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Rheological and Thermodynamic Behaviour of PSf/ ZnO: Effect of Zinc Oxide

Mohamad Luqman Harith Abu Mansor[1], Muhamad Zaini Yunos[2*], Zawati Harun[2], Mohamed Nasrul Mohamed Hatta[2], Rosniza Hussin[3], Azlinnorazia Ahmad[2], Aina Syazwana Zulkefli[2]

[1]Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400 Batu Pahat, Johor

[2]Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400 Batu Pahat, Johor

[3]Faculty of Engineering Technology,
Institute Integrated Engineering (I^2E),
Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400 Batu Pahat, Johor

*Corresponding Author

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Abstract: The synthesis of zinc oxide nanoparticle normally involves zinc precursor and reduction during the preparation. To improve the dispersion of nanoparticle, the ZnO synthesis is the most promising option since the particles can stabilize in dope solution. However, the process of ZnO synthesis required the addition of polar precursor and reduction agents which are expected to influence the rheological and phase inversion properties of membrane dope solution. It is worth to mention that the rheological properties and phase inversion behaviour of the dope solutions play a critical role in determining the membrane morphology and separation performance. The PSf/ZnO dope solution was prepared via in-situ synthesis using three different precursors and reducing agents. The concentration was varied from 0 wt. %, 1 wt.% and 2 wt.% before dissolving in N-Methyl-2-pyrrolidone (NMP) as it will completely dissolved together. Three different precursors used were Zinc Chloride, Zinc Nitrate and Zinc Acetate while Sodium Borohydride, Hydrazine Hydrate and Urea are three different reduction agents. The thermal stability of the dope solutions was analyzed using cloud test measurement and the rheological properties were measured using viscometer toward the viscosity of the dope solution. Thermodynamic stability analysis denotes that the hydrazine hydrate has the lowest non-solvent percentage which is 3.30 %. Meanwhile, zinc nitrate with hydrazine hydrate have the lowest non-solvent percentage which is 1.59 %. This also shows that the zinc nitrate with urea binodal line nearly to the solvent/polymer axis which might resulted on faster demixing rate and miscibility gap become shorter. The viscosity results of urea as reducing agent in dope solution is highest as compared with two other reducing agents. Thus, as the concentration of zinc oxide increases, the viscosity and thermodynamic instability of the solution increased at the room temperature.

Keywords: Rheology, thermodynamic, zinc oxide, membrane, polysulfone, ternary diagram, viscosity

1. Introduction

Membrane separation technology is the most popular method used for cleaning water and drinking water production [1]. The increasing gap between water supply and its demand leads to the consistency growing of membrane demand. The removing process of microbiological contaminants and organic compounds will be conducted by using membrane filters. Membrane fouling occur due to its hydrophobic properties. Meanwhile, membrane surface is one of

*Corresponding author: mzaini@uthm.edu.my

the most onerous problems retarding the practical application in the membrane system [2]. Improving surface hydrophilicity has shown less fouling potential [3]. However, hydrophilic membrane surfaces are prone to be exposed to higher bacterial growth which can lead to the formation of protein layer and eventually block membrane pores [4]. Zinc oxide synthesis normally involve zinc precursor and reduction during membrane preparation. However, most of the reduction agent are polar materials, which can influence rheological properties and phase inversion of membrane dope solution. It is also worth to mention that the rheological properties and phase inversion behaviour of the dope solutions play a critical role in determining the membrane morphology and separation performance. This is because the membrane dope rheology has influenced the exchange rates between the dope solvent and coagulant in which at the same time affect phase inversion kinetics during membrane fabrication [5]. Knowledge of the rheological properties of fluid is important in the design of flow processes in the quality control, storage and the processing stability, and in understanding and designing texture [6].

Moreover, the microstructure and mechanical properties of the membranes are largely dependent on solvent exchange kinetic and dope rheologies such as shear viscosity and viscoelasticity [7]. Thus, it is essential to investigate the influence of in-situ synthesis of ZnO on rheological and phase inversion during membrane fabrication. In order to improve the dispersion of nanoparticle, the ZnO synthesis of the nanoparticle is the most promising option since the particles can stabilize in dope solution. However, the process of ZnO synthesis required the addition of polar precursor and reduction agents which are expected to influence the rheological and phase inversion properties of membrane dope solution. The investigation of the effect of reducing agent towards PSf membrane polymer science and engineering place the rheology and viscoelasticity as very importance discipline and it is the study about the science flow and deformation of matter which are elasticity, flow, and molecular motion [7 & 8]. These properties will in turn affected the microstructure formation during phase inversion process. Thus, the study aims to investigate the effect of synthesis of ZnO in PSf dope membrane, characterized the rheological, and phase inversion properties of membrane dope solution for membrane fabrication.

2. Material and Method

PSf used as the base polymer. While, the solvent is N-methyl-2-pyrroolidone (NMP) were purchased from Sigma Aldrich together with the precursors (zinc chloride, zinc nitrate and zinc acetate) and reducing agent (hydrazine hydrate, sodium borohydride and urea) were used for the experiment. Lastly, the additive in dope solution is Polyethylene glycol (PEG) was added. The entire chemical used were analytical grade.

The composition of different type and concentration of reducing agents with different concentration of PSf shows in Table 1. The PSf mixed as the reducing agent dissolve in NMP and PEG as a stabilizer also added at the end of experiment.

Table 1: The compositions of different type and concentration of reducing agents towards PSf dope solution.

Polymer	*Solvent*	*Reducing Agents*
15 wt.% of PSf	85 wt.% of NMP	0 wt.% of Hydrazine Hydrate 0 wt.% of Sodium Borohydride 0 wt.% of Urea 1 wt.% of Hydrazine Hydrate 1 wt.% of Sodium Borohydride 1 wt.% of Urea 2 wt.% of Hydrazine Hydrate 2 wt.% of Sodium Borohydride 2 wt.% of Urea

For preparation synthesis of Zinc Oxide started by stirring 1:2 ratio aqueous solution of Zinc Nitrate / Zinc Acetate / Zinc Chloride and hydrazine hydrate / sodium borohydride / urea as reducing agent at 90 ˚C until it produces clear solution. Then, the solution was heated in microwave oven at 360 W until it produces white precipitate after 2 – 3 min. The precipitate then was centrifuged, washed with distilled water and crystallized with methanol. After that, the precipitate was dried at 100 °C for 3 hours. The white precipitate produced were blend with PSf/NMP dope solution. The composition of the experiment as shown in **Error! Reference source not found.**.

Table 2: The compositions of different precursor and different reducing agent towards PSf dope solution.

`Polymer	Solvent	Precursors	Reducing Agents
15 wt.% of PSf	85 wt.% of NMP	1 wt.% of Zinc Chloride	1 wt.% of Hydrazine Hydrate 1 wt.% of Sodium Borohydride 1 wt.% of Urea
		1 wt.% of Zinc Nitrate	1 wt.% of Hydrazine Hydrate 1 wt.% of Sodium Borohydride 1 wt.% of Urea
		1 wt.% of Zinc Acetate	1 wt.% of Hydrazine Hydrate 1 wt.% of Sodium Borohydride 1 wt.% of Urea

The example of chemical mechanism for the formation of ZnO explained by the following equations by using Zinc Chloride as precursor and hydrazine hydrate [10]:

$$ZnCl_2 + nN_2H_4 \rightarrow ZnCl_2(N_2H_4)_n \quad (1)$$

$$ZnCl_2(N_2H_4)_n \rightarrow Zn^{2+} + 2Cl^- + nN_2H_4 \quad (2)$$

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \quad (3)$$

$$2NH_3 + H_2O + Zn^{2+} \rightarrow Zn(OH)_2 + N_2 + 2H_2 \quad (4)$$

Via reaction (4)

$$Zn(OH)_2 \rightarrow Zn^{2+} + 2OH^- \rightarrow ZnO\ (NP) + H_2O \quad (5)$$

Via reaction (4)

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4{}^{2-} \rightarrow ZnO\ (NR) + H_2O + 2OH^- \quad (6)$$

The rheological properties focusing on the dynamic (absolute) viscosity of dope solution measured by using rotational viscometer. The viscometer with prepared dope solution measured the dynamic viscosity of the dope solution with an adjustable speed at 6 rpm, 12 rpm, 30 rpm and 30 rpm in one flow. The dynamic viscosity results calculated the shear rate using the formula as follows

$$\dot{\gamma} = \frac{v}{h} = \omega \times \left(\frac{2R_c{}^2}{R_c{}^2 - R_b{}^2}\right) \quad (7)$$

Where $\dot{\gamma}$ is the shear rate (1/s), v is the velocity of the moving spindle, (m/s), h is the distance between the spindle and the wall solution container, (m), ω is angular velocity of spindle, (rad/sec). ω = (2π/60) x N where N is RPM, R_b is radius of container, (m).

Thermodynamic stability analysis is to determine the composition at which the solution is no longer thermodynamically stable. The ternary phase diagram as shown in Figure 1 plotted based on turbidity or cloud-point method. This cloud point divide into two parts. The first part is to investigate the effect of reducing agent towards the PSf dope solution and the second part to study the effect of different precursor and reduction agent towards the ZnO/PSf dope solution. These studies were using bi-nodal line of polymer-solvent-nonsolvent system. This method studies the stability of the dope solution by adding the distilled water into dope solution. The distilled water was slowly titrated into the homogeneous dope solutions until precipitation occurred. The amount of water needed to exceed the cloud-point are measured. The cloud-point exceed as the solution turns into cloudy and the gelation points resulting from both liquid–liquid and solid–liquid. The composition of the mixture at precipitation was determined based on the amount of water added.

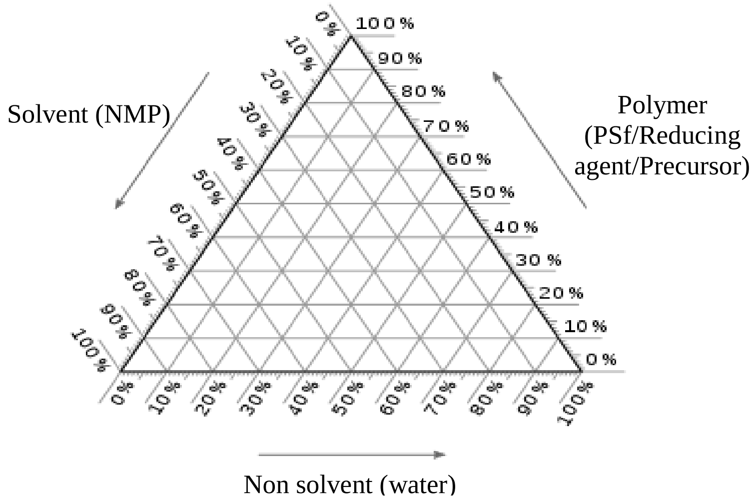

Fig. 1: The ternary phase diagram

3. Result

3. 1. Rheological properties

The viscosity test results for the dynamic viscosity against weight percent of PSf dope solution at different type and concentration of reducing agents shows in Figure 1. The most significant result was shown by the zinc nitrate precursor with the presence of different reducing agents. From Figure 1 obviously shows that urea has the highest viscosity compare to sodium borohydride and hydrazine hydrate. According to research by A.F. Ismail and P.Y. Lai [11] the viscosity of solution increased due to the intermolecular chain which has stronger interaction of solvent and polymer that can reduce the break down power of solvent for polymer in situation of chain entanglement and promote aggregation of polymer molecules. This result supported by Feng et al. (2003), where high viscosity as the interaction between polymer became more stronger in polymer chain and the deformation of polymer chain have more resistant [12]. A.F. Ismail and P.Y. Lai et al. [11] also mention that the high viscosity of polymer will lead to higher interaction between solvent and non-solvent in casting process. This is because slower rate phase inversion process formed a close cell substructure with dense and thin skin layer of asymmetric membrane .

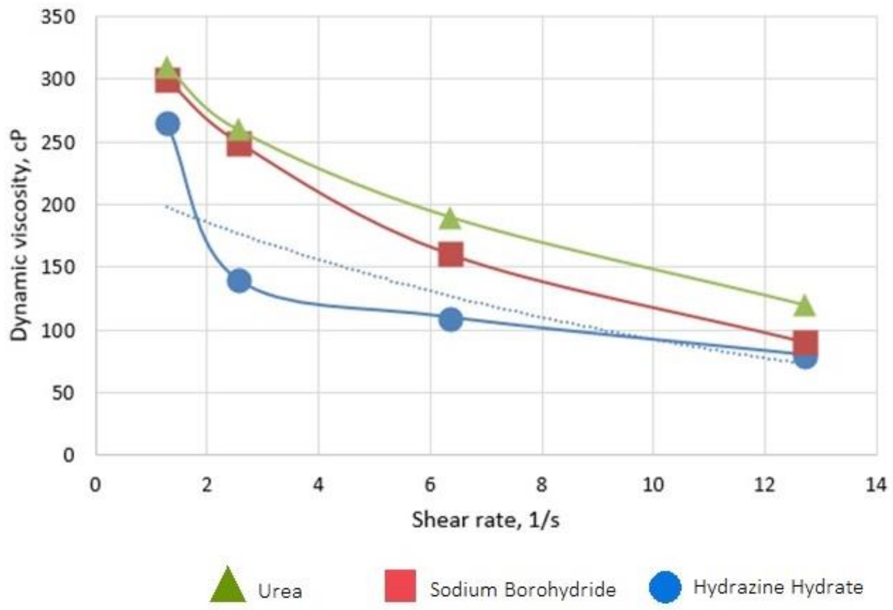

Fig. 1 - The graph of dynamic viscosity of ZnO/PSf dope solution against shear rate for zinc nitrate with different reducing agents.

3.2 Thermodynamic Stability

Thermodynamic stability results from cloud point measurement as shown in Figure 2 for the effect of reducing agents towards PSf dope solution plotted in the ternary diagram as shown in Figure 3. The result shows by increasing the concentration of PSf with constant of reducing agent will decrease the miscibility of the solution with the non-solvent or distilled water. The hydrazine hydrate has the lowest water percentage with the value 3.30 % compare to sodium borohydride and urea which are 1.98 % and 2.46 % respectively. It shows that the hydrazine hydrate is more unstable thermodynamic reducing agent compare to sodium borohydride and urea in which it approaches towards the solvent/polymer axis in dope solution. The hydrazine hydrate is likely increasing the speed formation of phase inversion. According to Sajjad Mohsenpoura et al. [8], as the binodal lines move towards the polymer/solvent axis in which the thermodynamic instable increases and more porous membrane expected. Therefore, hydrazine hydrate as additive is more unstable thermodynamic and the results is nearly to binodal line polymer/solvent axis have considered having more porous membrane compare to sodium borohydride and urea [13]. The hydrazine hydrate reduces the non-solvent (water) for precipitation of casting solution and tendency for demixing is increases.

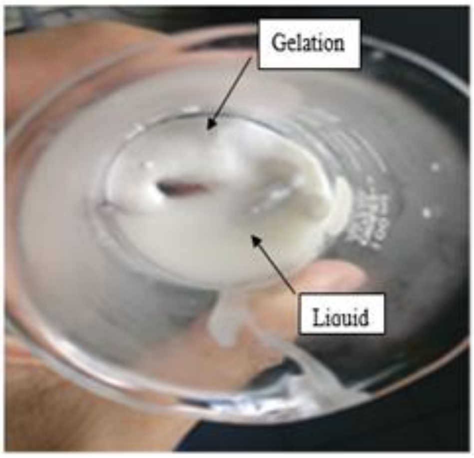

Fig. 2 - Cloud point condition

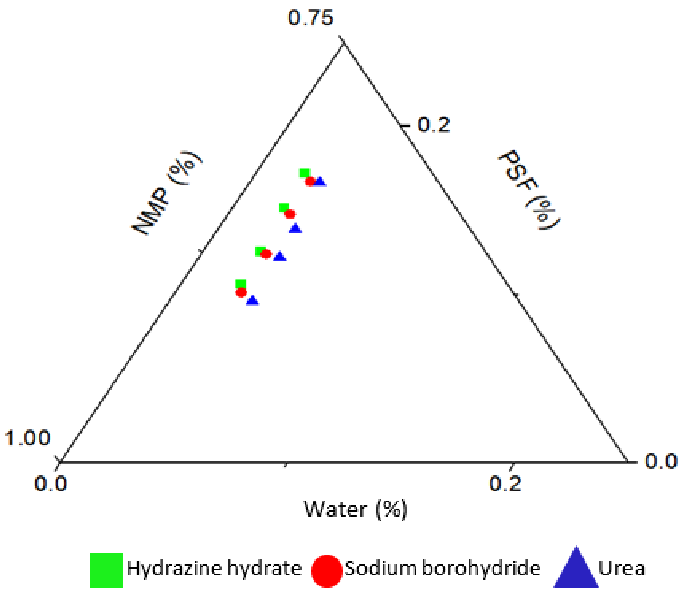

Fig. 3 - Ternary diagram of ZnO/PSf dope solution with three different reducing agents.

Moreover, thermodynamic stability analysis for the effect of ZnO with different precursors and reducing agents plotted in ternary diagram in Figure 4. The results show the water contain percentages at cloud point shows zinc nitrate with hydrazine hydrate have the lowest water percentage which is 1.59 %. This also shows that the zinc nitrate binodal line nearly to the solvent/polymer axis. A different research studies by Sajjad Mohsenpoura et al. [9] reported that the faster demixing rate and miscibility gap become shorter as the binodal line towards the solvent/polymer axis. The faster the membrane formed structure that is more open created and high permeability expected includes less sensitivity membrane. Therefore, the hydrazine hydrate as additive will increase the permeability compare with the sodium borohydride and urea as well as the structure more open formed because of the demixing rate is very highest compare to the others.

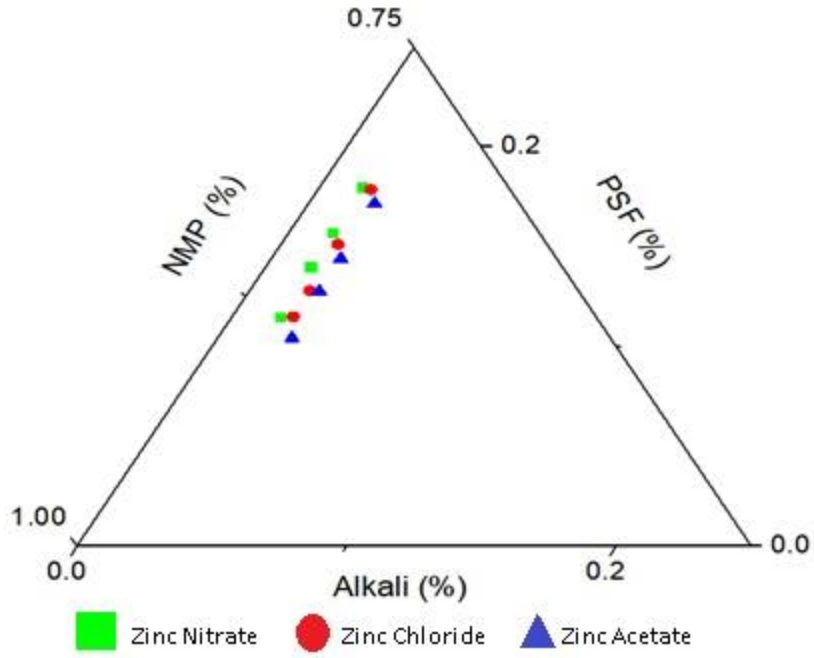

Fig. 4 - Ternary diagram of ZnO/PSf dope solution and three different precursors and reducing agents.

4. Conclusion

From this study, thermodynamic stability analysis denotes that the hydrazine hydrate has the lowest water percentage with the value 3.30 % from the effect of reducing agents towards 15 wt.% of PSf dope solution. Meanwhile, based on the effect of ZnO with different precursors and reducing agents results shows that zinc nitrate with hydrazine hydrate indicates the lowest water percentage of which is 1.59 %. As the result from viscosity measured shows that urea as reducing agent in dope solution have the highest viscosity as compared with hydrazine hydrate and sodium borohydride. High viscous solution has higher thermodynamic stability. Thus, the presence of precursor (zinc nitrate) and reducing agent (hydrazine hydrate) increase in ZnO dope solution instability where fast liquid–liquid demixing results in the formation of porous membranes, reduce the miscibility area of the system and increased the phase-inversion rate of the solutions.

5. Acknowledgement

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