Poly(methyl methacrylate)/SiO$_2$ Hybrid Membranes: Effect of Solvents on Structural and Thermal Properties

Muhammad Ali Zulfikar,[1] A. Wahab Mohammad,[1] Abdul Amir Kadhum,[1] Nidal Hilal[2]

[1]Department of Chemical and Process Engineering, Universiti Kebangsaan, Malaysia 43600 UKM Bangi Selangor Darul Ehsan, Malaysia
[2]School of Chemical, Environmental and Mining Engineering, The University of Nottingham, NE7 2RD, United Kingdom

ABSTRACT: In this paper, hybrid organic–inorganic membranes were prepared using three different solvents and characterized. The hybrid membranes were fabricated using sol–gel technique, which had polymethyl-methacrylate (PMMA) and tetraethyl orthosilicate (TEOS) as materials, with 80/20 ratio. The thin films were then characterized using FTIR, SEM, EDX, and mapping techniques. From the preliminary characterization, hybrid membranes were found to have nano and ultra scale tight-pores ranges, which was influenced by the solvent used. The SEM images clearly show that hybrid membranes have homogenous and smooth surface. FTIR 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 were also present. From DSC analysis, the T_g value of the PMMA moieties in hybrids membranes was in the order H-15-Toluene < Pure PMMA < H-15-THF < H-15-DMF. Furthermore, from TGA analysis it was found that the hybrid membranes have higher thermal stability compared with that of pure PMMA. EDX and mapping analysis showed that the composition and distribution of particles in the membranes were different and dependent on the solvents used. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3163–3171, 2006

Key words: hybrid membrane; inorganic–organic; sol–gel; permeability; PMMA/TEOS

INTRODUCTION

In recent years, preparation of hybrid organic–inorganic composites has attracted much interest because such hybrid may show controllable properties such as thermal, optical, electrical, optoelectronic, and mechanical behaviors by combining the properties of both inorganic glasses and organic polymers. Hybrid organic–inorganic materials have become an area of intense research, focusing on applications such as optic and electronic materials, biochemical sensors, catalyst, adsorbents, solid electrolytes, contact lenses, solar cell, and biomedical.[1–5] Only recently, hybrid materials have become membrane materials.[6–15] The sol–gel process, with its associated mild conditions, offers an approach to synthesis of hybrid materials.[1,2,9–14,16–27] These methods include hydrolysis of metal alkoxides with water to resulting of metal hydroxides, followed by a condensation of hydroxyl groups to form a three dimensional metal oxides network. Tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) have been used extensively in the sol–gel process to produce monolithic glasses from low temperature processes. The network forming polymerization of the alkoxide, for example TEOS, proceeds by the mechanisms of hydrolysis, alcohol condensation, water condensation, and SiO2 network, respectively, as has been reported previously.[19,24,28] These reaction mechanisms are concurrent[2,12,14,19,20] and exhibit reversibility.[20] The relative rate of each is governed by pH, solvent, water to alkoxide ratio, concentration, catalyst, and temperature.[10,12,14,21,23,29]

The development of new membrane material plays a very important role in membrane science and technology. Currently, various studies have shown that by incorporating minerals into polymers, there are possibilities for improving network structure, enhancing physical, chemical, and mechanical properties, increasing thermal stability, permeability and permselectivity, as well as modifying the pore structure and pore size distribution of membranes. The combined properties exhibit some characteristics of both ceramics and organic polymers.[13]

The purpose of this study then was to examine the properties of hybrid membranes prepared by reaction of polymethyl–methacrylate (PMMA) with tetraethyl

orthosilicate (TEOS) by means of sol–gel process, using three different solvents, namely tetrahydrofuran (THF), toluene, and dimethylformamide (DMF). Membranes prepared from the polymer hybrid mentioned earlier were evaluated for water permeability as well as characterization with various techniques such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Energy Dispersive X-Ray (EDX), and differential scanning calorimetric (DSC) to understand the effect of different solvents on structural and thermal properties of the membranes.
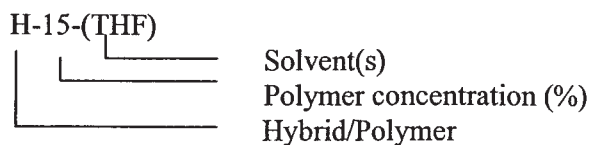
Experimental

Materials

Poly(methyl methacrylate) (PMMA, M_w = 350,000) and tetraethyl orthosilicate (TEOS; 98%) were purchased from Aldrich. Hydrochloric acid (HCl) that was used as catalyst was purchased from Merck. The solvents: tetrahydrofuran (THF), toluene, and dimethylformamide (DMF) were also purchased from Merck. All materials were used without further purification. Distilled water was used in all preparation.

Fabrication of hybrid membranes

PMMA was thoroughly dissolved in the respective solvent at 15% concentration polymer (w/w) in solution 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 acidic solution (pH = 2) was added in stoichiometric amount (TEOS:H_2O = 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 mentioned earlier was left for 24 h to release air bubbles. It was then cast on a drawing paper placed on a glass plate by means of a proper knife (Doctor Blade) to form thin films (thickness ~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 h. The nomenclature adopted herein specifies each sample as follows:

H-15-(THF)
Solvent(s)
Polymer concentration (%)
Hybrid/Polymer

Scheme 1

Permeation measurements

Permeation measurements were carried out using 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. Twenty milliliters of the permeate was collected in a graduated cylinder.

Characterizations

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) 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 form of KBr pellets method. A minimum of 18 scans signal was averaged with a resolution of 2 cm^{-1} at the 4000–450 cm^{-1} range.

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.

Differential scanning calorimetric

DSC (DSC 822e METTLER TOLEDO) was used for the investigation of glass transition temperature variation of synthesized hybrid materials. Appropriate amount of samples (~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^{-1} from 20 to 250°C.

Thermal gravimetric analysis

The thermogravimetric data was obtained from thermogravimetry analyzer (TGA, TA 951) performed under dry nitrogen atmosphere over a temperature range of 35–800°C at a heating rate of 10°C min^{-1}. The samples were ground into fine powder. The measurements were taken using 3–5 mg samples. Weight-loss/temperature curves were recorded.

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

TABLE I
Appearance of PMMA/Silica Hybrid Membranes

Membrane(s)	Appearance
H-15-DMF	Opaque
H-15-THF	Transparent
H-15-Toluene	Translucent

TABLE II
Water Permeabilities of the Hybrid Membranes

Membranes	Lp (L/m^2 h bar)
H-15-DMF	39.57
H-15-THF	3.69
H-15-TOL	2.79

by sputtering. Analysis was carried out on selected areas of 50 μm^2.

Si mapping technology

The distributions of Si atoms in the hybrid membranes were obtained by SEM EDX mapping (Oxford Instrument, 7353, England). The points in the figures denote C, O, and Si atoms.

RESULTS AND DISCUSSION

Physical appearances

Optical transparency is used as an initial criterion for the formation of homogeneous phase composition of the inorganic and organic constituents.[2,18,22] As shown in Table I, transparent hybrid membrane could be only obtained from hybrid membrane use THF as solvent. 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 SiO2 formed, which is generated by a hydrolysis of TEOS[19,22] and is necessary to prevent macroscopic phase separation.[2,19,22] From FTIR analysis, it can be seen that the hybrid membrane that is using THF as

solvent was observed to be made via hydrogen bonded, whereas in DMF and toluene solvents, no hydrogen bonding was present in both. More evidences and possible explanation would be presented and discussed with the data of FTIR and SEM analysis.

Permeation measurements

The results of permeation measurement are shown in Figure 1, while the water permeability values are shown in Table II. On the basis of this result, it can be seen that the different solvents affect the water permeabilities very much. The hybrid membranes prepared using the DMF solvent was significantly more porous compared with that of the membranes prepared using toluene and THF solvents. Further explanation of this behavior will be discussed in the following sections.

FTIR analysis

Infra red spectra of pure PMMA and synthesized hybrid membrane film were shown in Figure 2(a–d), respectively. As shown in the figures, all materials showed distinct infrared absorptions. In all hybrid membrane films, it can be observed that the absorp-
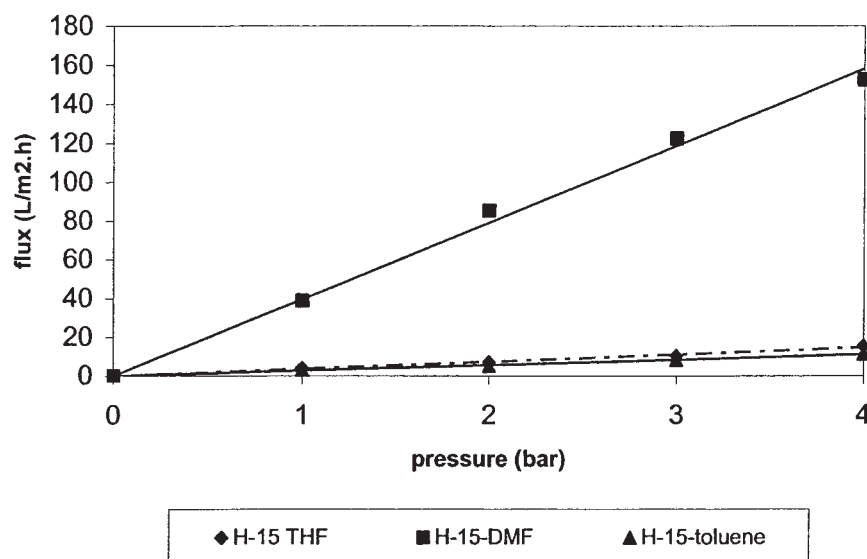

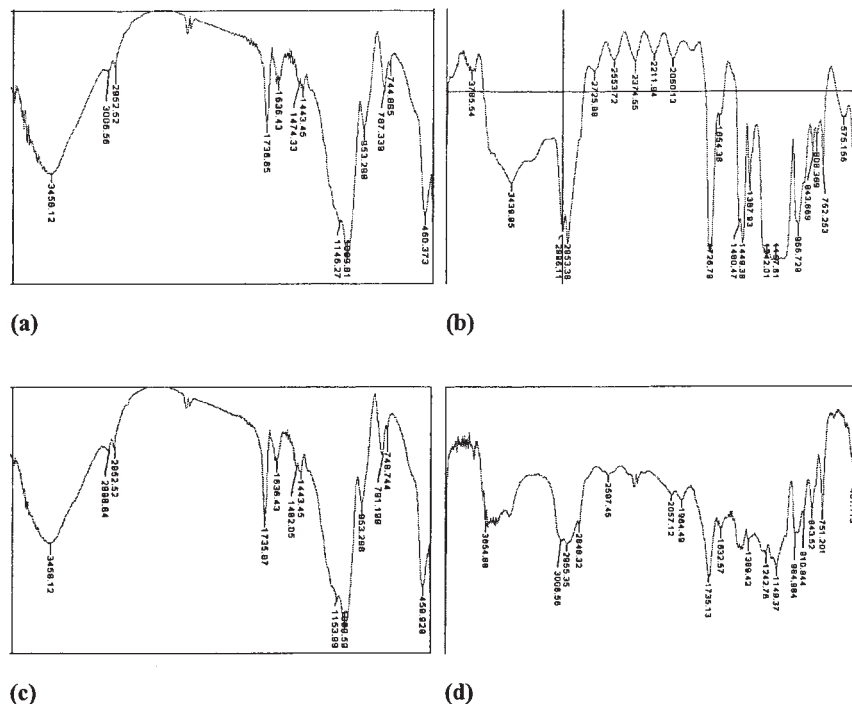**Figure 1** Water Permeability of the hybrid membranes.

Figure 2 Infra red spectra of (a) H-15-(DMF) hybrid membrane, (b) H-15-(THF) hybrid membrane, (c) H-15-(Toluene) hybrid membrane, and (d) pure PMMA.

tion peak of Si—O—Si asymmetric stretching at ~802 and 460 cm−1, which was due to the formation of silica structure via sol–gel process with the added TEOS. The two companion peaks in this region arise from Si—O—Si groups at ≈1072 and 1181 cm−1 that have cyclic and linear molecular substructures.[30] The hypothetical, linear, and cyclic molecular subunits in silicate structures are illustrated in Figure 3. In THF solvent, a derivative bond that indicates a partial shift in the C=O also appears in spectra, this being due to the presence of hydrogen bond in the system,[2,21,27] whereas in the DMF and toluene solvents, no hydrogen bonds were observed. Simultaneously, absorption peak of silanol groups (Si—OH) at 949 and 3469 cm−1 were also found, which resulted from the existence of unreacted silanol group on TEOS to formation of silica network.[27] In this research, hybrid organic–inorganic membrane was postulated to be formed by the assembly between SiO2 nanoparticle and polymer with
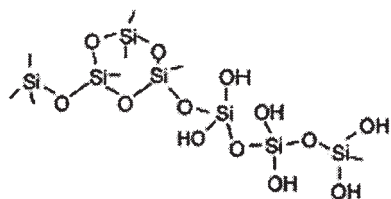
C=O groups via hydrogen bonding, especially for THF system, as shown in Figure 4.

Scanning electron microscopy

The surface of the hybrid membrane films were observed using SEM, which can give important information about the morphology of these materials. The SEM images in Figure 5(a–c) clearly show that hybrid membranes have homogenous and smooth surface. The morphology is closely related to the nature of the interactions between phases because morphology results from a competition between the crosslinking kinetics (formation of SiO_2 clusters and bonding to PMMA) and the phase separation kinetics because of the immiscibility of SiO_2 clusters in the polymer.

In hybrid systems based on high molar mass organic preformed polymers (for example PMMA), without designed functionalization, gelation is generally attributed to strong physical links such as hydro-
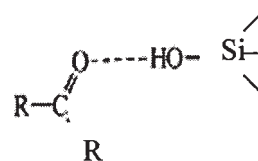

Figure 3 Depiction of hypothetical linear and cyclic molecular subunits in silicate structures.

Figure 4 Mechanism of assembly of SiO_2 nanoparticles in polymer matrix.
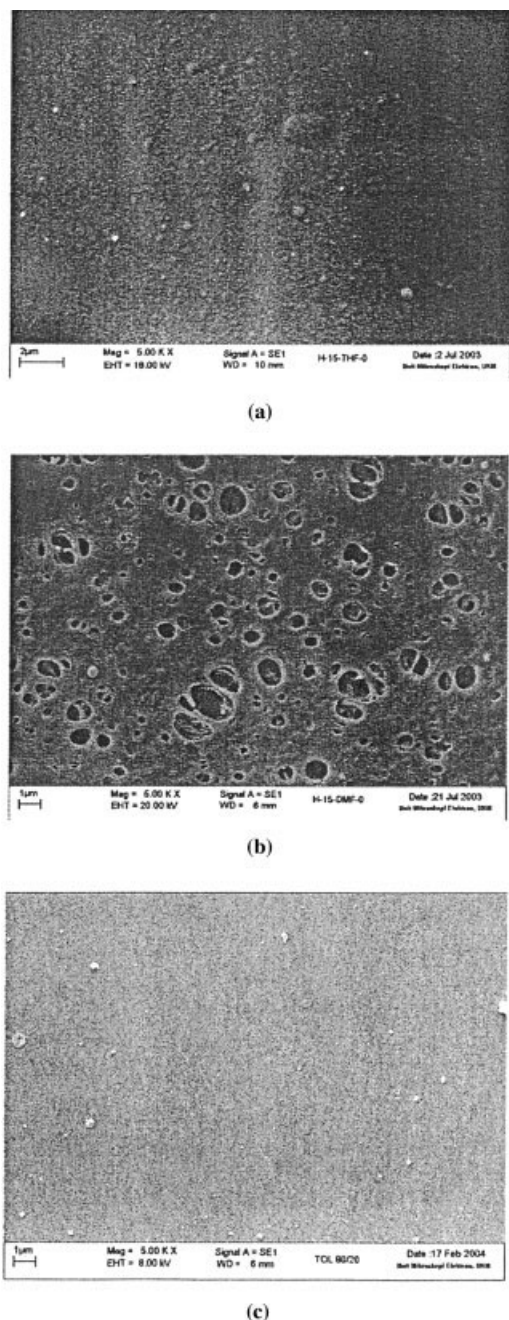
Figure 5 SEM of (a) H-15-(THF) hybrid membrane, (b) H-15-(DMF) hybrid membrane, and (c) H-15-(Toluene) hybrid membrane.

gen bonding between uncondensed alcohol functions of the inorganic clusters and carbonyl groups of the polymer chains.[31,32]

During PMMA/TEOS formation, TEOS is initially homogeneously dispersed in PMMA solution. As the hydrolysis/condensation reaction goes on, the inorganic SiO_2 network is formed. The growth of SiO_2 network is entropically unfavorable toward miscibility and the enthalpy interaction between the PMMA

segments and the inorganic component also deteriorates, and this condition can be due to macroscopic phase separation. A strong interaction between the PMMA and the SiO_2 is necessary to prevent these phase separation.

It is quite obvious from Table I that the solvent has an extremely important effect on the membrane appearance. The use of N, N dimethylacetamide, DMF, generally leads to a phase separated membrane, while THF favors the formation of optically transparent membranes. This observation can be explained in terms of hydrogen bonding interactions between the solvent and the polymer.

The solvents of this study can be broadly grouped into two categories: (1) dipolar aprotic (DMF) and (2) nonpolar (THF and toluene). Dipolar aprotic solvents, like DMF, can form hydrogen bond with the polymer's carbonyl group, hindering the molecular interaction between the PMMA and the SiO_2 domains, thus, leading to a phase separated system. In comparison, weak polar interactions between the THF molecules and the polymer repeat unit favors interaction between the PMMA and the SiO_2 domains, thus, inhibiting phase separation. THF solvent also function as solvent swelling the growing network and diluting the unfavorable interaction between PMMA and SiO_2, as described earlier.

Compared with toluene system, THF system has smooth and compact spherical polymeric particles. This observation can be explained by the steric effect theory. The steric hindrance effect is biggest in the toluene than in the THF system, thus, leading to hindering the molecular interaction between the PMMA and the SiO_2 domains. Furthermore, a translucent membrane film will be obtained when using toluene as solvent.

The cross section of the hybrid membranes are shown in Figure 6(a–c). Membranes obtained from PMMA solution in THF solvent have cocontinuous structure [Fig. 6(a)]. With DMF solvent, the membrane morphology progressively changes from cocontinuous structures (in THF solvent) to a cellular structure [Fig. 6(b)]. The same phenomenon also can be seen in toluene solvent system. The membrane structure in this system was bead (particulate) structure [Fig. 6(c)]. These observations may explain the water permeation results (section 3.2). It can be postulated that the membrane by DMF, because of the cellular structure, allows water to penetrate through the membrane *via* continuous channels (in the form of hydrodynamic flow) and thus, the high permeability value. However, the dense structure of the membrane by THF solvent reduced the permeability significantly. For the membrane with toluene solvent, the permeability is also much lower.
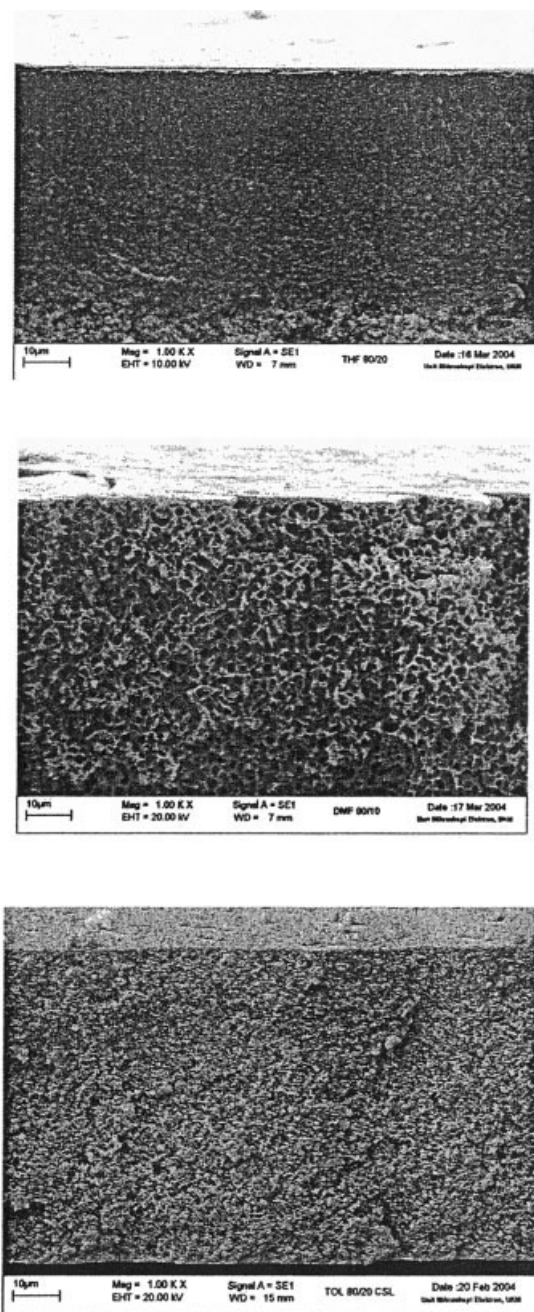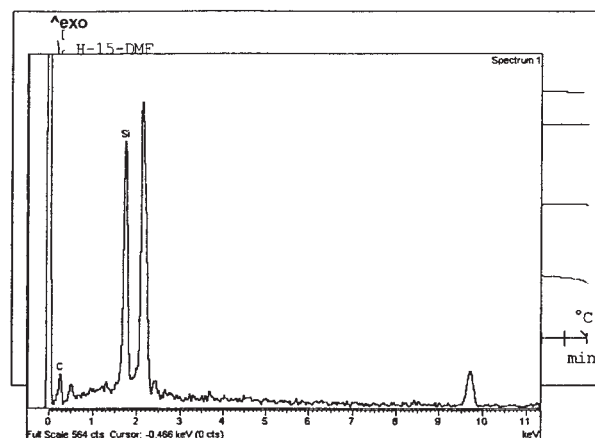
Figure 7 DSC Curve of hybrid membranes.

higher than that of pure PMMA, while the other one, H-15-Toluene was lower than that of pure PMMA. The T_g for H-15-THF and H-15-DMF were 118.40 and 120.91°C, respectively.

The lower T_g obtained for H-15-toluene hybrid membrane indicates the possibility that there were residual low molecular weight species in the sample, possibly TEOS. This residual molecule act as plasticizer and suppress the Tg of sample.[21] Another possibility might be the absence of hydrogen bond within the hybrid membrane,[27] as described earlier. In addition, the process of acid catalysis would pull the organic side chain together for a sol–gel reaction to form a tiny Si—O—Si structure. It also made a greater contribution to prohibiting the organic chain segments from coming together and increased the free volume around the stretched chain segments for further chain movement. Consequently, the Tg of the system decreased.[27] For H-15 THF hybrid membrane exhibited only single but tremendous wide profile of glass transition in DSC measurement (118.40°C). These results indicate that phase separation still existed in the hybrid materials.[19,27] Nevertheless, from the result of Tg measurements, it can be recognized that hybrid membrane of H-15-THF has obvious higher miscibility of organic and inorganic phases. Also could be seen that the Tg of H-15-THF hybrid membrane was higher than that of pure PMMA, which indicated that the

Figure 6 SEM of cross section of (a) H-15-(THF) hybrid membrane, (b) H-15-(DMF) hybrid membrane, and (c) H-15-(Toluene) hybrid membrane.

Differential scanning calorimetric

Glass transition temperatures (T_g) of these organic–inorganic hybrid membranes were investigated by DSC. The thermoscan profiles were shown in Figure 7 for hybrid membranes. All the T_g values were tabulated in Table III. It can be seen that pure PMMA has an obvious single T_g at 116.27°C. However, synthesized PMMA/silica hybrid membranes of various solvents also exhibited single T_g. The T_g of these two hybrid membranes, H-15-THF and H-15-DMF, were

TABLE III
Glass Transition Temperatures of PMMA/Silica Hybrid Membranes

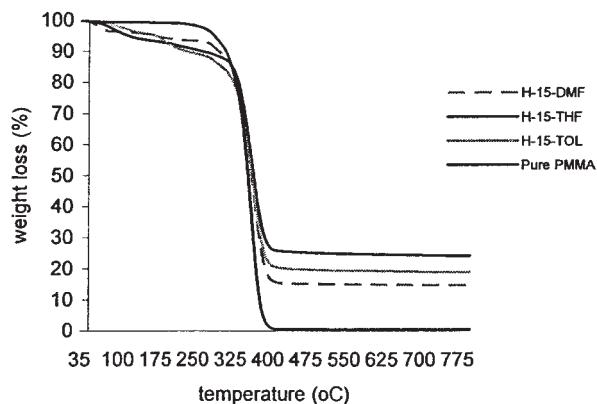| Membrane(s)	Glass transition temperature (°C)
PMMA	116.27
H-15-DMF	120.91
H-15-THF	118.40
H-15-Toluene	87.86

Figure 8 TGA Curve of hybrid membranes.

incorporation of minerals promotes the polymer thermal properties, which was due to the 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 because of increased rigidity structure of polymer.[21,27,33,34] According to Mulder,[34] factors that lead to an increase in thermal and also the chemical stability, are: increased Tg and Tm and increase in the crystallinity. Chain interactions, especially, induced by hydrogen bonding can increase the crystallinity and Tg. The other factor that can increase thermal stability is the presence of resonance structure in the system. For H-15-DMF hybrid membrane, although its Tg is higher than others, it was not due to the existence of interaction between the silica and polymer, but it might be caused the self condensation of silanols generated by hydrolysis of silicon alkoxide, then the silicon oxide networks with large size are easier to form in this system.[2] It is noteworthy to recall at this time that the catalyst was added to PMMA/TEOS solution 24 h before coating process. Thus, the TEOS was allowed to polymerize and to develop some structure in the solution. More evidences and possible explanation would be presented and discussed with the data of thermogravimetric analysis.

Thermal gravimetric analysis

Figure 8 shows the results of differential thermogravimetric analysis of pure PMMA and synthesized hybrid membranes. For pure PMMA there was only a single degradation stage found on TGA measurement, which was at 399.5°C. Nevertheless, the hybrid membranes have three degradation stages. It is interesting to notice that an obvious difference was found between H-15-THF, H-15-DMF, and H-15-toluene hybrid membranes. The first stage of the hybrid membranes was 147.5, 147.0, and 76°C for H-15-THF, H-15-toluene, and H-15-DMF, respectively. It resulted from

the elimination of ethanol and water generated from further condensation process, which had not been released during the vacuum drying process.[16,18,19] The second stage at ~300°C might be ascribed to a decomposition of the chain end from vinylidene end.[35,36] In the third stage, the polymer residues were further degraded at ~400°C, corresponding to the decomposition of main chain of PMMA.[35,36] The values of Td10 (the temperature of degradation at which the weight loss is 10%) for pure PMMA and hybrid membranes in THF, DMF, and toluene solvents are 248.0, 267.0, 299.5, and 235.5°C, respectively. The thermal stability of hybrid membranes at a low temperature is not superior to that of the pure PMMA; however, the char yield of hybrid membranes is higher than that of the pure PMMA at 800°C.

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.[37] The char yield of pure PMMA is 0.89 and that of hybrid membranes are 24.28, 12.89, and 18.99% for H-15-THF, H-15-DMF, and H-15-Toluene at 800°C, respectively. Consequently, the thermal stability of hybrid membranes at high temperatures exceeds that of pure PMMA, which suggests the successful incorporation
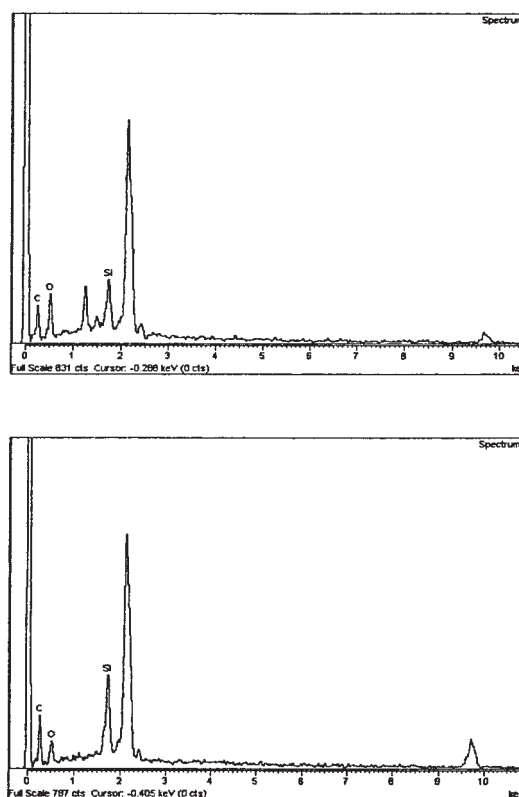

Figure 9 EDX of top surface of (a) H-15-(THF) hybrid membrane, (b) H-15-(Toluene) hybrid membrane, and (c) H-15-(DMF) hybrid membrane.
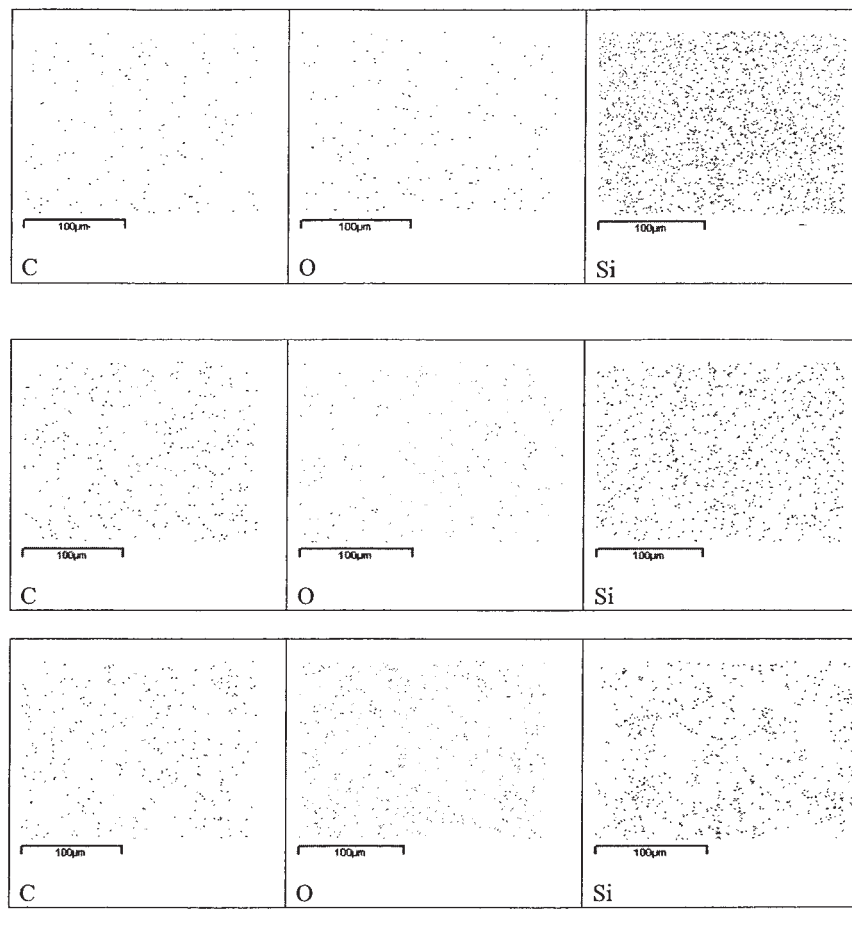
Figure 10 Mapping of top surface of (a) H-15-(THF) hybrid membrane, (b) H-15-(DMF) hybrid membrane, and (c) H-15-(Toluene) hybrid membrane.

of the silica moiety into the hybrid membranes. 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.[38] As shown in Figure 7, the hybrid membrane with THF solvent has higher thermal stability than the other. It was due to existence of the hydrogen bond between silica and polymer matrix, and also presence of Si—O—Si linkages in this membrane, as seen in FTIR spectra previously reported. For the other hybrid membranes, it was only due to the presence of Si—O—Si linkages, because in both, no hydrogen bonds were present in the hybrid systems.

Flame resistance can be quantified from the char residue on pyrolysis. Van Krevelen established a linear relationship between LOI and char residue for halogen-free polymers.[39] Increasing the char formation can limit the production of combustible carbon containing gases, decrease the exothermicity due to pyrolysis reactions, and decrease the thermal conductivity of the surface of burning materials. A higher char yield will enhance flame retardance.[39] The LOI of pure PMMA and hybrid membranes in

THF, DMF, and Toluene solvents are 0.89, 24.28, 12.89, and 18.99%, respectively, indicating that hybrid membranes exhibit better flame retardance than pure PMMA. This behavior is similar as observed in the addition of nanosilica particles to PMMA.[9,10] However, it can be concluded that the type of solvents used play an important role in their degradation behavior.

EDX analysis

As shown in Figure 9(a–c), the chemical analysis of the top and bottom layer of membrane film by EDX analysis showed that the top face contains the carbon, oxygen, and silicon elements. On the basis of this analysis, the hybrid membrane, which was prepared in THF solvent, has higher content of silicon than those prepared using toluene and DMF solvents. The reason for this has been explained in the previous section.

Mapping analysis

Figure 10(a–c) shows Si mapping of hybrid membranes. Based on these figures, the particles were uni-

formly dispersed throughout the polymer matrix with sizes below 100 nm, especially, for the membrane using THF solvent. This result showed that the hybrid membranes exhibit good miscibility between organic and inorganic phases.[23] The particles were well distributed and were of different sizes.

CONCLUSIONS

Hybrid organic–inorganic membranes, based on a PMMA polymer matrix and a SiO₂ component, have been successfully fabricated using the sol–gel method. In this study, it was found that transparent hybrid membrane could be only obtained from the one using THF as solvent. 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 SiO₂, whereas with DMF and Toluene solvents, no hydrogen bonding was present in both systems, which lead to opaque and white appearances. The water permeability measurements indicate that the membranes were within the ultrafiltration range. Type of solvent used affected the permeability values markedly. FTIR spectroscopy successfully uncovered all of the signature peaks that are characteristic of silicate structures in the membrane near-surface regions. More specifically, signs of Si—O—Si groups that are in cyclic and linear molecular substructures, as well as SiOH were present. SEM imaging of the membranes showed that the membranes have visible nanomicropores. From DSC analysis, the T_g value of the PMMA moieties in hybrid membranes was in the order H-15-Toluene < Pure PMMA < H-15-THF < H-15-DMF. Furthermore, from TGA analysis it was found that the hybrid membranes have higher thermal stability compared with that of pure PMMA. EDX and mapping analysis showed that the top face of hybrid contains the carbon, oxygen, and silicon elements and silica particles, which were uniformly dispersed throughout the polymer matrix.

References

1. Bescher, E.; Mackenzie, J. D. Mater Sci Eng 1998, C6, 145.
2. Huang, Z. H.; Qiu, K. Y. Polymer 1997, 38, 521.
3. Guizard, C.; Bac, A.; Barboiu, M.; Hovnanian, N. Separ Purif Technol 2001, 25, 167.
4. Lee, R. H.; Hsiue, G. H.; Jeng, R. J. J Appl Polym Sci 2001, 79, 1852.
5. Ahmad, Z.; Mark, J. E. Mater Sci Eng 1998, C6, 183.
6. Joly, C.; Goizet, S.; Schrotter, J. C.; Sanchez, J.; Escoubes, M. J Membr Sci 1997, 130, 63.
7. Nagasaki, Y.; Hashimoto, Y.; Kato, M.; Kimijima, T. J Membr Sci 1996, 110, 91.
8. Parvulescu, V.; Buhoci, L.; Roman, G.; Albu, B.; Popescu, G. Separ Purif Technol 2001, 25, 25.
9. Smaihi, M.; Jermoumi, T.; Marignan, J.; Noble, R. D. J Membr Sci 1996, 116, 211.
10. Kim, J. H.; Lee, Y. M. J Membr Sci 2001, 193, 209.
11. Sforca, M. L.; Yoshida, I. V. P.; Nunes, S. P. J Membr Sci 1999, 159, 197.
12. Hu, Q.; Marand, E.; Dhingra, S.; Fritsch, D.; Wen, J.; Wilkes, G. J Membr Sci 1997, 135, 65.
13. Kusakabe, K.; Ichiki, K.; Hayashi, J.; Maeda, H.; Morooka, S. J Membr Sci 1996, 115, 65.
14. Hibshman, C.; Cornelius, C. J.; Marand, E. J Membr Sci 2003, 211, 25.
15. Zimmerman, C. M.; Singh, A.; Koros, W. J. J Membr Sci 1997, 168, 39.
16. Young, S. K. Polymer 2002, 43, 6101.
17. Yu, Y. Y.; Chen, C. Y.; Chen, W. C. Polymer 2003, 44, 593.
18. Cho, J. W.; Sul, K. I. Polymer 2001, 42, 727.
19. Chan, C. K.; Peng, S. L.; Chu, I. M.; Ni, S. C. Polymer 2001, 42, 4189.
20. Huang, Z. H.; Qiu, K. Y. Polym Bull 1995, 35, 607.
21. Landry, C. J. T.; Coltrain, B. K.; Brady, B. K. Polymer 1992, 33, 1486.
22. Landry, C. J. T.; Coltrain, B. K.; Wesson, J. A.; Zumbulydis, N.; Lippert, J. L. Polymer 1992, 33, 1496.
23. Chiang, Chin-Lung; Ma, C. C. M. Eur Polym J 2002, 38, 2219.
24. Silveira, K. F.; Valéria, I.; Yoshida, P.; Nunes, S. P. Polymer 1995, 36, 1425.
25. Qiu, K. Y.; Wei, Y.; Jin, D.; Yang, C.; Kels, M. C. Mater Sci Eng 1998, C6, 91.
26. Wang, Y. T.; Chang, T. C.; Hong, Y. S.; Chen, H. B. Thermochim Acta 2003, 397, 219.
27. Chan, C. K.; Chu, I. M. Polymer 2001, 42, 6089.
28. Loy, D. A.; Shea, K. J. Chem Rev 1995, 95, 1431.
29. Klein, L. C. Annu Rev Mater Sci 1985, 15, 227.
30. Kenneth, A. M.; Payne, J. T. J Membr Sci 2000, 168, 39.
31. Judeinstein, P.; Sanchez, C. J Mater Chem 1996, 6, 511.
32. Pope, E. J. A.; Mackenzie, J. D. J Non-Cryst Solids 1986, 87, 185.
33. Zhu, Z. K.; Yang, Y.; Yin, J.; Qi, Z. N. J Appl Polym Sci 1999, 73, 2977.
34. Mulder, M. Basic Principles of Membrane Technology; Kluwer Academic: Netherland, 1991.
35. Kashiwagi, T.; Morgan, A. B.; Antonucci, J. M.; van Landingham, M. R.; Harris, R. H.; Awad, W. H.; Shields, J. R. J Appl Polym Sci 2002, 89, 2072.
36. Morgan, B.; Antonucci, J. M.; van Landingham, M. R.; Harris, R. H.; Kashiwagi, T. Polym Mater Sci Eng 2003, 83, 57.
37. Schrotter, J. C.; Smaihi, M.; Guizard, C. J Appl Polym Sci 1996, 61, 2137.
38. Huang, J. C.; Zhu, Z. K.; Yin, J.; Zhang, D. M.; Qian, X. F. J Appl Polym Sci 2001, 79, 794.
39. Van Krevelen, D. W. Polymer 1975, 16, 615.