

Fabrication and evaluation of polyurethane-based asymmetric membranes

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Abstract For preparation of an ideal wound dressing, a series of novel polyurethane-based asymmetric membranes with acetic starch and poly (ethylene glycol) as fillers were successfully fabricated by a combination of polymer-filler hybridization and immersion precipitation phase inversion. These resultant polyurethane-based asymmetric membranes consisted of an integral and dense skin layer supported by a porous sublayer as designed. The porosity and internal substructure of asymmetric membranes could be controlled by adjusting species and amount of fillers. The polyurethane-based asymmetric membranes showed promoted fluid absorption capability and controlled water vapor transmission, but could inhibit exogenous microorganisms invasion deriving from its dense skin layer. In vitro biodegradation assay indicated that the polyurethane/acetic starch composite membrane exhibited faster degradation behavior. These results indicated that the polyurethane-based asymmetric membranes prepared in this study has potential for application as an ideal wound dressing.

Abbreviations

PU	Polyurethane
ASt	Acetic starch
PEG	Poly (ethylene glycol)
WVTR	Water vapor transmission rate
DMF	<i>N,N</i> -dimethyl formamide

SEM	Scanning electron microscope
EWC	Equilibrium water content
PBS	Phosphate buffer saline

Introduction

Immediate coverage of wound bed with a dressing is necessary for rapid and optimum healing in the treatment of burns, skin ulcers, and surgical wounds. According to modern medical insights, an ideal wound dressing should possess the following properties: (1) high fluid absorption capability to remove excessive exudates from the wound bed; (2) suitable water vapor transmission rate (WVTR) to produce a moist environment preventing dehydration or exudates accumulation; (3) sufficient gas permeability for oxygen-requiring reparative processes; (4) good barrier against the penetration of infection causing microorganisms; and (5) nontoxic, non-allergenic, non-adherent, and easily removed without trauma [1–5].

Among various commercial wound dressings, polyurethane (PU) membrane dressing under trade names of TegadermTM and Op-Site[®] has been extensively used for its outstanding properties such as excellent tissue compatibility, abrasion resistance, and good mechanical strength [6–8]. However, as conventional wound dressing, totally dense structure of PU membrane results in its low water vapor or gas transmission rate and poor fluid absorption capability which cause exudates accumulation and infection-related complications in clinic cases [9, 10]. Meanwhile, low gas permeability inhibits oxygen exchange through the dressings, which decreases the regeneration of tissue cell or makes possible the proliferation of anaerobic bacteria. Thus, it seems that PU membrane currently

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available is far from ideal dressings, and modification is necessary to overcome their limitations.

Polymer composites have been attracting significant interest due to their superior performances. Acetic starch (ASt) and poly(ethylene glycol) (PEG) are all hydrophilic, biodegradable, nontoxic, and biocompatible; therefore, they all find use in a broad spectrum of applications [11–14]. As filler, ASt particles can uniformly disperse in PU matrix [15], thereafter improved water absorption capability and moisture permeability of PU membrane deriving from adsorption-diffusion-desorption for hydrophilic group. For PEG, previous works have shown that PEG has the ability to introduce porous features of polymer matrix due to its solubility in water during the phase change process [16, 17]. So, it was believed that the water absorbability and moisture permeability of PU-based membrane using PEG as a pore former would be enhanced depending on the permanent pore structure.

On the other hand, the nonsolvent induced phase inversion process has been widely used as a reliable method for preparing or modifying asymmetric membranes [18–20]. In this method, the porous cellular structure of most membranes is liquid–liquid demixing by nucleation and growth of a polymer-poor phase. The ratio of the solvent outflow to coagulant inflow can be illustrated by the composition path in a ternary phase diagram. When the ratio is large, the path enters the gelation region directly and brings about a dense structure. But if the ratio is small, the path intersects the liquid–liquid phase-separation region and the casting solution separates into polymer-rich and polymer-poor phases. The former forms the polymer matrices, and the latter forms the pores in membranes. So asymmetric polymer membranes having a compact top layer with porous substructure can be obtained. As a wound dressing, the asymmetric membranes could meet both requirements, i.e., the prevention of bacterial invasion and the controlling of evaporative water loss.

In this work, to fabricate an ideal wound dressing, the ASt and PEG were introduced into the PU matrix as the fillers. A series of novel PU-based asymmetric membranes were designed by combining polymer-filler blending and immersion precipitation phase inversion. According to this design, the PU-based asymmetric membrane consisted of an integral, dense skin layer supported by a porous sublayer with well-dispersed ASt particles or interconnected macropores caused by dissolution of PEG. The dense skin layer could prevent bacterial penetration and dehydration of wound bed but allows the drainage of wound exudates. The porous sublayer exhibits high adsorption capability for fluids and performs drainage of the wound by capillary and enhancement of tissue regeneration. Because of this special structure, the good performance of PU membrane would be achieved. Finally, the enzymatic degradation of the PU-based asymmetric membranes was evaluated by *in vitro*.

Materials and methods

Materials

Biomedical PU was supplied by Zhende Medical Dressing Co. Ltd, China. *N,N*-dimethyl formamide (DMF) of analytical grade was obtained from Yongda Chemical Co. Ltd, China. Poly(ethylene glycol) (PEG, $M_n = 4000$) was purchased from Gaonan Chemical Co., China. ASt with degree of substitution of 0.5 was obtained from Laite Chemical Co. Ltd, China.

Preparation of PU-based asymmetric membranes

PU-based asymmetric membranes were prepared by immersion precipitation phase inversion method using a casting process. Briefly, a certain amount of PU particles were dissolved in DMF with vigorously stirring for 1 h at 50 °C. Homogeneous suspension of ASt was prepared by dispersing ASt particles into DMF under stirring continuously. The blend solutions with constant solid content of 30 wt% were obtained by mixing PU solution with ASt suspension in the mass ratios (i.e., PU/ASt, w/w): 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50. After stirring at room temperature for 1 h, a transparent and homogeneous solution was obtained. Then the solution was cast on a plane glassine, subsequently immersed in a coagulation bath of distilled water at ambient temperature for allowing the exchange of solvent and nonsolvent. Finally, the obtained membranes were washed and dried at 70 °C.

Similarly, the asymmetric PU membranes using PEG as a pore former were produced as described above. The difference was that PEG was dissolved in DMF, and finally was removed from PU/PEG composite membranes during soaking and washing procedure due to its solubility in water. In this paper, for easy to compare PU/ASt membrane and PU membrane with PEG as a pore former, these resultant PU porous membranes will be defined as PU/PEG composite membranes although the PEG was leached.

Morphology

The surface and cross-sectional morphologies of PU-based asymmetric membranes were observed using a scanning electron microscope (SEM, JSM-5610, JOEL, Japan) after gold coating.

Density and porosity

The density (ρ_t) of the PU-based asymmetric membranes was calculated as follows [21]:

$$\rho_t = \frac{m}{D \times A} \quad (1)$$

where m is the weight of the polymer membranes and D is the average thickness of the polymer membranes, which was measured at five different places of each sample by dry membrane thickness gauge. A is the area of the polymer membranes.

The porosity of the PU-based asymmetric membranes was calculated as follows [22, 23].

$$\rho = \rho_a \times a \% + \rho_b \times b \% \quad (2)$$

$$\text{Porosity (\%)} = \frac{D \times A - m/\rho}{D \times A} \times 100 \quad (3)$$

For PU/ASt membrane, ρ is the solid density of the membranes, ρ_a is density of PU, 1.26 g/cm³, and a % is PU content in the composite. ρ_b is particle density of ASt, 1.48 g/cm³, and b % is ASt content in the composite. But for PU/PEG membranes, we consider that ρ is the density of pure PU (1.26 g/cm³).

Water absorption and equilibrium water content

The water absorption and equilibrium water content of PU-based asymmetric membranes were measured by swelling the samples in distilled water at 37 °C. Five square samples (5 × 5 cm²) of each composition were first dried for 24 h at 70 °C and cooled to room temperature in a desiccator. The dried samples were accurately weighed (W_d) and then soaked in distilled water for 24 h to reach equilibrium. The swollen samples were weighted (W_s) immediately after they were squeezed gently with filter papers to remove excessive surface water. The water absorption rate and equilibrium water content (EWC) were calculated as follows [24]:

$$\text{Water absorption (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (4)$$

$$\text{EWC (\%)} = \frac{W_s - W_d}{W_s} \times 100 \quad (5)$$

Water vapor transmission rate

WVTR of the PU-based asymmetric membranes was determined according to YY/T 0471.2-2004 (Test methods for primary wound dressings—Part 2: moisture vapors transmission rate of permeable film dressings, China) [25]. The samples (20 g/m²) were mounted on the top of cylindrical cups (diameter: 35.7 mm) containing 20 mL of distilled water, which were then placed in an incubator at 37 ± 1 °C and 20 % relative humidity. The weight change of permeation cup was recorded after 24 h, and the WVTR was calculated as follows

$$\text{WVTR (g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}) = \frac{\Delta W}{A \times \Delta t} \times 24 \quad (6)$$

where ΔW is the weight loss over the time interval (g), A is the area covering the cylindrical cup (m²), and Δt is the time interval (h).

Mechanical properties

All samples were cut into 40 × 5 mm² and placed overnight in the conditioning room (20 °C, 60 % RH). The mechanical properties of PU-based asymmetric membranes were tested on a Universal Testing Machine (KES-G1, Kato-Tech, Japan) at a crosshead speed of 10 mm/min.

Bacteria penetration

Escherichia coli (*E. coli*, ATCC 25922) and *Staphylococcus aureus* (*S. aureus*, ATCC 6538) were selected as test bacteria. The bacteria penetration test was performed according to the method reported by Mi et al. [26]. In general, the samples with diameter of 1.5 cm were sterilized and placed on the agar plates. Subsequently, the samples were inoculated with a suspension (0.2 mL) of *E. coli* and *S. aureus* (1 × 10⁴ cfu/mL) on its center area. After 5 days of incubation at 37 °C, the samples were checked for bacterial penetration.

Biodegradation

The in vitro biodegradation of the PU-based asymmetric membranes was evaluated by incubating samples in an enzymatic solution and then monitoring their weight losses at different incubation times. Samples were cut into 2 × 1 cm² in size and were accurately weighed. Then samples were incubated in 10 mL of phosphate buffer saline (PBS, pH 7.4) with 1.5 mg/mL lysozyme at 37 °C. At pre-determined time intervals, samples were taken out from the incubation medium, washed with distilled water, and dried. The morphologies of those degraded samples were examined by SEM observation, and the weight loss of sample was measured to calculate the degradation rate (DR) as follows.

$$\text{DR (\%)} = \frac{W_0 - W_1}{W_0} \times 100 \quad (7)$$

where W_1 is the weight of degraded sample and W_0 is the initial sample weight.

Results and discussion

Morphology

A series of novel PU-based asymmetric membranes mixed with ASt or PEG were prepared by combining polymer-

filler blending and immersion precipitation phase inversion. Figure 1 showed SEM images of surface and cross-sectional morphologies of pure PU membrane. It was found that pure PU membrane exhibited a totally dense structure with thickness of about 20 μm . The bottom surface of this membrane was smooth, while the upper surface was relatively rough. But obvious influence on microstructure of PU-based asymmetric membranes occurred when fillers were introduced. All the PU-based asymmetric membranes presented a double-layer structure as designed. For PU/ASt composite membrane, nearly spherical ASt particles with diameter of 10 μm were dispersed in sublayer, and gaps were clearly observed between particles and particles or matrix (Fig. 2a–c). In contrast, PU/PEG composite membranes with asymmetric pore structure were obtained, which consisted of a dense skin-covered microporous top layer supported by a finger-like macroporous sublayer (Fig. 2d–f).

Commonly, asymmetric membranes with a compact top layer supported by a porous substructure can be prepared by wet phase inversion method. However, a totally dense structure of pure PU membrane was obtained in this study. As already known, in the most commonly used technique, the casting solution was preheated at 50 $^{\circ}\text{C}$ for 5–60 min for solvent evaporation before immersed into a coagulation bath. During the solvent evaporation process, the loss of solvent drove the outermost region of the original polymer solution to form an integral and dense skin layer. The underlying polymer solution with formed skin layer was then immersed into a coagulation bath, in which wet phase inversion was induced by diffusion of nonsolvent into and solvent out of the polymer solution. Because of this solvent/nonsolvent exchange, the underlying polymer solution separated into a polymer-rich and a polymer-poor phase. Because of delayed phase separation at the outmost interface region of the casting solution, a dense top layer with porous sublayer can be obtained. But if casting solution is not pre-evaporated, the ratio of solvent outflow to coagulant inflow is large, therefore, bringing a dense structure.

While, addition of fillers, the phase-separation process is induced, different structure of membranes could be produced.

Density and porosity

The density and porosity of PU-based asymmetric membranes were determined to characterize the pore information. The recorded values are shown in Fig. 3. Compared with pure PU membrane, the density of all composite membranes was dramatically decreased with the increase of fillers content, which indicated that the addition of fillers created extra pores in the PU membranes; the pore size and/or quantity were increased with the increasing fillers content which was presumed to be deriving from apparent change tendency of the density of composite membranes when the content of fillers was more than 30 % (Fig. 3a).

Another evidence for the presence of extra pores in PU-based asymmetric membranes could be obtained from the analysis of porosity of composite membranes. As shown in Fig. 3b, the measured values were increased with increasing fillers content as expected. The more filler added, the larger porosity exhibited. This revealed that more pores did exist in the PU-based asymmetric membranes and the size of these extra pores increased with the content increase of fillers. The difference found in the changing tendency of density and porosity of PU/ASt was more noticeable than those of PU/PEG. The result indicated that the improved effect of ASt on performances of composite membranes was more prominent than PEG owing to its incompatibility-induced interfacial pores.

Water absorption and equilibrium water content

Exudates drainage ability of various membranes was evaluated by carrying out the water absorption of the asymmetric PU-based membranes. In general, commercially available PU membrane dressing exhibit low fluid absorption capability due to their totally dense structure, which resulted in

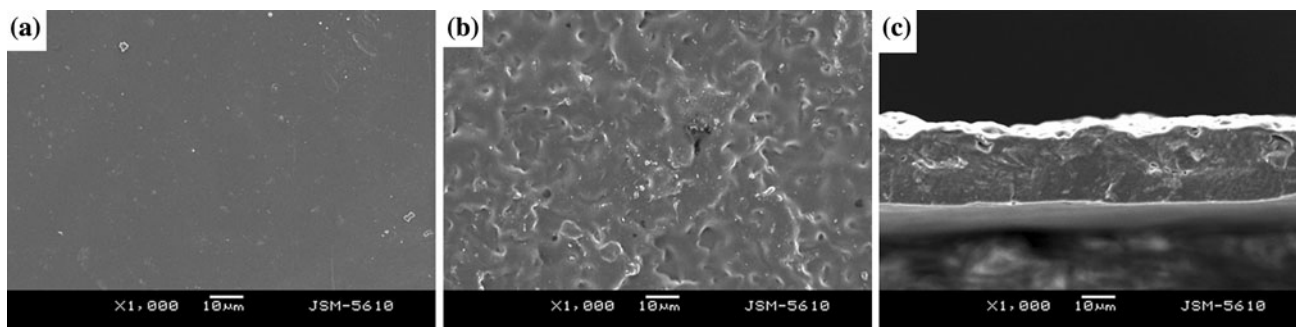


Fig. 1 Bottom surface (a), upper surface (b), and cross-sectional (c) morphologies of pure PU membranes

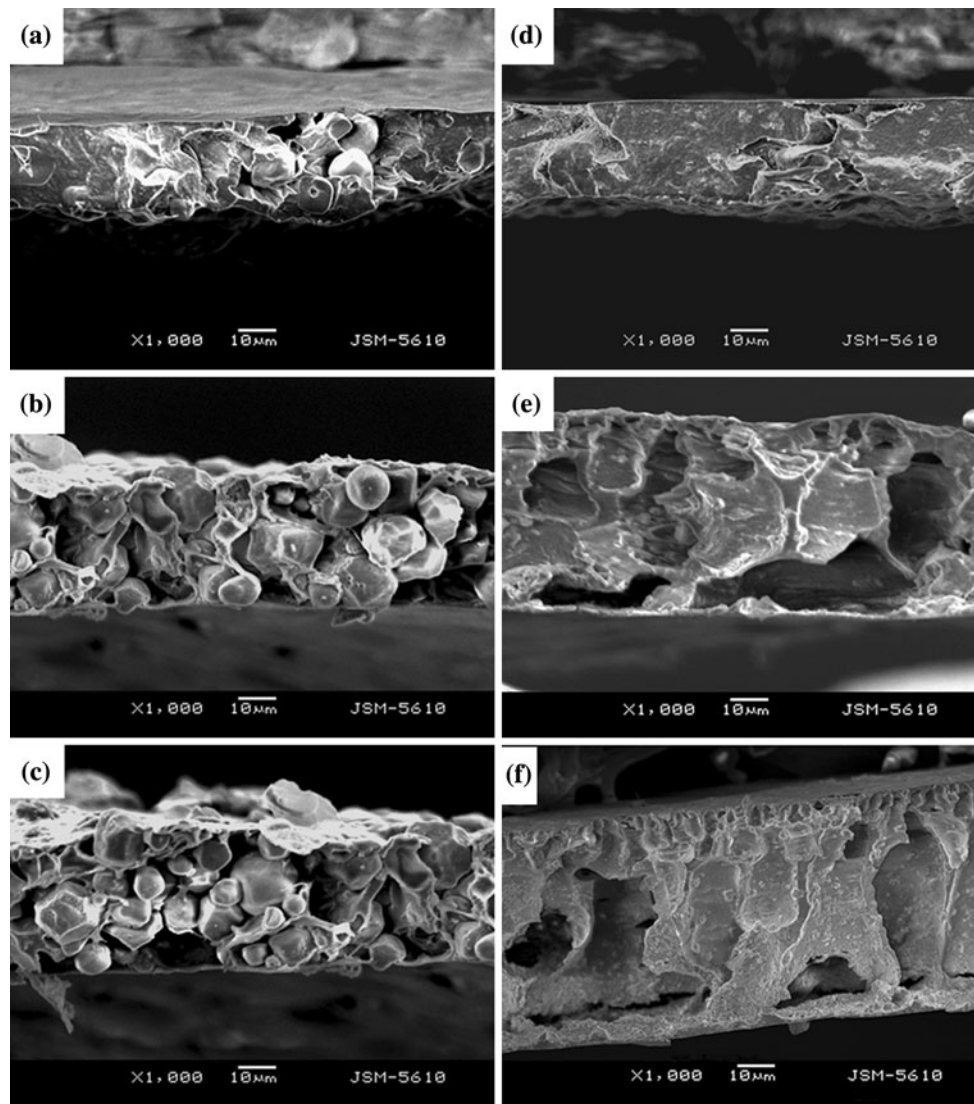
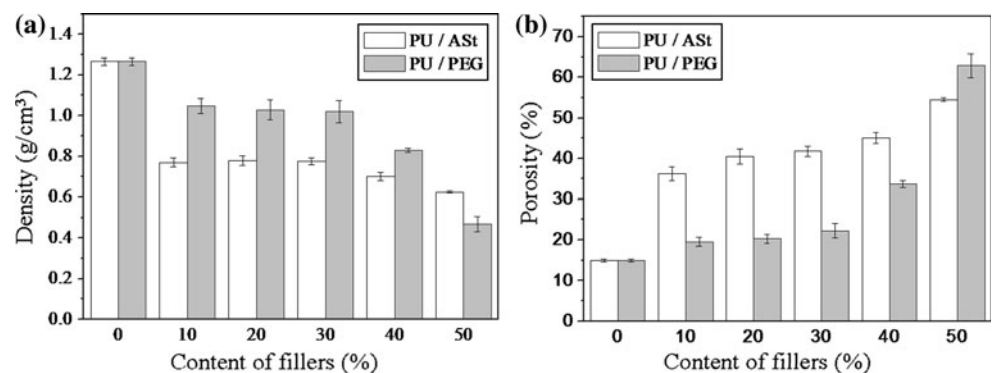


Fig. 2 Cross-sectional morphologies of asymmetric PU/ASt (a–c) and PU/PEG (d–f) composite membranes with filler contents of 30 % (a, d), 40 % (b, e), and 50 % (c, f)

Fig. 3 Density and porosity of PU-based composite membranes with different filler contents



limiting their application to low exudates case or exudates accumulations, and infection occurs. Figure 4 showed the water absorption and equilibrium water content of various PU membranes. Because of the increased porosity of porous

sublayer, the water absorption capacity of PU-based asymmetric membranes was increased with increasing filler content, ranged in 33.4–129.4 % for PU/ASt and 25.2–108.7 % for PU/PEG composite membranes, respectively. The

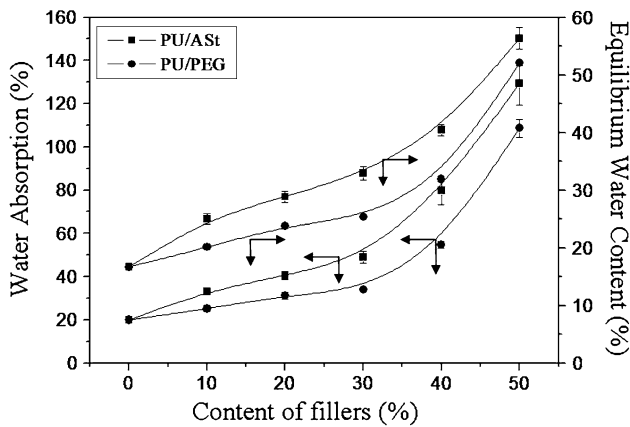


Fig. 4 Water absorption and equilibrium water content of PU-based composite membranes with different filler contents

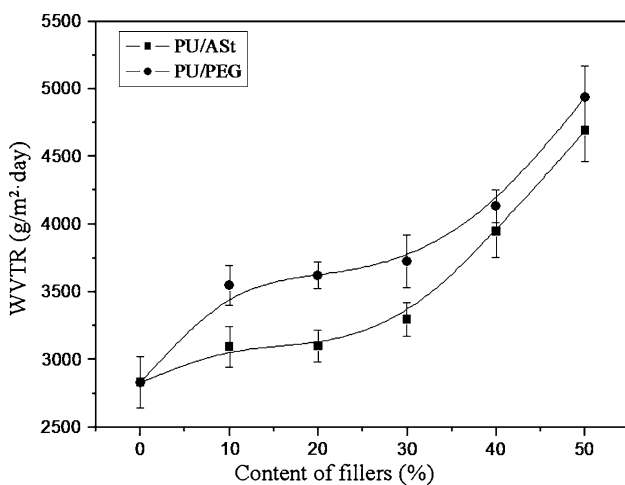


Fig. 5 Water vapor transmission rates of PU-based composite membranes with different filler contents

improved water absorption capability was beneficial to prevent exudates accumulation. On the other hand, the equilibrium water content of PU-based asymmetric membranes was also much higher than that of pure PU membranes, which was as low as 16.7 %. High equilibrium water content guaranteed a moist environment over the wound beds [22, 27] (Fig. 5).

Water vapor transmission rate

An ideal dressing should control the evaporative water loss from a wound at an optimal rate to prevent excessive dehydration and exudates accumulation. Wu and Yusof et al. reported that the WVTR of normal skin is 204 g/m² day, while that of injured skin can range from 279 g/m² day for a first-degree burn to 5138 g/m² day for a granulating wound [28, 29]. It was further recommended by Queen et al. [30, 31] that wound dressings with WVTR of 2500 g/m² day, mid-range of loss rates from injures skin, would be sufficient to

give adequate moisture without risking wound dehydration. In this work, the WVTR of PU-based asymmetric membranes ranged from 2830.01 to 4938.69 g/m²·day depending on the filler content, and increased with the increase of filler content. According to the previous reports, it seemed that those PU-based asymmetric membranes were quite suitable as dressing membranes applied on the different degrees of wound or different times of wound healing.

While, different from the porosity and water absorption of composite membranes, the WVTR of PU/PEG composite membrane was higher than that of PU/ASt membrane including the same content of filler. The permeation of water vapor through the asymmetric membranes consists of two steps—adsorption and diffusion. Thus, it was presumed that such barrier phenomenon of PU/ASt could be attributed to the good water absorption as well as an increased diffusion path length for interfacial pores structure, as penetrants are forced to take a tortuous course around filler particles to traverse a membrane [21]. In contrast, the microporous top layer supported by a macroporous finger-like sublayer structure of PU/PEG accelerated the diffusion of penetrants, and consequently resulted in an increase in permeability. The schematic permeation was illustrated by Fig. 6.

Mechanical properties

For application as a wound dressing, it should be both robust and flexible so as to adhere to the wound surface for a period time, and should be resistant to the damage during the period of healing, while also maximizing patient comfort and convenience [32, 33]. Table 1 showed the tensile strength, elongation at break, and elastic modulus of different PU membranes. With increasing the fillers content, the tensile strength and elongation at break decreased a little, while the elastic modulus slightly increased. However, when the content of fillers was more than 30 %, the strength declined obviously. Here, the tensile strength and elastic modulus of PU/ASt composite membranes were 5.1 ± 0.1 and 11.3 ± 1.3 MPa, and those of PU/PEG were 7.9 ± 0.9 and 10.9 ± 0.9 MPa, respectively. For PU/ASt composite membranes, the decrease of tensile strength was believed to be due to the addition of ASt particles, which destroyed the regular and uniform internal structure of PU matrix. It was well known that PU is a segmented polymer consisting of hard and soft segments. After addition of ASt particles, ASt as the rigid particles was considered as dispersed phase in PU soft continuous phase which could result in a stress concentration. When the composite membranes were stretched, the points of stress concentration were preferentially damaged. Thus the mechanical properties of PU/ASt composite membranes decreased with the increase of ASt amount [34]. On the other hand, from the Fig. 2, some gaps as interface pores were observed at the interface between the particles and PU matrix.

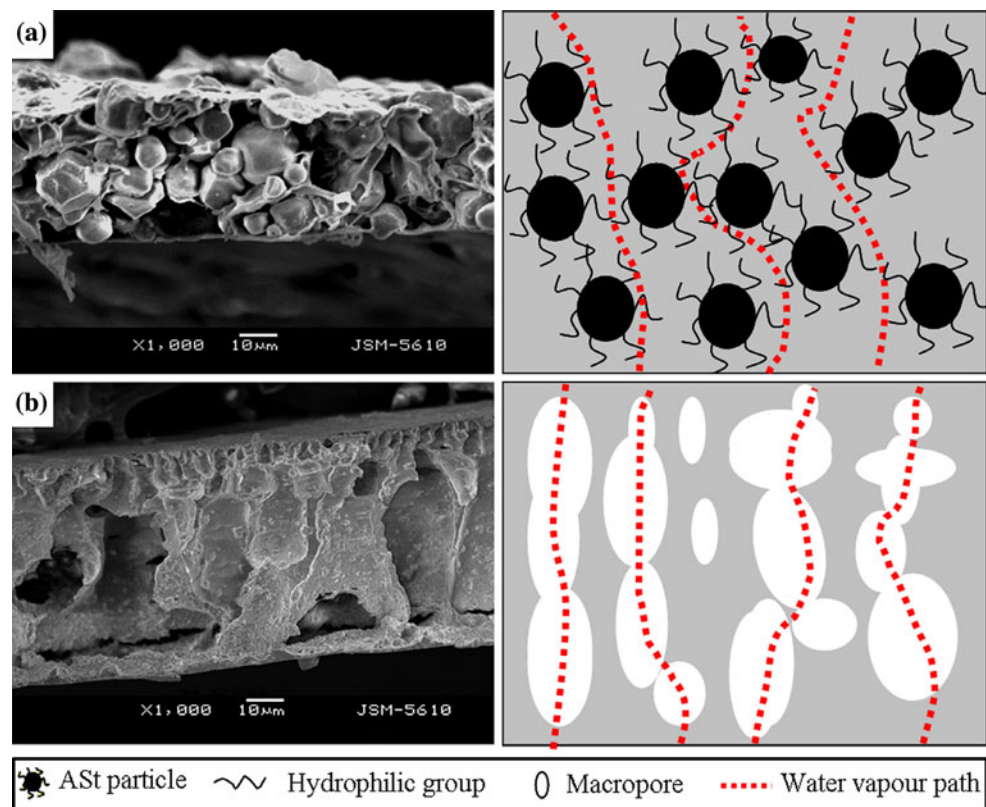


Fig. 6 Schematic permeation of water vapor transmission of PU/ASt (a) and PU/PEG (b) composite membranes

Table 1 Tensile strength, elongation at break, and elastic modulus of pure PU, PU/ASt, and PU/PEG composite membranes with different filler contents

Filler contents (%)	Tensile strength (MPa)		Elongation at break (%)		Elastic modulus (MPa)	
	PU/ASt	PU/PEG	PU/ASt	PU/PEG	PU/ASt	PU/PEG
0	13.2 ± 0.2		613.3 ± 29.7		11.7 ± 1.1	
10	9.1 ± 0.4	8.7 ± 0.4	589.3 ± 24.7	510.0 ± 25.8	12.1 ± 0.2	11.1 ± 0.7
20	8.6 ± 0.5	8.7 ± 0.8	665.2 ± 22.4	487.6 ± 16.6	11.8 ± 1.2	11.8 ± 0.6
30	5.1 ± 0.1	7.9 ± 0.9	485.1 ± 35.1	453.0 ± 34.5	11.3 ± 1.3	10.9 ± 0.9
40	4.4 ± 0.3	6.7 ± 0.5	489.5 ± 23.6	421.3 ± 37.5	8.0 ± 0.7	8.8 ± 0.7
50	3.2 ± 0.4	4.0 ± 0.3	484.2 ± 13.6	380.6 ± 8.7	4.0 ± 0.8	3.8 ± 1.5

These gaps could be another reason for the reduction in tensile strength of composite membranes. When the content of ASt was less than 30 %, the effect of destruction was weak deriving from most particles wrapped by PU in composite membrane. But when the content of ASt was more than 30 %, this destruction effect became more obvious. Whereas, even as the content of ASt particles reached 50 %, the PU/ASt composite membrane also had good elasticity with the elongation at break of 484.2 ± 13.6 %. While the decrease of tensile strength of PU/PEG composite membranes might be due to the porous sponge-like structure, which destroyed the physical properties of PU matrix. Although our results suggested that both ASt

and PEG particles weakened the tensile strength, the PU-based asymmetric membrane also presented excellent elasticity, and could be satisfied to clinical application.

Bacteria penetration

In order to protect the wound beds from outside bacterial infection, an ideal dressing should act as a barrier against microorganism penetration. In this work, in vitro bacteriologic test showed that no bacterial plaque was observed on the other side of composite membranes after cultivation for 5 days, suggesting that both *E. coli* and *S. aureus* did

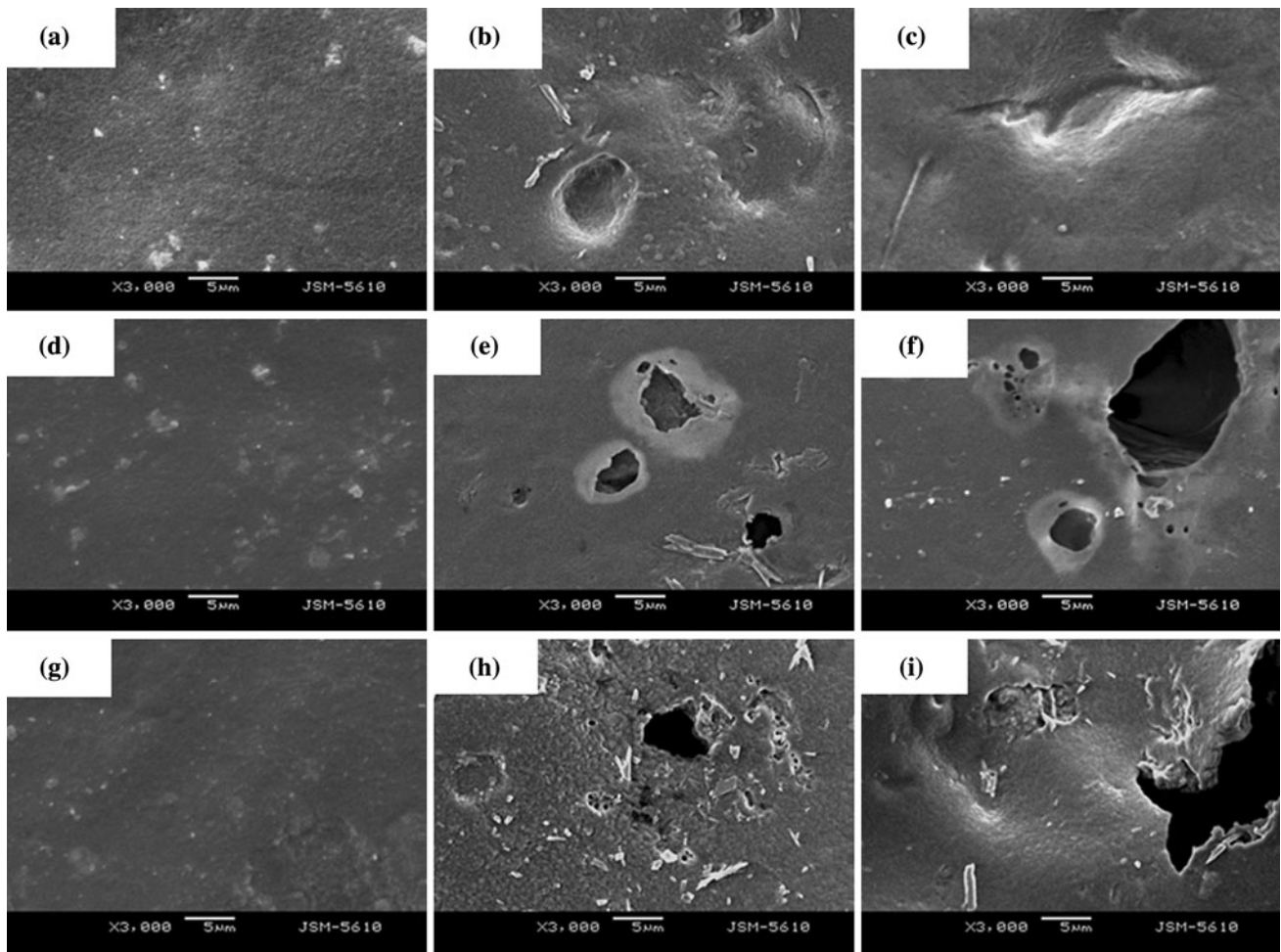


Fig. 7 Morphologies of pure PU membrane (a–c), PU/Ast (d–f), and PU/PEG (g–i) composite membranes with 40 % of filler content after biodegradation for different times: a, d, g for 0 week; b, e, h for 4 weeks; c, f, i for 7 weeks

not penetrate the membranes despite the fact that the pore size at the sublayer of the PU-based asymmetric membranes was much larger than the minimal size of bacteria. This result indicated that the PU-based asymmetric membranes exhibited excellent inhibition of bacteria penetration due to its dense skin surface.

Biodegradation

Figures 7 and 8 showed the biodegradable behavior of PU-based asymmetric membranes after incubation in 10 mL of PBS solution (pH 7.4) with 1.5 mg/mL lysozyme at 37 °C. During the degradation period, the dense skin surface of pure PU membrane remained almost intact except for crack, whereas no obvious collapse occurred in its internal structure. After adding the fillers, the degradation degree of PU-based asymmetric membranes was enhanced, and the

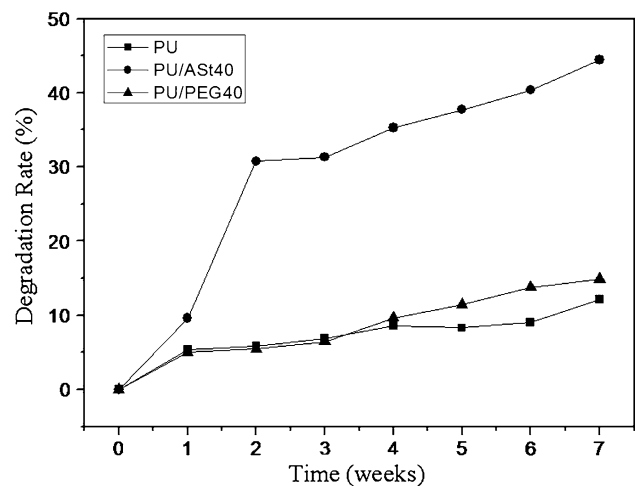


Fig. 8 Degradation rate of pure PU membrane and PU-based composite membranes with 40 % of filler content after biodegradation for different times

holes were formed in the skin surface due to the degradation, and further extended after 7 weeks of degradation. Meanwhile, the substructure became loose. Compared with the feeble degradation of pure PU membrane, the DRs of PU/ASt and PU/PEG composite membranes with 40 % of filler content were increased to 44.4 and 14.9 %, respectively; this result indicated that higher porosity, water absorbability as well as biodegradation of ASt particles themselves resulted in faster biodegradable behavior of PU/ASt composite membranes than that of PU/PEG composite membranes.

Conclusions

A series of novel PU-based asymmetric membranes designed for the application as an ideal wound dressing was fabricated by combining polymer-filler hybridization and immersion precipitation phase inversion. An integral and dense skin layer supported by a porous sublayer was formed during the wet phase inversion process, and evenly distributed the ASt particles throughout the PU/ASt samples. The asymmetric membranes exhibited the characteristics of high porosity, promoted fluid absorption capability, controlled water vapor transmission, but inhibited the exogenous microorganisms invasion deriving from its dense skin layer. The evaluation of these properties suggested that the obtained PU-based asymmetric membranes could be a good candidate to be used as an ideal wound dressing.

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