 1985; Yilmaz and McHugh, 1986; Reuvers,1987; Zeman and Tkacik, 1988; Lin, 1995; Kim etal., 1997; Lai etal., 1998].

Ternary phase diagrams can predict, whether or not a solution of a certain polymer in a certain solvent is suitable for membrane formation. Binary phase diagrams indicates the phase boundaries as a function of

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temperature and composition that provides information for the phase inversion process, whereas ternary isothermal phase diagrams are useful for the prediction of the phase transitions that can occur when phase separation is induced according to one of the other methods[Chunsheng etal., 2011; Homolová etal., 2012].
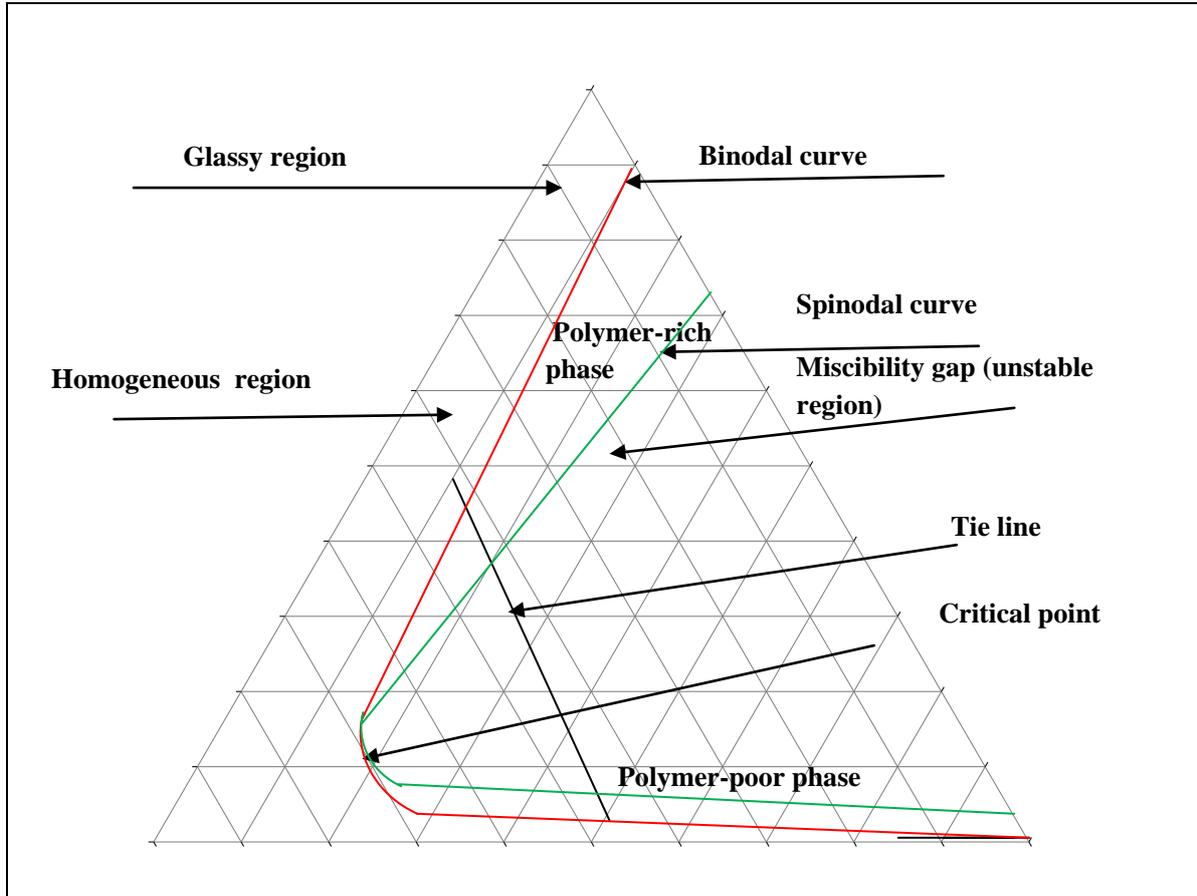

Fig. 1: Ternary-phase diagram of polymer (P)–solvent(S)–nonsolvent(NS) system.

It should be kept in mind, that phase diagrams only predict the phase transition of a polymer solution which can undergo during a membrane formation process. An equilibrium phase diagram provides a map for the different phase transitions that are favoured thermodynamically. The kinetics of phase separation processes determine whether or not the thermodynamically favoured transition will occur, and also to indicate the extention of the transition which will take place. Non equilibrium processes can play an important role during membrane formation. The polymer/solvent/nonsolvent systems were investigated in this paper to report the agreement between experimental and miscibility gaps with the evaluations of a membrane-forming system**.**

The composition of the membrane has been determined by experimental work, which consumes a lot of chemicals, may be with no significant result. Thus this work seeks to optimize the operation of the membrane composition and the manufacturing process with helping of ternary phase diagram.

Experimental:
Materials:

Polyamide-6 (PA-6) is used as a polymer with bulk density 0.25 gm/ml, particle size 50–160 μm was purchased from LeunaWerke AG (Germany). Formic acid (FA) is used as a solvent (FA) 85% by weight, its density at 20°C is 1.198 gm/cm3, boiling point 100.7°C. Formic acid and methanol both of analytical grade were purchased from Sigma-Aldrich chemical company and used without further purification.

Preparation of Asymmetric Polyamide-6 (PA-6) Membranes:

The Polyamide-6 (PA-6) asymmetric membrane was prepared using phase inversion method. The polymer dope solution (20 wt.% in formic acid) was casted onto a glass plate using a doctor blade at 20°C and the evaporation time was 1 minute. The glass plate was subsequently immersed in a gelation bath consisting of pure water at 28°C. It was then rinsed in pure water to remove residual solvent. The effect of water as additive (5-

10%) to polymer casting solution was studied. The schematic flow diagram for preparation of polyamide -6 membranes by casting techenique is depicted in Fig. (2).
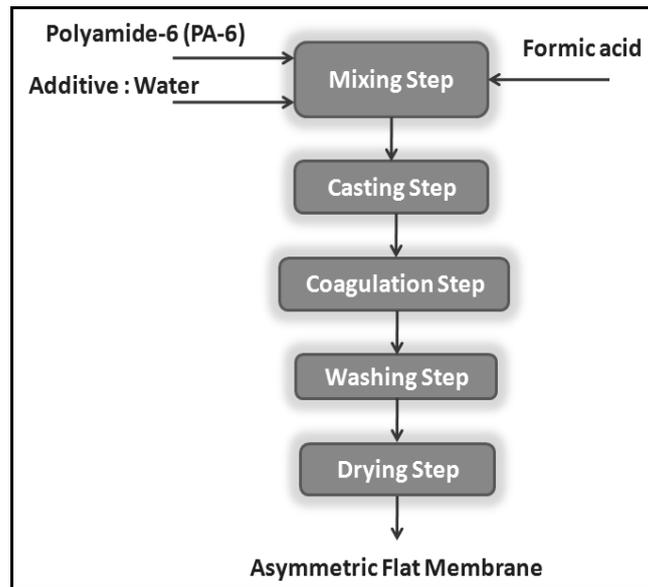

Fig. 2: Process Block Flow Diagram for Preparing Polyamide-6 Membranes by Casting.

Membrane Characterizations:
Scanning Electron Microscopy (SEM):

Scanning electron microscopy (SEM) was used to observe the morphology of Polyamide-6 (PA-6) membranes; however samples of membranes were coated with gold to provide electrical conductivity. The top and bottom Snapshots of membranes were taken on a JEOL 5410 scanning electron microscope (SEM) was operating at 10 kV. Where, significant views of surfaces were recorded.

Phase Diagram:

In the ternary phase diagram (polymer (p)/solvent (s)/nonsolvent (ns)) a miscibility gap exists with metastable regions. According to the theory of phase separation, three modes of phase separation can take place in such ternary system: nucleation and growth of the polymer lean phase, spinodal phase separation and nucleation and growth of the polymer rich phase. Since, the polymer is one of the components in the ternary system, where the solidification of this part in this system can take place.

Determination of Turbid Points Values and Phase Diagrams:

In this researsh we intended to study PA6/FA/water (non solvent) systems to report the agreement between experimental work to get asymmetric polyamide membranes and the ternary phase diagram miscibility gaps for the evaluations of the membrane-forming system. Thus, the ternary phase diagrams with experimental cloud point data were constructed for PA6/FA//Water system. The phase diagram of the polymer/solvent/nonsolvent combination systems was determined by cloud point measurement. Hence, the ternary phase diagram (turbid points curve) was obtained by the following method: PA6 solutions with different compositions were placed in glass-ware reactor under stirring and the coagulant was slowly added to the PA6 solutions until the clear solutions remain milky-like.

For this purpose, starting polymer solutions with concentrations of 1, 2, 5, 10, and 20 wt% PA6 in FA were carried out in the glass-ware reactor to achieve homogeneous polymer solutions, these mixtures were stirred by a magnetic stirrer. The ternary phase diagram was obtained from the turbid points.

To reach the turbid point, pure water was added slowly into the polymer solution under stirring. During titration, the solution temperature was controlled at 30°C with water bath and the addition of pure water was continued until the clear polymer solution visually turned to look milky-like. After, the observation of the first sign of turbidity, addition of nonsolvent was stopped and the solution was stirred for an additional 20-40 min to see whether the turbid solution changes to a clear solution or not. If the solution turned to a clear solution, more nonsolvent was added, otherwise the determined point was considered as the onset of real turbid point.The ternary composition of turbid point was then calculated from the amount of nonsolvent, solvent and polymer present in the glass-ware.

Pervaporation Experiments:
Experimental Setup:

The experiments were carried out on pervaporation system technique, Fig. (3), which contained flat sheet membrane module had three opening for feeding, recycling and vacuum pressure. The feed was continuously fed to the membrane module from an open feeding tank (glass flask) using peristaltic feeding pump. Vacuum pressure was obtained using a vacuum pump. The feed mixture was heated using hot plate and the temperature was controlled by thermostat of hot plate and recorded by thermometer. Water condenser was used as cooling system which using recycling of cold water with temperature 5 ^{0}C, inlet and outlet in condenser jacket, the recycling system of cooling water to condenser was done using another peristaltic pump. Product was collected from downstream of the condenser.

PV Experiments with mixture of 90wt%methanol/10wt%, water mixture were carried out to characterize the PA6 membrane. All experiments were carried out in a state of continuous balance with a vacuum downstream and a constant temperature for feed mixtures. The composition of permeate which was collected from condenser downstream was determined for each mixture, the permeate enrichment and flux of permeation (J) were measured for several membrane samples (specific membrane area of 3.14×10^{-4} m^2). The feed tank of the capacity of 100 gm was filled with 90 wt% methanol and 10 wt%, water. The downstream side pressure of the process was maintained at 200 mbar with a vacuum pump. The weight of permeate was determined using a precise balance. The permeation flux (J) was calculated using the expression:

$$J = \frac{Q}{(A * T_t)} \tag{3}$$

where Q (Kg) is the total mass of the permeate collected through the effective area of membrane A (m^2) and during the time T_t (h), once the state has been reached .
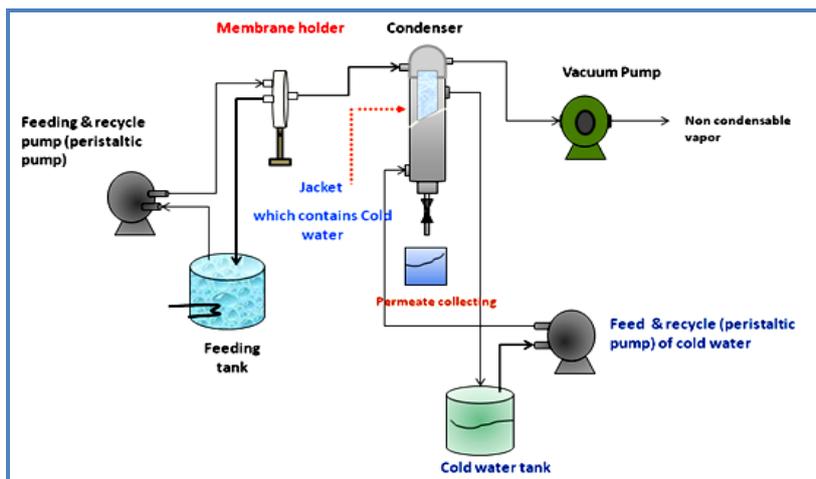

Fig. 3: Schematic diagram of the pervaporation experimental set-up.

RESULTS AND DISCUSIONS

Turbid Points Values (Binodal Demixing Curve) and Phase Diagrams:

The investigated miscibility gaps of the (PA6/FA/H$_2$O) system with the evaluations of a membrane-forming system have explained the agreement with the experimental work.

The evaluations of a membrane-forming system is available with helping of the SEM snapshots on the prepared membranes to show the agreement between the experimental work for the preparation of PA6 membranes and miscibility gaps in the ternary phase diagram. The phase diagram for the system PA6/FA/H$_2$O represents a detailed picture of the three components miscibility and it contains useful thermodynamic information about the phase separation (inversion) process. The ternary phase diagram and the determination of the binodal demixing curve of the polymer/solvent/nonsolvent combination systems were obtained from the turbid (cloud) points measurements which are presented in Fig.4. The operating parameters for preparation of PA-6 membranes were represented in table 1.

Table 1: Operating parameters for preparation of PA-6 membranes.

*Membrane	Casting solution			Permeate flux gm hr^{-1} m^{-2}	Thickness
	PA-6%	FA%	Water%		
M1	20	80	0	17000	160μm
	"	"	"		
	"	"	"		
	"				
M2	19	76	5	32500	180μm
	"	"	"		
	"	"	"		
M3	18	72	10	38500	210μm
M4	10	60	30	-	

*Pre-concentration time (1 min), immersion in water bath 1 hour at 28±2°C. Where; P: polymer, W: Water, FA: formic acid, M1; M $_{20wt \%P}$,M2; M $_{19wt \%P,5W}$, M3; M $_{18wt \%P,10W}$.
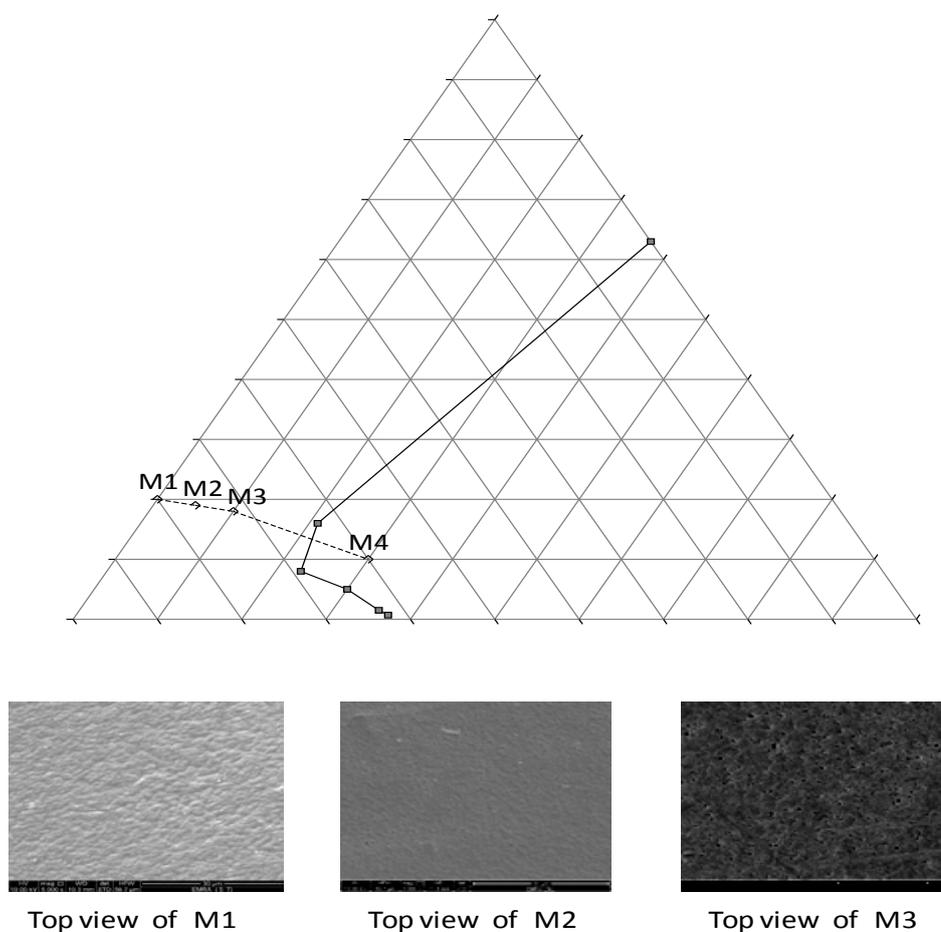

Fig. 4: Schematic ternary phase diagram with membrane morphology (ternary solution of PA6 membranes M$_1$-M$_4$ --○-- ; binodal demixing curve ■).M1; M $_{20wt \%P}$,M2; M $_{19wt \%P,5W}$, M3; M $_{18wt \%P,10W}$.

The effect of variations of the casting solution composition with water addition for membranes (M$_1$-M$_4$) is displayed schematically in Fig.4, it reports the agreement between experimental work and miscibility (mixing) gaps with the evaluations of a membrane-forming system. From the resulted miscibility gap of the ternary phase digram (Fig.4) and snapshots of SEM for membranes (M$_1$-M$_4$), it was found that increasing in water concentration can lead to change in membrane morphology from less porous to highly porous membranes, thus the addition of water was not possible since the actual concentration (i.e.: 22 wt% water in 20 wt.% PAA in DMF) which was already very close to the binodal demixing curve in the ternary phase diagram (i.e.: M$_4$). Fig.4 illustrates the experimental cloud points data for PA6/FA/H$_2$O system. According to this figure, the cloud point curve of PA6/FA/H$_2$O system is closer to the solvent-nonsolvent axis (FA-H$_2$O axis), which indicates that more water (33 wt %) is needed for the precipitation of PA6 in this system because there is a large mixing gap. On the other hand, the lowest binodal points near the FA/H$_2$O axis were very dilute, which were close to the critical point. Consequently, the liquid-liquid miscibility gap almost overlapped the FA/H$_2$O axis. In addition, the

observed results show that the FA is a good solvent for PA6, therefore a small demixing gap should be observed for PA6/FA/H$_2$O system compared to the other systems reported in literature review as a reported result by Barzin *et.al* 2007 who studied the theoretical phase diagram calculation for water/solvent (NMP or DMAc)/polyethersulfone systems, which was found that water was needed for the precipitation of polyethersulfone in these systems is in range (20 to 25 wt%) because there is a small mixing gap. In general, expected trends on the basis of the phase diagram were in reasonable agreement with the observed membrane morphology. Hence, the concluded results can be reported in the range of addition of non-solvent to polymer solution, the effect of this range on the membrane morphology was studied to predict the behaviour of (PA6/FA/non solvent) systems with helping of these tests. Thus, the predicted results can indicate that the membranes cannot be prepared when the addition of nonsolvent (water) is greater or equal than turbid points such as M4. It was observed from table 1 that permeate flux increased with increasing water wt% in membrane polymer solution; these results were in agreement with membrane morphology, according to the pores in the top layer, where denser layer can lead to low flux.

Conclusions:

The feasibility of the preparation of PA6 membranes has been established clearly, where the morphology of the PA6 membrane structure can be controlled by the conditions of phase inversion, and either to the formation of a thin dense layer with a very porous support.

The final membrane morphology which has been formed during phase inversion method is dependent on the kinetics as well as the thermodynamics of the phase separation. The equilibrium ternary phase diagram system is a good tool for understanding the controlling of the membrane morphology and the membrane structure. A large amount of water (26-39 wt. % water) was needed to achieve liquid–liquid phase separation in the PA6/FA/Water ternary system. The systems required a large amounts of nonsolvent to achieve precipitation, and to obtain liquid-liquid phase separation to form membranes with nanofiltration and reverse osmosis properties. This observation was related to the thermodynamic properties of the systems.

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