Chapter 19

Surface Modification of Polymeric Membranes by UV Grafting

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Polypropylene and polysulfone membranes were surface modified by UV grafting with acrylic acid. ATR and XPS analyses confirmed that acrylic acid was well grafted to the membrane surface. Grafting of acrylic acid hydrophilized the membrane surfaces, which enhanced the membrane water flux up to 10 times. It also improved the rejection properties of the membranes, which is an unusual trend compared to those of conventional membranes. The hydrophilized membrane surface exhibited strongly reduced membrane fouling. Various parameters of the UV grafting process were investigated, such as reaction time, monomer and photo-initiator concentration, irradiating distance, reaction temperature, and solvent type. The effect of each parameter was explored to optimize the membrane performance of these materials.

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its hydrophilicity. 1 μL of water was dropped from a micropipet onto the leveled surface of the membrane to make a single drop. A CCD camera installed perpendicular to the surface captured the image of the drop at a magnification of 100, which helped us confirm that the membrane surface at the contact point is horizontal. The captured image was processed by an image analyzer system (ImagePro, Mediacybernetics Co.). Each contact angle was measured at least 5 times and averaged to avoid errors from surface roughness. Membrane structure was examined by scanning electron microscopy (SEM) using a Stereoscan 440 from Leica Co. Chemical analyses of the membrane surfaces were performed by FT-IR (ATR) (Perkin Elmer 2000) and XPS (ESCA 2000, VG Microtech).

Results and Discussion

Effect of UV Grafting Time

When acrylic acid was grafted to the PP and PSf membrane surfaces, UV grafting time was varied from 30 sec to 6 min. As shown in Figures 1 and 2, the carbonyl stretching peak at 1,720 cm^{-1} in the ATR spectra was observed for both PP and PSf membranes; this peak confirmed the presence of acrylic acid on the membrane surface. Even though the carbonyl stretching peak was confirmed from membrane surfaces that were washed with solvent to remove ungrafted acrylic acid, it was not clear that the carbonyl stretching peak directly represented grafted acrylic acid. XPS analysis was performed to confirm the grafting reaction by showing the formation of new chemical bonds at the surface. The C 1s spectra of untreated PP and UV grafted PP membrane are compared in Figure 3. An untreated PP sample exhibits only a C-C peak, whereas a UV grafted sample contained O=C-O and O=C peaks in addition to the C-C peak, which confirmed the grafting of acrylic acid to the membrane surface.

In ATR spectra, the carbonyl peaks in both samples increased with increasing grafting time. However, after optimum points, the carbonyl peaks decreased in both cases. The optimum wavelength range for benzophenone was 300 – 350 nm; UV irradiation below 300 nm might damage the grafted acrylic acid as well as the membrane matrix after long grafting times. As shown in Figure 4, the thickness of the sponge layer on PSf membranes decreased with grafting time, which reflected the damage of the sample by the UV irradiation. Unfortunately, preparation of SEM samples for cross sectional views was not possible for PP membranes.

In Figures 5 and 6, the effect of grafting time on flux and rejection of PP and PSf membranes is illustrated. Each membrane showed the best flux at the maximum absorbance seen in the FTIR in Figures 1 and 2. The pure water flux was compared with the solution flux for each membrane. The solution flux for

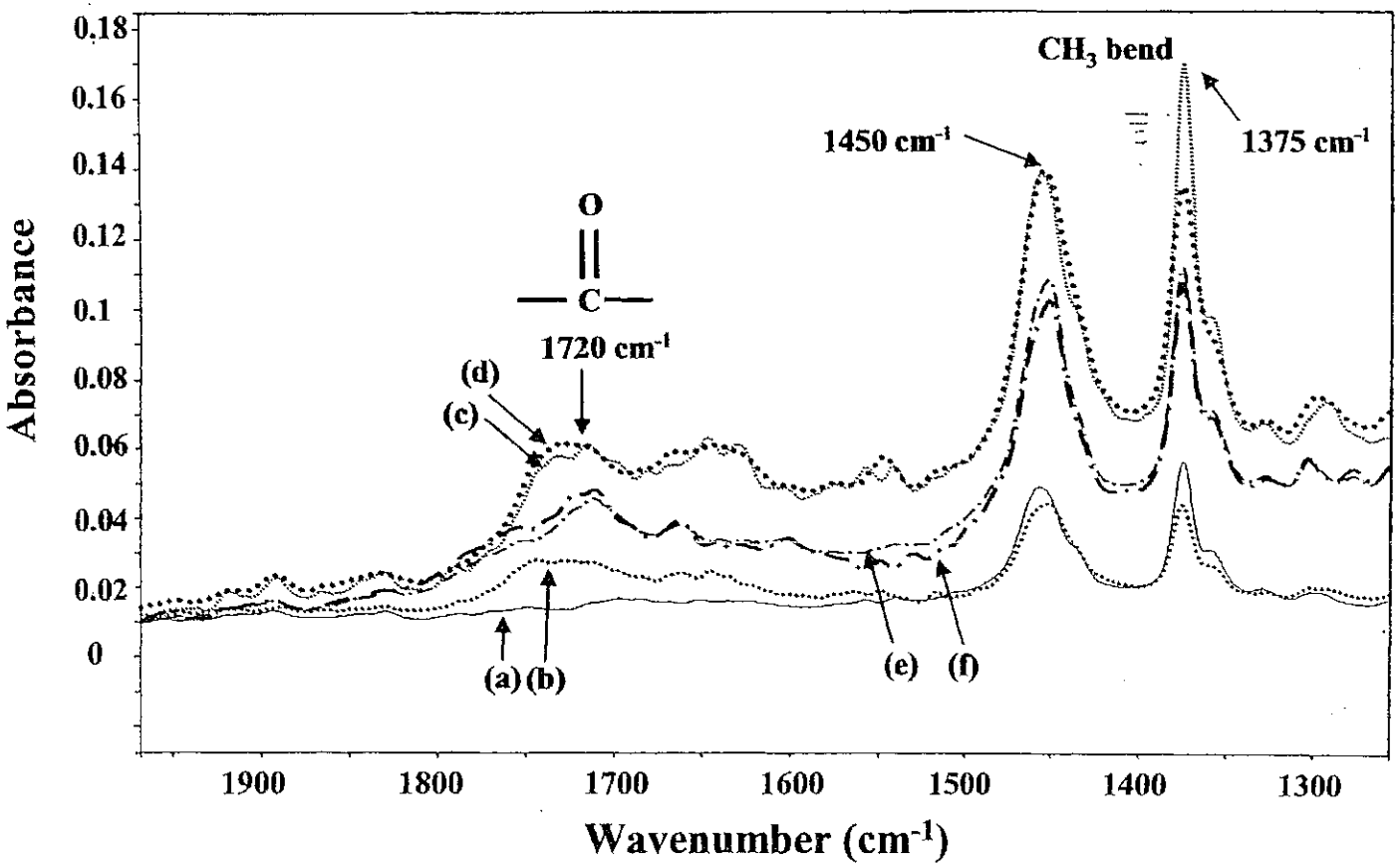


Figure 1. ATR spectra of PP membrane UV grafted with acrylic acid (irradiation distance: 16 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.03 mole/l, temperature: 60 °C, solvent: acetone): (a) untreated, (b) 0.5 min, (c) 1 min, (d) 2 min, (e) 3 min and (f) 4 min.

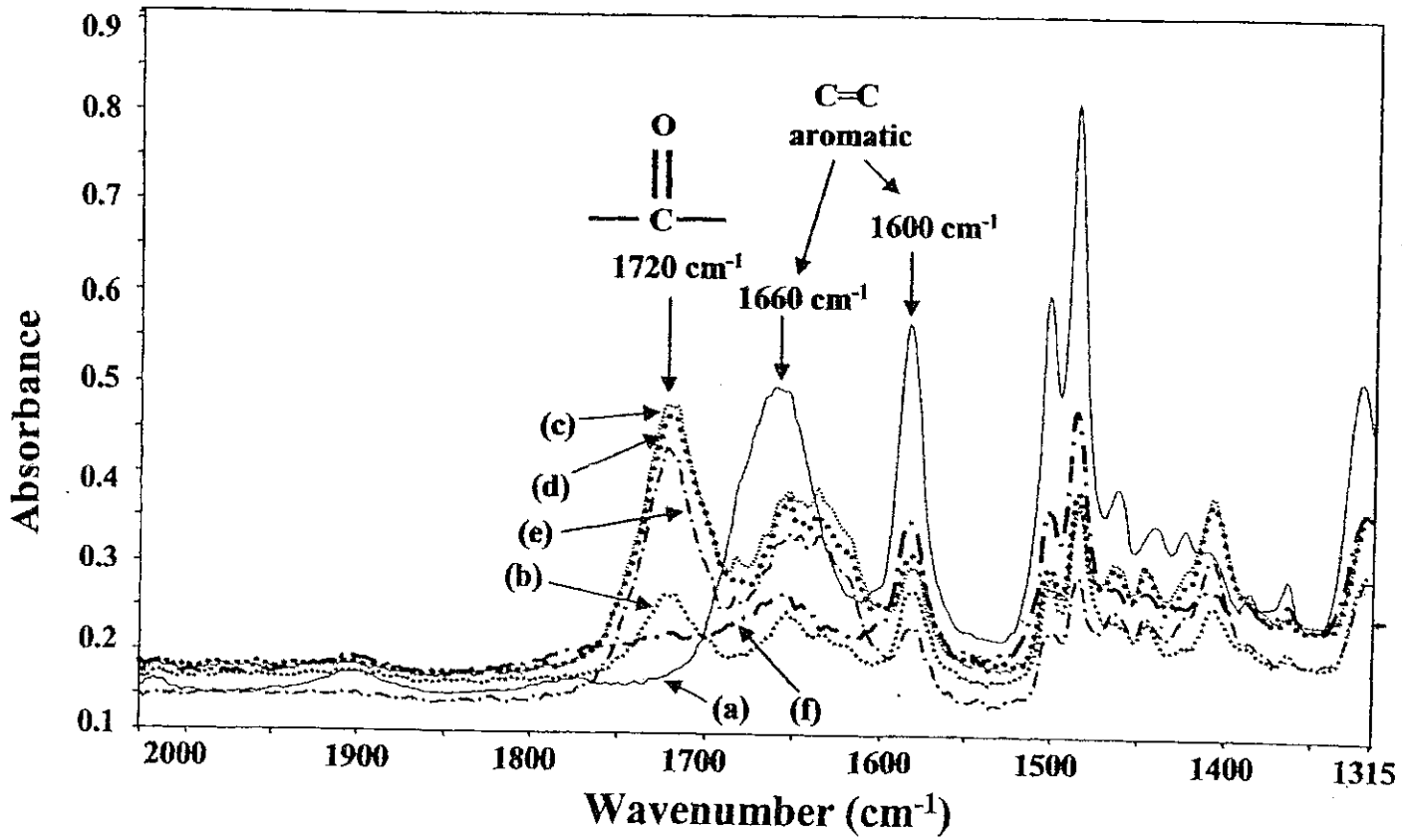
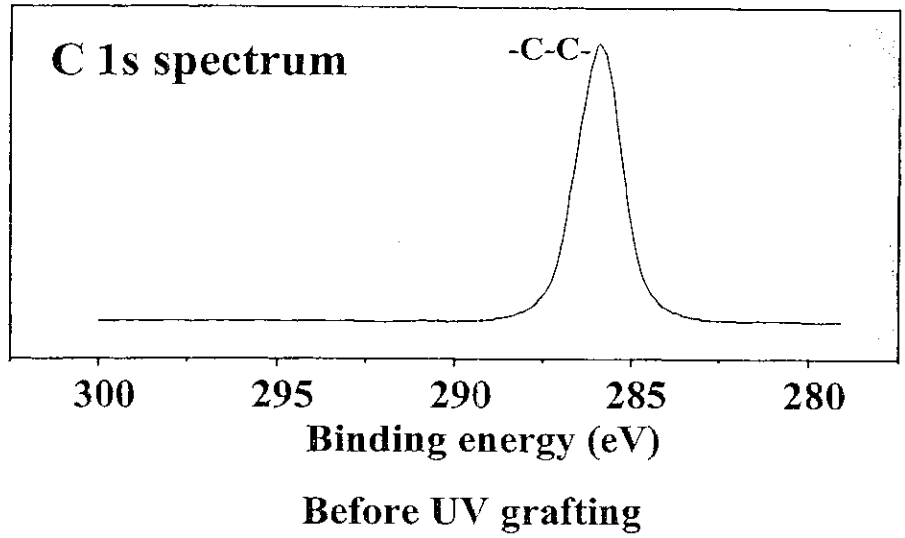


Figure 2. ATR spectra of PSf membrane UV grafted with acrylic acid (irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l, temperature: 60 °C, solvent: acetone): (a) untreated, (b) 0.5 min, (c) 1 min, (d) 2 min, (e) 3 min and (f) 4 min.



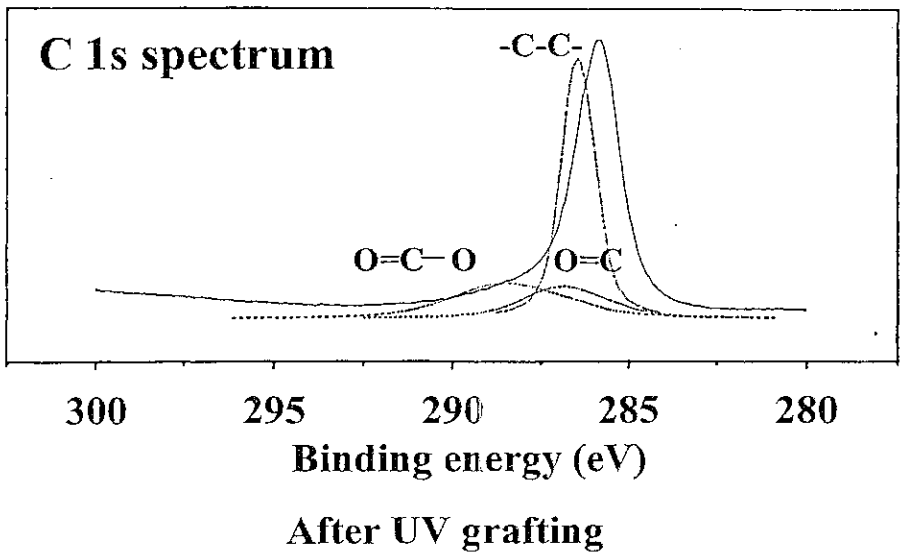
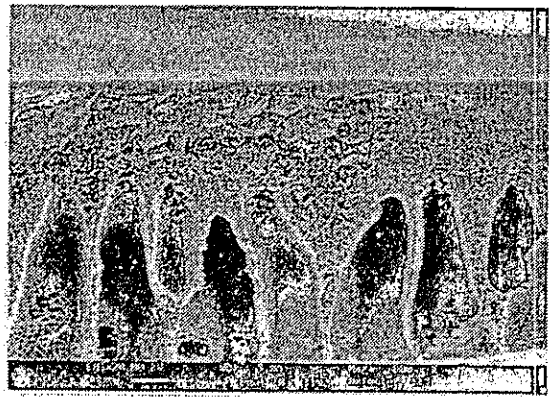
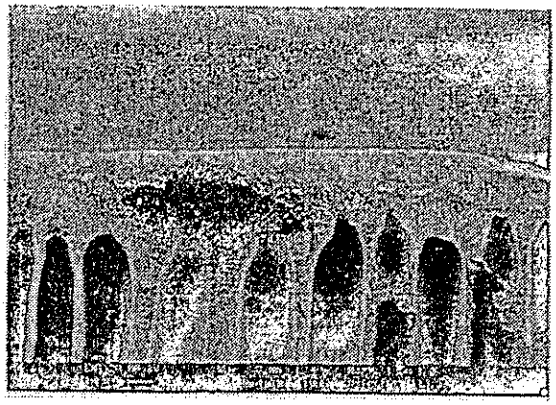


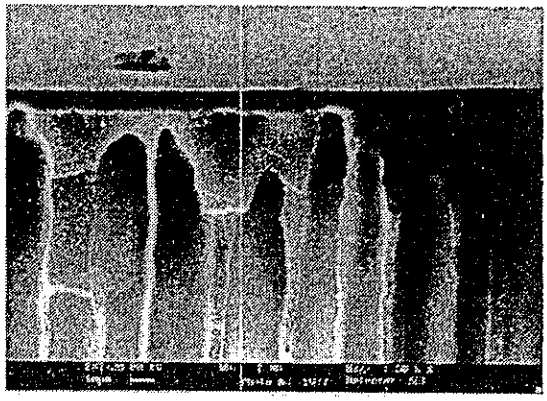
Figure 3. XPS spectra of PP membrane UV grafted with acrylic acid (irradiation distance: 16 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.03 mole/l, temperature: 60 °C, solvent: acetone).



Original PSf



Grafted for 1 min



Grafted for 3 min

Figure 4. Cross sectional images of PSf membranes UV grafted with acrylic acid (irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l, temperature: 60 °C, solvent: acetone).

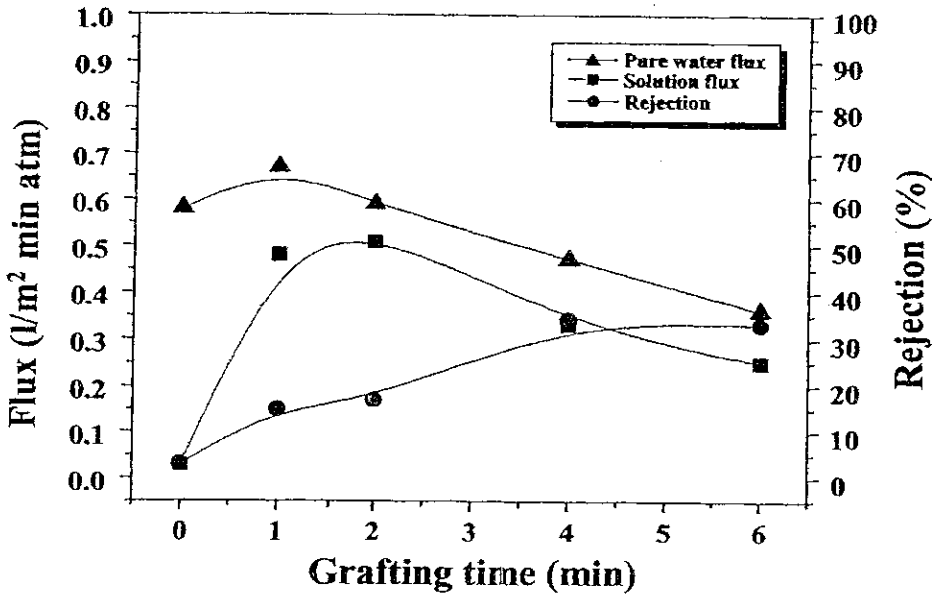


Figure 5. Effect of grafting time on performance of PP membrane UV grafted with acrylic acid (irradiation distance: 16 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.03 mole/l, temperature: 60 °C, solvent: acetone).

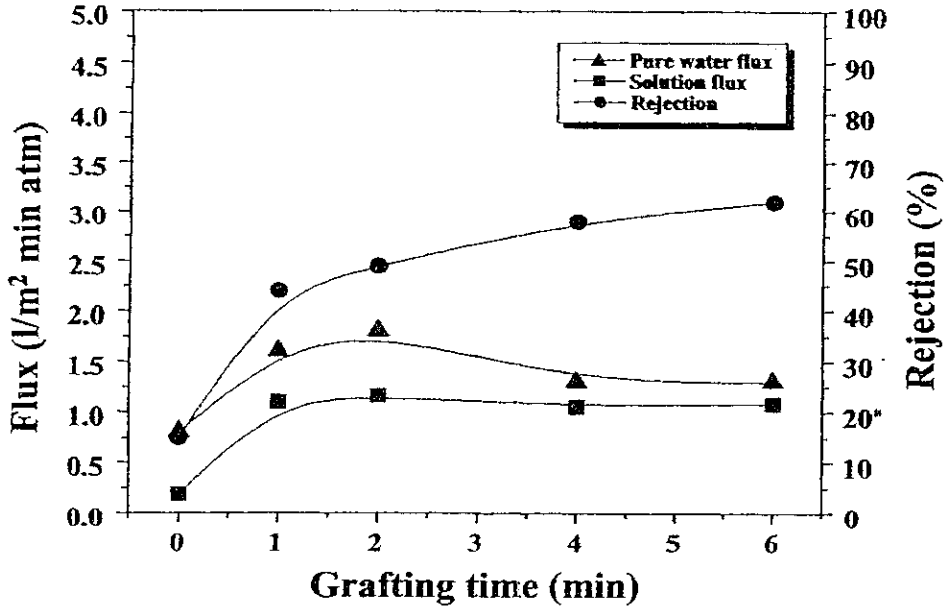


Figure 6. Effect of grafting time on performance of PSf membrane UV grafted with acrylic acid (irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l, temperature: 60 °C, solvent: acetone).

each membrane is smaller than the pure water flux, which can be attributed to membrane fouling by the dextran in the solution. The solution flux through untreated PP membranes was significantly reduced relative to the pure water flux value. Since PP is a hydrophobic material, membrane fouling was a serious issue for this sample. After UV grafting, the solution flux through the PP membranes greatly increased, and they reached values comparable to those of pure water. For both membranes, dextran rejection steadily increased with grafting time, which could be attributed to the damage of the microporous structure by the UV irradiation.

UV grafting with acrylic acid strongly reduced the contact angle with water as shown in Figure 7 for PP membranes. Surface roughness of microfiltration membranes could cause errors in measuring contact angle. In this work, the contacting image of the drop with the membrane surface was magnified by 1,000 times to assure correct measurements. Increasing grafting time reduced the contact angle of water drops on the membrane surface. However, there were also an optimum UV grafting time for minimizing the contact angle.

UV grafting with acrylic acid reduced the BSA adsorption for both PP and PSf membranes as shown in Figure 8. This result is believed to be associated with the increasingly hydrophilic character of the surface with increasing grafting time. PP membranes showed minimum adsorption at the optimum grafting time observed in other measurements.

Effect of UV Irradiation Distance

The distance between the sample and the UV source determined the beam intensity and influenced the membrane as shown in Figure 9. The hydrophobic PP membrane surface was hydrophilized at short distances with high beam intensity, and water flux increased. An increase in the source to sample distance reduced the beam intensity, the membrane surface was less hydrophilic after grafting, and the water flux was reduced. However, if the source to sample distance was too short, the sample was damaged, which decreased rejection, and it is shown in Figure 9 that there is an optimum distance for UV irradiation. For PP membranes, the optimum distance was 18 cm.

Effect of Monomer Concentration

Different amounts of acrylic acid were applied to the surface of PP membranes prior to the UV grafting reaction. As shown in Figure 10, an increase in the monomer concentration resulted in more grafting and a more hydrophilic surface, which increased water flux. However, if there was too much

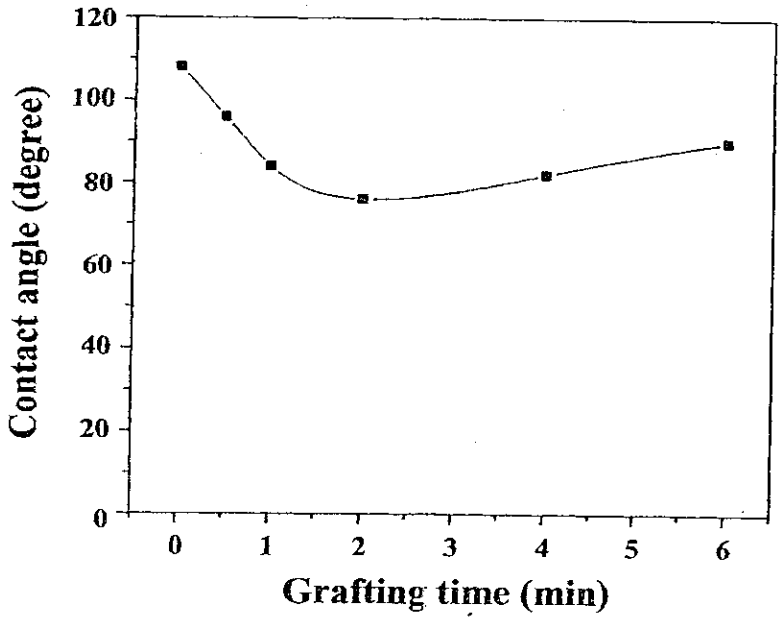


Figure 7. Effect of grafting time on contact angle of PP membranes UV grafted with acrylic acid (irradiation distance: 16 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.03 mole/l, temperature: 60 °C, solvent: acetone).

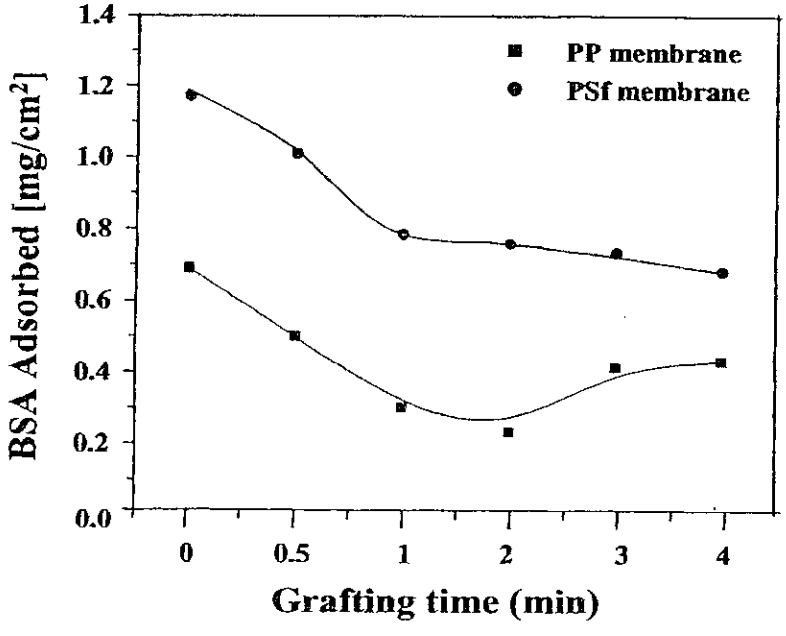


Figure 8. Effect of grafting time on BSA adsorption to PP and PSf membranes UV grafted with acrylic acid (irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l, temperature: 60 °C, solvent: acetone).

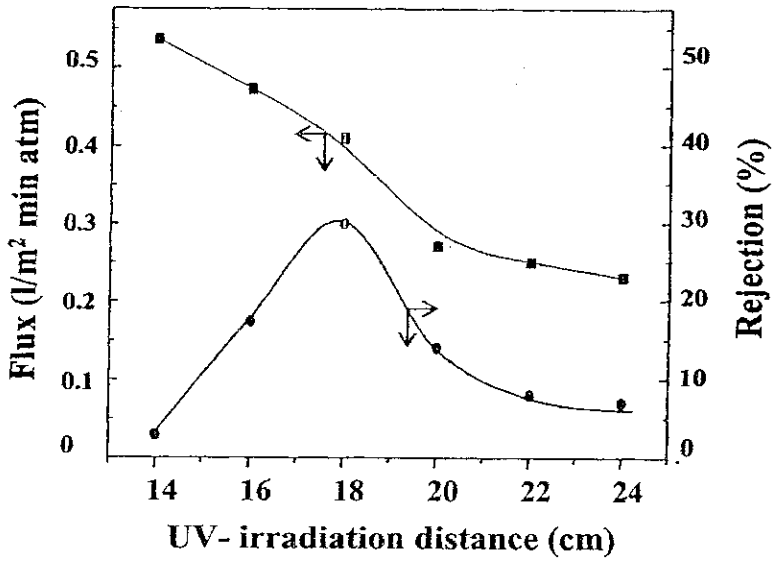


Figure 9. Effect of irradiation distance on performance of PP membranes UV grafted with acrylic acid (grafting time: 2min, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l, temperature: 60 °C, solvent: acetone).

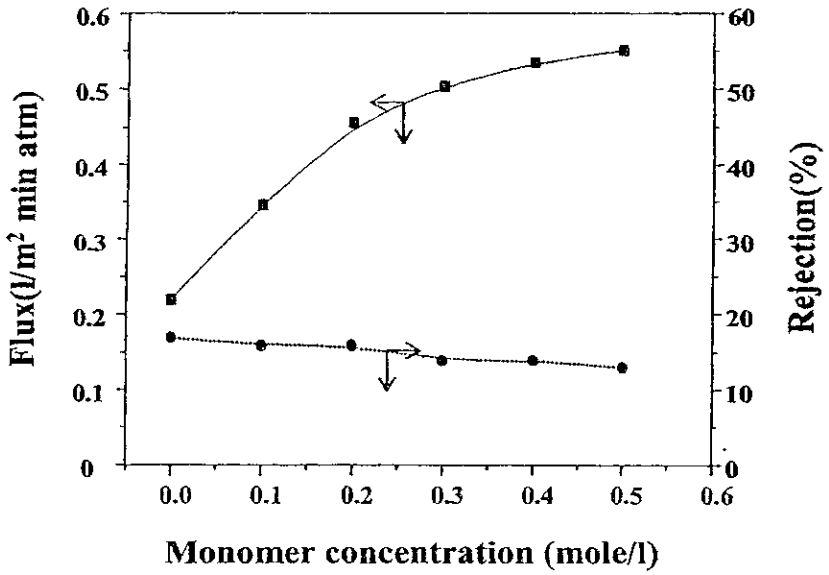


Figure 10. Effect of irradiation distance on performance of PSf membranes UV grafted with acrylic acid (grafting time: 2min, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l, temperature: 60 °C, solvent: acetone).

monomer, then monomer homopolymerization instead of grafting to the membrane surface occurred, and the rate at which flux increased with increasing monomer concentration was reduced. Rejection was low within the monomer concentration range considered. As shown in Figure 11, BSA adsorption was also reduced and reached a constant value at concentrations greater than 0.3 mole/l despite the increase of monomer concentration.

After the UV grafting reaction, the sample was solvent leached in a Soxhlet apparatus. Therefore, any unreacted monomer and ungrafted homopolymer were properly removed from the sample. The grafting ratio of each sample was determined by comparing the characteristic peak heights of acrylic acid and PP. Acrylic acid showed a characteristic peak at 1,710 cm^{-1} and PP has one at 710 cm^{-1}. The ratio of absorbance, $A_{1710\ cm^{-1}}/A_{710\ cm^{-1}}$ represented the relative grafting ratio. Relative grafting ratio increased with monomer concentration as shown in Figure 12. After the Soxhlet leaching, the relative grafting ratio was reduced by elimination of unreacted monomer and homopolymer. At high monomer concentration, Soxhlet leaching strongly reduced the relative grafting ratio. Therefore, there should be an optimum monomer concentration for effective grafting with little homopolymerization.

Effect of Photoinitiator Concentration

Different amounts of photoinitiator, benzophenone, were introduced into the UV grafting reaction of acrylic acid to the PP membrane. As shown in Figure 13, an increase in photoinitiator concentration enhanced the membrane performance to some extent by forming more radicals. However, too much radical formation inhibited the propagation reaction and terminated the chain reaction for grafting. Excessive photoinitiator resulted in a poor grafting reaction and deteriorated the membrane performance.

Effect of Reaction Temperature

UV grafting of acrylic acid to PP membranes was performed at various temperatures. An increase in reaction temperature helped the grafting reaction, and it enhanced the flux while slightly decreasing the rejection as shown in Figure 14. Figure 15 shows that BSA adsorption gradually decreased as reaction temperature increased. However, it must be remembered that a reaction temperature that is too high might damage the sample, so there is probably an optimum temperature for fast reaction, low BSA adsorption, and mimimal damage to the sample.

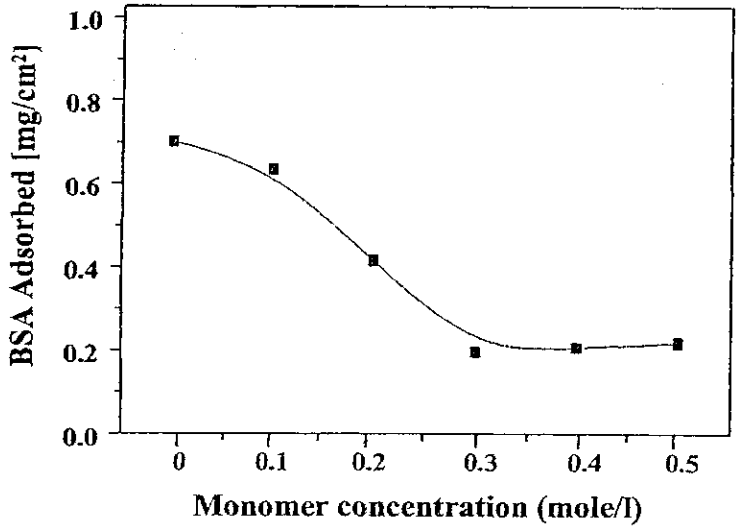


Figure 11. Effect of monomer concentration on performance of PP membranes UV grafted with acrylic acid (grafting time: 2min, irradiation distance: 16 cm, benzophenone concentration: 0.02 mole/l, temperature: 60 °C, solvent: acetone).

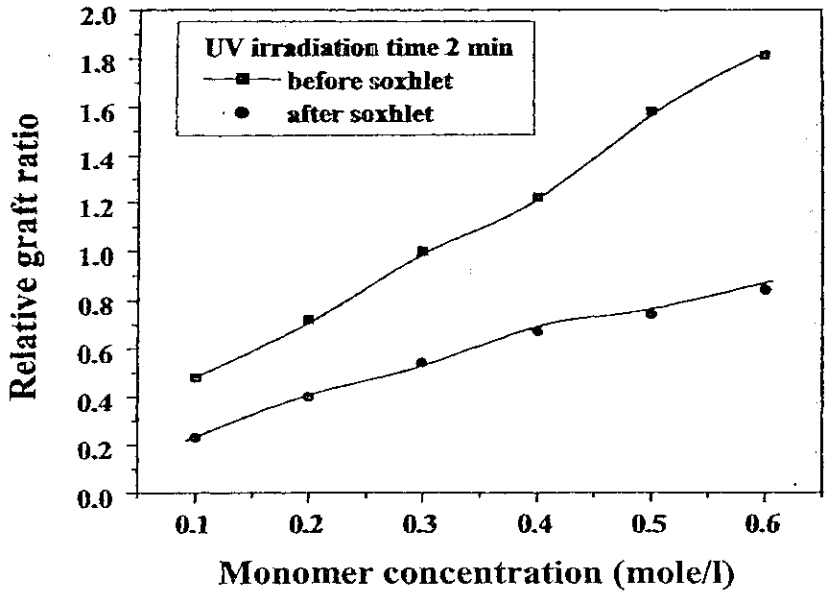


Figure 12. Effect of monomer concentration on relative grafting ratio of PP membranes UV grafted with acrylic acid (grafting time: 2min, irradiation distance: 22 cm, benzophenone concentration: 0.02 mole/l, temperature: 60 °C, solvent: acetone).

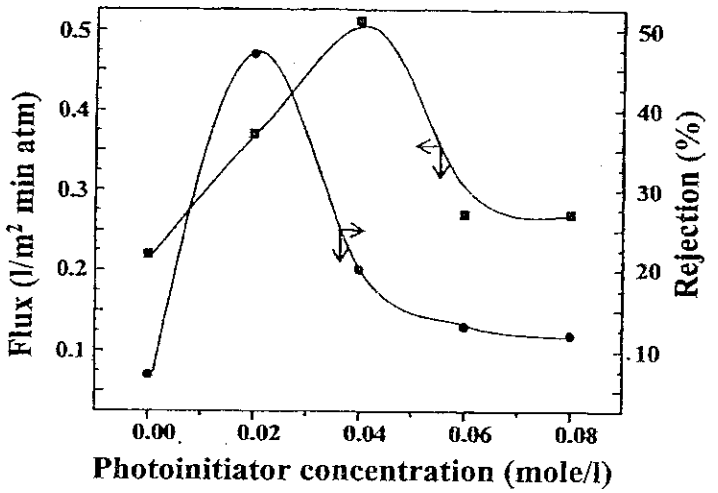


Figure 13. Effect of photoinitiator concentration on performance of PP membranes UV grafted with acrylic acid (grafting time: 2min, irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, temperature: 60 °C, solvent: acetone).

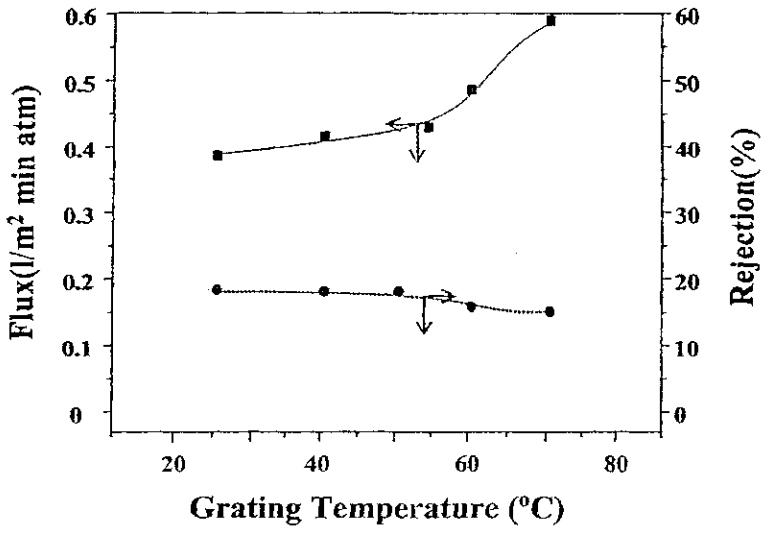


Figure 14. Effect of reaction temperature on performance of PP membranes UV grafted with acrylic acid (grafting time: 2min, irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.04 mole/l, solvent: acetone).

Effect of Solvent

UV grafting of acrylic acid to PP membranes was performed using various solvents, and performance variations were observed as shown in Figure 16. If acrylic acid itself was applied to the membrane without any solvent, the flux of the membrane was improved. Hsiue has reported that mobility of the monomer plays an important role in the grafting reaction (*18*). The mobility of monomer without any solvent should be low, and this is the likely reason that the grafting reaction was not successful. When acrylic acid was dissolved in several solvents for the grafting reaction, they showed better performance than the membrane treated with monomer without solvent. Three solvents were selected in this work; methanol, ethanol, and acetone, each at a concentration of 0.3 mole/L. Acetone is known to absorb UV light below 320 nm and can be excited even without any initiator (*7*). Therefore, acetone was the best solvent among those considered, and it enabled more grafting and better performance than the other solvents. The solubility parameter of the solvent was also an important factor. The solubility parameter difference between the solvent and acrylic acid made a difference in performance between methanol and ethanol. Reduction in BSA adsorption with different solvents was in the same order as separation performance enhancement, as shown in Figure 17.

Conclusion

UV grafting of acrylic acid to PP and PSf membranes was successfully developed. UV grafting enhanced membrane performance and reduced membrane fouling. The best performance and fouling resistance data for PP and PSf membranes after UV grafting are listed in Table I. The optimum grafting time resulted in the best performance without sample damage. Irradiating distance should also be controlled for the best grafting effects. Monomer and photoinitiator concentration should be optimized to prevent homopolymerization and termination. The grafting reaction was accelerated at high reaction temperature. The mobility of the monomer determined the reaction rate, and solubility differences and UV absorbing characteristics determined the performance and fouling resistance after UV grafting reaction. Acetone was the best solvent for the acrylic acid grafting reaction.

Acknowledgement

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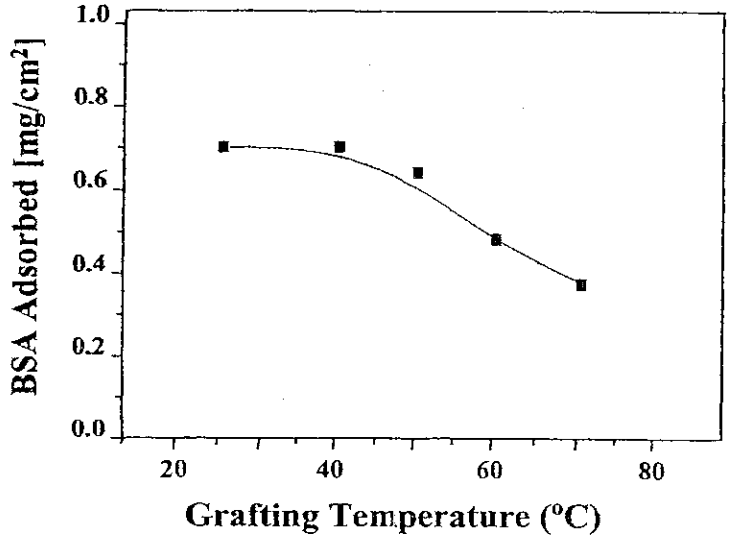

Figure 15. Effect of reaction temperature on BSA adsorption to PP membranes UV grafted with acrylic acid (grafting time: 2min, irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l, solvent: acetone).

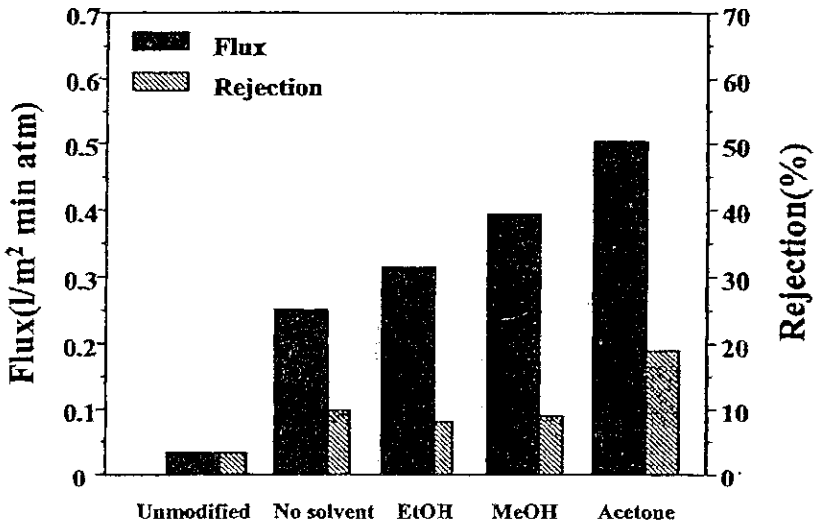

Figure 16. Effect of solvent on performance of PP membranes UV grafted with acrylic acid (grafting time: 2min, irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l solvent: acetone).

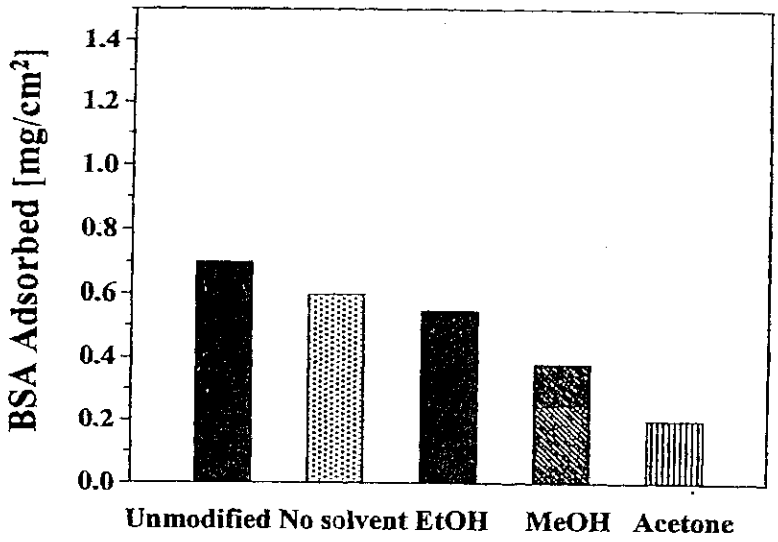

Figure 17. Effect of solvent on BSA adsorption to PP membranes UV grafted with acrylic acid (grafting time: 2min, irradiation distance: 22 cm, acrylic acid concentration: 0.3 mole/l, benzophenone concentration: 0.02 mole/l solvent: acetone).

Table I. Comparison of Flux, Dextran Rejection, and Protein Adsorption Before and After UV Grafting Acrylic Acid to PP and PSf Membranes.

Membrane	*Flux (l/m^2 atm min)*	*Rejection (%)*	*BSA adsorbed (mg/cm^2)*
Untreated PP	0.03	3	0.7
UV grafted PP	0.53	18	0.2
Untreated PSf	0.19	15	1.2
UV grafted PSf	1.08	51	0.8

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