ORIGINAL ARTICLE

Effect of sintering temperature on the morphology and mechanical properties of PTFE membranes as a base substrate for proton exchange membrane

Nor Aida Zubir[1] and Ahmad Fauzi Ismail[2]

Abstract

Zubir, N.A. and Ismail, A.F.

Effect of sintering temperature on the morphology and mechanical properties of PTFE membranes as a base substrate for proton exchange membrane

Songklanakarin J. Sci. Technol., 2002, 24(Suppl.) : 823-831

This paper reports the development of PTFE membranes as the base substrates for producing proton exchange membrane by using radiation-grafting technique. An aqueous dispersion of PTFE, which includes sodium benzoate, is cast in order to form suitable membranes. The casting was done by using a pneumatically controlled flat sheet membrane-casting machine. The membrane is then sintered to fuse the polymer particles and cooled. After cooling process, the salt crystals are leached from the membrane by dissolution in hot bath to leave a microporous structure, which is suitable for such uses as a filtration membrane or as a base substrate for radiation grafted membrane in PEMFC. The effects of sintering temperature on the membrane morphology and tensile strength were investigated at 350°C and 385°C by using scanning electron microscopy (SEM) and EX 20, respectively. The pore size and total void space are significantly smaller at higher sintering temperature employed with an average pore diameter of 11.78 nm. The tensile strength and tensile strain of sintered PTFE membrane at 385°C are approximately 19.02 ± 1.46 MPa and 351.04 ± 23.13 %, respectively. These results were indicated at 385°C, which represents significant improvements in tensile strength and tensile strain, which are nearly twice those at 350°C.

Key words : proton exchange membrane, sintering temperature, radiation-grafted membrane

---

[1]M.Sc. (Gas Engineering), Post graduate student, [2]Ph.D. (Chemical Engineering), Prof., Membrane Research Unit, Faculty of Chemical Engineering and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 Johor, Malaysia.

Corresponding e-mail : afauzi@utm.my

Received, 9 January 2003 Accepted, 2 July 2003

Membrane prepared by radiation-induced grafting is receiving increasing attention in the field of polymer and separation technology. This is due to its potential to substitute similar membranes prepared by conventional polymerization methods in various application of industrial interest such as pervaporation, dialysis, water electrolysers, sensors and proton exchange membrane fuel cells (PEMFCs) (Gupta and Scherer, 1993).

In the development of the alternative proton exchange membranes, modification of preformed polymers by grafting of chemical functionality is a versatile means of incorporating new functionalities and properties into the existing films or membranes (Holmberg *et al.*, 1998). Moreover, this technique shows a superior advantage where the difficulty of shaping the graft copolymer into a thin membrane of a uniform thickness could be circumvented by the possibility of starting the process with a thin film already having the shape of a membrane.

It is observed that the selection of a suitable polymeric membrane material for the radiation induced graft copolymerization is based on fluorine containing polymers. Fluoropolymers are chosen because of their superior thermal stability and radiation resistance. Thus, many fluoropolymers have been studied as potential proton exchange membranes substrates for grafting, including polytetrafluoroethylene (Nasef *et al.*, 2000-b, c), polytetrafluoroethylene-co-hexafluoropropylene (Büchi *et al.*, 1995; Gupta *et al.*, 1998; Nasef *et al.*, 2000-d, e), polytetrafluoroethylene-co-perfluorovinylether (Nasef and Saidi, 2000-a), polyethylene-alt-tetrafluoroethylene (Brack *et al.*, 2000), polyfluorovinylidene (Filnt ans Slade, 1997; Walsby *et al.*, 2001-b), polyvinylfluoride (Ostrovskii *et al.*, 1999; Vie *et al.*, 2002), polychlorotrifluoroethylene and copolymers thereof. The chemical structures of the base fluoropolymers used for grafting are shown in Table 1.

In the course of this study, polytetrafluoroethylene (PTFE) was selected as the precursor membrane material because of its satisfactory thermal, chemical and mechanical stability, despite its radiation sensitivity, that suited it better for more rigorous working environments. In addition, PTFE also has the advantage in terms of its widespread use as a commercial polymer (Hashida and Namio, 1989). These properties with its relative low cost and local availability, established PTFE the choice for use as a standard material for the fabrication of membranes. Not much study has been conducted in relation to the effect of sintering temperature on the membrane morphology and properties. Therefore, the objectives of present study are to provide a rapid process for forming PTFE membranes and to study the effects of sintering temperature on morphology and tensile strength of PTFE membranes as base substrates for producing proton exchange membrane by using radiation-grafting technique.

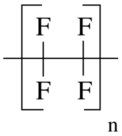
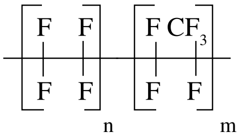
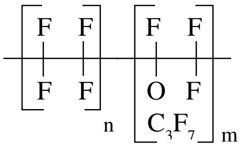
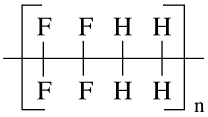
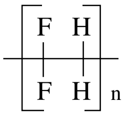
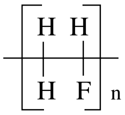
Experimental

Materials

Polytetrafluoroethylene (PTFE) polymer with the commercial name of “Teflon® PTFE 30 Aqueous Dispersion” was supplied by DuPont de Nemours (Japan). Because of the presence of surfactant in the polymer dispersion, it has a tendency to foam during mixing. This behavior must be obstructed in order to prevent the formation of the undesirable pinholes in the final PTFE membranes. Accordingly, an additive such as ethylene glycol of molecular weight 6207, supplied by Merck was added as a foam suppressant for the dispersion during mixing (Chao and Porter, 1980). Ethylene glycol also serves as a viscosity-increasing agent to assist casting process. Besides that, a salt, i.e. sodium benzoate of molecular weight 144.11, supplied by Riedel-de Haën, which acts as pore forming agent, was mixed with the foregoing casting solution. The salt used should include the following characteristics:

1) Sufficient solubility in water to be completely dissolved in the aqueous PTFE dispersion prior to formation into a sheet;
2) A propensity to grow dendritic crystals in the drying environment step;
3) An ability to grow a fine crystal size from a PTFE dispersion;

Table 1. Base fluoropolymers used for grafting

Fluoropolymers	**Abbreviation**	**Structure**
Poly(tetrafluoroethylene)	PTFE	 $-\left[\mathrm{CF_2-CF_2}\right]_n-$
Poly(tetrafluoroethylene-co-hexafluoropropylene)	FEP	 $-\left[\mathrm{CF_2-CF_2}\right]_n-\left[\mathrm{CF_2-CF(CF_3)}\right]_m-$
Poly(tetrafluoroethylene-co-perfluorovinylether)	PFA	 $-\left[\mathrm{CF_2-CF_2}\right]_n-\left[\mathrm{CF(OC_3F_7)-CF_2}\right]_m-$
Poly(ethylene-alt-tetrafluoroethylene)	ETFE	 $-\left[\mathrm{CF_2-CF_2-CH_2-CH_2}\right]_n-$
Poly(fluorovinylidene)	PVDF	 $-\left[\mathrm{CF_2-CH_2}\right]_n-$
Poly(vinylfluoride)	PVF	 $-\left[\mathrm{CH_2-CHF}\right]_n-$

4) Stability at the temperature of sintering step; a neutral or slightly alkaline pH in an aqueous dissociated state (to avoid precipitation of the PTFE particles).

The casting solution used in this study consists of 100 cc PTFE aqueous dispersion (polymer), 10 cc ethylene glycol (additive) and 25 gm sodium benzoate (salt) in the polymer-additive-salt mixture.

Preparation of PTFE membranes by using sintering technique

The PTFE flat sheet membranes were prepared according to the sintering process, as illustrated in Figure 1. The basic process includes casting, drying and salt crystallizing, polymer sintering, cooling and salt leaching.

The polymer solution was casted on a clean stainless steel plate at ambient temperature using a special fabricated pneumatically controlled flat sheet membrane-casting machine. The casting knife is used to evenly spread polymer solution across a plate. Basically, the casting knife consists of a steel blade, resting on two runners arranged to form a precise gap between the blade and plate. Depending on the desired final film thickness, casting knife with slit height ranging from 100µm – 200 µm were used.

The exposed surfaces of the wet casted membranes are dried in a vacuum oven at temp-

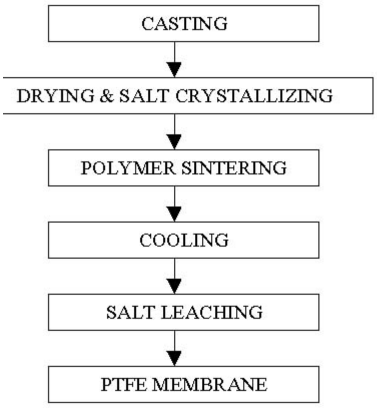


Figure 1. Process steps for the preparation of sintered PTFE membrane

erature of 30°C – 40°C in order to grow crystals of the dispersion salt, which are dispersed throughout the dried membranes. The rate of drying affects the permeation characteristic of the final product by modifying the type of salt growth and hence ultimate pore configuration (Chao and Porter, 1980).

After that, the dried membranes are sintered in a furnace to cause an interparticle bonding of the polymer to increase their structural strength. The membrane is then maintained at 385°C for 30 minutes to assure that essentially all portions of the membranes have reached the same temperature. Figure 2 shows the flow diagram of a method for sintering PTFE membrane process in accordance with the present study. Then the sintered membranes are permitted to cool, say, to room temperature. The rate of cooling will determine the crystallinity of the PTFE in the final products.

The salt crystals are leached from the cool membranes by immersion to a hot water bath for at least 24 hrs and then the ultimate bulk membrane structure is formed. Finally, the resulting membranes are then removed and being air-dried at room temperature.

Scanning electron microscopy

SEM has been found to be a reliable method for investigating general membrane morphology (Walsby, 2001-a). Membrane structure and dimensions were determined with a Philip XL-40 scanning electron microscope (SEM). The preparation of membrane samples was crucial. Cross sections of the membrane were obtained by freeze facturing the immersion of the sample in liquid nitrogen. PTFE membranes were mounted on aluminium disk with double-surface tape. The sample holder was then placed and evacuated in a sputter-coater with gold at a working voltage of 20 kV. The purpose of membrane coating with a thin layer of gold is to facilitate the transport of electrons from the electron beams that were not reflected or transformed to secondary electrons.

Mechanical properties

Dumb-bell-shaped specimens of 50 mm long with a neck of 28 mm and 4 mm wide (ASTM D882) were used. The measurements of tensile

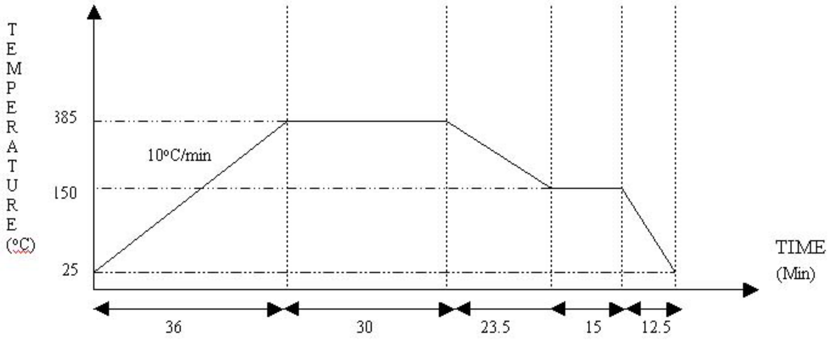


Figure 2. The sintering process flow diagram.

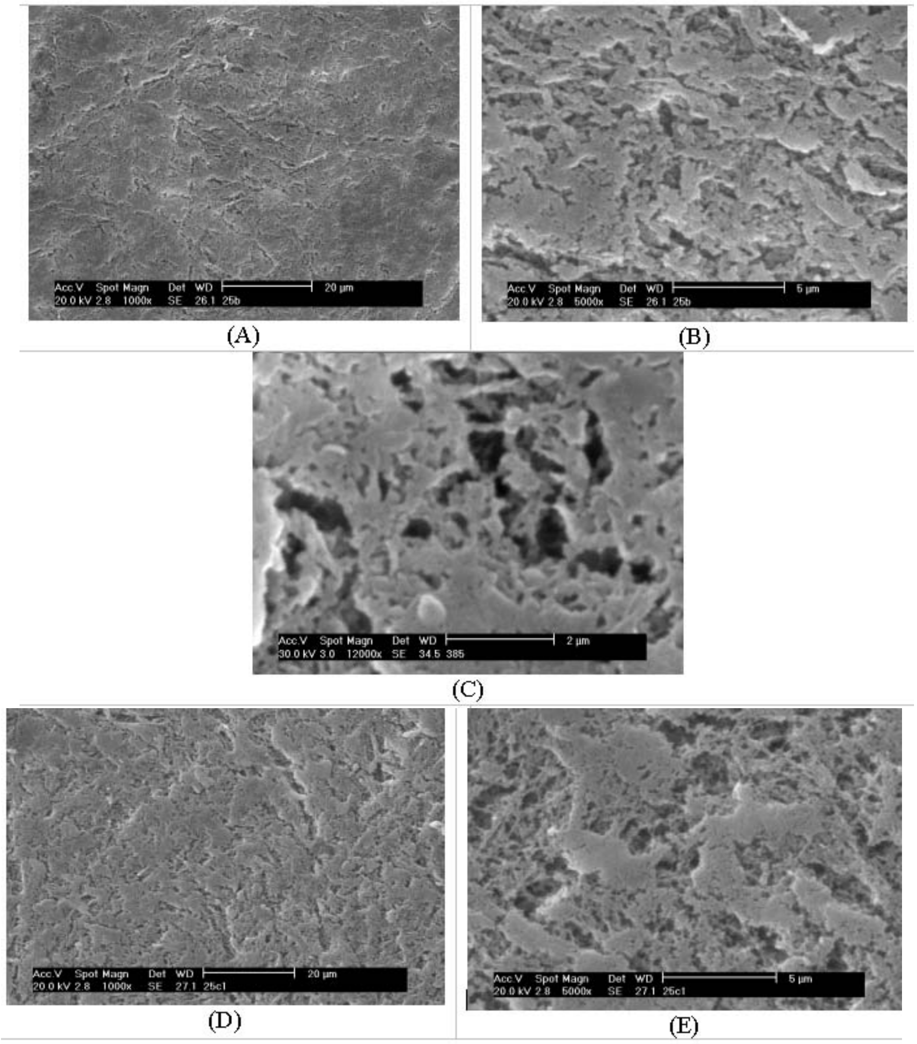
strength and elongation percent at break were recorded on an EZ 20 at room temperature. The crosshead speed was fixed at 50mm/min. A minimums of five specimens was tested for each sample.

Results and Discussion

Effects of sintering temperature on PTFE membrane morphology

The morphology of the top and bottom surface with the cross-section of PTFE membrane was observed by using scanning electron micrograph (SEM). Figure 3, shows the matte and porous top surface of the PTFE membrane which is the one that formed by exposure to the surrounding environment during drying and sintering processes. The lighter color comprises the solid portion of the membrane, while the darker comprises the pores or voids. This specific membrane composition consists of 25 grams of sodium benzoate, 10 ml ethylene glycol and 100 ml PTFE 30.

It is apparent in Figure 3 (C) that the pores are interconnected within the bulk of the mem-



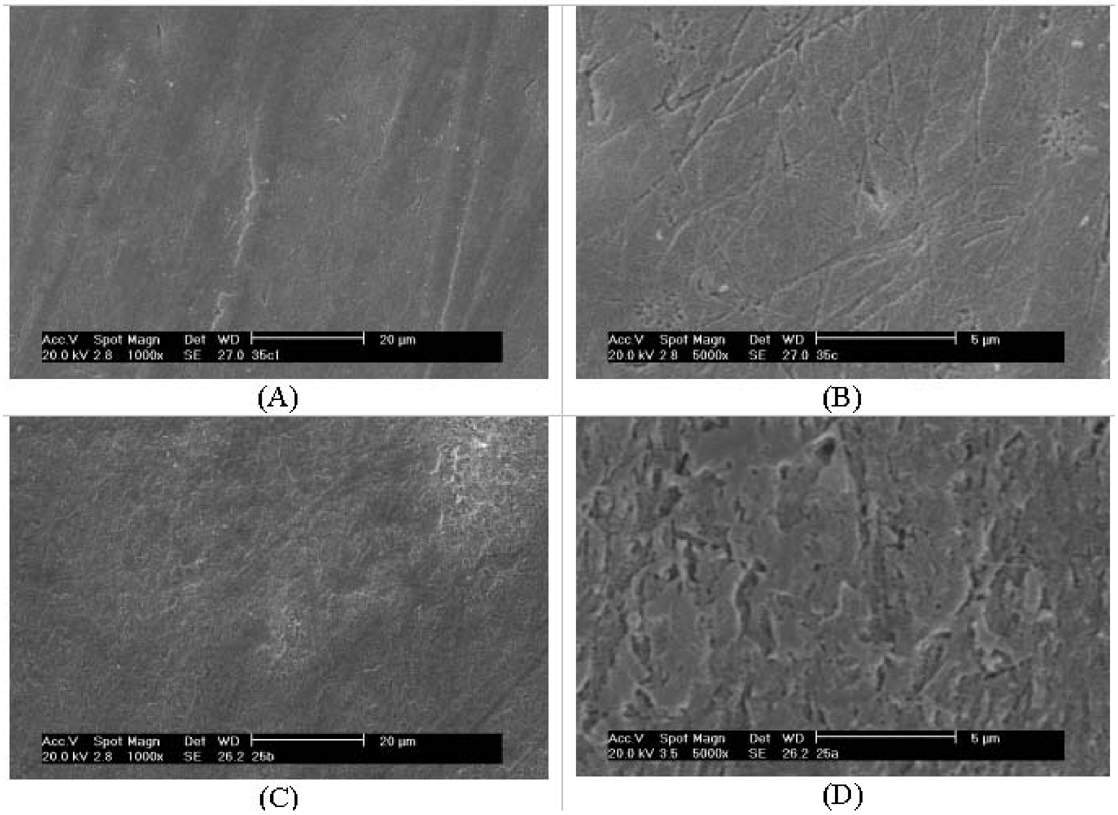
(A) (B) (C) (D) (E)

Figure 3. Scanning electron micrographs of top surface of PTFE membrane sintered at 385°C; A) at 1000 magnification; B) at 5000 magnification; C) at 12000 magnification and at 350°C; D) at 1000 magnification; E) at 5000 magnification.

brane and are interlaced and intertwined into a void network of intersecting shafts forming a matte and porous surface in a sponge-like configuration on the top surface of PTFE membrane (Chao and Porter, 1980). The morphological change in the membrane is clearly different between the sintering temperatures employed. At 385°C, the membrane surface is smoother than 350°C membrane surface. This is due to the shrinkage of the voids at the lateral and also throughout the membrane. Therefore finer form of voids will appear at the higher sintering temperature employed.

Due to the mechanism of crystal growth, essentially all of the pores are open to the rough matt surface of the membrane, so that essentially none of the salt is encapsulated by the PTFE polymer. Hence, this microporous membrane consists only the polymer without extraneous material. This condition can be explained as follows. Crystal growth occurs by evaporation of the water during the drying and salt crystallizing process to a sufficient extent that the salt becomes supersaturated in the remaining water. Such salt concentration occurs first at the surface of the membrane that exposed in the oven's condition. Crystallization proceeds from this surface supersaturated solution into the interior of the membrane. Then, all of the salt crystals of any size grow in the membrane are being exposed and diluted to water during the leaching process.

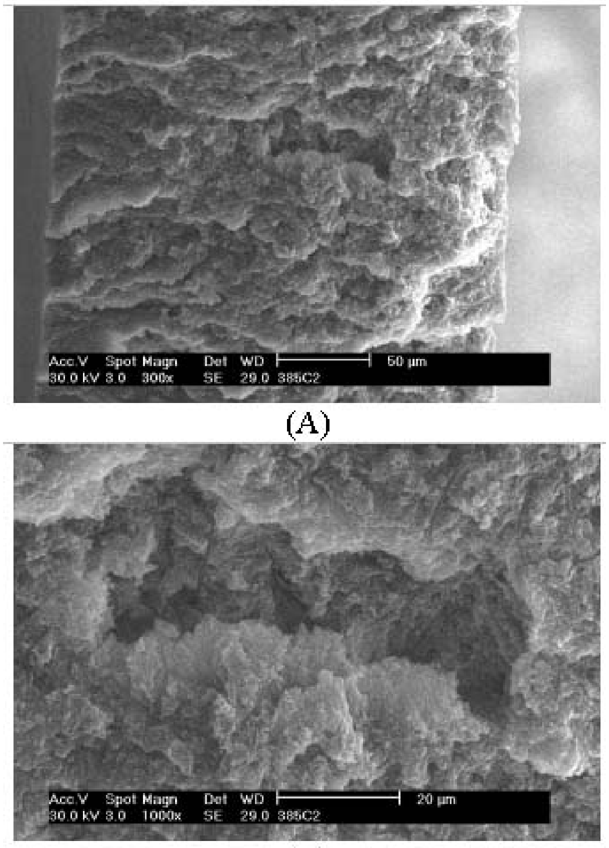
Figure 4 shows the morphologies of the bottom and unexposed of the PTFE membranes obtained by drawing at 385°C and 350°C, respectively. Smooth bottom membranes are clearly seen in the Figure 4 if were compared to the top



(A) (B)

(C) (D)

Figure 4. Scanning electron micrographs of bottom surface of PTFE membrane sintered at 385°C; A) at 1000 magnification; B) at 5000 magnification and at 350°C; C) at 1000 magnification; D) at 5000 magnification.



(A)

(B)

Figure 5. Scanning electron micrographs of the cross-section of PTFE membrane sintered at 385°C; A) at 300 magnification; B) at 1000 magnification.

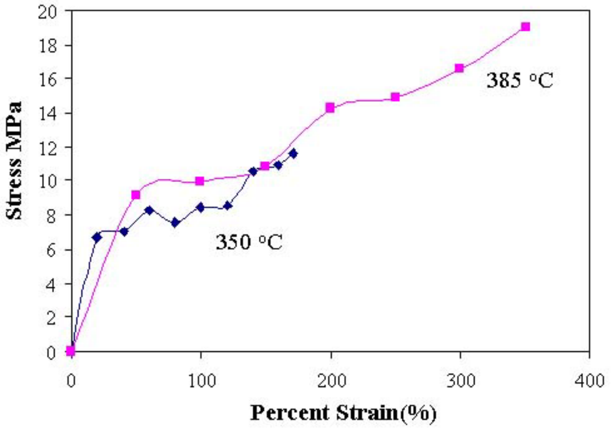


Figure 6. Stress - strain curves of the sintered PTFE membranes

surface of the PTFE membranes (Figure 3). Furthermore, it is obvious that the pore size and total void space is significantly smaller on the smooth bottom surface than on the rough matt top surface of the PTFE membrane. As mentioned above, the membrane surface is smoother at 385°C than as 350°C. We suppose that the void structure pattern (Figure 4-B and D) is essentially same as rodlike entities that observed by Hashida and Namio (1989) at the bottom surface of the membrane.

The cross-section of PTFE membrane structure is illustrated in Figure 5. The resulting membranes made by this technique are symmetric membranes (Figure 5-A) with a very irregular porous structure in a fingerlike configuration, as can be seen in Figure 5-B. It is assumed that the void space network on the top surface continues downwardly into the interior of the membrane forming intertwined pore paths. This provides a three-dimensional labyrinthic network or maze for passage of grafting monomer solutions to provide excellent degree of grafting formed in the membrane. By using the Dubinin-Radushkevich micro pore area method the total micro pore volume is 0.04033 cc/g with the average pore diameter is 11.78 nm acquired.

Effects of sintering temperature on tensile properties of PTFE membranes

Figure 6 shows the stress–strain curves of the PTFE membrane sintered at 385°C and 350°C, respectively. At 350°C, the PTFE membrane had a tensile strength of approximately 11.59 ± 1.50 MPa. Its initial Young's modulus was approximately 20478.00 ± 51.10 MPa and elongation was about 172.55 ± 25.42 %. Meanwhile, at higher sintering temperature of 385°C, the resultant PTFE membrane had a tensile strength of about 19.02 ± 1.46 MPa. The initial Young's modulus reduced to about 14177.00 ± 35.15 MPa, which is nearly twice of list of the PTFE membrane sintered at 350°C. The elongation was higher than the former, which is approximately 351.04 ± 23.13 %. The initial Young's modulus represents the stiffness of the material,

Table 2. Tensile properties of the sintered PTFE membranes

Sintering Temperature (°C)	Tensile Strength (MPa)	Tensile Strain (%)	Young's modulus (MPa)	Energy to break point (J)
350°C	11.59±1.50	172.55±25.42	20478.00±51.10	0.42±1.01
385°C	19.02±1.46	351.04±23.13	14177.00±35.15	1.29±0.59

that is, its resistance to elastic strain. Therefore, it is assumed that when this membrane was subjected to sintering process, a distinct improvement was detected in the tensile strength and strain, as well as the tensile toughness and ductility of the sintered membrane at 350°C compared with the sintered membrane at 385°C.

Lastly, Table 2 summarizes the data obtained from the tensile tests of the PTFE membranes sintered at 350°C and 385°C, respectively. These results indicate that a significant improvement in the tensile properties of the porous PTFE membranes was achieved by the increasing of the sintering temperature. It is believed that the matt and rough configuration of the microporous membrane formed of intertwined pores lends considerable structural strength when higher sintering temperature is employed. Furthermore, the crystallization and recrystallization of the PTFE polymer into the membranes are found and credited to the significant improvement on the mechanical performance of the resultant membranes.

Conclusion

We have successfully produced PTFE membranes by using sintering technique in accordance with the foregoing process. The results show that the morphology and mechanical properties of the membranes strongly depend on the sintering temperature employed. At higher sintering temperature, the resultant membranes showed better pore sizes configuration that served as a maze for passage of grafting monomer solutions to provide excellent degree of grafting formed in the membranes. A significant improvement on tensile properties is achieved through sintering the PTFE membranes at 385°C due to considerable structural strength changes, crystallization and recrystallization of the PTFE polymer into the membranes. Thus, the membranes produced are particularly useful to be used as the base substrates for radiation grafted membranes, which are employed in PEMFC or as separator in an electrolytic cell such as battery and also in a variety of other applications.

References

Brack, H.B., Buchrer, H.G., Bonorand, L. and Scherer, G.G. 2000. Grafting of pre-irradiated poly(Ethylene-Alt-Tetrafluoroethylene) films with styrene: Influence of base polymer film properties & processing parameters. J. Mater. Chem. 10. 1795 - 1803.

Büchi, F.N., Gupta, B., Haas, O. and Scherer, G.G. 1995. Study of radiation-grafted FEP-G-polystyrene membranes as polymer electrolyte in fuel cells. Electrochem. Acta. 40. 345 - 353.

Chao, K.C. and Porter, M.C. 1980. Method For Forming Microporous Fluorocarbon Polymer Sheet And Product. US Patent 4196070.

Filnt, S.D and Slade, R.C.T. 1997. Investigation of radiation-grafted PVDF-G-polystyrene-sulfonic-acid ion exchange membranes for use in hydrogen oxygen fuel cells. Solid State Ionics. 97. 299 - 307.

Gupta, B. and Scherer, G.G. 1993. Proton exchange membranes by radiation grafting of styrene onto FEP films. I. Thermal characteristics of copolymer Membranes. J. Appl. Polym. Sci. 50. 2129 - 2134.

Gupta, B., Scherer, G.G. and Highfield, J.G. 1998. Thermal stability of proton exchange membranes prepared by grafting of styrene into pre-irradited FEP films and the effect of crosslinking. Angew. Makromol. Chem. 256. 81 – 84.

Hashida, S. and Namio, H. 1989. Surface morphology and crystalline orientation of uniaxially drawn polytetrafluoroethylene films. J. Appl Polym Sci. 37**.** 2897 - 2906.

Holmberg, S., Näsman, J. A. and Sundholm, F. 1998. Synthesis and properties of sulfonated and crosslinked poly[(vinylidene fluoride)-graft-styrene] Membranes. Polym. Adv. Technol. 9. 121 - 127.

Nasef, M.M. and Saidi, H. 2000-a. Thermal degradation behaviour of radiation grafted FEP-G-polystyrene sulfonic acid membranes. Polym. degradation and stability. 70. 497 - 504.

Nasef, M.M., Saidi, H., Dessouki, A.M. and El-Nesr, E.M. 2000-b. Radiation-induced grafting of styrene onto poly(tetrafluoroethylene) (PTFE) films. I. Effect of grafting conditions and properties of the grafted films. Polym. Int. 49. 399 – 406.

Nasef, M.M., Saidi, H., Nor, H. and Ooi, M.F. 2000-c. Radiation-induced grafting of styrene onto poly(tetrafluoroethylene) films. II. Properties of the grafted and sulfonated membranes. Polym. Int. 49. 1572 - 1579.

Nasef, M.M., Saidi, H. and Nor, H. 2000-d. Proton exchange membranes prepared by simultaneous radiation grafting of styrene onto poly(tetrafluoroethylene-co-Hexafluoropropylene) flims. I. Effect of grafting conditions. J. Appl Polym Sci. 76. 220 - 227.

Nasef, M.M., Saidi, H., Nor, H. and Ooi, M.F. 2000-e. Proton exchange membranes prepared by simultaneous radiation grafting of styrene onto poly(tetrafluoroethylene-co-hexafluoropropylene) flims. II. Properties of sulfonated membranes. J. Appl Polym Sci. 78. 2443 - 2453.

Ostrovskii, D., Paronen, M., Sundholm, F. and Torell, L.M. 1999. State of water in sulfonated poly-(vinyl fluoride) membranes: An FTIR study. Solid State Ionics. 116. 301 - 310.

Vie, P., Paronen, M., Stromgard, M., Rauhala, E. and Sundholm, F. 2002. Fuel cell performance of proton irradiated and subsequently sulfonated poly(vinyl fluoride) membranes. J. Membrane Sci. 204. 295 - 301.

Walsby, N. 2001-a. Preparation and Characterization of Radiation-grafted Membranes for Fuel Cells. Helsinki University of Technology: Msc. Thesis. ISBN 952-91-3646-3.

Walsby, N., Paronen, M., Juhanoja, J. and Sundhoulm, F. 2001-b. Sulfonation of styrene-grafted poly-(vinylidene fluoride) films. J. Appl Polym Sci. 81. 1572 - 1580.