

Synthesis and characterization of poly(methyl methacrylate)/SiO₂ hybrid membrane

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Abstract

Hybrid organic-inorganic membranes were fabricated using sol-gel technique using poly (methyl methacrylate) (PMMA) and tetraethyl orthosilicate (TEOS) with 80/20 (w/w) ratios with THF solvent. The thin films were then characterized using FTIR, SEM, EDX, DSC, TGA, water permeability and also its molecular weight cut-off. From the preliminary characterization, the hybrid membrane was found to have nano and ultra scale tight pore ranges. FT-IR spectroscopy uncovered all the signature peaks characteristic of silicate structures in the near-surface regions. Fingerprints of Si–O–Si groups in cyclic and linear molecular substructures are present. The SEM image clearly shows that hybrid membranes have homogenous and smooth surface. EDX analysis shows the composition of particles in the membrane. DSC analysis of the membrane show-interesting phenomenon regarding glass transition temperature (T_g). The hybrid membrane was found to have higher T_g than pure PMMA. From TGA analysis, the hybrid membranes were observed to have higher thermal stability than pure PMMA.

Keywords: Hybrid membrane, inorganic-organic, sol-gel, PMMA, TEOS.

1. Introduction

Recently, much effort has been devoted to the development of organically modified sol gel derived ceramics, which are regarded as a new family of hybrid materials. They are called ‘ceramers’, ‘organoceramic’, ‘policeram’, ‘ceramers’ or ‘ormosils’^[1,2]. In these materials, organic polymers are chemically incorporated into an inorganic network at molecular level, and changing the overall composition ratio of organic to inorganic varies their properties. Many new types of organic/inorganic hybrid materials have the potential to combine the desired properties of inorganic and organic systems. The properties of the hybrid materials could be tuned through the functionality or segment size of each component, including thermal, mechanical, electronic, optical and optoelectronic properties^[3,4]. These properties depend not only upon the properties of the individual component phases, but also upon their interaction, polymer phase morphology and interfacial properties with the other component^[5,6]. One of the widely studied hybrid materials is poly(methyl methacrylate)(PMMA)/inorganic oxide^[3,4]. PMMA has been widely used in optical devices due to its excellent optical properties and processibility^[3,7]. However, its thermal and mechanical properties have limited its applications. One possible solution to address the above problem is to hybridize with inorganic oxides such as silica or titania^[4,8]. The other solution is addition of nanoscale silica or titania particles to polymers^[3,4,5]. Nanoscale silica

particles also can have a large interfacial area as long as the diameter of particles is in the range of nanometers. Although they do not have the narrow gallery structure of layered clay, the improvement in physical properties ^[3,5] and also some improvement in thermal stability ^[3,6] by the addition of nanoscale silica particles to polymers were reported.

In this study, the hybrid membrane films were prepared from in-situ polymerization of tetraethoxy orthosilane (TEOS) in a poly(methyl methacrylate) as previously reported ^[9]. Preliminary results on the preparation and characterization of this membrane are also reported.

2. Experimental

2.1. Materials

Poly (methyl methacrylate) (PMMA, $M_w = 350,000$) and tetraethyl orthosilicate (TEOS) (98%) were purchased from Aldrich. Hydrochloric acid (HCl) was applied as catalyst was purchased from Merck. The solvent: tetrahydrofuran (THF) was purchased from Merck. Water used was generated from distillation system. All materials were used without further purification.

2.2. Fabrication of hybrid membranes

In general, the samples were prepared as previously described ^[9] by dissolution PMMA in THF at 15% concentration polymer (w/w) first. TEOS was added directly to the solution under continuous agitation. The TEOS was well dispersed and the solution became clear within a few minutes. Then water ($\text{pH} = 2$) were added in stoichiometric amount ($\text{TEOS:H}_2\text{O} = 1:4$) and mixed for 24 h more at ambient temperature. The final composition solution of PMMA/TEOS was 80/20 (w/w). The homogeneous solution above was allowed for 24 hours to release of the bubbles. It was then cast in paper placed on the glass plate by means of a proper knife (DR. Blade) to form thin films (thickness ca 350 μm) and was allowed to stand at room temperature for 20 days for gelation. Finally, the gelled samples were obtained and then dried at 60 °C in vacuum for 5 hours.

2.3. Permeation measurements

Permeation measurements were carried out with distilled water. A stirred dead-end Amicon ultrafiltration cell model 8200 was used in these experiments. It had a volume capacity of 200 mL. The effective area of the membrane was 28.7 cm^2 . The operating pressure of experiment was 1-5 bar in the range. The permeate was collected in a vessel at 20 ml volume.

2.4. Characterizations

2.4.1. Determination of molecular weight cut off

The Molecular Weight Cut Off was determined by dextran with different molecular weights (12.2 to 505 kDalton). Dextran concentration was 200 ppm by weight. The concentrations of feed and permeate solutions were determined by colorimetric method [10] and then the solute separation, R , was obtained by:

$$R = 1 - (C_p/C_f)$$

where C_p : permeate concentration, C_f : feed concentration

2.4.2. Differential scanning calorimetric

Differential scanning calorimeter (DSC 822e METTLER TOLEDO) was used for the investigation of glass transition temperature variation of synthesized hybrid materials. Appropriate amount of samples (ca. 3 mg) were ground into fine powder and then were sealed in aluminum sample pans. DSC analyses of these hybrid materials were then conducted under dry nitrogen at a heating rate of 10 °C/min from 20 to 250 °C.

2.4.3. Thermal gravimetric analysis

The thermogravimetric data was obtained from thermogravimetry analyzer (TGA, TA 951) performed under dry nitrogen atmosphere over a temperature range of 35 to 800 °C at a heating rate of 10 °C/min. The samples were ground into fine powder. The measurements were taken using 3-5 mg samples. Weight-loss/temperature curves were recorded.

2.4.4. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) spectra of the hybrid membranes were recorded between 4000 and 450 cm^{-1} on a Bio-Rad, FTS 165 spectrometer. Samples for FTIR were prepared in the film method. A minimum of 18 scans was signal averaged with a resolution of 2 cm^{-1} at the 4000 - 450 cm^{-1} ranges.

2.4.5. Morphological properties

The structure of the surface of the membrane film was analyzed by Scanning Electron Microscopy, SEM (Oxford Instrument, 7353, England). The hybrid membranes were fractured in liquid nitrogen and coated with Au by sputtering.

2.4.6. EDX analysis

The chemical analysis of the hybrid membranes was analyzed by Energy Dispersive X-Ray, EDX (Oxford Instrument, 7353, England). The hybrid membranes were fractured in

liquid nitrogen and coated with Au by sputtering. Analysis was carried out on selected areas of $50 \mu\text{m}^2$.

3. Results and discussion

3.1. Permeation measurements

Using the constant volume carried out permeation measurements. The results of permeation measurement can be seen at Table 1. It can be shown that the hybrid membrane has ultra scale tight pores ranges. The explanation of this behavior would be described more detail in the next sessions.

3.2. Determination of molecular weight cut off

The molecular weight cut-off is key parameter for membranes and were determined using inert, stable molecules having various higher molecular weights. For hybrid membrane the MWCO was found to be 350 kD, revealing that the addition of silica increases the pore size of the membrane, as seen in Table 1.

Table 1
Physical properties of hybrid membrane.

Membrane(s)	Lp ($\text{m}^3/\text{m}^2 \cdot \text{s} \cdot \text{bar}$)	MWCO	Tg ($^{\circ}\text{C}$)	Char Yield (800 $^{\circ}\text{C}$) (%)
Pure PMMA	small	-	116.27	0.89
PMMA/SiO ₂	1.0696×10^{-6}	380 kD	118.40	24.28

3.3. Differential scanning calorimetric

Glass transition temperatures (T_g) of these organic-inorganic hybrid membranes were investigated by DSC. The thermo-scan profiles were sketched in Figure 1 for hybrid and PMMA membranes. The T_g values were tabulated in Table 1. It can be found that neat PMMA has an obvious single T_g at 116.27 $^{\circ}\text{C}$. However, synthesized PMMA/silica hybrid membranes also exhibited single T_g . The hybrid membrane exhibited only single but tremendous wide profile of glass transition in DSC measurement (118.40 $^{\circ}\text{C}$). These results indicate that phase separation still existed in the hybrid materials [8,11]. Nevertheless, from the result of T_g measurements it can be recognized that hybrid membrane has obvious higher miscibility of organic and inorganic phases. Also could be seen that the T_g of hybrid membrane was higher than that of neat PMMA, which indicated that the incorporation of minerals by promoted the polymer thermal properties, which was due to existence of the strong interactions between the silica network and the polymer matrix. These strong interactions limit the movement/motions of the polymer chains segments due to increase rigidity structure of polymer [12,13]. More evidences and possible explanation would be presented and discussed with the data of thermogravimetric analysis.

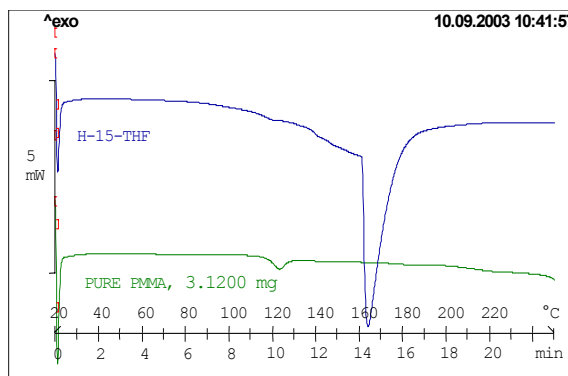


FIGURE 1. DSC curve of hybrid membrane.

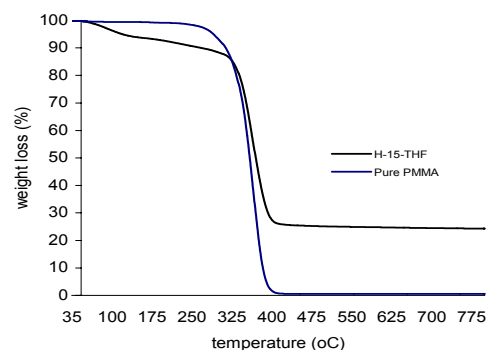


FIGURE 2. TGA curve of hybrid membrane.

3.4. Thermal gravimetric analysis

Figure 2 show the results of differential thermogravimetric analysis of neat PMMA and synthesized hybrid membranes. Furthermore, degradation temperatures of all the synthesized hybrid materials were tabulated explicitly in Table 1. It is well know that for neat PMMA there was only single degradation stage found on TGA measurement, which were at 399.5 °C. Nevertheless, the hybrid membranes have three degradation stages. The first stage of the hybrid membranes was 147.5 °C. It was resulted from the elimination of ethanol and water generated from further condensation process, which have not been released during the vacuum drying process ^[1,8,14]. The second stage at approximately 300 °C might be ascribed to a decomposition of the chain end from vinylidene end ^[5,6]. In the third stage, the polymer residues were further degraded at approximately 400 °C, corresponding to the decomposition of main chain of PMMA ^[5,6].

The behavior follows from the presence of Si-O-Si linkages in the hybrid membranes, which increases the polymer degradation temperature by shifting the weight loss to higher temperatures ^[15]. The char yield of pure PMMA is 0.89 and that of hybrid membrane is 24.28 at 800 °C. Consequently, the thermal stability of hybrid membranes at high temperatures exceeds that of pure PMMA, which suggests the successful incorporation of the silica moiety into the hybrid membranes ^[3]. This increase in the thermal stability can be attributed to the high thermal stability of silica and the existence of the strong interaction between the silica particles and the polymer matrix ^[16,17].

3.5. FTIR analysis

Infra red spectra of synthesized hybrid membrane film were sketched in Figure 3. In hybrid membrane film, it can be easily found that the absorption peak of Si-O-Si asymmetric stretching at ca 802 cm^{-1} and 460 cm^{-1} , which was due to the formation of silica structure via sol-gel process with TEOS added. The two companion peaks in this region arise from Si-O-Si groups at ca 1072 and 1181 cm^{-1} that are in cyclic and linear molecular sub-structures ^[18]. A derivative bond which indicates a partial shift in the C=O also appears in spectra, this being

due to the presence of hydrogen bond in the system [8,11,12,19]. Simultaneously, absorption peak of silanol groups (Si-OH) at 949 cm⁻¹ and 3469 cm⁻¹ were also found, which resulted from the existence of unreacted silanol group on TEOS to formation of silica network [8].

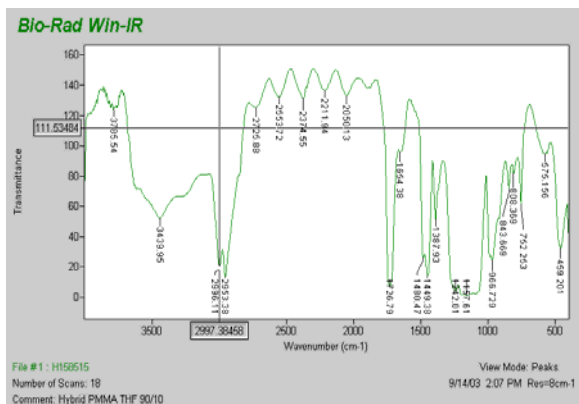


FIGURE 3. FTIR spectra of hybrid membrane.

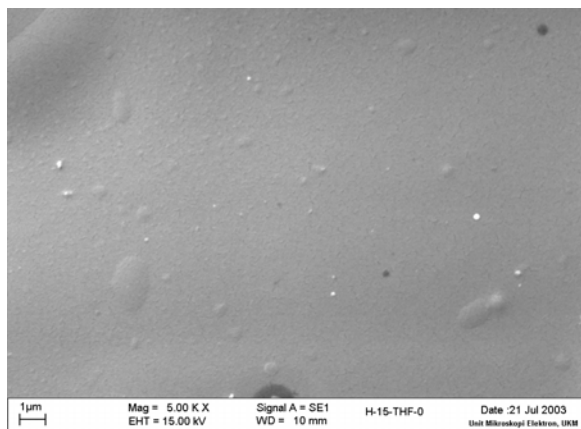
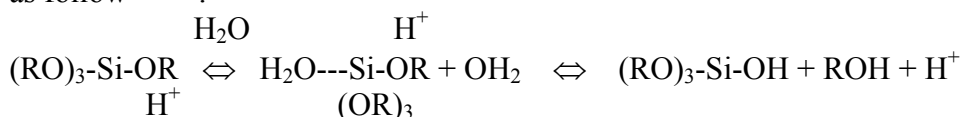


FIGURE 4. SEM of hybrid membrane.

3.6. Scanning electron microscopy

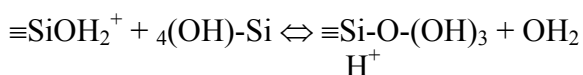
The fractured surface of the hybrid membrane films were observed using SEM, which can give important information about the morphology of these materials. The SEM image in Figure 5 clearly show that hybrid membranes have homogenous and smooth surface and have a finer morphology with smaller pores. It is correspondent to hydrolysis and condensation mechanisms and therefore the nature and size of the resulting polymeric particles.

The mechanism for hydrolysis reaction in the low pH is electrophilic substitution [20,21] as follow [21,22].



An alkoxide group is protonated in a rapid first step. Electron density is withdrawn from silicon making it more electrophilic and thus more susceptible to attack by water. The water molecule attacks from rear and acquires a partial positive charge. The positive charge of the protonated alkoxide is correspondingly reduced making alcohol a better leaving group. The transition state decays by displacement of alcohol [22]. In this sense, the absence of an alcohol in the reaction medium, encourages the forward reaction to occur, thus speeding up the entire process [23]. The solvents of this study can be grouped into category non-polar. In non polar solvents, it cannot form hydrogen bond to hydronium ion (from acid catalyst), therefore, process of hydrolysis is complete. It is caused by formation which silanol group, subsequently would affect condensation process.

In the low pH the condensation reaction proceeds by an electrophilic substitution mechanism whereby a protonated silanol species dissociates according to [24].



The additional proton is later removed either by a water of another $\text{Si}(\text{OH})_4$ molecule. It is obvious from the above mechanism that the polymerization rate in this pH is directly proportional to the H^+ concentration. As is well known, hydrogen bonding as well as electrostatic interactions between the solvent and the electrophile are of fundamental importance in bimolecular electrophilic substitutions. The condensation reaction is most efficient in non-polar solvents, which lack the ability to interact both electrostatically, and through hydrogen bonding to either the reactants or the activated complex. THF does not possess a dipole moment, nor any electronegative atoms capable of deactivating the electrophile through hydrogen bonding and should result in a significant enhancement of the condensation rate. It is due to system has smooth and compact spherical polymeric particles

3.7. EDX analysis

The chemical analysis of the top and bottom layer of membrane film by EDX analysis shows that the top face contains the carbon, oxygen and silicon elements and also shows that the bottom face of hybrid membrane has higher contain silicon than top face. It might be correspondent to process of membrane production.

4. Conclusion

Hybrid organic-inorganic membranes, based on a PMMA polymer matrix and a SiO_2 component, have been successfully fabricated by a sol-gel method. From results of permeability measurements indicating that membranes were of ultrafiltration range. In this study, it was found that transparent hybrid membrane could be obtained. It is suggested that the polymer which result in optically transparent composites with polymerized TEOS are those capable of hydrogen bond formation with residual hydroxyls present on the surface of the SiO_2 as revealed from FTIR analysis. From DSC analysis, the T_g value of the hybrid membranes was higher than pure PMMA membrane. Furthermore, from TGA analysis it was found that the hybrid membranes have higher thermal stability compared to pure PMMA. SEM imaging of membranes show that the membranes have nano scale tight pores. EDX analysis shows that the top face of hybrid contains the carbon, oxygen and silicon elements and the bottom face of hybrid membrane has higher contain silicon than top face.

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