Research Article

Weiye Li, Zhihong Chang*, Liming Lin, and Xiaoyan Xu

Effect of montmorillonite on PEBAX® 1074-based mixed matrix membranes to be used in humidifiers in proton exchange membrane fuel cells<https://doi.org/10.1515/epoly-2020-0022>

received February 08, 2020; accepted March 21, 2020

Abstract: To meet the increasing requirements of membrane humidification in proton exchange membrane fuel cells (PEMFCs), a series of montmorillonite (MMT)/PEBAX® 1074 mixed matrix membranes (MMMs) were fabricated using the solvent casting method. Pristine MMT and poly(oxyalkylene)amine (APOP)-modified MMT were added as the filler. Using the XRD, FT-IR, SEM, and TEM, the morphology and chemical structure of MMT during modification were investigated. Using the tests of water vapor permeability, air permeability, water contact angle, and crystallinity, the effects of montmorillonite on membrane properties were investigated. The results showed that surface hydrophilicity and crystallinity of MMMs increased as the MMT content increases, which leads to higher vapor permeability and selectivity than the pure PEBAX® 1074 membrane. After modification, APOP-MMT/PEBAX® 1074 MMMs showed better performance in vapor permeability and vapor/air selectivity. The best selectivity was 1.7×10^5 , which is three times higher than that of pure PEBAX® 1074 membrane.

Keywords: mixed matrix membrane, membrane humidifier, vapor permeability, PEBAX® 1074, montmorillonite

1 Introduction

Electricity is essential to the development of mankind in the new millennium, in which fuel cells are the strategically electrochemical device to convert the chemical energy of fuels effectively and directly into electricity.

Among these fuel cells, proton exchange membrane fuel cells (PEMFCs) are considered to be one of the most desirable power sources for transportation and portable equipment due to their high power density, high reliability, and low operating temperature (1). However, the major hurdle to PEMFC's development is reaching a durability of 5,000 h recommended by the US Department of Energy. Gas humidification in the PEMFC system is a necessary method to ensure the best performance as well as long-term stability (2,3). The humidification of air is achieved by the membrane humidifier and utilizing stack cathode exhaust for humidification can significantly decrease the system complexity (4,5).

The pervaporation membrane is a key component of membrane humidifier, which needs to have good vapor permeability and low air permeability (6). Nafion®-based membranes are usually used for membrane humidifiers for their high permeability and selectivity of water (7,8). However, the price of Nafion®-based membranes is high. By adding inorganic hydrophilic materials into Nafion® membrane, better water uptake performance can be obtained (9–13). According to the permeation mechanism of gas through dense membranes, the vapor permeation in the membrane also can be divided into three steps: adsorption, diffusion, and desorption (14). Such improvement on water uptake of the membrane may decrease the desorption rate of water in the membrane. These modifications still cannot help the membrane for humidifier improving its vapor permeability, and the price of the membrane is still high. Therefore, many studies have focused on developing inexpensive polymer-based membranes having a good performance. Samimi et al. (15) constructed porous polyethersulfone, polysulfone, and mixed polymer with nanoparticle TiO₂ membranes using the wet-inversion method; the water flux of the membrane was in the range of 0.16–0.22 L/m² h. Ramya et al. (16) studied a polytetrafluoroethylene porous membrane-based humidifier; the humidification performance is comparable to the bubble humidifier, but the membrane has a high air permeability of 12 L/cm² min. Jesswein et al. (17)

* Corresponding author: Zhihong Chang, Department of Polymeric Materials, School of Materials Science and Engineering, Tongji University, Shanghai 200092, China, e-mail: changzh@tongji.edu.cn, tel: +86 21 69580143, fax: +86 21 69580143

Weiye Li, Liming Lin, Xiaoyan Xu: Department of Polymeric Materials, School of Materials Science and Engineering, Tongji University, Shanghai 200092, China

fabricated a series of polyvinylidene fluoride (PVDF) hollow fiber membrane and coated with polyvinyl acetate (PVA) layer, $\text{H}_2\text{O}/\text{N}_2$ selectivity improved as coating thickness increases and reached a maximum of 289 at $1.75\ \mu\text{m}$ coating thickness. Borduin *et al.* (18) investigated foamed polyethersulfone–zeolite porous membranes; the foamed membrane had high vapor permeability close to Nafion[®], but the gas permeability also increased greatly. Most studies have focused on building a porous structure to improve the permeability. However, the gas permeability also increased due to the porous structure, which is bad for the membrane to block exhausted gas. Therefore, it is of great value to improve the vapor permeability without increasing the gas permeability of the membrane.

The selection of polymer matrix material is essential for the membrane. A polymer with higher hydrophilicity leads to a concentration polarization phenomenon downstream to the membrane. However, a polymer with poor hydrophilicity has poor penetration rate. Therefore, choosing a matrix material for the humidifier membranes largely depends on finding the proper hydrophilicity of the polymer. PEBAX[®] is a series of polyethylene oxide (PEO)-based block copolymer. The crystalline amide block acts as an impermeable phase and provides mechanical strength. The polyether block serves as the permeable phase for its good chain mobility (19,20). The hydrophilicity of these copolymers can be adjusted by changing the content of each block. PEBAX[®] 1074 is composed of 45 wt% polyamide 12 (PA 12) as the hard block and 55 wt% polyethylene oxide as the soft block. The structure of PEBAX[®] 1074 is shown in Figure 1. Because of the strong affinity among ether oxide (EO) units in the polymer and CO_2 , PEBAX[®] 1074 was one of the most suitable materials for CO_2 separation (21–24). In a previous work (25), the vapor permeability of PEBAX[®] 1074 was found to increase exponentially with the increase in vapor activity, while the nitrogen permeability decreased slightly with the increase in vapor activity. This result highlighted the good selectivity of PEBAX[®] 1074, which indicated its potential use as the polymeric matrix material for the membrane in a humidifier. However, the performance of PEBAX[®] 1074 membranes, especially the air-barrier property, still needs to be improved to meet the demands for fuel cell humidification.

Figure 1: Chemical structure of PEBAX[®] 1074.

Mixing the polymeric membrane materials with inorganic particles is a method for improving the gas barrier property of the membrane. Such membranes are called mixed matrix membranes (MMMs), which have gained more and more attention due to the advantages of separation versatility, easy processing, and economic feasibility (26–32). One of the effective inorganic particles is layer silicate, which helped the membrane reducing permeability after exfoliated as selectivity-improving filler in the polymer matrix (33). Montmorillonite (MMT) is a type of layer silicate, with layered structure used as fillers in membranes to enhance the separation performance (34,35). However, the presence of dangling hydroxyl end groups at the surface of MMT makes it easy to absorb water and swell. These groups also make it difficult to mix and form interfacial interaction with large-sized polymer molecules (36). Therefore, it is necessary to modify MMT to improve its performance in membranes. Generally, the modification has two advantages: first, the modification process enhances the distance between the layers, due to which the macromolecules can intercalate into MMT; and second, the organics bonded to layered silicates make MMT more compatible with the polymer matrix (37). Alkylammonium salts were the common reagents used to modify MMT. However, these salts may lead to a hydrophobic character and a great interlayer space of MMT, which are bad for the vapor sorption and transport process (38). For the membrane used in PEMFC's humidifier, MMT is a good candidate as an air barrier in the membrane. But MMT needs to be modified with hydrophilic reagents, which contain groups that are compatible with the hydrophilic matrix. In this area, detailed and systematic analysis linking to the separation performance of MMT/PEBAX[®] 1074 MMMs is scarce in the literature.

In this paper, poly(oxyalkylene)amine (APOP) was used to modify MMT to improve its compatibility with PEBAX[®] 1074 matrix without decreasing the hydrophilicity of MMT. The MMT/PEBAX[®] 1074 and APOP-MMT/PEBAX[®] 1074 MMMs were prepared. The effects of MMT on the water contact angle, crystallinity, vapor permeability, and water/air selectivity of the PEBAX[®] 1074-based membranes were investigated.

2 Experimental

2.1 Materials

PEBAX[®] 1074 was supplied by Arkema Inc., France. Poly(oxyalkylene)amine (D400) was purchased from Shanghai

Aladdin Bio-Chem Technology Co., Ltd, China. Na-montmorillonite (MMT) was supplied by Shandong Yousuo Chemical Co., Ltd, China. *N*-butyl alcohol (AR) was purchased from Shanghai Titan Technology Co., Ltd, China. Hydrochloric acid (HCl, CMOS) and acetone (AR) were purchased from Shanghai Wokai Biotechnology Co., Ltd, China. All these reagents were used without any further purification.

2.2 Preparation of modified montmorillonite

First, 3.87 g APOP-D400 and 1.776 g aqueous hydrochloric acid (37 wt%) were dispersed in 484 mL of water/acetone mixture (molar ratio of water/acetone was 1:3, respectively) for 3 h while cooling in iced water. Meanwhile, 4 g MMT was added to deionized water and stirred for 2 h using magnetic stirrer under room temperature. The APOP solution was then added slowly into the MMT suspension with stirring. The mixed solution was stirred steadily for 6 h at 70°C. As a result, APOP-modified montmorillonite (APOP-MMT) was obtained. The APOP-MMT was separated using suction filtration. The APOP-MMT was washed thrice using deionized water and dried under vacuum at 70°C for 48 h. The experimental procedure was similar to that reported in a previous work (39).

2.3 Preparation of MMT/PEBAX® 1074 MMMs

The MMMs were prepared using the casting method. First, 0.5 g PEBAX® 1074 was added into a 50-mL round bottom flask containing 25 mL *n*-butyl alcohol. The mixture was stirred at 90°C for 5 h, as a result of which, PEBAX® 1074 solution was obtained. Then, different

amounts of MMT or APOP-MMT were added to the solution. After 3 h of ultrasonic dispersion, the membrane solution was obtained. The amount of MMT was calculated according to Table 1. The MMT/PEBAX® 1074 MMMs were named as P/M-ratio No., as presented in Table 1. For example, when the ratio of MMT to PEBAX® 1074 was 12:100, the membrane sample was named as P/M-12. The amount of APOP-MMT in APOP-MMT/PEBAX® 1074 MMMs was same as that of MMT (see Table 1), and this series of membranes was named as P/PM-ratio No. The thickness of the P/M MMMs was $51.1 \pm 5.2 \mu\text{m}$, and the thickness of P/PM MMMs was $51.0 \pm 5.8 \mu\text{m}$.

2.4 Characterization

X-ray diffraction (XRD) was carried out using a Rigaku X-ray diffractometer (D/max 2,550, Rigaku, Japan) with Ni-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The 2θ variations were recorded within the range of 3–40° at the speed of 5°/min. XRD experiments were performed on MMMs to obtain their crystallinity. The crystallinity of MMMs was calculated using the Jade software, which used the peak separation method within the 2θ range of 3–40° in the spectra.

The FTIR spectra of MMT and APOP-MMT were recorded using a Thermo Scientific Nicolet IS5 FTIR spectrometer (Nicolet Instruments Inc., Madison, Wisconsin, USA) using KBr pellet. Each sample was scanned 16 times over the range of 400–4,000 cm^{-1} with a resolution of 4 cm^{-1} . The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of pure PEBAX® 1074 and MMMs were also investigated on this instrument at a resolution of 4 cm^{-1} , and the scanning range was 570–4,000 cm^{-1} .

MMT and APOP-MMT were observed using transmission electron microscopy (TEM; JEM-2100F, Japan). First, 1.5 wt% MMT or APOP-MMT was dispersed in water. The resulting suspension was dropped on the copper grids

Table 1: Composition of MMT/PEBAX® 1074 membrane solutions

	MMT (g)	PEBAX® 1074 (g)	MMT:PEBAX	MMT content (wt%)
P/M-0	0	0.5	0:1	0
P/M-3	0.015	0.5	3:100	2.9
P/M-5	0.025	0.5	5:100	4.8
P/M-7	0.035	0.5	7:100	6.5
P/M-10	0.05	0.5	10:100	9.1
P/M-12	0.06	0.5	12:100	10.7

and dried at room temperature. After the specimen was coated with a thin layer of gold, the morphologies of MMT, APOP-MMT, and the cross-sections of MMMs were observed by using a scanning electron microscope (SEM; S-4800, Hitachi Co, Japan). The cross-sectional specimens of the membranes were prepared by breaking the membrane manually after cooling in liquid nitrogen.

Water contact angle tests were performed using an OCA15EC contact angle meter (Data Physics GmbH, Germany) and used to measure the hydrophilicity of the membrane surface. To this end, 2.0 μL distilled water drop was deposited on the membrane's surface at five different spots. Each value was obtained using the supporting software through image recognition. The average value for the five observations was adopted as the contact angle.

Vapor permeability (WVP) of the membrane was tested according to GB/T 1,037–1,988. Three membrane samples were cut into round pieces and fixed on three permeability cups with an internal diameter of 6 cm. The cups were placed into a constant temperature and humidity cabinet where the temperature and relative humidity were maintained at 30.0°C and 60.0%, respectively. After stabilizing the conditions for 30 min, the membrane was weighted using an analytical balance (Shimadzu Co., China). The initial weight (m_1 , g) was obtained. After 3 h, the final weight (m_2 , g) was measured. The WVP of the film was calculated using equation (1):

$$\text{WVP} = \frac{m_1 - m_2}{\Delta t \times A} \quad (1)$$

where Δt (s) is the total test duration and A (m^2) stands for the membrane exposure surface.

Vapor permeability (P_v) was calculated using equation (2):

$$P_v = \frac{\text{WVP} \times d}{\Delta p} \quad (2)$$

where d (m) is the thickness of the membrane and Δp (Pa) is the pressure differential of vapor across the sample.

The air permeability of membrane samples was tested at 25°C according to GB/T 1,038–2,000 by using a custom-built gas permeation test rig employing the manometric method. The schematic of the apparatus is shown in Figure 2. The membrane sample was fixed into the test cell, and the whole system was vacuumed at -27 Pa for at least 3 h to remove adsorbed vapors or gases. Before each test, a gas leak test was performed on the system to make sure that there was no gas leak in the system. The low-pressure valve was closed, and the high-pressure valve and air valve were opened. Pressure variations over time were recorded during the test. Three membrane samples were used for these tests.

Air permeability coefficient (P_g) and vapor selectivity (α) were calculated using equations (3) and (4), respectively.

$$P_g = \frac{\Delta P}{\Delta t} \times \frac{V}{A} \times \frac{T_0}{P_0 T} \times \frac{D}{(P_1 - P_2)} \quad (3)$$

$$\alpha = \frac{P_v}{P_g} \quad (4)$$

where $\frac{\Delta P}{\Delta t}$ is the rate of pressure variation over time (Pa/s), V is the volume of the low gas pressure chamber (m^3),

Figure 2: Schematic of the gas permeation test rig.

A is the effective penetration area (m^2), T_0 (273.15 K) and P_0 (1.0133×10^5 Pa) are the standard temperature and pressure, respectively, T is the temperature of the test environment (K), D is the thickness of the membrane (m), and $(P_1 - P_2)$ is the pressure difference across the two sides of the membrane (Pa).

The tensile strength and elongation at break of the membranes were measured using a universal material testing machine (Kaiqiang Machinery Co., China) according to ASTM D882-02. The stretching speed was 5 mm/min.

3 Results and discussion

3.1 Modification of montmorillonite

3.1.1 XRD analyses

XRD analysis was used to characterize the crystallographic structure of MMT. The XRD patterns of MMT and APOP-MMT are shown in Figure 3. The pristine MMT shows a diffraction peak of (001) crystal plane at 5.88° (2θ). After modification, the diffraction peak of (001) plane shifts to a lower angle ($2\theta = 5.46^\circ$).

The interlayer space can be calculated using the Bragg equation (see equation (5)):

$$2d \sin \theta = n\lambda \quad (5)$$

where θ represents the half of the diffraction angle and λ is the wavelength of X-ray (0.154 nm).

The results show that the interlayer space of MMT increases from 1.50 to 1.62 nm after MMT was modified

Figure 3: XRD patterns of MMT and APOP-MMT.

with APOP. The change in the interlayer space indicates that APOP was successfully intercalated into the layer of MMT. Meanwhile, the peak intensity of APOP-MMT was lower, while the peak shape was much wider than the pristine MMT, which indicates that the random orientation of APOP-MMT lamellae may have formed (40).

3.1.2 FTIR analyses

The chemical structures of pristine MMT and APOP-MMT were analyzed using FTIR, and the corresponding results are shown in Figure 4. As seen in the FTIR spectrum of MMT, peaks at 521 cm^{-1} (Al–O bending vibration) and $1,033 \text{ cm}^{-1}$ (Si–O stretching vibration) are the characteristic absorption peaks of MMT, whereas the peaks at 3,620 and $3,435 \text{ cm}^{-1}$ are assigned to the stretching vibrations of Al–O–H bond and H–O–H bond, respectively. These results prove the presence of absorbed water (41).

Figure 4: FTIR spectra of pristine MMT and APOP-MMT.

After modification with APOP, as seen in the FTIR spectrum of APOP-MMT, new peaks can be observed. These new peaks lie at $3,252 \text{ cm}^{-1}$ (–NH stretching vibration of NH_3^+), $2,972 \text{ cm}^{-1}$ (–CH₂– asymmetric stretching vibration), $2,880 \text{ cm}^{-1}$ (–CH₂– symmetric vibration), $1,480 \text{ cm}^{-1}$ (–CH₂– asymmetric bending vibration), and $1,382 \text{ cm}^{-1}$ (–CH₃ symmetric bending vibration). These changes represent the interaction between APOP and MMT.

3.1.3 Morphology of pristine MMT and APOP-MMT

Figure 5 shows the TEM photos of pristine MMT and APOP-MMT at different magnifications. As shown in Figure 5a and b, pristine MMT has a very obvious edge,

Figure 5: TEM images of MMT and APOP-MMT: (a and b) pristine MMT, (c and d) APOP-MMT.

which is derived from the unique lamellar structure of MMT. Figure 5c and d shows that the edge of APOP-MMT became blurred, which may be due to the formation of a partially exfoliated structure in APOP-MMT or the attachment of APOP on the surface of MMT.

SEM images were taken to determine the morphology and size distribution of MMT and APOP-MMT. The size of MMT in SEM photos was measured using the Nano Measure software, and about 120 particles were used for measurement. Figure 6 shows the pristine MMT and APOP-MMT at different magnifications and their size distribution. As seen in Figure 6a and b, MMT has a typical lamellar structure and layers are tightly bonded to each other. Therefore, MMT has a compact and homogeneous structure. With regard to APOP-MMT, many exfoliated sheets are observed (see Figure 6c and d). Meanwhile, larger MMT particles can also be observed. When these results are combined with the XRD results, it can be inferred that MMT formed a partially exfoliated structure after being modified by APOP. Figure 6c and f shows the size distribution of pristine MMT and APOP-MMT particles. The APOP-MMT particles were smaller than the pristine MMT particles. APOP-MMT (mean size: 2.22 μm) had a 38% smaller size than the pristine MMT (mean size: 3.57 μm). Reduction in the size of the modified MMT can be

attributed to the intercalation of APOP. Intercalated APOP caused MMT sheet peeled off from MMT particles, as a result smaller MMT particles were obtained.

3.2 Properties of the MMMs

3.2.1 Chemical structure of MMMs

ATR-FTIR was performed to analyze intermolecular interaction between the PEBAX[®] 1074 and MMT at different loading of MMT, and spectra are shown in Figure 7. The peak at 1,120 cm^{-1} of the pure PEBAX[®] 1074 membrane belongs to the symmetric vibration of the C–O–C group in the PEO segment. Peaks at 1,646 cm^{-1} and 1,734 cm^{-1} are related to H–N–C=O and O–C=O groups in the PA segment, respectively. Aliphatic C–H bond is assigned by the peak at 2,922 cm^{-1} . The peak at 3,308 cm^{-1} is associated with N–H groups in the PA segment (42). When pristine MMT or APOP-MMT was added into PEBAX[®] 1074 matrix, a new peak at 1,033 cm^{-1} appeared, which is attributed to the stretching vibration of Si–O of MMT. It can be seen that except for the peak of Si–O, other peaks had little difference in the peak wavenumbers or peak intensity. Such results

Figure 6: SEM images and size distribution of pristine MMT and APOP-MMT: (a–c) pristine MMT, (d–f) APOP-MMT.

Figure 7: ATR-FTIR spectra of MMMs: (a) pristine MMT/PEBAX® 1074, (b) APOP-MMT/PEBAX® 1074.

indicate that no chemical bond was formed between fillers and PEBAX® 1074 matrix.

3.2.2 Surface hydrophilicity of MMT/PEBAX® 1074 MMMs

The permeation of gas through dense membranes can be divided into three steps: adsorption, diffusion,

and desorption (14). The first step is the adsorption and dissolution of gas molecules on the upstream side of the membrane. The rate of adsorption and dissolution is determined by the properties of gas molecules and the interaction between the gas molecules and membrane materials.

The dissolution of vapor on the surface of the membrane is affected by many factors, including the

number of hydrogen bonds in the membrane, the density of the polymer chain, and the conformation of the polymer chain. The interaction between the water molecules and polymer is critical to the dissolution process. The strong polar polymer contains more hydrophilic groups, due to which, the membrane contains more hydrogen bonds and coordination, which is beneficial to the dissolution of water molecules. The solubility coefficient of water molecules increases with the improvement in the hydrophilicity of the membrane (43,44). Analyzing the contact angle is a common method to investigate the hydrophilicity of the membrane.

Figure 8 shows the effect of MMT (APOP-MMT) content on the contact angle of the membrane's surface. The water contact angle decreases from $99.8 \pm 2.3^\circ$ to $85.8 \pm 1.6^\circ$ as the MMT content increase from 0% to 9.1% and tend to stabilize at high MMT contents. MMT is a kind of hydrophilic material as it contains large amounts of inorganic ions between the layers (34). When added to the membrane, MMT is dispersed in the membrane, increasing the hydrophilicity of membrane (35). However, the water contact angle of the membranes decreases to $76.5 \pm 1.3^\circ$ when 9.1% APOP-MMT was added, which is quite lower than that of MMT/PEBAX[®] 1074 MMM containing the same content of MMT. These results highlight the better hydrophilicity of membranes containing APOP-MMT. When the APOP-MMT was intercalated into the polymer, due to the presence of APOP molecules on the surface of MMT, the polyether structure improved the compatibility between MMT and PEBAX[®] 1074. Moreover, the presence of $-\text{NH}_2$ groups in APOP increased the hydrophilicity of the membrane to a certain degree.

Figure 8: Water contact angle of the MMMs.

3.2.3 Crystallinity of MMT/PEBAX[®] 1074 MMMs

The rate of gas permeation through the polymer is related to the segmental motion of the polymer. Factors that limit the movement of polymer segments are beneficial for reducing gas permeation. Crystal regions of the polymer are considered to be the regions, in which the gas is impermeable, which is due to the strong interaction of regularly arranged molecular chains. Generally, the gas permeability decreases with the increase in polymer crystallinity (45).

XRD spectra were obtained to determine the crystallinities of the MMMs. As seen in Figure 9, diffraction peaks at 22.6° and 5.6° (2θ) are observed in the spectra, which correspond to (001) and (020) diffractions, respectively, of the γ form of crystal phase of polyamide (46). Moreover, the diffraction peak at 11.3° (2θ) is the characteristic diffraction peak of PEBAX[®] 1074 that is related to polyether regions (47,48). After MMT or APOP-MMT was added to PEBAX[®] 1074 matrix, a new peak at 19.7° (2θ) emerges, which corresponds to (020) diffraction peak of MMT (49). As the content of MMT increases, the intensity of the peak at 22.6° (2θ) increases, while the intensities of the peaks at 11.3° and 5.6° (2θ) decrease, which indicates the change in membrane crystallinities. The crystallinities of the PEBAX[®] 1074 matrix were determined from the XRD spectra using the Jade software that employed the peak separation program. To eliminate the randomness of the peak separation process, pristine PEBAX[®] 1074 membrane was heated to 155°C , which is higher than the melting temperature of PEBAX[®] 1074. Then, the membrane was immediately immersed into liquid nitrogen to reduce the crystallinity as much as possible. This sample was analyzed using XRD, while the XRD spectrum was used as a standard for the peak separation process, as shown in Figure 9c. The results show that four peak profiles fit the pattern, and the calculated crystallinity was 3.23%. All subsequent calculations were based on this separation method, and the corresponding results are shown in Figure 9d. The crystallinity of the membranes increases from 27.6% to 41.2% when the APOP-MMT content increases from 0% to 9.1%. Meanwhile, the crystallinity of the membrane containing MMT only increases to 37.1%. During crystallization, MMT most likely acted as a nucleating agent, and the polymer segments tended to aggregate and crystallize around it. Good compatibility between APOP-MMT and PEBAX[®] 1074 matrix resulted in high dispersion of inorganic sheets, and thus led to high crystallinity of the polymer. Therefore, the addition of MMT into MMMs promoted the crystallization of PEBAX[®]

Figure 9: XRD spectra of MMMs: (a) pristine MMT/PEBAX® 1074, (b) APOP-MMT/PEBAX® 1074, (c) peak fitting results of quenched pure PEBAX® 1074 membrane, (d) crystallinities of the MMMs.

1074 matrix, especially when MMT was modified using APOP.

between MMT and PEBAX® 1074 may improve. Therefore, after MMT was modified with APOP, the membrane became compact.

3.2.4 Morphology of cross-sections of MMT/PEBAX® 1074 MMMs

Figure 10 shows the SEM images of the cross-sections of the MMMs containing 6.5 wt%. MMT. As compared in Figure 10, it is obvious that the cross-section of the membrane containing APOP-modified MMT is smoother than that containing pristine MMT, after the membranes were broken in liquid nitrogen. As we know, the aggregation of MMT and the low compatibility between MMT and PEBAX® 1074 may result in the fragility of the membrane. Figure 6 shows more aggregation of pristine MMT than that of APOP-MMT. Meantime, owing to the polyether structure in APOP-MMT, the compatibility

3.2.5 Vapor permeability of MMT/PEBAX® 1074 MMMs

Figure 11 shows the vapor permeability coefficients (P_v) of MMT/PEBAX® 1074 MMMs. As the pristine MMT content increases, the value of P_v first increases and then decreases. The maximum value of P_v is $(7.98 \pm 0.15) \times 10^4$ Barrer ($1.67 \times 10^{-17} \text{ m}^3 \text{ m/m}^2 \text{ s Pa}$) when 4.8% MMT was in the membrane. With regard to APOP-MMT/PEBAX® 1074 MMMs, the P_v value first increases and then decreases. The maximum P_v value is $(8.49 \pm 0.17) \times 10^4$ Barrer for the APOP-MMT content of 4.8%. After comparing these results, it is apparent that APOP-MMT had a significantly positive impact on the vapor

Figure 10: SEM images of the cross-section of the MMMs containing 6.5 wt%: (a and c) pristine MMT, (b and d) APOP-MMT.

Figure 11: Vapor permeability coefficient for the MMMs.

permeation than what MMT did to the MMMs. As explained in Section 3.2.1, MMT increased the water contact angle of the membranes, which indicates that MMT improved the dissolution coefficient of the PEBAX[®] 1074 MMMs. Therefore, the addition of MMT in the membrane may result in the acceleration of vapor dissolution in the membrane. However, as explained in Section 3.2.2, MMT also increased the crystallinity of MMMs, which is detrimental to the penetration of vapors

and gases in membrane (50). These two effects of MMT worked at the same time, and the changes to the vapor permeability may rely on the dominating effect of MMT for various contents of MMT in PEBAX[®] 1074. At a low MMT content, the increase of hydrophilicity has a greater influence on the vapor permeability, and therefore, the vapor permeability coefficient increased with the increase in the content of MMT. When the MMT content increased to beyond 5%, the crystallinity of membrane increased continuously, and the large crystallization region blocked the permeation of vapor. Therefore, the vapor permeability coefficient of the membrane decreased with the increase in the content of MMT.

3.2.6 Air permeability and selectivity of MMT/PEBAX[®] 1074 MMMs

For air permeation, the permeation rate is expressed as the air permeability coefficient (P_g). The air permeability coefficient and the selectivity of MMT/PEBAX[®] 1074 MMMs are shown in Figure 12. As seen in Figure 12a, the air permeability coefficient has a rapid decline from 1.54

Figure 12: Air permeability coefficient (a) and selectivity (b) of the MMT/PEBAX® 1074 MMMs.

to 0.47 Barrer when 2.9% MMT was added to the membrane. With the content of MMT increasing to 9.1%, the air permeability remains in a relatively stable range. When the content of MMT increased to 10.7%, the air permeability coefficient increases. It is well known that O_2 and N_2 (main components in the air) have little interaction with PEBAX® 1074. Therefore, the addition of MMT has little effect on the solubility coefficient of air. The increase in the crystallinity makes it hard for air to penetrate through membranes. At the same time, the laminar structure of MMT makes the penetration path of air tortuous (51), which may slow down the air penetration. For low MMT content, it dispersed evenly, and therefore, the laminar structure formed evenly, which did well in increasing the crystallinity and penetration path. Therefore, the air penetration coefficient drops at low loadings of MMT. When the content of MMT is high, it aggregates, which is detrimental to increasing the crystallinity and penetration path, and therefore, the air permeability coefficient increases. Owing to the improved comparability of APOP-MMT and polymer resin, the MMT distributes evenly and then the air is blocked effectively. Therefore, at the high loading of MMT, the membranes containing APOP-MMT have a lower air permeability coefficient than the membranes containing pristine MMT.

The selectivity of a membrane for a certain set of gases or vapors is a measurement of its separation performance. It shows the ability of the membrane to separate different gaseous components. The selectivity of a membrane is an important parameter for its use in a humidifier. Figure 12b shows the water/air selectivity (α) of the MMMs. Water/air selectivity of MMT/PEBAX® 1074 MMM reached the maximum value of $(16.44 \pm 0.66) \times 10^4$

for the pristine MMT content of 2.9%, which is 3.6 times more than that of the pure PEBAX® 1074 membrane. Additionally, the water/air selectivity of APOP-MMT/PEBAX® 1074 MMM reaches the maximum value of $(17.26 \pm 0.69) \times 10^4$ for the APOP-MMT content of 4.8%, which is 3.8 times higher than that of the pure PEBAX® 1074 membrane. These results show that MMT accelerates the vapor penetration and blocks air permeation, while the modification of MMT with APOP helps improve the performance of MMMs.

3.2.7 Mechanical properties of MMT/PEBAX® 1074 MMMs

The effects of MMT content on the mechanical properties of MMT/PEBAX® 1074 MMMs are shown in Figure 13. Apparently, as the pristine MMT content increases from 0% to 6.5%, the tensile strength of the membrane increases from 7.6 ± 0.5 to 9.5 ± 0.4 MPa, whereas the elongation at break increases from $83 \pm 12\%$ to $181 \pm 13\%$. When used in the membrane-based plate-and-frame humidifier, the membrane needs to have good tensile strength and elongation at break, which meets the needs for fixation and operation in a humidifier (15,18). These results indicate the good mechanical properties of PEBAX® 1074 MMMs. This enhancement behavior may be attributed to the strong interfacial interaction between the PEBAX® 1074 matrix and the well-dispersed pristine MMT (52) and the increase in crystallinities. However, with further increase in the content of MMT, the pristine MMT particles trends to aggregate, which would invalidate the enhancement effect of MMT in MMMs, and therefore, the sharp drops

in elongation at break and tensile strength can be observed. Moreover, APOP-MMT shows similar effects on strengthening the mechanical properties of MMMs. It can also be concluded that this kind of modification of MMT has little effect on the mechanical properties of PEBAX[®] 1074 MMMs.

Figure 13: Mechanical properties of the MMT/PEBAX[®] 1074 MMMs.

4 Conclusions

Polymer membranes have been widely used in membrane humidification technology. However, they cannot meet the increasing requirements of membrane humidification in PEMFCs. In this paper, MMT/PEBAX[®] 1074 MMMs were fabricated using the solvent casting method. The pristine MMT and APOP-modified MMT were added as fillers. Using the XRD, FTIR, SEM, and TEM techniques, the morphology and the chemical structure of MMT during modification were investigated. Based upon the analysis of vapor permeability, air permeability, water contact angle, FTIR, and crystallinity of MMT/PEBAX[®] 1074 MMMs, the effects of MMT on the properties of membranes were investigated. The results showed that, when MMT fillers were blended into PEBAX[®] 1074, the surface hydrophilicity and the crystallinity of MMT/PEBAX[®] 1074 MMMs increased with the increase in the content of MMT, and higher vapor permeability and selectivity than those of the pure PEBAX[®] 1074 membranes can be obtained. After modification with APOP, APOP-MMT showed better performance in improving the comparability of MMT and polymer resin, vapor permeability and vapor/air selectivity of MMT/PEBAX[®] 1074 MMMs than pristine MMT. The best selectivity for the membrane containing APOP-MMT was $(17.26 \pm 0.69) \times 10^4$, which is 3.8 times

higher than that of the pure PEBAX[®] 1074 membrane. The improved selectivity of MMT/PEBAX[®] 1074 MMMs shows that it is a promising candidate to be used as a humidifier membrane in PEMFCs.

Acknowledgments: This project was supported by the Natural Science Foundation of China (51203119) and Fundamental Research Funds for the Central Universities.

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