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Surface-Modified Polysulfone Membranes: Aqueous Phase Oxidation via Persulfate Radical

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ABSTRACT: Polysulfone (Udel P1800) ultrafiltration membranes were surface modified using potassium persulfate ($K_2S_2O_8$) as a free radical source in the aqueous phase. The expected modification was hydrogen abstraction leading to hydroxylation at one or two sites on the isopropylidene linkage. Reaction time, $K_2S_2O_8$ concentration, and temperature were optimized based on two criteria: (1) minimal change in pure water fluxes after surface modification and (2) reduction of adsorptive fouling with a pulp mill effluent. The pure water flux retention for an unmodified membrane was $\sim 20\%$ after adsorptive fouling with the pulp mill effluent and was increased to 70% after reaction with $K_2S_2O_8$. Angle-resolved XPS indicated increased oxygen and a new

carbon peak consistent with an aldehyde reaction occurring in the top 3.5 nm. NMR solution analysis was inconclusive because of the low sensitivity of the experiment. Further analysis of oxidation products was carried out on finely dispersed polymer. Fourier transform infrared, internal reflection spectroscopy suggested oxidation by the formation of an aldehyde which was further oxidized to carboxylic acid. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1723–1730, 2006

Key words: polysulfone; membrane; fouling; persulfate; oxidation; ESCA-XPS; FT-IR

INTRODUCTION

Polysulfone is a thermoplastic widely used for the production of ultrafiltration membranes. This material is available from several producers in various grades. Polysulfone has excellent film forming characteristics and mechanical and chemical resistance, but is highly hydrophobic, which is one of the factors leading to adsorptive fouling.

Many applications using membrane processes contain feed components which can adsorb on the membrane and degrade performance. This can occur over either long- or short-term operation and is dependent on the nature and concentration of the adsorbing components. Meireles et al.¹ described how the original membrane properties could be masked or altered by the adsorption of different proteins. Hanemaaijer et al.² and Dal-Cin et al.³ showed how adsorptive fouling could account for permeability reductions of $\geq 90\%$ with proteins and pulp mill effluents, respectively.

The degree of adsorptive fouling is determined by solute–membrane interactions. These can consist of electrostatic forces, van der Waals forces, hydrogen

bonding, hydrophobic interactions, and others. A common strategy for reducing adsorptive fouling has been to use hydrophilic materials for membranes, which show a preference for adsorbing water rather than solutes at the membrane surface. Regenerated cellulose is one such material and its low adsorptive fouling properties are well documented.^{2–5} However, this material does not have the mechanical strength or chemical resistance of polysulfones.

An alternative strategy has been to increase the hydrophilicity of polysulfone by chemical modification. This allows one to retain the desirable properties of polysulfone membranes and to reduce its tendency to foul via adsorption. Modification may be accomplished either on the bulk polymer or the membrane surface. In practice, bulk modification involves altering the chemical properties of polysulfone before forming a membrane, whereas surface modification involves alteration of surface properties after membrane formation.

Typical surface modification methods include chemical oxidation, organic chemical reaction, plasma treatment, and grafting.⁶ The present work focuses on the surface modification of polysulfone membranes with peroxydisulfates. This approach is particularly attractive because of the low cost of the reagents used, aqueous phase reaction conditions, and fast reaction times. Bamford and Al-Lamee⁷ functionalized aliphatic polymers with $K_2S_2O_8$ via a hydroxylated in-

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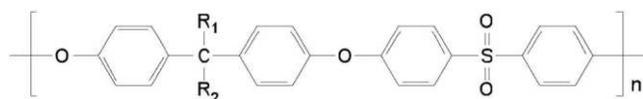


Figure 1 Molecular structure of polysulfone showing expected oxidation sites where R_1 and R_2 can be a methyl (CH_3), an alcohol ($-\text{CH}_2-\text{(OH)}$), aldehyde ($-\text{CH}=\text{O}$), or carboxylic acid ($-\text{C}(=\text{O})-\text{OH}$) group.

intermediate. The anticipated benefit was improved biocompatibility of these materials for *in vivo* medical implants and polypropylene dialysis fibers. Biocompatibility would be improved by changing the hydrophobic surface to a hydrophilic surface by substitution of aliphatic hydrogens with hydroxyl groups.

The expected modifications on Udel are depicted in Figure 1, where $R_{1,2}$ could be, by extension of the work of Bamford and Al-Lamee,⁷ one or, possibly, two alcohols, $-\text{CH}_2-\text{(OH)}$, at each site. Further oxidation could yield an aldehyde, $-\text{CH}=\text{O}$, or carboxylic acid, $-\text{C}(=\text{O})-\text{OH}$.^{8,9} The ease of implementing this modification is of great benefit. Existing spiral wound, plate and frame or hollow fiber modules could be modified *in situ* by recirculating $\text{K}_2\text{S}_2\text{O}_8$ solution at the appropriate temperature, concentration, and time.

A pulping effluent, plug screw feeder pressate (PSFP), from our previous work,³ was used to evaluate the effectiveness of the proposed modification to reduce adsorptive fouling. Unmodified and modified membranes were contacted with the mill effluent in nonpermeation conditions. Permeation tests would introduce additional effects, such as pore plugging or cake formation, and would confound the effect of changes to the membrane surface characteristics. Pure water fluxes were reduced to $\sim 20\%$ of the initial value by adsorptive fouling alone for unmodified membranes. Changes in FTIR-IRS (Fourier transform infrared, internal reflection spectroscopy) spectra, as a function of time, suggested that adsorptive fouling was initiated by the deposition of lignin sulfonates followed by cellulosic oligomers.¹⁰

EXPERIMENTAL

Materials

Udel P1800 (Solvay Advanced Polymers, Alpharetta, GA) was dissolved (20 and 22 wt %) in *N*-methylpyrrolidinone (NMP) (reagent grade, Aldrich, Sigma-Aldrich Canada Ltd., Oakville, Ontario, Canada), both used as received. Membranes were produced in our laboratory on an automated casting machine on a nonwoven polyester backing (Hollitex 3296, Ahlstrom Filtration, Inc., Windsor Locks, CT) with a casting gap of 250 μm . The casting speed was 5 cm/s with a standing time of ~ 20 s. The gelation bath was reverse osmosis (RO) water permeate at 2°C. The membranes were exchanged daily with fresh RO water for 3 days. Coupons were cut and stored in 25% aqueous ethanol. Samples were prescreened with pure water fluxes to avoid complicating interpretation of the degree of fouling due to pore sizes,^{1,3} assuming the water flux was an indicator of the nonfouled pore size for a given casting solution composition. This procedure also removed any residual NMP that may have been present.

The PSFP was obtained from a semichemical (sulfite) mechanical pulping mill. The plug screw feeder is used to feed wood chips to a sodium sulfite digester. After digestion, the pulp is sent to a press and then pulp refining and paper making is done. This postdigestion pressate, or sulfonated liquor, is recycled to wash the wood chips before going to the digester. The run-off from the wood chip feeder is the PSFP. A typical composition of the PSFP is shown in Table I. Attempts to prepare representative PSFP samples in the laboratory did not produce a product with the same fouling propensity as samples obtained at the mill.¹¹ Attempts to study adsorptive fouling in our laboratory, using pure components (dehydroabietic acid, oleic acid, sulfonated lignin, and lignin sulfonate at various concentrations and pH), were not successful. Peroxydisulfate solutions were prepared from potassium persulfate, ($\text{K}_2\text{S}_2\text{O}_8$, Sigma 7727-21-1) dissolved in RO water which had been degassed by

TABLE I
Composition of Unfiltered PSFP

pH	Cond ^a ($\mu\Omega$)	DS ^b (mg/L)	SS ^c (mg/L)	TOC ^d (mg/L)	BOD ^e (mg/L)	RFA ^f (mg/L)	Lignin sol (mg/L)	Lignin insol (mg/L)	Volatile acids (g/L)	Sugars (mg/L)
5.7	5100	12,600	1700	5670	5250	432	2400	1900	920	2680

^a Electrical conductivity.

^b Dissolved solids.

^c Suspended solids.

^d Total organic carbon.

^e Biological oxygen demand.

^f Resin and fatty acids.

boiling, and all reactions were carried out under nitrogen blanketing.⁷

Chemical analysis

FTIR-IRS analysis was described in detail in Ref. 10, and performed on a Midac M1200-SP3 (Midac Corp., Costa Mesa, CA). In this work, rather than placing a membrane sample in contact with the Ge crystal, the reacted, dispersed polymer was dissolved in tetrahydrofuran (THF) and deposited directly on the Ge crystal. This allowed rapid and complete evaporation of the THF and, more importantly, any absorbed water. This was essential to allow differentiation of the expected —OH additions from adsorbed water. Analysis was facilitated by derivatization of —C—OH groups using sulfur tetrafluoride which would produce —C(=O)—F or —C—F from a carboxylic acid and hydroxyl group respectively (absorption between 1810 and 1850 cm^{-1})¹².

XPS data were obtained with a Kratos Axis HS X-ray photoelectron spectrometer (Kratos, UK). The size of the analyzed area was about 1 mm^2 . Monochromatized Al K radiation was used for excitation and a 180° hemispherical analyzer with a three-channel detector was employed. The X-ray gun was operated at 15 kV and 20 mA. High-resolution XPS spectra were collected using 40-eV pass energy and are the average of three scans. An electron flood gun neutralized sample charging during the experiment. The take-off angle data on flat membrane samples were obtained by changing sample orientation versus the normal from 0 to 60°. This corresponds approximately to a change in the probing depth of 8.0 to 3.5 nm.¹³

¹H NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.95 MHz. Deuterated dimethylsulfoxide (DMSO-*d*₆) was the NMR solvent for heterogeneous samples, and the DMSO signal at 2.50 ppm was used as the chemical shift reference.

Scanning electron micrographs (SEM) were obtained on a Joel JSM 840A (Dearborn, MA) after air drying, vacuum drying, and gold coating under vacuum, at a magnification of 10,000.

Oxidation reactions

As will be discussed subsequently, XPS analysis suggested chemical changes were occurring on the very top layers of the membrane, less than 3.5 nm, making detection by FTIR-IRS insensitive on membrane samples. Oxidation reactions on membranes were thus restricted to evaluating changes in adsorptive fouling. Characterization studies were further supported by carrying out heterogeneous reactions on finely dispersed polysulfone, so as to maximize the surface to mass ratio and the degree of oxidation. Homogeneous

reactions were also attempted on water-soluble, highly carboxylated polysulfone for NMR analysis.

Membrane samples: Heterogeneous oxidation and adsorptive fouling

Reactions with $\text{K}_2\text{S}_2\text{O}_8$ and adsorptive fouling experiments on membranes were carried out in a 4-L beaker heated with a hot plate stirrer with an immersion probe for temperature control. Membranes were mounted in a retainer (316 stainless steel) designed to hold the membranes at the circumference of the beaker wall, skin side facing in. Reaction conditions were optimized using the following procedure:

1. Initial pure water flux, J_{0r} , was measured.
2. Three membrane samples were reacted in $\text{K}_2\text{S}_2\text{O}_8$ solutions; three concentrations (5, 10, 20 wt %), two reaction times (10 and 60 min), and temperatures ranging from 60 to 100°C.
3. The pure water flux for the modified membrane, J_{mr} , was measured.
4. Adsorption on membrane samples was accomplished by exposure to the PSFP at 50°C for 3 h with no permeation.
5. The pure water flux after adsorptive fouling, J_{ar} , was measured after membranes had been vigorously rinsed with RO water but no physical or chemical cleaning.

The adsorptive fouling tests were carried out at 50°C, as this was the anticipated temperature for processing the PSFP. The 3-h time was chosen to match the preselected time for the permeation test used in a previous study for this effluent.³

Heterogeneous oxidations: Dispersed polymer

Fine dispersions of polymer were prepared by precipitation from a 1 wt % Udel solution in THF, which was added slowly to hot water with vigorous stirring. The THF was driven off by heating, leaving a very fine suspension. Reactions with $\text{K}_2\text{S}_2\text{O}_8$ were carried out at 70 and 90°C with 5 wt % $\text{K}_2\text{S}_2\text{O}_8$. Samples were collected at 10, 30, and 60 min and quenched by mixing with approximately the same volume of RO water at 2°C.

Addition of the $\text{K}_2\text{S}_2\text{O}_8$ promoted flocculation and thereby potentially reduced the surface area. An ultrasonic probe (Sonics and Materials Inc.; VCX 750 controller with CV33 head, Sonics and Materials Inc., Newton, CT) immersed in the suspension during the reaction helped to maintain the polysulfone dispersion. It should be noted that this sonication technique may have increased the degree of oxidation, as reported by Price et al.,⁸ during persulfate oxidation of polyethylene surfaces. Price et al. used sonication over

a fixed sample area, whereas, in this work, the polymer dispersion was highly agitated and sonication would be expected to have less impact on the degree of reaction.

Polymer modified in the dispersed form was washed with RO water several times to eliminate $K_2S_2O_8$ and by products. This was verified by comparing FTIR transmission spectra of new and used $K_2S_2O_8$ with polymer FTIR-IRS spectra. Centrifugation or settling was used to collect the dispersed polymer, followed by decanting and remixing/washing and vacuum oven drying at 40°C in petri dishes. All samples were dissolved in THF or $CHCl_3$ and coated on both sides of a Ge crystal for FTIR-IRS analysis. THF was subsequently the preferred solvent for films, as it could be more readily eliminated from films on the Ge crystal compared to $CHCl_3$. Moreover, increasing the hydrophilicity of polysulfone reduces its solubility in $CHCl_3$,¹⁴ which could have resulted in the converted material being lost during the sample preparation.

The SF_4 derivatization was carried out on a film deposited on a Ge crystal. The sample was placed in a 2-L polyethylene bottle flooded with SF_4 for 6 h. The conversion of the postulated carboxylic acid group on the reaction product to the salt form was attempted on one of the recovered samples described earlier. The petri dish, containing a thin polymer film remaining after dissolving the polymer with THF for coating a Ge crystal, was half filled with NaOH (pH \geq 11) for 1 h, washed, vacuum oven dried, redissolved with THF, and coated on a Ge crystal.

Homogeneous reactions

Homogeneous reactions were attempted using carboxylated Udel polysulfone, with two carboxylic acid groups, ortho to the sulfone, per repeat unit¹⁴; the carboxylic salt form is water soluble. A homogeneous reaction was expected to increase the degree of reaction significantly and yield indications of the reaction product by NMR. The acid form of carboxylated polysulfone was dissolved (1 wt %) in water with NaOH to a final pH of 9–10. Homogeneous reactions of carboxylated polysulfone in aqueous $K_2S_2O_8$ solutions were not productive. A pH of 9–10 required to keep the salt form of the carboxylated polysulfone may also have exhausted the $K_2S_2O_8$ and the polymer precipitated within 1 min after adding the $K_2S_2O_8$. No changes were detected by FTIR-IRS or NMR.

RESULTS AND DISCUSSION

Adsorptive fouling with PSFP

The ideal set of reaction conditions for modification of a membrane would leave the membrane morphology unchanged, i.e., the of J_m/J_0 ratio = 1. A second addi-

tional criterion would be to maximize J_a/J_m , thereby minimizing adsorptive fouling. The J_a/J_0 ratio is not a suitable measure of the reaction's effectiveness for reducing fouling. As will be seen, numerous cases exist where J_a/J_0 is ≥ 1 but also coupled with $J_m/J_0 \gg 1$.

Table II and Figures 2 and 3 show the J_m/J_0 ratios for various temperatures, concentrations, and times. A J_m/J_0 ratio of ≤ 1.5 was chosen as an acceptable increase of the pure water flux after surface modification. Exposing the Udel membranes to overly aggressive conditions resulted in large increases in J_m , suggesting degradation of the membrane, which was confirmed with SEMs (Fig. 4). The pure water flux increased by an unacceptable amount, for any time and temperature combination with 10 wt % $K_2S_2O_8$. As expected, combinations of higher temperatures and times at 5 wt % $K_2S_2O_8$ also degraded the membrane morphology. Some values of J_m/J_0 ratio were slightly lower than unity; this was most likely caused by reclamping the membrane samples in the same cell and a compressed portion of the membrane being located in the permeation area for measuring J_m .

J_m/J_0 was close to unity at 5 wt % and 60°C for persulfate-treated membranes, but the J_a/J_m ratio was 0.20, indicating severe adsorptive fouling. Previously reported flux retentions, J_a/J_0 , were typically 0.2³ after adsorptive fouling with PSFP. Bamford and Al-Lamee⁷ performed their modifications at 75°C, and Price et al.⁸ needed ultrasound to see any changes at 35°C; hence, the lack of a measurable effect on the membrane surface is not unexpected. Lower temperatures and longer reaction times were investigated in an attempt to broaden the range of reaction conditions. This would facilitate modification of premade membrane modules.

Several conditions can be identified (see footnote in Table II), which improved the flux retention, with J_a/J_m considerably higher than the 20% for unmodified membranes, while keeping J_m/J_0 close to 1.5. Flux retentions of 0.6–0.75 are a significant improvement. The lower $K_2S_2O_8$ concentration is appropriate with large scale use to minimize reagent costs. The lower concentration and temperature required longer reaction times, which is also advantageous when trying to work with large membrane areas or trying to modify prefabricated spiral wound modules or tubular membranes.

XPS analysis of heterogeneous reactions: Membrane samples

Angle-resolved XPS is a useful technique for reaction depth profiling. This technique applied to membrane surfaces suggested that the depth of reaction on the membrane surface was restricted to the exposed surface. Changes in the relative atomic composition were detected only at a take-off angle of 60°, suggesting that

TABLE II
Reaction Conditions, Pure Water Fluxes, and Ratios for J_m/J_0 , J_a/J_0 , and J_a/J_m (see Membrane Samples: Heterogeneous Oxidation and Adsorptive Fouling for definitions) for Heterogeneous Reactions on Membranes and PSFP as Adsorptive Foultant

K ₂ S ₂ O ₈ (wt %)	Temp (°C)	Time (min)	J ₀ (L/(m ² hr (bar)))	J _m /J ₀		J _a /J ₀		J _a /J _m	
				Average	SD	Average	SD	Average	SD
5	70	10	59	0.8	0.02	0.23	0.1	0.3	0.13
5	75	10	49	0.63	0.02	0.24	0.06	0.39	0.1
5	80	10	56	0.77	0.12	0.43	0.04	0.56	0.04
5 ^a	85	10	51	0.66	0.21	0.42	0.14	0.65	0.02
5 ^a	90	10	55	1.36	0.1	1.02	0.06	0.75	0.04
5	100	10	143	2.71	0.4	1.39	0.12	0.52	0.04
5	60	60	152	1.09	0.2	0.22	0.05	0.2	0.01
5	70	60	118	1.12	0.11	0.16	0.04	0.14	0.02
5 ^a	70	60	56	1.13	0.21	0.72	0.2	0.63	0.06
5 ^a	75	60	48	1.46	0.03	1.01	0.02	0.69	0.01
5 ^a	75	60	48	1.24	0.32	0.86	0.29	0.68	0.07
5	80	60	45	1.87	0.05	1.37	0.09	0.73	0.04
5	90	60	54	3.88	0.3	3.19	0.33	0.82	0.02
5	100	60	146	5.7	0.31	3.17	0.34	0.56	0.08
10	85	10	105	1.79	0.13	1.4	0.06	0.79	0.07
10	94	10	125	3.52	0.39	2.65	0.25	0.75	0.04
10	100	10	106	3.16	0.17	2.74	0.79	0.86	0.24
10	85	60	127	7.58	0.81	5.28	0.49	0.7	0.01
10	94	60	134	9.34	1.3	7.37	0.86	0.79	0.02
10	100	60	87	7.64	2.02	7.98	2.53	1.04	0.18

^a Indicates preferred reaction conditions. Averages and standard deviations are for three coupons in all cases.

oxidation was occurring only on the uppermost membrane layer (3.5 nm). Figure 5 shows the spectra of a sample reacted with 5 wt % K₂S₂O₈, at 90°C and 60 min.

The peaks positioned at 284.7, 285.3, and 286.2 eV were assigned to C—C, C—S, and C—O—C carbons in the unreacted polysulfone. Peak assignments and

shifts are based on reported data in Ref. 15. At a 60° take-off angle, a new peak appears at 287.6 eV. This represents a shift of 2.9 eV, which is much less than the expected shift for carboxylic acid (4.18–4.33 eV) but is more similar to an aldehyde (2.81–2.97 eV). The relative concentration ratio of C—O to C—C also increased at the highest take-off angle.

At a 60° take-off angle, two new oxygen peaks appear at around 534.0 and 535.5 eV. The peak at 534.0

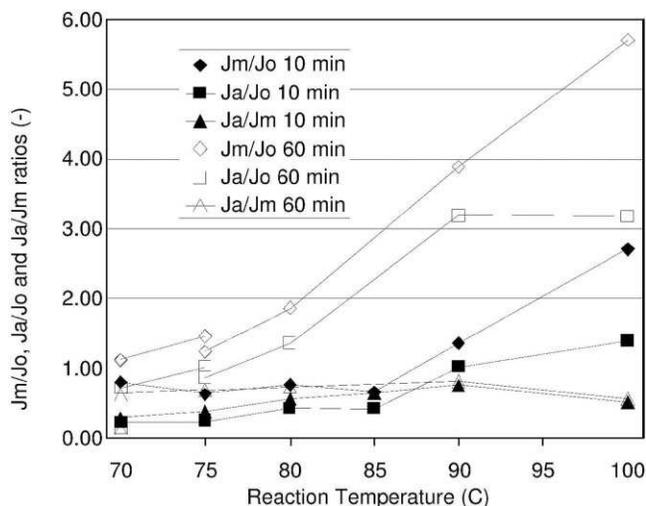


Figure 2 J_m/J_0 and J_a/J_m ratios as a function of reaction time and temperature for 5 wt % K₂S₂O₈. Contact with PSFP at 50°C for 3 h.

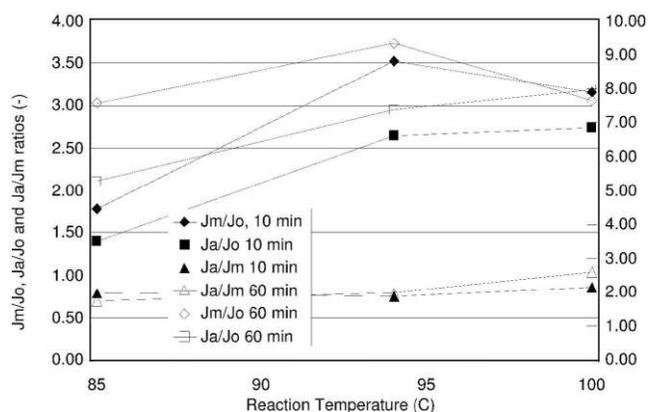


Figure 3 J_m/J_0 and J_a/J_m ratios as a function of reaction time and temperature for 10 wt % K₂S₂O₈. J_m/J_0 , J_a/J_0 for 60 min are on right hand axis. Contact with PSFP at 50°C for 3 h.

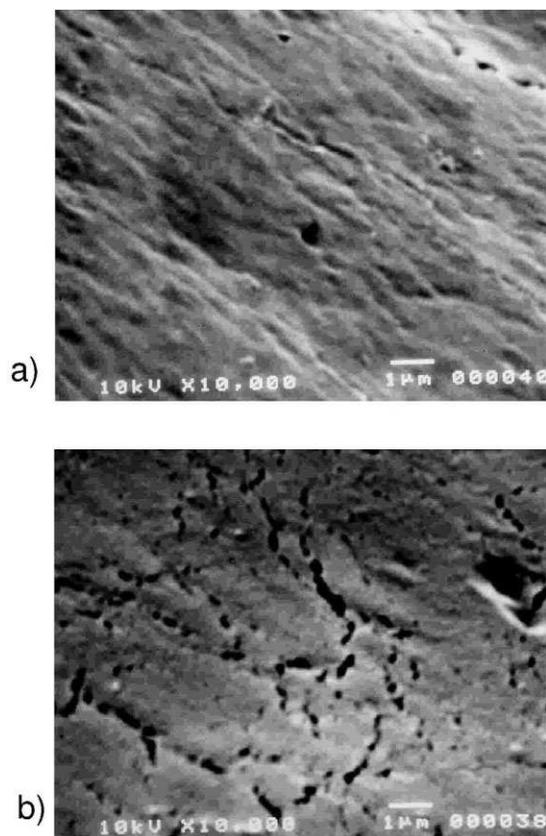


Figure 4 Udel membrane before (a) and after (b) exposure to $K_2S_2O_8$ (5 wt %), 60 min and $90^\circ C$, showing surface crazing.

was difficult to assign and the peak at 535.5 eV was tentatively assigned to a sulfate group. The sulfate assignment was corroborated with changes of the sulfur peak features at high take-off angle. Indeed, the fitted $S2p_{1/2}$ peak at 60° take-off angle was too broad and too high due to the suspected presence of an additional sulfur peak around 169 eV consistent with a sulfate group.¹⁶ There appears to be a trace of oxidizing agent remaining on the uppermost surface of the membrane.

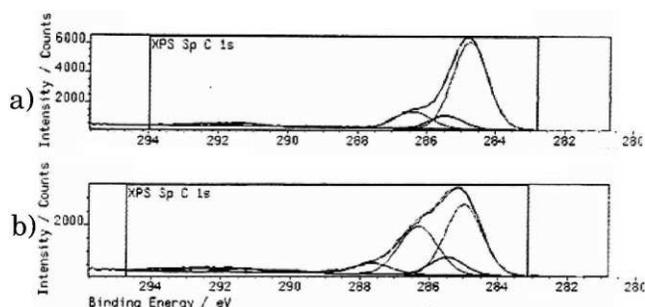


Figure 5 High-resolution spectra of carbon C1s at (a) 40° and (b) 60° take-off angles. Reaction at $90^\circ C$, 5 wt % $K_2S_2O_8$, and 60 min. Peaks corrected to 284.7 eV for C—C bonds.

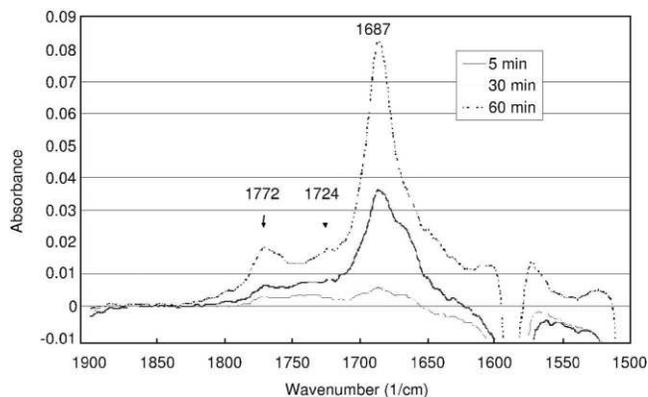


Figure 6 FTIR-IRS spectral subtracts (see text) showing absorbances in the carbonyl region after oxidation at $70^\circ C$ and various reaction times.

FTIR-IRS analysis of heterogeneous reactions: Dispersed polysulfone

The sensitivity of FTIR-IRS analysis of membrane surfaces in previous work¹⁰ was increased by clamping two membrane samples to a Ge crystal, providing 25 internal reflections. In the current work, this was not sufficient to detect any changes. This, coupled with indications from angle-resolved XPS analysis, led to attempts to increase the degree of reaction by increasing the surface area to mass ratio for the polymer, as described earlier in *Heterogeneous Oxidations: Dispersed Polymer*.

Recovery of the dispersed polymer was qualitatively observed to be more difficult with greater reaction times and temperature. This suggests a change in the surface properties and a change in the particle size distribution of dispersed polymer.

No changes were seen in the region expected for —OH species; however, other changes were observed. The FTIR-IRS spectra for a series of reaction times at $70^\circ C$ (with ultrasound to maintain the dispersion) and 5 wt % $K_2S_2O_8$ are shown in Figure 6 from 1500 to 1900 cm^{-1} . The spectra for unmodified Udel was subtracted from the spectra for reaction times of 5, 30, and 60 min, and then a uniform baseline correction was applied to give zero absorbance at $\sim 1900\text{ cm}^{-1}$. After 5 min, no changes were observed, and at 30 min, there was some absorbance at 1687 cm^{-1} , which increased at 60 min reaction time. A second peak appears at 1772 cm^{-1} at 60 min reaction time. The absorbance at 1687 cm^{-1} is consistent with an aldehyde (diphenylacetaldehyde in Ref. 17), which would be an expected intermediate product in oxidizing an alcohol to a carboxylic acid.

The spectra in the same region at $90^\circ C$ with ultrasound, 5 wt % $K_2S_2O_8$ for 10-, 30-, and 60-min reaction times are shown in Figure 7. The absorbance at 1687 cm^{-1} is still present but relatively small compared with the new absorbance at 1725 cm^{-1} , which is rela-

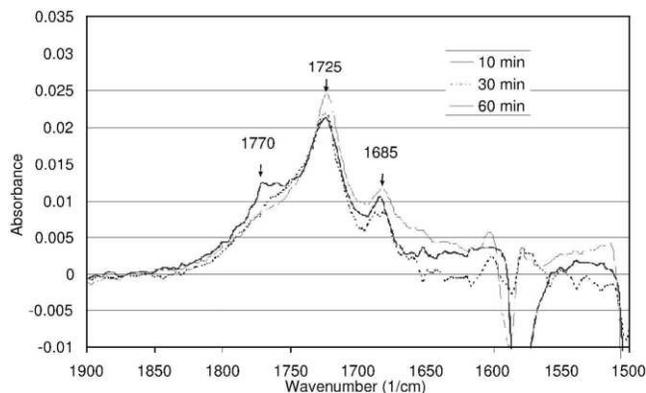


Figure 7 FTIR-IRS spectral subtracts (see text) showing absorbance in the carbonyl region after oxidation at 90°C and various reaction times.

tively similar for all the reaction times. This is somewhat lower than the absorbance reported for the acid form of carboxylated polysulfone¹⁴ at 1740 cm^{-1} , but consistent with the absorbance of carboxylated polysulfone repeated on the current FTIR instrument (not shown). A new absorbance in the range 1770–1772 cm^{-1} appears at 60 min reaction time, similar to that observed at 70°C and 60-min reaction conditions, but has not been identified.

Further information about the absorbance at 1725 cm^{-1} was obtained by both derivatization of the group with SF_4 and attempting to convert the acid form to the salt using sodium hydroxide (Fig. 8). In this figure some quantity was added to the absorbance to separate the spectra. The “control” and “persulfate” spectra are those used in Figure 7 at 60 min.

Derivatization of the carboxylic acid group using SF_4 is expected to produce $-\text{C}(=\text{O})-\text{F}$ or $-\text{C}-\text{F}$

from a carboxylic acid or hydroxyl group. The expected absorbance is seen at 1851 cm^{-1} together with some diminution of the peak at 1724 cm^{-1} . The two new adsorptions at 1788 and 1774 cm^{-1} are not accounted for.

Salt formation should shift the carboxylic acid absorption to 1625 cm^{-1} . The persulfate sample was immersed in strong NaOH, but there was no appearance of a new peak in the expected range and little diminution of the peak at 1725 cm^{-1} . This may be the result of a low conversion of the acid to the salt, because it was performed on a film, rather than on the dispersed polymer.

In summary, the formation of an alcohol was not detected by FTIR at any reaction condition. A new absorbance at 1687 cm^{-1} , consistent with an aldehyde, increased with reaction time at 70°C. It would appear that, if any alcohol formation occurred, it was oxidized to an aldehyde. An absorbance at 1725 cm^{-1} , consistent with a carboxylic acid group, was observed at 90°C but showed no change with reaction time. SF_4 derivatization supports the existence of the carboxylic acid group.

CONCLUSIONS

Unmodified polysulfone membranes retained only 20% of their pure water flux due to adsorptive fouling after exposure to a pulp mill waste stream. The pure water flux retention was increased to 60–75% after the membranes were pretreated with oxidizing aqueous $\text{K}_2\text{S}_2\text{O}_8$ solutions. Reaction conditions were optimized such that changes to the membrane morphology, as measured by the pure water flux, were minimized. Large-scale modifications of premade membranes/

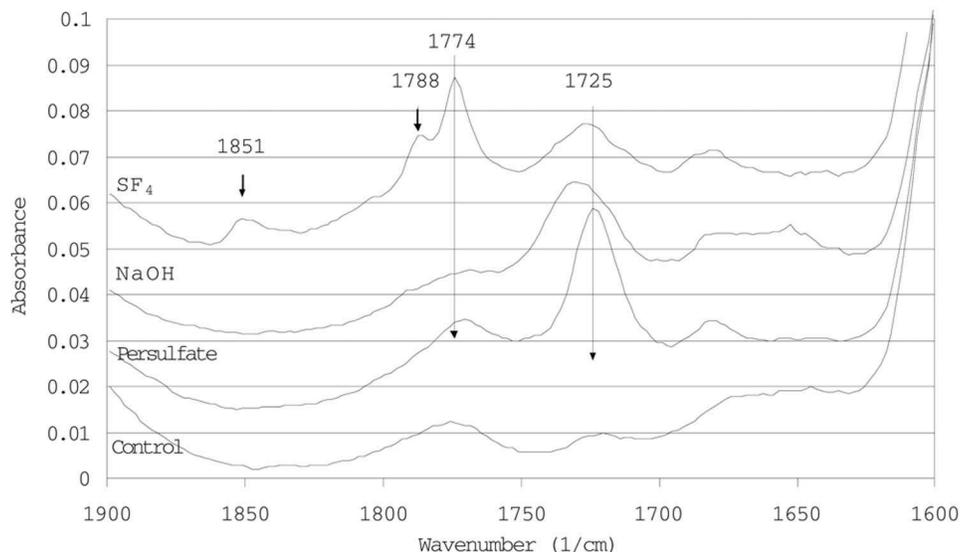


Figure 8 FTIR-IRS spectra showing absorbance in the carbonyl and C—F range, reaction with 5 wt % $\text{K}_2\text{S}_2\text{O}_8$ at 90°C and 60 min.

membrane modules would be most economical and easily implemented at: (a) low $K_2S_2O_8$ concentrations (5 wt %), (b) a temperature of 70°C, and longer reaction times (60 min).

Oxidation products on membrane samples were difficult to detect. FTIR-IRS analysis was not sensitive enough to detect changes, and angle-resolved XPS suggested that any oxidation that occurred was restricted to the top 3.5 nm. XPS was not conclusive but suggested an increased C—O to C—S ratio and a new carbon peak consistent with an aldehyde group.

Changes to Udel polysulfone were detected by FTIR-IRS more readily only after reactions were carried out on fine dispersions of the polymer. An ultrasound probe was required to avoid agglomeration after the addition of $K_2S_2O_8$. The expected reaction product, a polysulfone with hydroxylation at the isopropylidene linkage, was not identified. An increasing amount of aldehyde with increasing reaction time was detected for reaction conditions at 70°C and 5 wt % $K_2S_2O_8$. The aldehyde was no longer detected at 90°C and was likely completely oxidized to a carboxylic acid at the minimum reaction time of 5 min. Carboxylic acid formation was corroborated by derivatization with SF_4 and a new absorbance at 1851 cm^{-1} , consistent with the formation of $-C(=O)-F$.

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