Preparation of Anti-Oil Stained Membrane by Grafting Polyethylene Glycol Macromer onto Polysulfone Membrane

HIROO IWATA,[1,*] MARIA I. IVANCHENKO,[1] and YOSHIYUKI MIYAKI[2]

[1]National Cardiovascular Center Research Institute, 5-7-1, Fujishiro-dai, Suita, Osaka 565, Japan, and [2]TOSOH Corporation, Shinnanyo, Yamaguchi, Japan

SYNOPSIS

In this study, anti-oil stained ultrafiltration membrane was prepared by grafting a polyethylene glycol diacrylate macromer onto a plasma-activated polysulfone membrane. The macromer formed a hydrate layer which prevented oil in emulsion from directly contacting the membrane surface, thus preventing the oil from staining the membrane. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polysulfone (PS) is a polymer with a high glass transition temperature, thermal and oxidative stability, and low creep even at elevated temperatures. Membranes made from PS are widely utilized in ultrafiltration (UF) and microfiltration. However, the hydrophobicity of PS causes adsorption of hydrophobic and amphoteric solutes onto the membrane in aqueous environments. This impairs, and may eliminate, the functionality of the membrane. A surface with a hydrated layer interacts to a lesser extent with hydrophobic and amphoteric solutes.[1,2] We have developed techniques to form a hydrate layer using surface graft polymerization.[3] These could be applied to create hydrophilic UF membranes. However, with membrane pores measuring 100–1,000 Å, the length of the grafted polymer must be controlled to avoid closing off membrane pores.[4] In the current study, we created anti-oil stained membrane by forming a hydrated layer on a PS membrane by grafting polyethylene glycol onto its surface.

EXPERIMENTAL

PS membranes (TOSOH Corp., Shinnanyo, Japan) with a molecular weight cut-off of 3×10^6 Da were immersed in deionized water for 2 days to remove glycerol. They were then immersed for 1 day in 0.2% polyethylene glycol with acrylate functional groups at both ends (PEGDA) (Polyscience Inc., Warrington, PA) in a solution of 25% isopropyl alcohol and water, then air-dried. Molecular weight of PEGDA is 4×10^3 Da. The PS membranes were then treated with plasma using a glow discharge reactor (Model LCVD-19, Shimadzu Corp., Kyoto, Japan) in argon (Ar) at 0.1 Torr by supplying 13.56 MHz high frequent current at 30 W between the two electrodes for 10 sec. Ungrafted PEGDA was then removed from the PS membranes by extraction with deionized water (PEGDA-membrane). The same procedure was used with polyethylene glycol (WAKO Pure Chemicals, Osaka, Japan) in place of PEGDA (PEG-membrane). PEG has a molecular weight of 5×10^3 Da, and no terminal acrylates. This allowed observations on the effect of the acrylate functional groups of PEGDA.

RESULTS AND DISCUSSION

The membrane surfaces were characterized by X-ray photoelectron spectroscopy (XPS) (ESCA 750,

* To whom correspondence should be addressed.

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Shimadzu Co., Ltd., Kyoto, Japan). The stoichiometrical atomic ratio of carbon : oxygen : sulfur (C : O : S) of the native PS membrane was 1.0 : 0.168 : 0.038, which coincides well with that calculated from the molecular structure of PS. After PEGDA grafting, the atomic ratio of C : O : S became 1.0 : 0.357 : 0.019. The atomic O : C ratio increased and the atomic S : C ratio decreased. However, the atomic O : C ratio was still less than 0.5, as calculated from the molecular structure of PEG, and sulfur was still observed in the spectrum after PEGDA grafting. This analysis indicates that the membrane surface was not thoroughly covered by the thick layer of the grafted PEGDA chains, but PEGDA grafting clearly occurred.

The XPS spectra of C_{1S} could be resolved into four components: $-C^*H_2-$, $-C^*-S-$, $-C^*-O-$, and $-C^*=O$. The C_{1S} spectrum of the PS membrane is composed of a broad peak at a lower binding energy from the carbon of $-C^*H_2-$ and peaks at higher binding energies from the carbon of $-C^*-S-$ and $-C^*-O-$ (Fig. 1). After PEGDA grafting, the intensity of the $-C^*-O-$ component increased. It also supports the grafting of PEGDA.

Phosphate-buffered saline (PBS) containing 0.3% olive-oil emulsion was filtered under a pressure of 0.5 kgf/cm^2 using a stirred ultrafiltration cell. The filtration sequence started with 5-min filtration followed by 20-min exposure to the oil emulsion without filtering or agitation. This was followed by another 5-min filtration, then 24-h exposure without agitation. This was followed by a final 5-min filtration period. To determine the effluent flux during filtration, the filtrate was collected into sampling cups during 1-min intervals and weighed.

Figure 2 shows normalized levels of effluent flux during each period of filtration. The untreated PS membrane demonstrated quite high effluent flux (J_0 = 1.4 ml/cm^2 min) of PBS without olive oil. When olive oil was emulsified into the PBS, however, effluent flux quickly decreased to zero after filtration of only a few ml/cm^2. The oil in the emulsion adhered to the hydrophobic membrane surface and closed the pores of the membrane. Figure 2 also shows the effluent flux through an Ar plasma-treated membrane without adsorbed macromers, and those through the PEG- and PEGDA-membranes. The Ar-treated membrane with no adsorbed macromers and the PEG-membrane remained functional after 5-min filtration, each treatment clearly having imparted some oil-resistant properties to the PS membrane. Effluent flux through the PEGDA membrane

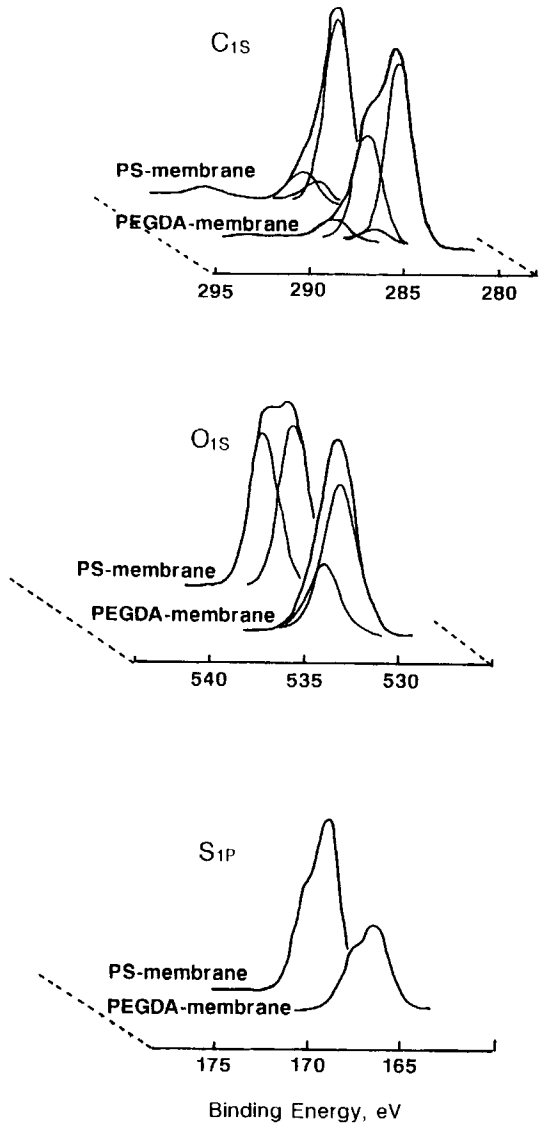

Figure 1 XPS spectra of the membrane surfaces. PS membrane: a PS membrane washed with deionized water to remove glycerol. PEGDA-membrane: a PS membrane with absorbed PEGDA treated by Ar plasma.

decreased, but the rate of effluent flux approached a constant. The efficacy of PEGDA grafting was more clearly pronounced after stationary exposure of the membrane to the oil emulsion. Rates of effluent flux through the PEGDA-membrane remained constant after the 20-min and 24-h exposures. However, the effluent flux of the plasma-treated membrane decreased to one third after 20-min stationary exposure, and after 24 h it completely lost its filtration ability. The PEG-membrane

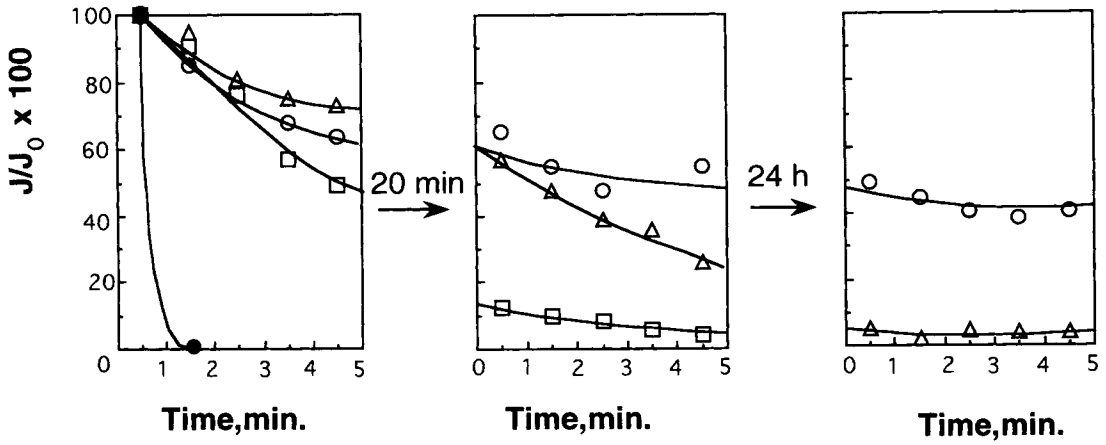

Figure 2 Effect of surface modification of PS membranes on the effluent flux of a 0.3% olive-oil emulsion in the PBS under a pressure of 0.5 kgf/cm^2. Normalized effluent fluxes J/J_0 are shown, where J_0 is the effluent flux in the first min of filtration for each membrane. The filtration sequence started with 5-min filtration followed by 20-min exposure to the oil emulsion without filtering or agitation. This was followed by another 5-min filtration followed by 24-h exposure without agitation. This was followed by a final 5-min filtration period. (●), PS membrane (J_0 = 0.1 mL/cm^2 min); (○), PEGDA-membrane (J_0 = 1.4 mL/cm^2 min); (□), Ar plasma-treated PS membrane (J_0 = 2.0 mL/cm^2 min); (△), PEG-membrane (J_0 = 1.75 mL/cm^2 min).

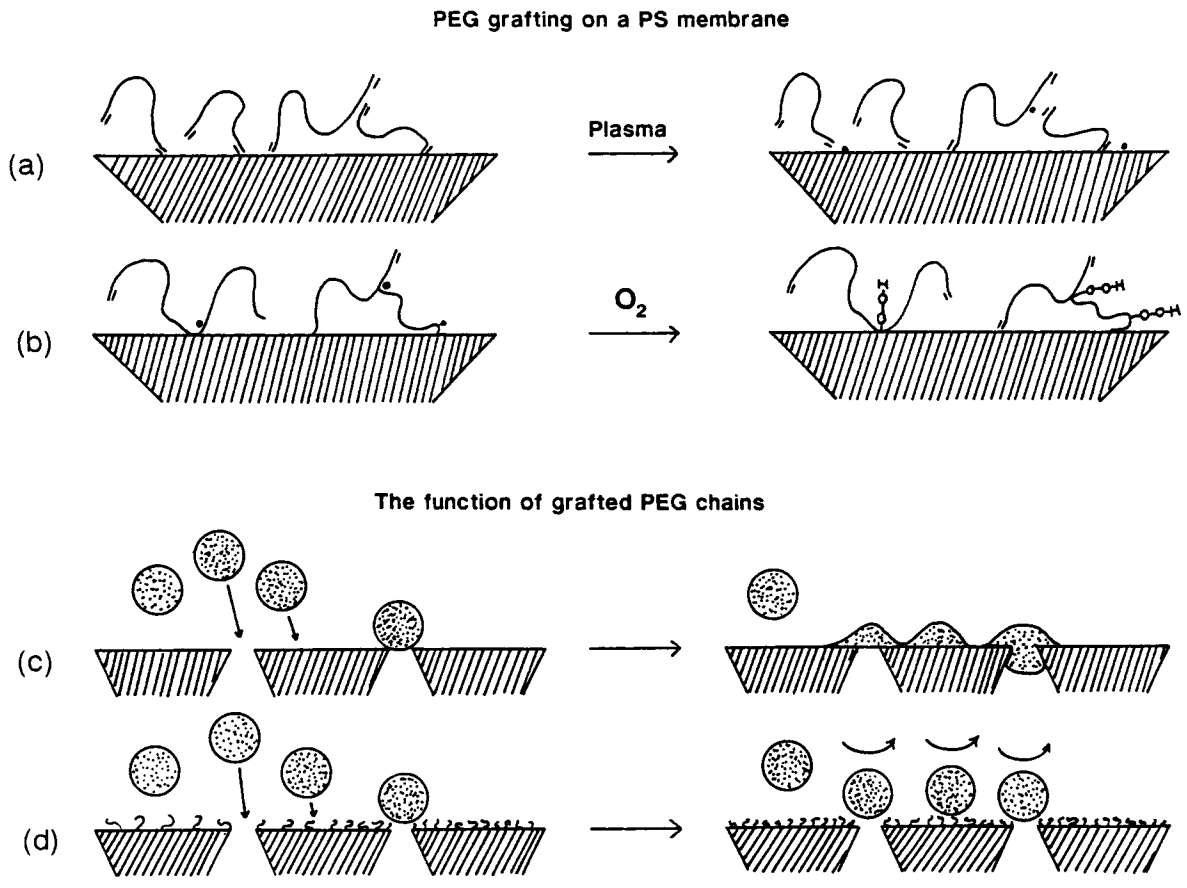

Figure 3 Schematic representation of the grafting of the PEG macromer on a PS membrane and the resulting effect of the grafted PEG. The schema (c) shows oil adsorbed onto the hydrophobic surface of an untreated PS membrane. The schema (d) shows how the hydrophilic PEG chains prevent the oil from contacting the surface of the PS membrane.

showed anti-oil stained properties, but did decrease in its filtration rate after 24 h of stationary exposure to the oil emulsion. This decrease was probably due to insufficient grafting of PEG chains.

Figure 3 schematically shows the suspected role of the PEGDA chains in making the membrane less susceptible to oil-staining. The chains dissolved into emulsion prevent oil from directly contacting the surface of the membrane, and is likely to be the primary mechanism contributing to the membrane's resistance to oil-staining. A hydrophobic membrane can be rendered resistant to oil-staining by grafting a hydrophilic polymer.

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