Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.781727

51 (2013) 3814–3820
May

Taylor & Francis
Taylor & Francis Group

Preparation and properties of PVDF/PPTA blend membranes

Jiaojiao Dong*, Dongqing Liu*, Yufeng Zhang, Cong Wang

State Key Laboratory of Hollow Fiber Membrane Material and Membrane Process, State Key Laboratory of Hollow Fiber Membrane Science and Membrane Process, Tianjin Polytechnic University, Tianjin 300387, China
Email: djj87101@163.com

Received 8 August 2012; Accepted 25 February 2013

ABSTRACT

In this article, the interweave polymer structure of the polyvinylidene fluoride/poly (p–phenylene terephtalamide) (PVDF/PPTA) was prepared and the mass ratio of m (PVDF)/m (PPTA) was 2:1. The blend membrane was obtained by phase inversion method. The effects of the preparation parameters were systematically investigated, such as the component of coagulation bath, addictive content, and the concentration of polymer on the performance of PVDF/PPTA blend membrane. The structure and properties of the blend membranes were examined using scanning electron microscope; fourier transform infrared spectroscopy; and contact angle meter. The permeation performance was characterized by measuring pure water flux and the retention of bovine serum albumin and poly (ethylene glycol) of different molecular weight. Meanwhile, porosity, average pore size, and fouling resistance performance were also estimated. The experiment results confirmed that PVDF/PPTA blend membrane displays enhanced hydrophilicity and fouling resistance performance compared with neat PVDF membrane and have improved pure water flux and protein rejection ratio.

Keywords: PVDF/PPTA blend membrane; Flux; Retention; Permeability; Morphology

1. Introduction

Blending is often used to improve the performance of polymeric materials. In this experiment, poly (p-phenylene terephtalamide) (PPTA) and polyvinylidene fluoride (PVDF) were selected as the blending components. PPTA was synthesized by low-temperature polycondensation of p-phenylenediamine (PPD) and terephthaloyl dichloride (TPC) in mixed solvents of N-methyl pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc). Owing to the extreme rigidity of the molecule, PPTA has excellent mechanical properties, thermostability, and has been extensively used in ocean engineering, space navigation, military, and defense areas. But PPTA is difficult to dissolve and melt unless under special conditions and requires a very high level of equipment and production process [1,2]. Therefore, the material is poor in processing performance.

As one of excellent polymer material, PVDF is a semi-crystalline polymer and widely used in separation membrane material, which not only has good chemical resistance, thermal stability, and flexibility, but also has other special properties, such as piezoelectricity and dielectric properties [3,4]. However,

---

*Corresponding author.

Presented at the 2012 Qingdao International Desalination Conference June 26–29, 2012, Qingdao, China

the hydrophobicity of PVDF is a major factor in limiting its scope of application. In practice, protein absorption and deposition of PVDF membrane surface is easy to produce and causes serious membrane fouling which gives rise to rapid decline of permeability. Meanwhile, the water treatment process of membrane requires a higher pressure leading to reduce the lifespan of membrane components and increase the cost [5,6].

However, a blend of PPTA and PVDF may overcome the machining problems of PPTA and improve the hydrophilicity of PVDF.

In this study, PVDF/PPTA blend membranes were prepared using phase inversion method. The morphology and properties of these membranes were investigated by using scanning electron microscope (SEM), contact angle goniometer, and Fourier transform infrared spectroscopy (FTIR)

2. Experimental

2.1. Materials

PVDF (FR904) powder was obtained from the Shanghai San Ai Fu Co. Ltd. (China) and dried in the vacuum oven for approximately 6 h at 80℃ to remove its water content. PPD and TPC were used to synthesize PPTA; the solvent N,N-DMAc (>99%, reagent) and NMP (>99%, reagent) were purchased from Tianjin KeMiOu Chemical Reagent Co. Ltd. Anhydrous $CaCl_2$, ethanol, bovine serum albumin (BSA), and polyethylene glycol (PEG) 6,000, 20,000 were obtained from the Tianjin Guang Fu, respectively.

2.2. Preparation of PVDF/PPTA blend membrane

The membranes were prepared by the phase inversion method. The casting solution was prepared by dissolving PVDF, PPD, and TPC polymers in mixed solvents of NMP and DMAc according to a certain ratio (NMP/DMAC = 3:1) and adding anhydrous $CaCl_2$ as cosolvent. The PPTA was formed by the low-temperature solution polymerization of PPD and TPC. Then, the homogeneous polymer solution was kept in a vacuum oven at 60℃ to remove air bubbles. The solution was poured and cast on glass plates with a homemade casting knife. The membrane was immediately moved to the coagulation bath for immersion at 25℃ without any evaporation. The prepared membranes were washed and stored in pure water for at least 1 day to completely wipe out the residual solvents and additives and then kept in deionized water before testing.

2.3. Membrane characterization

2.3.1. Scanning electron microscopy (SEM)

The surface and cross-section morphologies of PVDF/PPTA blend membranes were inspected by SEM (JEOL Model JSM-6,360 LV, Japan) with image acquisition via a digital camera connected to the microscope.

2.3.2. Permeation flux (J) and rejection (R) of PVDF/PPTA blend membranes

The pure water permeability of blend membrane was measured with a cross-flow filtration system. The blend membrane was previously compressed with pure water for 30 min at 0.1 Mpa to obtain a steady value, and then the rejection was tested using a 200 ppm PEG solution with a molecular weight distribution from 6,000 to 20,000 and BSA aqueous solution. The concentration of PEG and BSA was determined by ultraviolet absorption (UV Shimadzu UV-2,450) at $\lambda_{\max}$ of 595 nm. Pure water flux (J_w) of the membrane was calculated using the following equation:

$$J_W = \frac{Q}{A \times \Delta t}$$

where Q was the quantity of permeated water (L); t was the permeation time (h) and A was the membrane area (m^2).

The rejection was determined by the following equation:

$$R = \left(1 - \frac{C_P}{C_f}\right) \times 100\%$$

where C_P was the concentration of permeate solution, C_f was the concentration of feed solution.

2.3.3. Contact angle, porosity and the mean pore size

The water contact angle measurement is a common method to estimate the hydrophilicity of membrane. In this study, static contact angles of pure PVDF and blend membranes surface were investigated by an automated contact angle goniometer equipped with video capture and the value was observed after 20 s at room temperature. For each membrane sample, five measurements from various positions of the surface were done to calculate the average value.

The porosity of the fabricated membrane was measured in the method dry/wet weight. The membrane was immersed into water before the removal of excess water of the membrane surface by filter paper. Then, the same sample was dried in an oven at 60℃. The porosity was calculated using the following equation:

$$\text{Porosity } (\%) = \frac{W_1 - W_2}{\rho(\text{water}) \times v}$$

where W_1 and W_2 are the weights of the wet and dry membrane, respectively, ρ(water) is the density of pure water at 25℃, and V is the apparent volume of the membrane.

The mean pore size r_m can be acquired as follows:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q_T}{\varepsilon \times A \times \Delta P}}$$

where ϵ is porosity, l is the membrane thickness (m), Q_t is the volume of the permeate water per unit time (m^3/h), A is the effective area of the membrane (m^2), and ΔP is the measuring pressure (0.1 MPa).

2.3.4. FTIR analysis

FTIR spectra were obtained on a spectrometer TENSOR37, which were collected in the wave number range of 3,700–500 cm^{-1}.

3. Results and discussion

3.1. FT-IR characterization of PVDF/PPTA blend membrane

The PPTA was synthesized by low-temperature solution polymerization of PPD and TPC. The resulting material was characterized with FTIR-ATR spectroscopy (Fig. 1). The stretching vibration at 3,312.32 cm^{-1} was originated from the N–H, and the presence of adsorption at 1,646.82 cm^{-1} was assigned to the carbonyl group of the first band in the acid amide; the strong adsorption at 1,545.38 cm^{-1} and 1,513.92 cm^{-1} were associated with the N–H bend vibration and the C–N stretching vibration of the second band in the acid amide. The third band adsorption of the acid amide was at 1,258.66 cm^{-1}, which was caused by coupling vibration of the N–H and C–N groups, and the adsorption at 824.68 cm^{-1} was associated with the substituted benzene ring. These adsorptions indicated the successful synthesized reaction of the PPTA.

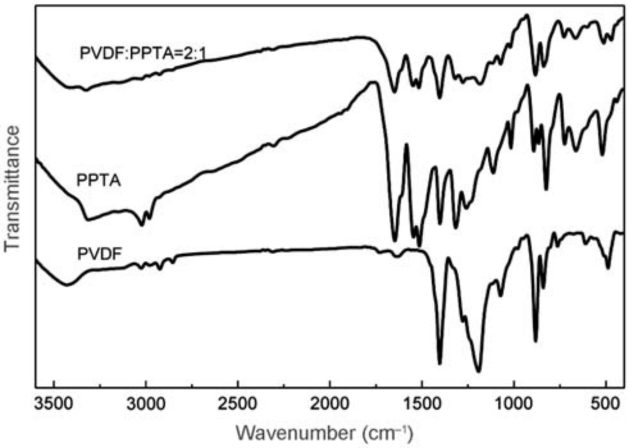

Fig. 1. FTIR spectra of PVDF/PPTA blend membrane, pure PVDF and pure PPTA.

The N–H stretching vibration at 3,312.32 cm^{-1}, C=O adsorption at 1,646.82 cm^{-1}, and N–H stretching vibration at 1545.38 cm^{-1} become weaker and these vibration widths become narrow after blending with PVDF and PPTA. This is because the hydrogen bond between N–H and C=O vibration intensity becomes stronger and because of low down stretching vibration frequency of N–H and C=O. In contrast to the PPTA, there is a strong absorption peak at 1,184.05 cm^{-1} *I* of the blend membrane, which is the C–F stretching vibration. And there are also three characteristic frequencies at 883, 1,072, and 1,403 cm^{-1} from the C–F radical bond. All these adsorptions prove that the PPTA and PVDF have good compatibility; they can form a macrohomogeneous system after blending. But in contrast to PVDF and PPTA, all the wavelength of the characteristic peaks and vibration intensity have minor changes in the blend membrane, which illustrate that there are molecular interactions between PPTA and PVDF.

3.2. Effects of PVDF/PPTA concentrations in dope solutions

Several species of blend membranes were prepared in order to investigate the effects of PVDF/PPTA concentrations. The weight ratio of PVDF/PPTA was kept at 2:1, while the total weight of PVDF and PPTA was varied.

The compositions and characteristics of blend membranes are listed in Table 1. The addition of PPTA may enhance the hydrophilic property of PVDF membrane, the significant decrease in water drop contact angle with blended PPTA in cast solution. Meanwhile, with an increase in PVDF/PPTA concentration from 9 to 18 wt.%, the contact angle of blend membrane slightly increased from 60.36° to 74.68°, but it was still smaller than PVDF membrane (88.03°), porosity, and mean pore size diminishingly.

The performance of PVDF/PPTA blend membrane with different concentrations is shown in Fig. 2 and in order to evaluate the fouling resistance performance

Table 1
Compositions and characteristics of PVDF/PPTA blend membranes

Samples	Solid content (%)	Dope solution (wt.%) (PVDF/PPTA/$CaCl_2$/NMP-DMAc)	Porosity (%)	Mean pore size (nm)	Contact angle (°)
M-1	12	12/0/2/83	68.81	226	88.03
M-2	9	6/3/2/89	49.82	345	64.36
M-3	12	8/4/2/86	43.16	337	66.15
M-4	15	10/5/2/83	41.73	331	74.39
M-5	18	12/6/2/80	38.41	321	78.68

of PVDF/PPTA blend membrane, BSA (Mw = 67,000), PEG6000 (Mw = 6,000), and PEG20000 (Mw = 20,000) were chosen as solutes. This figure shows that the pure water flux decreases while the rejection ratio of PEG and BSA increase with PVDF/PPTA concentration increase. This is because the viscosity of casting solution and film thickness improved. In general, the higher viscosity enhanced the mass transfer resistance between solvent and nonsolvent during the process of phase separation; so higher the polymer content, lower the precipitation rate, and the surface of the film is more dense, while adding film thickness leads to the higher resistance in membrane filtration. Therefore, the PVDF/PPTA blend membranes have a good antifouling performance.

The effect of PVDF/PPTA concentrations on morphology of the modified membrane is shown by SEM images in Fig. 3. In the above analysis, the denser surface layer of blend membrane was observed with the increase in polymer concentrations of the casting solution. Meanwhile, the film of average size and porosity were gradually reduced. Compared to the cross-section of blend membrane, M-2 and M-3 possess a macroporous structure; there was no obvious distinction of finger-like holes and sponge-like holes when the polymer concentration was low. This is due to the casting solution contact with the water instantly, which led to the phase separation to occur extremely quickly, almost taking place simultaneously in the skin layer and the internal layer. However, the finger-like voids gradually developed in the cross-section when the concentration of polymer increased to 15 wt.% (M-3 and M-4). But, the existence of a higher polymer concentration induced phase inversion is not possible at the same time. The surface layer immediately contacted with the water; so, the phase separation appeared rapidly and the finger-like voids were formed, while the sponge-like voids were generated inside the blend membrane due to the phase separation delay in the inner layer. Hence, the more dense membrane structure may be responsible for the increase in the retention rate and the decrease in the pure water flux.

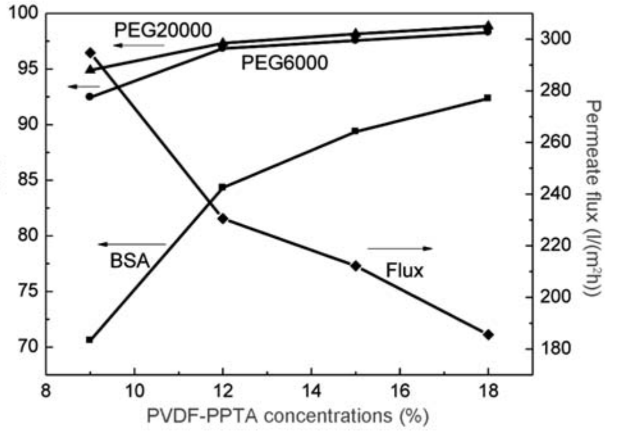

Fig. 2. Pure water flux and retention rate for PPTA/PVDF blend membranes with different polymer concentrations.

3.3. Effects of additive in dope solutions

Different concentrations $CaCl_2$ particles (2, 4, and 6%) of polymer dopes consisting of NMP/DMAc and PVDF/PPTA (18%, weight) were prepared. The membrane characterization, such as SEM photographs, permeation flux (J), and porosity have been conducted. Table 2 indicates that all the membranes to which $CaCl_2$ was added had high permeation flux and an increase of the $CaCl_2$ concentration led to an increase in the water permeate flux. The effect of $CaCl_2$ on water fluxes is interpreted as follows.

Some $CaCl_2$ particles could be lost in the phase separation process, leaving pores behind, due to the fact that they were easy to dissolve in water. As a result, the surface porosity of the blend membrane increased as the content of $CaCl_2$ improved, thereby further affecting the pure water flux of the membrane. Therefore, the enhancement in pure water flux resulted from the growing amount of $CaCl_2$ particles in the casting solution. However, the blend membrane is made up of more amounts $CaCl_2$ particles, causing reunited phenomena; so, the pure water flux cannot

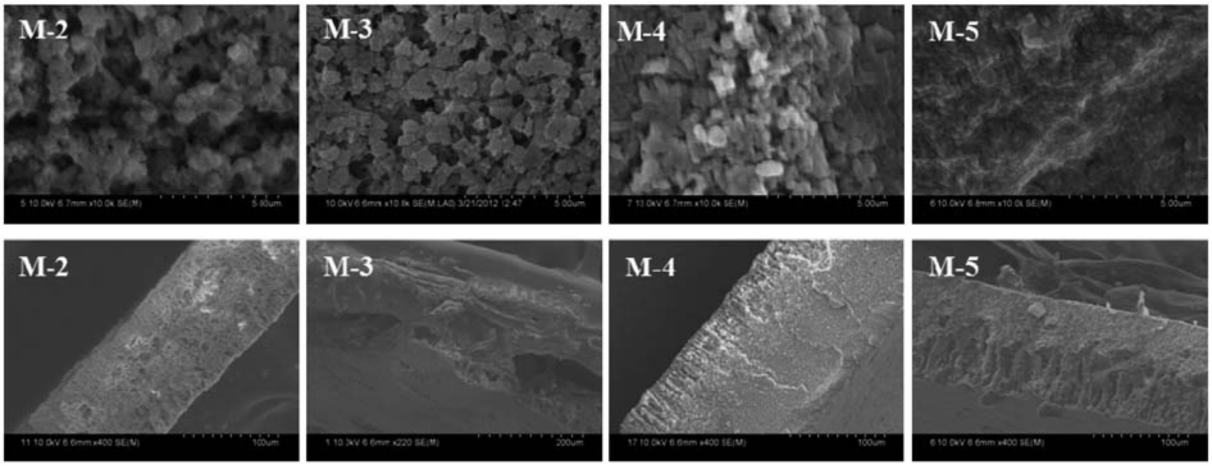

Fig. 3. Membrane morphologies of PVDF/PPTA blend membrane: M-2(9%), M-3(12%), M-4(15%), and M-5(18%).

Table 2
Effect of different $CaCl_2$ content on membrane performance

Samples	M-5a	M-5b	M-5c
Additive content	2%	4%	6%
Porosity (%)	38.41	43.37	49.52
Mean pore size (nm)	321	311	288
Water flux (L/m^2 h)	185.579	198.248	202.893

be more increased. Considering the economy and practicability, 2% of $CaCl_2$ particles are more appropriate.

3.4. Effects of coagulation bath composition

Coagulation bath composition is one of the key factors in determining the exchange rate of solvent and coagulation bath via immersion precipitation process; thus, coagulation medium have important influence on pore structure and performance of PPTA/PVDF blend membranes.

In this section, the effect of coagulation bath composition on the membrane structure and performance were investigated using 10 wt.% DMAc/water mixture, 10 wt.% ethanol/water mixture, and 10 wt.% NaCl/water mixture, while the concentration of polymer was kept constant at 12%, and the coagulation bath temperature is maintained at 25℃. The porosity, mean pore size, and contact angle of the different membranes are given in Table 3. The surface and cross-section morphologies of these three blend membranes are shown in Fig. 4.

Compared with the SEM photograph, it can be found that the presence of ethanol as the coagulation medium leads to irregular crack holes on the membrane surface and the formation of membrane with sponge-like voids. So the blend membrane has high porosity and pure water flux. It is because water is a strong nonsolvent that often gives rise to rapid liquid–liquid demixing process; asymmetric membrane structure consisting of finger-like voids could be generated, while the employment of solvent or weak nonsolvent in the coagulation bath may reduce the mass transfer speed between solvent and coagulation bath, which eventually results in the formation of sponge-like structure. It is well known that ethanol acts as a weak nonsolvent; thus, the employment of ethanol delayed the speed of polymer precipitation favored by the formation of PVDF/PPTA blend membrane with sponge-like structures.

However, the finger-like structures appeared when 10 wt% DMAc and NaCl were used as internal

Table 3
Effect of coagulation bath composition on membrane performance

Samples	M-3a	M-3b	M-3c
Coagulating bath	90%water/10%DMAc	90%water/10%ethanol	90%water/10%NaCl
Porosity	47.86%	43.16%	41.75%
Mean pore size	314 nm	324 nm	308 nm
Contact angle	70.12°	66.15°	65.57°

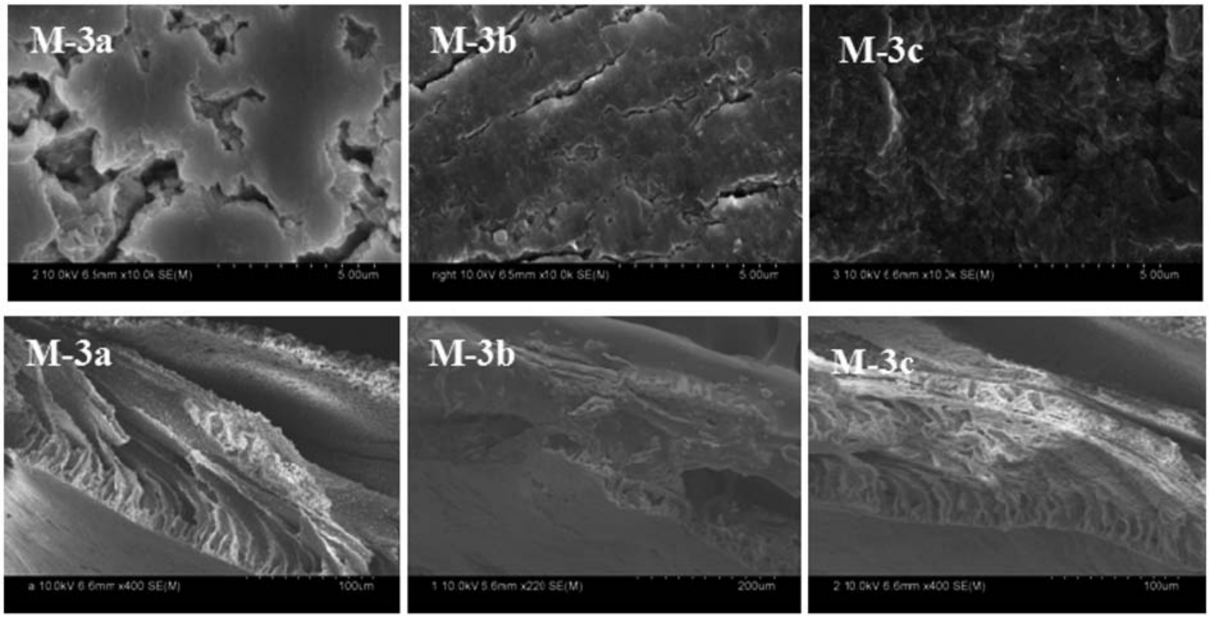

Fig. 4. SEM images of top surface (left) and cross-section (right) of M-3 with different coagulation bath composition: M-3a (DMAc/water), M-3b (ethanol/water), and M-3c (NaCl/water).

coagulant, respectively, and a dense surface of membrane was formed in the cross-section, which was immersed by using NaCl/water bath as shown in Fig. 4 (M-3c). This will cause a reduction in the porosity and water flux of membrane. The same conclusion can be obtained from Table 3. It can be seen that the membrane porosity revealed a minimum value when 10 wt% NaCl was added into the coagulation bath, while the water contact angles of the membranes show that coagulation bath composition may slightly affect the contact angle value.

Fig. 5 shows that the presence of NaCl as the coagulant medium yielded a relatively lower water flux compared to DMAc/water coagulant and ethanol/water coagulant. The addition of NaCl into the water bath may induce delayed phase separation, and the polymer chains have time to adjust the structure, forming a close membrane surface.

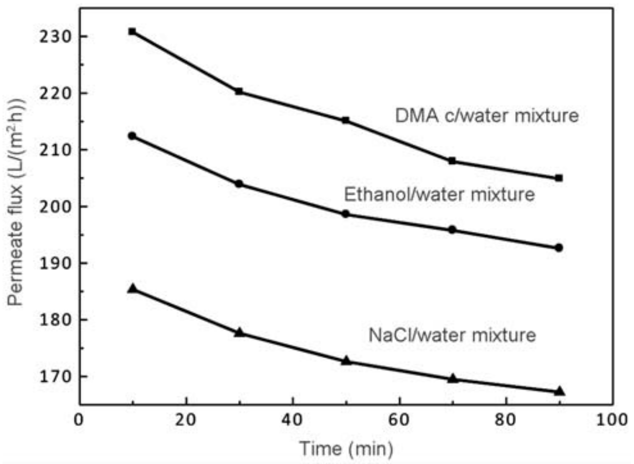

Fig. 5. The pure water flux for M-3 with different coagulant medium.

4. Conclusions

The PVDF/PPTA blend membranes with excellent performance were successfully synthesized by phase inversion process, which cause a porous structure of the membrane surface. The results of this study demonstrate that the membranes with different polymer concentrations have different morphologies and performances. The increasing concentration of PPTA/PVDF resulted in the formation of membranes with lower pure water flux and higher rejection of BSA, PEG6000, and PEG20000 solution, so the PVDF/PPTA blend membrane was provided with favorable antifouling properties. The addition of $CaCl_2$ particles could affect membrane pore sizes and porosity, and the pure water permeation flux increased with more use of $CaCl_2$ particles as an additive in casting solutions. Based on the experimental results, the employments of DMAc and ethanol in the coagulation bath have higher porosity and mean pore sizes than NaCl/water bath. Meanwhile, the addition of NaCl into water bath could generate a denser skin layer of blend membrane, while the performance property would be reduced.

Acknowledgments

The study was supported by the China High-Tech R and D Program (863 Program) No. 2012AA03A602.

References

[1] Y.-P. Wang, X.-H. Gao, R.-M. Wang, H.-G. Liu, C. Yang, Y.-B. Xiong, Effect of functionalized montmorillonite addition on the thermal properties and ionic conductivity of PVDF-PEG polymer electrolyte, React. Funct. Polym. 68 (2008) 1170–1177.

[2] F. Liu, N. Awanis Hashim, Y. Liu, M.R. Moghareh Abed, K. Li, Progress in the production and modification of PVDF membranes, J. Membr. Sci. 375 (2011) 1–27.

[3] N. Awanis Hashim, Fu Liu, K. Li, A simplified method for preparation of hydrophilic PVDF membranes from an amphiphilic graft copolymer, J. Membr. Sci. 345 (2009) 134–141.

[4] A. Bottino, G. Capannelli, A. Comite, Novel porous membranes from chemically modified poly(vinylidene fluoride), J. Membr. Sci. 273 (2006) 20–24.

[5] X. Flambard, S. Bourbigot, R. Kozlowski, M. Muzyczek, B. Mieleniak, M. Ferreira, B. Vermeulen, F. Poutch, Progress in safety, flame retardant textiles and flexible fire barriers for seats in transportation, Polym. Degrad. Stab. 88 (2005) 98–105.

[6] X. Flambard, S. Bourbigot, M. Ferreira, B. Vermeulen, F. Poutch, Wool/para-aramid fibres blended in spun yarns as heat and fire resistant fabrics, Polym. Degrad. Stab. 77 (2002) 279–284.