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Characterization of hybrid membranes from sol –gel method on PVA/Chitosan polymer blend

: Effect of silica hybrid nanocomposite on membrane structure

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***Abstract*— Hybrid membrane was prepared from polymer blend of PVA/Chitosan with tetraethyl orthosilicate (TEOS) as the inorganic cross linker. In this report, characteristics of hybrid membrane were analyzed by contact angle analysis, their mechanical performance using tensile strength and their thermal stabilities using thermogravimetry analysis (TGA) with various concentrations of TEOS. The increase in TEOS concentration resulted in the improvement of the mechanical and thermal structure of the membrane. The addition of TEOS in the solution of membrane made the hybrid membrane more hydrophilic. The incorporation of 3wt% till 5wt% TEOS concentration was found to produce high flexibility and good thermal stability of hybrid membrane. Results obtained from this study are used for further development in the application of thin film composite membrane.**

Keywords*— hybrid membrane ;sol –gel ;organic –inorganic polymer

I. INTRODUCTION

In recent years, membrane application process have received much attention as potential process for the separation water and gas [1]. The main advantages of membrane process compared with other separation unit are related to their faster operation, more effective process, and more economical than other conventional method [2]. On the other hand, they do not need any additives and can perform isothermally [2][3]. Due to their advantages, polymeric membranes for ultrafiltration, nanofiltration, pervaporation, gas separation, and fuel cells has been made for better performance on membrane technology [2].The major benefits from polymer membrane are low operational costs, relatively small footprint, and compliance with environmental regulations [2]. However, the polymer membranes efficiency decrease with time due to the chemical degradation, fouling, thermal instability, low fluxes and compaction [2].

Thus, polymer blending had been studied to solve the problem. It is one of the suitable ways to have a new material that has unique properties and has potential to be commercialized.This was due to by the realization that new molecules are not always required to meet the need for new materials because polymer blending usually can be implemented more rapidly and economically than the development of new materials [4]. The material of the membrane also has been improved by the interactions between blended polymer like poly(Vinyl Alcohol) (PVA) and chitosan (Cs) through hydrophobic side chain combination [4]. In principle, blending is an ideal technique for making optimum hydrophilicity in the hydrophobic membrane. Hydrophilicity of the synthetic polymers has great influence on the blend preparation and properties. Surface and bulk hydrophilicity of blended polymers affect mainly their biological behaviour. Many studies have been made by addition of nanoparticles or cross linker to form complex structure of the polymer blending. For instance, hybrid membrane is formed by the addition of inorganic cross linker like tetraethyl orthosilicate (TEOS) as silica nano precursor in mixed organic – inorganic polymer membrane were formed polymer hybrid membrane.

The combination of both organic and inorganic polymeric membranes as hybrid membrane was create an emerging research field and may contribute to solve some of the problems connected to each other's [2]. There are number of papers showed the extensive applications of hybrid membrane and better performance of hybrid membrane compared to the other mixed polymer membrane [5][6][7][8][9][10][11]. However, hybrid membranes cannot be prepared by common methods to prevent any effects for overall membrane properties. Generally, there are three ways to produce hybrid membrane. The first is the sol–gel process. The second is the phase inversion method or the in situ blending method, and the third is in situ or interfacial polymerization [2]. The sol –gel method have been chosen as method to produce hybrid membrane in this studies. The sol – gel method can produce homogenous materials combination with high thermal stability, density and hardness [12][13][14]. Besides, Sol-gel is a suitable method for the preparation of oxide films from precursors containing alkoxysilyl groups through continuous reaction steps of hydrolysis and condensation [12].

The aim of this paper is to identify the characteristic of hybrid membrane prepared frompolymer blending PVA with chitosan and cross linked with TEOS. These hybrid membranes were coated as thin film layer onto polysufone (PSF) membrane to form thin film composite membrane. Poly (vinyl alcohol) (PVA) are used for this studies as common material used in membrane preparation because of its hydrophilic in nature and contains pendant hydroxyl groups. High hydrophilicity is needed for membrane separation due to minimise the membrane fouling by organic matter [15]. The hydroxyl groups in the repeating units of the polymer are expected to produce strong secondary interactions with the residual silanol groups generated from acid catalyzed hydrolysis and polycondensations of TEOS [12]. Therefore the present work aims are not only investigating the mechanical properties and hydrophilicity of hybrid membrane on varying silica nanocomposite TEOS, but also their thermal stability between hybrid membrane materials in sol – gel method by using TGA.

II. Experimentals

A. Materials

In the preparation of thin film composite membrane, the material required were polyvinyl alcohol with a hydrolysis degree of 87-89% (M_W : 85,000 – 124,000), polysulfone resin pellet (M_W: 44,000 – 53,000), tetraorthosilicate (TEOS) with 99% purity and hydrochloric acid with 37% purity as catalyst and commercial chitosan (deacetylation degree 84.8 ± 1.2 %). These chemicals were obtained from Sigma Aldrich, Malaysia. 1-methyl-2-pyrrolidone (NMP) with purity of 99% was obtained from Merck, Malaysia. Deionized water was also used as solvent. All this material was employed without further purification.

B. Methods

Hybrid membrane were prepared by using sol gel method, an about 2 wt% of chitosan solution need was prepared. In order to produce chitosan solution, about 3g of chitosan was dissolved into 2 wt% acetic acid solution. Then, the mixture was stirred vigorously at room temperature for 6 hours [4]. After that, 10 wt% of polyvinyl alcohol (PVA) solution was prepared [4]. About 10g of polyvinyl alcohol pellet was dissolved into 90ml of distilled water to formed 10 wt% of PVA solution. The solution was heated at 90℃ for 6 hours and was stirred by using the magnetic stirrer until the PVA pellet is dissolved completely. Next, chitosan solution and PVA solution was mixed together and the mixture was heated again at 60℃ and stirred for 4 hours to create homogeneous solution. Then, the homogeneous solution was left to cool at room temperature. After that, tetraethylorthosilicate (TEOS) as a nano precursor was added to the solution at three different concentrations which are 1 wt%, 3 wt%, and 5wt% by using sol-gel method. Next, about 1ml of catalyst, which is hydrochloric acid at 37 wt.% was added to the solution and then the solution was heated again at 30℃ and stirred the solution continuously for 10 hours [16]. During the preparation of TFC membrane polysulfone (PSF) membrane was needed as porous support layer for hybrid membrane. The polysulfone membrane was placed on a glass plate. Then, a hybrid membrane solution was cast on the polysulfone as a thin layer to form a thin film composite membrane. Glass rod was used for the casting process. The composite membrane was left for 24 hours at room temperature and then, it was heated at 45°C in an oven for 1 hour. Fig. 1 and TABLE I is a summary of the preparation conditions for all TFC membrane formulated in this study:

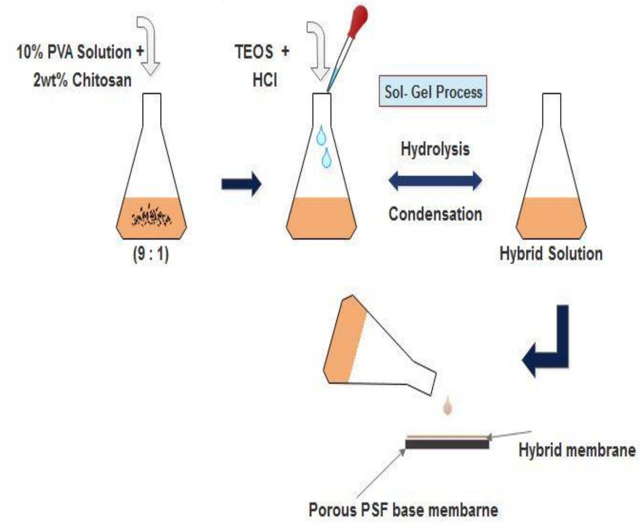

Fig. 1. Formulation of PVA/Cs/teos hybrid membranes with various teos content (wt%) using sol – gel technique

TABLE I. Summary of the preparation conditions for all TFC membrane formulated in this study

Membrane	Sample concentration (wt%)			
	PSF	*PVA*	*CS*	*TEOS*
M1	13	10	2	0
M2	13	10	2	1
M3	13	10	2	3
M4	13	10	2	5

III. Characterization of Membranes

A. Water Contact analysis

The water contact angle analysis was carried out with a VCA Water surface Analysis System (AST products Inc.). A piece of membrane was attached in a sample holder of the equipment [17]. A water droplet was dispensed onto the membrane strip from a Gilmart Instrument 0.2 ml micrometer syringe. Then, contact angles were measured through the water phase angles.The reported values were the averages of the contact angles of three droplets.

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B. Tensile strength

The sample was prepared in the dry states were carried out using Instron universal testing model. For the testing, the hybrid membranes were cut into a rectangular shape of 100mm length and 40 mm width. The speed of the machine is 5mm/min and the gauge length was set at 25 mm according to the standard method ASTM D 882 for a thin film [4]. The tensile strength, elongation, and tensile modulus of the samples were measured.

C. Thermogravimetry analysis (TGA)

The thermal stability of hybrid membrane was evaluated by using Thermogravimetry analysis but it more focused on temperature degradation and weight residue of the sample .The sample weight was ranged from 5 to 10 mg in the powder form. The sample was heated from 0ºC to 900°C at a heating rate of 10 °C/min.

IV. RESULTS AND DISCUSSIONS

A. Effect of TEOS concentration on membrane hdrophilicity

One of the important parameters for permeation through membrane is membrane hydrophilicity. This parameter is related to antifouling properties of membrane since the targeted application is dealing with foulant material. [11]. Commonly, membrane hydrophilicity is greater when its contact angle is smaller [11]. The contact angle (CA) with different concentration of cross linker TEOS data were shown in TABLE II. It can seen from the TABLE II, all the membrane samples showing hydrophilic properties.The presence of hybrid layer on the polysufone (PSF) membrane reduces the contact angle which showing increase in hydrphilicity. This is due to the polysulfone characteristic which is hydrophobic compared to TFC membrane that made up by PVA, which is high hydrophilic. Extra amount of cross linker agent like TEOS addition restrained the formation of crystallization and lowered the membrane porosity and roughness of membrane upper surface and the contact angle (CA) of the membrane were decreased [11]. On the other hand, pure PVA film showed lowest CA due to its properties good film- forming and high hydrphilicity [18]. PVA is sensitive during the mixing with other materials. Thus, TEOS is needed to increase the hydrophilicity of PVA/Cs blended polymer.

TABLE II. the differences of contact angle between membrane without cross linker and with cross linker TEOS.

Membrane	TEOS Concentration (Wt%)	Contact Angle (º)	Standard Deviation
Porous support (PSF)	-	78	±1.25
MI	0	60.9°	±4.25
M2	1	59.03°	±2.85
M3	3	51.53°	±1.05
M4	5	49.83°	±1.70

B. Effect of TEOS concentration on membrane mechanical properties

Tensile strength and elongation at break are two significant parameters to define the mechanical properties of membranes. As shown in fig.2 the tensile strength and percent strain increased with the increased of TEOS content. In general, TEOS content inhibites the formation of macrovoids and improved the mechanical properties of hybrid membrane [11]. Where more TEOS content in membrane made the membrane more rigid structure. Thus it needed more strength to fracture. From the tensile strength result, it also showed that silica nanocomposite like TEOS can disperse throughout the polymer matrix and silica can interact with polymer chain through hydrogen bonding. So, the polymer matrix becomes trapped between silica precipitates [19].The increasing of tensile strength with increasing TEOS content from the interaction of the hydrogen bond or other bond formed between PVA/CS and TEOS after the sol –gel process. As reported by Xiojuan Lu et. al (2008), the tensile strength of the membrane increases with increasing of TEOS content but excess amount of TEOS content will caused hybrid homogeneity decrease, thus, the strength will decreased. The elongation at break at higher TEOS content increase due to the film of hybrid membrane content high TEOS that can cause the film become more rigid and show decrease flexibility [4]. Generally, TEOS network restricted the movement of the polymer molecules, which weakened the flexibility of the membrane. Although, the membrane with higher content of TEOS has higher tensile strength but they have higher percent of strain which show ductile properties

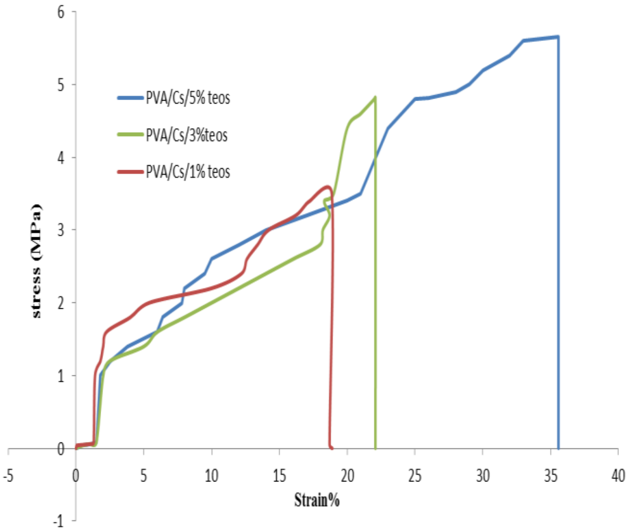

Fig. 2. Stress vs strain of PVA/Cs/teos hybrid membranes with various teos content (wt%)

TABLE IIII. the differences of contact angle between membrane without cross linker and with cross linker TEOS.

Membrane	TEOS (Wt%)	Tensile strength (MPa)	Break strain(%)	Elongation (mm)
M2	1	3.5	18.86	4.715
M3	3	4.82	22.08	5.52
M4	5	5.65	35.6	8.9

C. Thermogravimetry analysis (TGA)

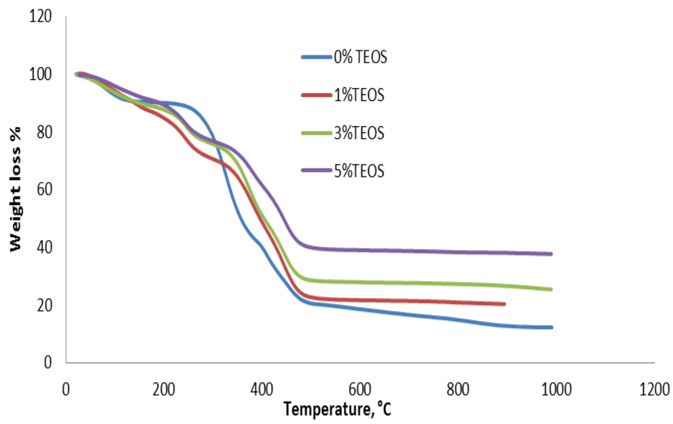

Fig. 3. TGA curves of the hybrid membrane sample, hybrid membrane with 0% TEOS, hybrid membrane with 1% TEOS, hybrid membrane with 3% TEOS, hybrid membrane with 5% TEOS.

TABLE IV. Thermal analysis data of samples in TGA curves

Membrane	The residual weight at temperature 500°C
M1	20.3
M2	22.6
M3	28.4
M4	39.75

The purpose of TGA analysis in this study is to examine the thermal degradation and stability of the effect of TEOS content in the hybrid membrane. The thermal stability of hybrid membrane with different amount of TEOS was determined by TGA curve shown in Fig.3. From Fig.3, it shown the trends in weight loss is similar and the weight change within the membrane steps can be clearly found. The TGA curve showed three main steps of weight lost. The first weight lost that occurred at a temperature below 150°C is the removal of the residual water from the sample [14], due to the exposure of the sample to air during preparation.The second weight loss is around 200ºC to 400ºC corresponds to the removal of hydroxyl group on PVA and chitosan [20].However, the curves are not clearly shown. The final weight loss is after 500°C was related to the degradation of the polymer backbones in the hybrid membrane [20]. TABLE IV showed the weight residue of the thermal degradation for hybrid membrane samples on the effect of TEOS content. The weight residue gradually increases around 400°C as the TEOS content increased. Therefore, the incorporation of inorganic polymer, TEOS into the polymer blending of PVA/chitosan significantly stabilized the thermal degradation of the membranes [20]. Besides that, it is also observed that the interaction of the hydrogen bond or other bonds between the TEOS inorganic network was formed after the sol–gel process. It was believed that the polymeric chains formed from the interaction can controlled the thermal action and increasing the rigidity of the membrane.In overall comparison, higher residual mass was achieved by chitosan/ PVA at 5% TEOS sample as compared to the other three membranes. The thermal degradation of the polymer occurs at higher temperature due to the higher presence of silica in TEOS. It requires more reaction activation energy and possesses higher order as higher content of TEOS provide strong incorporation of the silica with the polymer matrix of chitosan/PVA blended. Thus, a more thermal resistance and rigid structure of polymer are formed. Therefore, an increase in silica content contributes to higher weight residue when subjected to an increasing temperature and time [10].

V. CONCLUSIONS

The mechanical and thermal stability of hybrid membrane are improved apparently by an appropriate choice of TEOS concentration. The cross- linking of TEOS in polymeric chain formed rigid structure and high thermal resistances due to the increasing of silica contents. However, the membrane exhibit ductile properties due to lomger elongation. The contact angle also decreases with increasing of concentration of TEOS which show high hydrphilicity. High hydrophilicity is needed for membrane separation due to minimise the membrane fouling by organic matter Thus, the incorporation of 3%-5wt% TEOS concentration was found to produce high flexibility and good thermal stability of hybrid membrane. Results obtained from this study are used for further development in the application of thin film composite membrane.

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