Preparation of Polyimide Membrane and Its Application in Treatment of Exhausted Unhairing Liquor

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Abstract: A polyimide membrane has been prepared from the polyamic acid by chemical imidization, and used in the filtration of exhausted unhairing liquor for recovery and reuse of wastewater. The separation performances and chemical stability as well as thermal property of the membrane have been determined. The results show that the membrane has a rejection of 92% of COD, a rejection of 90% of suspended solids and a rejection of 48% of sulfide with a flux of 33L/m^{2}h for exhausted unhairing liquor at 0.09MPa. The membrane exhibits excellent stability in the range of pH3-11 with most unhairing chemicals. A reusable wastewater with less organic matter can be obtained by filtration with the polyimide membrane.

Key words: polyimide; polyimide membrane; ultra-filtration membrane; exhausted unhairing liquor

1 Introduction

Exhausted unhairing-liming baths are highly polluting for the presence of sulfide, amines, by-products coming from degradation of hair and epidermis and high concentration of alkalis. The COD of this bath ranges between 13000 and 43000 mg/L of consumed oxygen, and contributes to 55% of total COD of tannery effluent. In order to reduce the pollution of exhausted unhairing-liming baths, some researchers propose the adoption of the bath utrafiltration (UF) and water reuse technologies. In this way, the separation of pollutants from exhausted unhairing liquors were studied using various UF membranes[1, 2, 3, 4], and a protein concentrated stream and a permeate stream to be recycled to the unhairing drum were obtained respectively. In this process, rejections to proteins of 85% and sulfides of 2% as well as a water flux of 0.5–2.5 mL/cm^2 min were reached by a poly-vinyl-idene-fluorides (PVDF) UF tubular membrane[1], and rejections to proteins of 58% and sulfides of 2% as well as a permeate flux of 58–200L/m^2 h were achieved by a polysulfone UF spiral-wound module [2, 3]. Rejections to proteins of 79% and sulfides of 22% as well as a permeate flux of 35–45L/m^2 h were obtained by a cellulose-tri-acetate UF cross-flow membrane [4]. The separation efficiency is affected to a large extent by these commercially available membranes. In order to get an efficient membrane suitable for unhairing-liming baths, the preparation of separation membranes was studied in our work. In the present paper, a polyimide ultrafiltration membrane was prepared from a modified polyamic acid by phase inversion and chemical imidization, and used to separate the pollutants from unhairing-liming baths. The structure, separation performance, and chemical stability as well as thermal property of the membrane were investigated.

2 Experimental

2.1 Membrane preparation

Polyamic acid (PAA) solutions in N, N-dimethylacetamide (DMA) of 15% solid (w/w) content were prepared from pyromellitic dianhydride and 4,4'-Oxydianiline (PMDA/ODA) by a method as mentioned elsewhere. The η_{inh} values of the solution was 1.27 dl/g.

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The casting solution was prepared by mixing 8g of polyethylene glycol (PEG400) with 100g of PAA solution. This solution was cast on a glass plate and kept at 293K with 1min evaporation time, and then the nascent membrane was immersed in a deionized water coagulation bath. After the immersion, the membranes were dehydrated with absolute ethanol, and then imidized in a mixture of acetic anhydride/ triethylamine/acetone for 48 h. The wet membrane was washed in deionized water and finally air-dried to get the finished membrane.

2.2 Membrane structure and rejection measurement

The surface and cross-section structure of the polyimide ulrafiltration membrane was characterized by scanning electron microscopy (SEM).

The pure water flux was measured at 25℃ over 0.04-0.1mPa. The solute rejection rate was measured with polyethylene glycol (PEG20000, PEG10000, PEG6000, PEG1500) at 0.09Mpa. The initial concentration of polyethylene glycol was 1000 ppm in pure deionized water. The initial and the permeate concentrations were measured by visible spectrophotometry using Dragendoff reagent as a chromogenic agent according to HCRJ 066－1999. Rejection refers to the ability of the membrane to keep solute out of the permeate in a single stage process. It was calculated by

%rejection = [1-(solute in permeate / solute in initial solution)]×100.

2.3 Membrane thermal performance measurement

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a STA 409PC integrated thermal analyzer at a heating rate of 10℃ under nitrogen atmosphere. The glass transition temperature (Tg) was calculated at the intersection of the tangents to the corresponding DSC curve.

2.4 Separation of exhausted unhairing liquor with the membrane

The prepared polyimide plate membrane was installed on a module. Exhausted unhairing liquor was pumped through the membrane module at 25℃ under a transmembrane pressure of 0.09Mpa. Periodically permeate flux was determined. At the end of each experiment, COD, total nitrogen, sulphide, suspended solids and ash were analyzed. The rejection of the membrane to them were calculated.

2.5 Measurement of exhausted unhairing liquor and permeate stream

Chemical oxygen demand (COD) was determined by dichromate method according to GB11914－89. Total nitrogen (TN) was determined by alkaline potassium persulfate digestion-UV spectrophotometric method according to GB11894－89. Sulfides (S^{2-})was determined by iodometric method according to HJ/T60－2000. Suspended substance(SS) was determined by gravimetric method according to GB11901－89. Total ash was determined by gravimetric method.

2.6 Membrane chemical stability measurement

The chemical stability of the prepared membrane was examined by incubating the membrane samples in warm water (45 ˚C) , sulfuric acid solution(pH3), calcium hydroxide solution (pH11), 3g/L hydrogen peroxide solution, 2g/L sodium bisulphide solution for up to 12 days. The rejections and fluxes of the membrane were measured before and after the incubating using exhausted liming-unhairing liquor, and were used to investigate changes in membrane characteristics.

3 Results and discussions

3.1 Structure and molecular weight cut-off value of the membrane

Fig. 1a-d shows the results of the SEM observations of the asymmetric polyimide membranes. The surface structure (Fig. 1a) of the ulrafiltration membrane is dense and there is no any pinhole or crack. The cross-section of the membrane consisted of an air-side ultrathin skin layer, a porous finger-like

structure layer and a glass-side skin layer (Fig. 1b). The honeycomb-like holes of diameter up to 0.4-1.0μm or slightly higher are densely distributed on the surface (Fig. 1c) and cross-section (Fig.1d) of supporting wall of finger-like cavity.

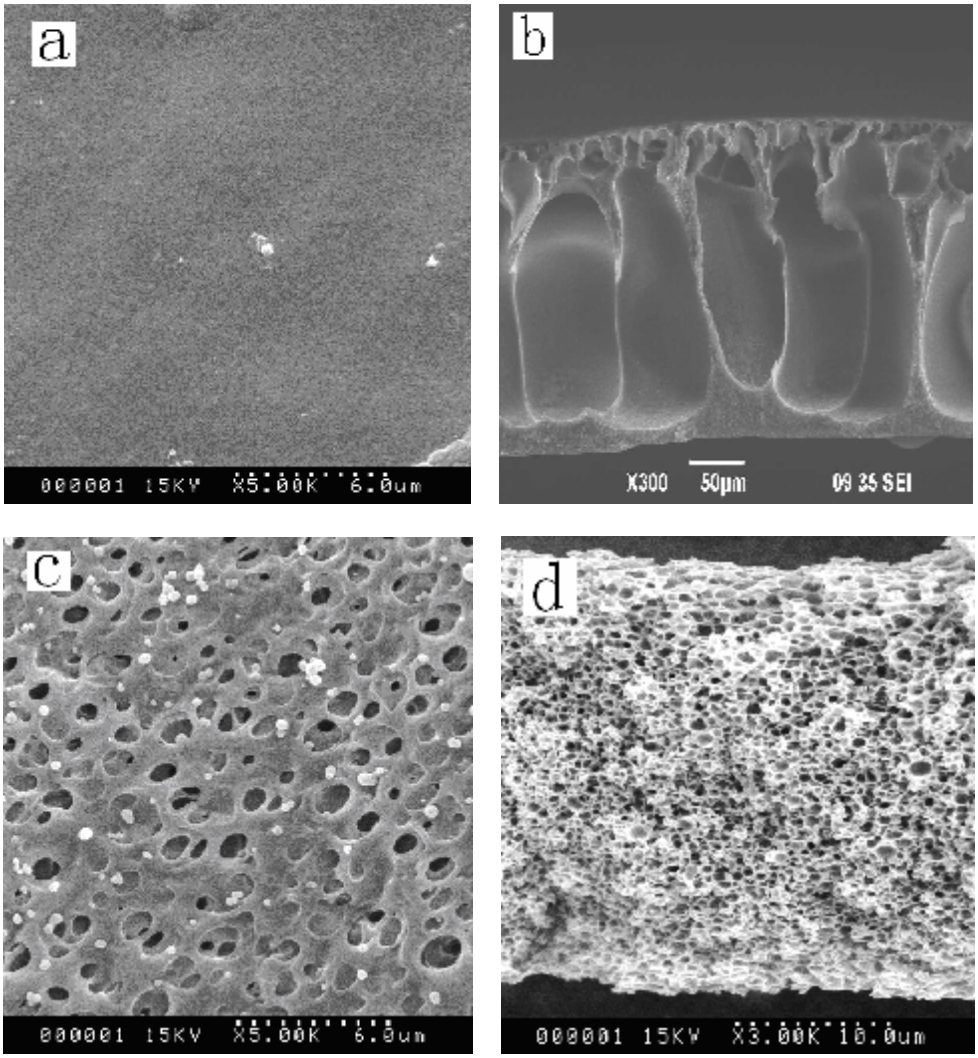

Fig.1 Scanning electron microscopy views of asymmetric polyimide membrane

(a) Membrane surface at 5000×magnification.

(b) Membrane cross-section at 300×magnification.

(c) Finger-like cavity surface at 5000×magnification.

(d) Supporting wall cross-section of finger-like cavity at 3000×magnification.

Table 1 shows the pure water fluxes at different transmembrane pressures for the polyimide utrafiltration membrane. As expected, the higher transmembrane pressure, the higher permeates fluxes were achieved, and at 0.09mPa a flux of 35 L/m^{2}h was obtained. Moreover, a rejection to PEG10000 of 92% was achieved at 0.09mPa (seen Table 2). This implies that the molecular weight cut-off (MWCO) value of the polyimide utrafiltration membrane is approximately (PEG)10000Da.

Table 1 Pure water fluxes of the membrane at different transmembrane pressures

Pressure/mPa	0.04	0.05	0.06	0.07	0.08	0.09	0.1
Flux/L/m^{2}h	2	4	12	21	29	35	41

Table 2 Rejections of the membrane to various molecular weight polyethylene glycol

PEG molecular mass/Da	800	1000	6000	10000	20000
Rejection/%	7.5	21	62	92	96

3.2 Thermal stability of the membrane

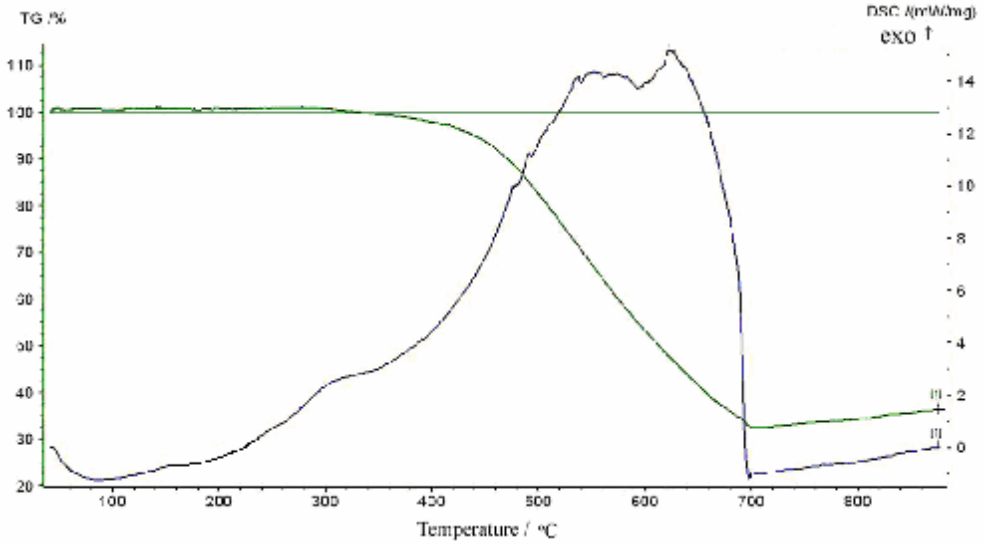

Fig. 2 TGA and DSC curves of polyimide utrafiltration membrane

The thermal stability of prepared membrane was evaluated by thermogravimetric (TGA) analysis. Fig. 2 presents the weight loss of the membrane. In general, it is seen that the degradation of the membranes occurs in two steps. The first step, from 330℃ to 470℃, represents the volatilization of the volatile matter and/or the evaporation of residual water. The second step, starts at 470℃ and ends at 700℃, represents the main thermal degradation of the polyimide chains. These indicate that the prepared membrane possesses much high thermal stability.

Fig. 2 also presents the DSC curve of the polyimide ultrafiltration membrane prepared in this study. A broad endothermic peak from 155℃ to 305℃ can be observed on the curve. The corresponding glass transition temperature (Tg) is 160℃. This higher glass transition temperature imply that the prepared membrane possess a looser structure because a higher Tg indicates that membrane possesses more free volume fraction and vice versa.

3.3 Separation performances of the membrane

Characteristics of three different exhausted unhairing-liming liquors and their permeate stream obtained by utralfiltration with the prepared membrane was shown in Table 3 and Table 4. It can be observed that the exhausted unhairing-liming liquors were considerably polluted due to the presence of sulfide, amines, by-products coming from degradation of hair and epidermis and high concentration of alkalis. After utrafiltration with the prepared membrane, the pollutants in the permeate stream were significantly reduced. The best separation results in terms of flux and rejection were obtained at 25℃ under a transmembrane pressure of 0.09Mpa and were shown in Table 5. For all three samples of exhausted unhairing-liming liquor, rejections more than 92% of COD, 87% of total nitrogen, 90% of suspended solids and 48% of sulfide were achieved. This indicates that the membrane cut-off on the hydrolyzed proteins is efficient since COD and total nitrogen were mainly consisting in hydrolyzed proteins. In addition, the membrane cut-off on the sulphide and other salts can not be ignored due to the adsorption of protein and membrane on the salts. Under this utrafiltration conditions, the highest flux was

achieved in the treatment of exhausted cattlehide unhairing liquor. This implied that the prepared membrane did not reject the peptide molecules of low molecular weights that clogged the membrane pores, decreasing the membrane fouling.

Table 3 Characteristics of exhausted unhairing liquor

Samples	COD(mg/L)	TN(mg/L)	Ash(mg/L)	Sulphide(mg/L)	SS(mg/L)
Goatskin unhairing liquor	42600	3864	30982	1273	8600
Cattlehide unhairing liquor	13000	2315	29563	1088	2766
Pigskin unhairing liquor	20000	4511	37456	4398	7586

Table 4 Characteristics of permeate stream after ultrafiltration with the prepared membrane

Samples	COD(mg/L)	TN(mg/L)	Ash(mg/L)	Sulphide(mg/L)	SS(mg/L)
Goatskin unhairing liquor	2556	502	8985	496	344
Cattlehide unhairing liquor	1040	278	8869	566	277
Pigskin unhairing liquor	1400	361	9364	1847	607

Table 5 Rejections and fluxes of the membrane in the ultrafiltration of exhausted unhairing liquor

Samples	Rejection COD(%)	Rejection TN(%)	Rejection Ash(%)	Rejection Sulphide(%)	Rejection SS(%)	Flux ($L/m^2 \cdot h$)
Goatskin unhairing liquor	94	87	71	61	96	21
Cattlehide unhairing liquor	92	88	70	48	90	33
Pigskin unhairing liquor	93	92	75	58	92	18

3.4 Chemical stability of the membrane

The rejections and fluxes of the membranes incubated with warm water and various dilute solution are shown in Table 6. No significant change in rejections to COD and SS was observed for the membranes after incubating in warm water (45℃), dilute sulfuric acid solution (pH3), 3g/L hydrogen peroxide solution and 2g/L sodium hydrosulfide solution for 12 days, while slight decrease was observed after incubating in calcium hydroxide solution (pH11) for 12 days. Increasing porosity as noticed by increase in flux would be the possible reason for this change. The slight increase in flux for membrane incubated with calcium hydroxide solution is possibly due to extraction of a small quantity of hydrophilic additive，and is still within the acceptable range for its application. In general, the prepared membrane exhibits excellent stability in the range of pH3-11 with most unhairing chemicals.

Table 6 Rejections and fluxes of the membranes incubated with warm water and various dilute solution

Samples	Rejection SS(%)	Rejection COD(%)	Rejection Sulphide(%)	Flux ($L/m^2 \cdot h$)
Untreated membrane	96	94	62	18
warm water treated membrane	94	93	56	20
Sulfuric acid treated membrane	95	93	58	23
Calcium hydroxide treated membrane	90	90	52	26
Hydrogen peroxide treated membrane	93	94	60	21
Sodium hydrosulfide treated membrane	92	93	59	22

4 Conclusions

A polyimide utrafiltration membrane with molecular weight cut-off value of (PEG) 10000Da was successfully prepared from modified polyamic acid by phase inversion and chemical imidation in this study. The surface structure of the membrane is dense and its cross-section consisted of an air-side ultrathin skin layer, a porous finger-like structure supporting layer and a glass-side skin layer. The honeycomb-like holes of diameter up to 0.4-1.0μm are densely distributed on the supporting wall of finger-like cavity. When the membrane was applied to separating the pollutants from exhausted liming-unhairing liquor at 25℃ under a transmembrane pressure of 0.09Mpa, rejections more than 92% of COD, 87% of total nitrogen, 90% of suspended solids and 48% of sulfide were achieved with a flux of 33L/m^2h. The membrane exhibits excellent rejection and flux stability to warm water(45℃), acid solution (pH3) and alkalis solution (pH11), as well as dilute oxidant and reductant solution. A reusable wastewater with less organic matter can be obtained by filtration with the polyimide membrane.

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