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# Use of a Temperature Sensitive Surface Gel to Reduce Fouling

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**Abstract:** Numerous surface modification strategies have been developed to improve the fouling resistance of filtration membranes. A novel approach in which a temperature sensitive polymer gel is deposited on the surface is reported. The gel switches from an expanded, lower permeability, fouling-resistant hydrophilic state to a collapsed, higher permeability, fouling-prone hydrophobic state as the temperature is increased. By alternating between these two states, it is hypothesized that fouling can be reduced while minimizing the permeability reduction due to the surface modification. The hypothesis was tested by depositing a hydroxypropyl cellulose (HPC) gel on the surface of the cellulose acetate ultrafiltration membranes (Osmonics SN32) using divinyl sulfone (DVS) as a crosslinker. Unmodified and modified membranes were used to filter yeast and the HPC suspensions. To induce the hydrophobic-hydrophilic transition, the feed was switched alternately between room temperature and 60°C solutions. The experimental results support the hypothesis. Unmodified membranes fouled severely when operated at room temperature, 60°C, or oscillating between the two temperatures. The modified membranes fouled severely at 60°C but little fouling occurred at room temperature or with temperature oscillation. The results suggest that permanent surface modification is not required to reduce the fouling rates. Transient fluctuations in the surface chemistry and the structure are equally effective. Moreover, one can achieve higher filtration rates in transient operation because pores possess a larger effective diameter/higher permeability in the collapsed state than the expanded state.

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**Keywords:** Filtration, fouling, membrane, membrane modification, transport properties

# INTRODUCTION

The development of new materials for liquid filtration has been the focus of significant research effort. However, membrane fouling remains a major obstacle to the industrial use of the membrane processes. Fouling refers to a decline in water permeability due to the accumulation of the solute or the particulates on the membrane surface or in membrane pores.

Fouling may be reversible or irreversible depending on its origins (1). Reversible fouling arises from the accumulation of rejected solutes or particulate matter near the membrane surface that are not strongly adsorbed. For osmotically active solutes, this concentration increase leads to an increase in osmotic pressure and a concomitant reduction in the driving force for liquid permeation. For rejected particulate matter, the surface accumulation poses an additional resistance to liquid permeation. In both cases, the accumulated matter may be removed when filtration stops by a combination of flowing liquid across the membrane surface and reversing the direction of fluid permeation, i.e., backflushing.

Irreversible (adhesive) fouling occurs when strong specific interactions exist between the membrane and the rejected solute or the particulate matter. These interactions lead to irreversible adsorption on the membrane surface or in the membrane pores. The adsorbed material may form a continuous gel or a cake layer on the membrane surface. The adsorbed material and cake cannot be removed when the filtration stops. The reduction in the permeation rate due to irreversible fouling ultimately requires membrane replacement—one of the largest costs associated with membrane processes in the water treatment, pharmaceutical, and biomedical industries (2).

The reversible contribution to fouling can be moderated by the control of fluid flows within the filtration device. However, efforts to control the irreversible contribution have been less successful.

A number of approaches have been tried to reduce the irreversible adsorption by modifying the membrane surface. These include the physical adsorption of water-soluble polymers (3), the formation of Langmuir-Blodgett films (4), the thermal grafting of a hydrophilic polymeric surface coating (5–6), the grafting via electron beam irradiation (7) and photografting with UV irradiation (8).

Although these surface modifications can reduce the adhesive adsorption relative to the unmodified membrane, the adsorption is not eliminated. Moreover, unmodified membranes made of materials that possess charge and hydrophilicity characteristics comparable to those of the surface layer exhibit similar adsorption characteristics (9).

To overcome these limitations, researchers proposed attaching polymer brushes or gels to membrane surfaces (10). They hypothesized that at a sufficiently high surface coverage, the adsorption would be eliminated by steric interactions between the extended polymeric chains and the solute attempting to find its way to the membrane surface. Although the brush did reduce adsorption, the adsorption was not reduced to the extent expected. At equilibrium, the entropic penalty incurred when the polymer chains align to let a solute molecule approach the surface is compensated for by the energy released when the solute adsorbs on the surface. The use of a hydrophilic surface brush or gel to reduce fouling during membrane filtration is widely reported in the literature (11–14); He et al. (15) provide an excellent review of photo-initiated pathways to membrane formation or modification to control the surface interactions.

Attaching a stimuli-responsive polymer brush or gel (such as n-isopropyl acrylamide or hydroxypropyl cellulose) on the surface offers the potential to collapse or expand the polymer surface layer. The phase change arises from the existence of a lower critical solution temperature (LCST) such that the polymer precipitates from the solution as the temperature is increased. This capability can be exploited to control the protein adsorption/desorption (16). At lower temperatures, the surface layer expands into a hydrophilic state while at higher temperatures it collapses into a hydrophobic state. Protein adsorption is reduced in the expanded, hydrophilic state relative to the collapsed, hydrophobic state. Although the equilibrium adsorption is reduced, adsorption can still occur.

Stimuli-responsive brushes have been used to control the membrane permeability as well (17–22). Large increases in water flux with temperature are observed for brush-coated membranes as the grafted polymer layer collapses upon passing through the LCST. However, for sufficiently small pores that are comparable in size to the thickness of the collapsed brush layer, the permeability can decrease with the increasing temperature as the collapsed polymer can cover the pore mouth and pose a greater resistance to water transport than the expanded, fully hydrated layer (22).

The effect of surface modification with a temperature-sensitive polymeric gel layer on membrane fouling is reported here. Experimentally, a thermally responsive hydroxypropyl cellulose (HPC) gel layer is deposited on the surface of a cellulose acetate membrane. Aqueous solutions of HPC possess a LCST of approximately 43°C; i.e., above this temperature the solution phase separates. When deposited on the surface, this aqueous solution forms a gel which collapses into a hydrophobic state upon increasing the temperature above the LCST and expands into a hydrophilic state at temperatures below the LCST.

It is hypothesized that triggering the phase transition (i.e., changing the membrane temperature such that the surface changes from the expanded hydrophilic state to the collapsed hydrophobic state or vice versa) continuously by oscillating the temperature of the membrane surface will provide fouling resistance while minimizing the impact of the surface modification on hydraulic permeability. In the expanded hydrophilic state, one expects the surface to be fouling resistant. The cellulose acetate membrane is not highly hydrophilic. Therefore, the presence of the extremely hydrophilic surface hydrogel should reduce interactions with hydrophobic foulants such as yeast and improve fouling resistance. Experimental measurements of fouling rates and atomic force microscopy support this hypothesis.

Upon collapsing the gel into a hydrophobic state, the surface becomes fouling prone. However, in the collapsed state one expects higher liquid permeabilities since the gel layer is thinner and may reduce the pore blockage as illustrated in Fig. 1. By expanding the gel again, the material that accumulates near the membrane surface ideally is forced away and the low permeability, fouling resistant surface is restored. Oscillating between the two states offers the potential to increase hydraulic permeability while retaining fouling resistance.

## METHODS AND MATERIALS

### Membranes

SN32 ultrafiltration membranes were modified (Osmonics Inc., Minnetonka, MN). These hydrophilic cellulose acetate membranes possess a molecular

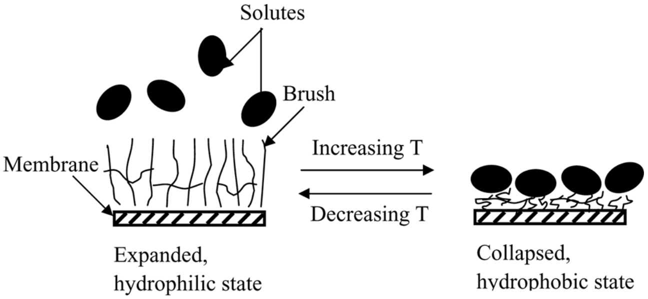


*Figure 1.* Equilibrium states of the hydroxypropyl cellulose gel.

weight cutoff (MWCO) of 20,000 Da and typically are operated at temperatures less than 30°C, pressures less than 0.34 MPa (50 psi), and pH between 2 and 9.

## HPC Gels

HPC gels were formed by crosslinking a 10 wt.% HPC solution with divinyl sulfone (DVS). The HPC solution was prepared in an amber bottle by adding 10 gm of HPC powder (MW = 100,000) to 100 ml of 0.1 M NaOH solution and mixing vigorously. An appropriate amount of DVS stock solution was added to the HPC solution to yield a final DVS concentration of 1.41 wt.%. After shaking for one minute, the liquid mixture was poured into a petri dish and allowed to react to completion. The resulting gels were dried in a hood.

Crosslinking occurs by the reaction of the DVS vinyl group with hydroxyl groups of cellulose (23):

$$\underset{\text{(HPC)}}{2R_{\text{cell}}\text{-}OH} + \underset{\text{(DVS)}}{(CH_2{=}CH)_2SO_2} \longrightarrow \underset{\text{(Crosslinked HPC)}}{R_{\text{cell}}\text{-}OCH_2CH_2SO_2CH_2CH_2O\text{-}R_{\text{cell}}}$$

When used to crosslink HPC and other cellulose ethers in isotropic aqueous solutions, DVS forms gels at pH 12 in less than an hour.

To evaluate the temperature dependence of gel swelling, the mass of a dry sample ($m_d$) was determined. Then the sample was immersed in water at a specified temperature for one minute and allowed to swell. The swollen sample was quickly removed, blotted dry using Kimwipes (to remove the surface water), and weighed. The mass of the wet sample ($m_w(T)$) was used to calculate the degree of swelling ($Q$) at one minute using $Q = (m_w(T) - m_d)/m_d$. Plotting $Q$ as a function of temperature allows the determination of the LCST—the critical point corresponds to the temperature at which $dQ/dT$ passes through a maximum.

## Membrane Surface Modification-Layer-Wise

The SN32 membranes were modified "layer-wise" by first coating the membrane with a DVS (Aldrich Chemical Company, Milwaukee, WI) solution and then casting an HPC (Aldrich Chemical Company, Milwaukee, WI) solution on top.

The DVS solutions of specified wt.% were prepared by adding stock DVS solution to deionized water in an amber bottle. The solution pH was adjusted to 7 by adding 0.1 M NaOH solution drop-wise. Concentrations ranging from 1 to 3 wt.% were used.

HPC solutions of specified wt.% were prepared by adding HPC powder (of various molecular weights) to 0.1 M NaOH. The final solution pH was adjusted to 12. Concentrations from 9 to 22 wt.% and molecular weights of 100,000 and 1,000,000 were used.

The membrane was coated with the DVS solution at room temperature by pouring the solution over it. Then the HPC solution was cast on the surface using a universal blade applicator to obtain a uniform film coating of thickness ~100 microns. The high pH of the HPC solution increased the reaction rate.

The coatings were allowed to dry for 48 hours in a fume hood. After drying, the membranes were kept overnight in DI to remove excess reactants. The notation (*x, y, z*) is used to identify the concentrations and molecular weight of the reactants used for membrane modification: *x* is the DVS solution wt.%, *y* the HPC solution wt.%, and *z* the HPC molecular weight.

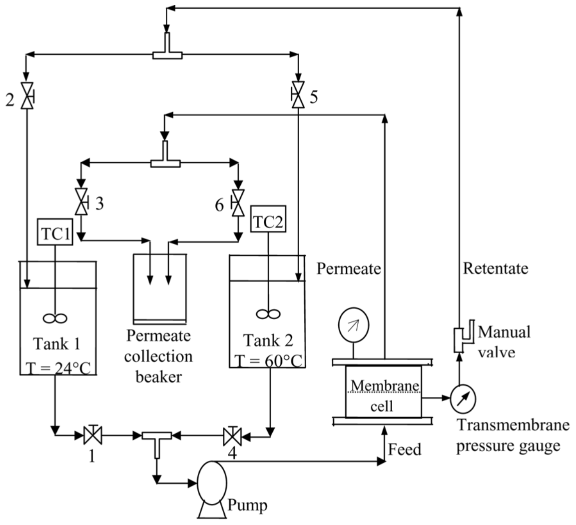
### Membrane Modification—Mixture-Wise

SN32 membranes were modified "mixture-wise" by the addition of stock DVS solution to HPC solutions, prepared as described for layer-wise modification, prior to coating the membrane. After the DVS addition, the solution was shaken for 1 minute and cast on the membrane using the universal blade applicator. The coating was allowed to dry for 48 hours and then kept overnight in DI before testing. The concentrations and molecular weight of the mixture used for coating are indicated using the same notation as for layer-wise modification.

## CHARACTERIZATION

Unmodified and modified membranes were characterized in several ways including tap water permeabilities at different temperatures, transient permeation rates during filtration of a yeast suspension, and HPC solution at different temperatures, and surface imaging using atomic force microscopy (AFM).

The experimental filtration setup is illustrated in Fig. 2. An Osmonics Sepa CF membrane cell (Osmonics Inc., Minnetonka, MN) is used to hold the membrane for filtration with standard feed and permeate spacers. Two feed tanks are used: one containing cold feed below the LCST (24°C) and the other hot feed above the LCST (60°C). The feed



LEGEND:

⊠ A solenoid valve interfaced with the computer.

T A tee fitting.

Bank 1 consists of valves 1, 2, 3; and Bank 2 consists of valves 4, 5, 6.
Bank 1 is the cold bank (T = 24°C) and Bank 2 is the hot bank (T = 60°C).

TC1 and TC2 are immersion circulators with temperature control.

***Figure 2.*** Diagram of experimental apparatus.

to the membrane cell may be taken continuously from either tank for a constant temperature run or alternately from both tanks to change the temperature of operation. The retentate is returned to the feed tank from which it came. Collected permeate volumes were returned as well to maintain the feed concentration at its initial level.

The feed tank and retentate return tank are selected by a set of solenoid valves controlled by a Labview 6.1 VI (National Instruments Corporation, Austin, TX). The feed to the membrane cell is controlled by switching the states of the valves in Bank 1 (the valves controlling feed from the cold tank) and Bank 2 (the valves controlling feed from the hot tank). Permeate is collected in a tared beaker, and the cumulative mass is recorded once a minute during the run. The membrane cell is held clamped together by a compressed air line. During operation the transmembrane pressure was maintained at 0.34 MPa (50 psi).

Filtration experiments at constant temperature and with temperature fluctuations were conducted with model hydrophilic and hydrophobic foulants: a yeast suspension (hydrophobic) and a HPC solution. The expanded HPC gel should reduce adsorption and fouling for the yeast solution while no benefit is expected for the HPC solution.

## Yeast Suspension Experiments

The yeast suspension was prepared following the procedure described in the literature (24). Washed yeast (Saccharomyces cerevisae, commercially available Fleischmann's active dry yeast) was added to phosphate buffer saline (PBS). The buffer solution (pH 7.4) was prepared by mixing 80 g of NaCl (Fisher Scientific), 2 g KCl (Fisher Scientific), 14.4 g $Na_2HPO_4$ (Fisher Scientific), and 2.4 g $KH_2PO_4$ (Fisher Scientific) in 10 l of tap water. A single yeast suspension concentration [0.00432 ($g/cm^3$)] was used for all experiments.

The yeast filtration experiments consisted of a series of transient permeation rate measurements at different temperatures. Experiments were performed at a constant temperature of 24°C and 60°C to establish the fouling characteristics of the surface layer in the expanded and collapsed structure, respectively. Experiments also were performed with the feed temperature fluctuating between 24°C and 60°C to determine if fouling is affected by transient variations in the surface structure.

During the filtration experiments, the permeation rates were measured with time to determine the extent of fouling. Additionally, the pure water hydraulic permeability at 24°C was measured before and after filtration runs; before each measurement the membrane cell was flushed with hot water and backflushed for 30 minutes using a reverse transmembrane pressure of 0.03–0.14 MPa (5–20 psi). Any decrease in permeability after filtration indicates the extent of irreversible fouling that occurred. Repeat measurements of pure water permeabilities differed by less than 5% demonstrating the reproducibility of the measurement.

The constant temperature filtration runs of 24°C and 60°C were conducted for 65 minutes. However, the runs with temperature fluctuations were limited to 45 minutes due to temperature changes in the feed tanks. The fluctuating temperature runs were conducted by feeding alternately from the hot and cold tanks for 10 seconds; this time interval was approximately the shortest that would allow the temperature of the membrane cell to reach the feed temperature.

The time interval between changes in the feed temperature is shorter than the time interval used to determine the equilibrium swelling. The experimental results indicate that attaining an equilibrium state is not required to impart the fouling resistance and increase the flux when switching the physical and the chemical state of the surface layer.

The temperature in the cold tank increased and that in the hot tank decreased during the experiment due to fluid mixing upon switching between the two tanks and the thermal inertia (heating and cooling) of the filtration apparatus. In a typical experiment, the hot tank temperature decreased from 60 to 53°C while the cold tank temperature increased from 24 to 40°C.

Hydraulic permeabilities were calculated from the collected permeate masses over 5 minute intervals. The values are expressed as $m^3/m^2/s/Pa$ based on the active membrane area.

Yeast growth was not monitored during the experiments. However, yeast batches were changed after each experiment and growth nutrients were not provided. One would expect aging of the yeast mixture to increase adherence and exacerbate fouling as reported in the literature (25) as cells rupture and aggregate. Retention of anti-fouling characteristics with time therefore will indicate that the surface gel provides robust resistance to fouling.

## HPC Solution Experiments

A 0.25 wt.% HPC solution was prepared in each of the two feed tanks by adding the corresponding mass of HPC powder (MW = 100,000). Both tanks were heated to 60°C to dissolve the powder before adjusting the temperature to the desired feed temperature. The experimental filtration procedure was identical to that used for the yeast suspension.

## AFM Analysis

Atomic force microscopy (AFM) was used to examine the surface structure and the morphology of the membranes. The AFM investigation was conducted using a scanning probe microscope (Nanoscope IIIa with a fluid cell attachment). The samples were tested in air. The surface roughness was evaluated as $R_a$, the mean value of the surface relative to the center plane, calculated as

$$R_a = \frac{1}{L_x L_y} \int_0^{L_y} \int_0^{L_x} |f(x,y)| \, dxdy \qquad (1)$$

where $f(x, y)$ is the surface position relative to the center plane and $L_x$ and $L_y$ are the dimensions of the surface.

Changes in the surface roughness provide an indirect measurement of fouling. Increases after a filtration run indicate the formation of a non-uniform cake layer deposited during the filtration run.

## RESULTS AND DISCUSSION

### HPC Gel Swelling

Figure 3 illustrates the swelling measurements for two HPC gels. As the temperature increases, the degree of swelling decreases. The slope of the swelling versus the temperature curve increases notably at a temperature of ~43°C. These observations are consistent with the existence of an LCST at 43°C as reported in the literature.

### Pure Water Hydraulic Permeability

Measurements of water hydraulic permeability ($K_p$) for an unmodified membrane and various layer-wise modified membranes are summarized in Table 1. The values are reported for measurements at 30 and 60°C.

For all membranes, the permeability at 60°C is higher than that at 30°C. The permeabilities of the modified membranes are lower than that of the unmodified membrane and the magnitude of the difference increases as the wt.% of the HPC solution used for the modification

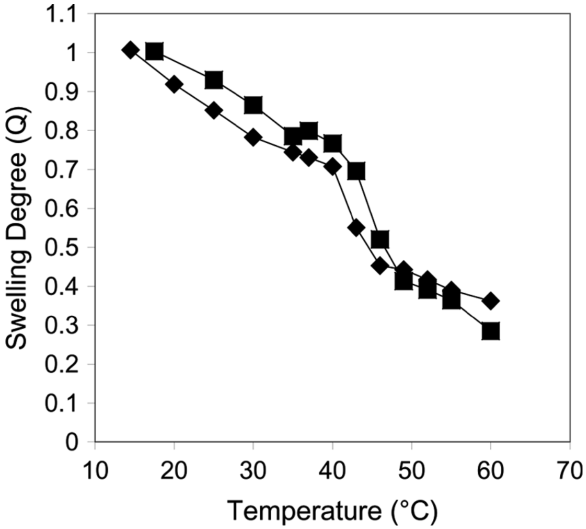


***Figure 3.*** The effect of temperature on the swelling of an HPC gel. Note the sharp transition at ~43°C indicating a transition between expanded and collapsed states. The two sets of symbols represent data for two samples.

**Table 1.** Pure water hydraulic permeability measurements for unmodified and layer-wise modified membranes

| Membrane | T (°C) | $K_p$ ($m^3/m^2/s/Pa$) | $K_{p,60}\mu_{60}/K_{p,30}\mu_{30}$ | $D_{60}/D_{30}$ |
|---|---|---|---|---|
| (0, 0, 0) | 30°C | 1.82E-10 | 0.92 | 0.98 |
| | 60°C | 2.86E-10 | | |
| (2, 9, 100,000) | 30°C | 5.19E-11 | 1.14 | 1.03 |
| | 60°C | 1.01E-10 | | |
| (2, 15, 100,000) | 30°C | 3.70E-11 | 1.30 | 1.07 |
| | 60°C | 8.21E-11 | | |
| (2, 21, 100,000) | 30°C | 2.16E-11 | 1.59 | 1.12 |
| | 60°C | 5.86E-11 | | |

increases. This is consistent with greater surface density of the HPC gel on membranes prepared with higher HPC concentrations.

The higher permeability at 60°C reflects both changes in membrane porosity and water viscosity. The viscosity of water decreases as the temperature increases and therefore contributes in part to the observed permeability increase.

To separate the effect of modification on permeability from the temperature dependence of viscosity, two quantities are calculated:

1. the ratio of (permeability × viscosity) at 60 to that at 30°C and
2. the ratio of the effective pore diameter (*D*) at 60 to that at 30°C. The pore size is calculated from the (permeability × viscosity) ratio as indicated in Eq. (2):

$$\frac{D_{60}}{D_{30}} = \left(\frac{K_{p,60}}{K_{p,30}}\frac{\mu_{60}}{\mu_{30}}\right)^{1/4} \tag{2}$$

where $\mu$ is water viscosity and the subscripts 30 and 60 indicate the temperature. Equation (2) assumes that the membrane may be treated as a number of equal length pores in parallel and flow through the pores follows the Hagen-Poiseuille law. The calculated effective pore size is not the true pore size of the composite membrane structure that results from surface modification. However, changes in the pore size or the product of the permeability and the viscosity (the viscosity normalized permeability) indicate changes in the composite permeability that cannot be accounted for by the change in water viscosity—the permeability of the surface layer must change as well due to a change in structure.

Table 1 indicates that for the unmodified membrane the effective pore diameter and viscosity normalized permeability decrease slightly as the temperature increases from 30 to 60°C. Such a change suggests that the membrane expands with increasing temperature which leads to a reduction in the pore volume. However, an increase in viscosity normalized the permeability and the pore size is observed for each of the modified membranes. The magnitude of the change increases as the concentration of the HPC solution used for the modification increases. For the 21% solution, the increase in the effective pore size is ~12%. Therefore, one can increase the membrane permeability significantly by collapsing the attached gel layer—for the 21% solution the increase in permeability after accounting for the temperature dependence of the viscosity is a factor of $1.12^4 \sim 1.6$ or 60%.

## Yeast Filtration

### Unmodified Membrane

Figure 4 illustrates the results obtained for yeast suspension filtration with unmodified membranes. During both the constant temperature

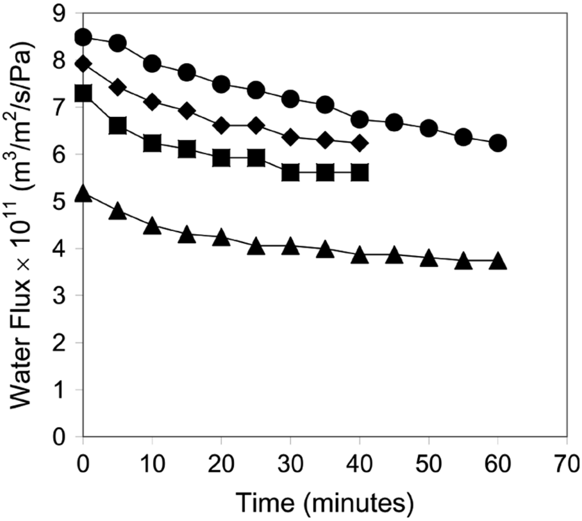


*Figure 4.* Water flux during yeast filtration with an unmodified membrane. The order of the experiments was: 1) fluctuating temperature run (diamonds), 2) fluctuating temperature run (squares), 3) constant T = 24°C run (triangles), and 4) constant T = 60°C run (circles). The initial pure water hydraulic permeability of 1.27E-10 $m^3/m^2/s/Pa$ dropped to 1.12E-10 $m^3/m^2/s/Pa$ after the first run.

and fluctuating temperature runs, water fluxes declined with time as the membrane fouled. The pure water hydraulic permeability measured after the first fluctuating temperature run decreased from 1.27E-10 to 1.12E-10 $m^3/m^2/s/Pa$. Note that pure water permeabilities measured in-between experiments differ from the permeabilities reported in the figures due to the presence of yeast in the solution and the effect of temperature on the membrane structure and water viscosity.

## Membranes Modified Layer-Wise

Figure 5 illustrates the results obtained for a (1, 9, 100,000) membrane modified using the layer-wise technique. The hydraulic permeability after modification, 7.39E-11 $m^3/m^2/s/Pa$, is lower than that of the unmodified membrane, 1.27E-10 $m^3/m^2/s/Pa$, providing evidence that a gel layer was attached which posed an additional resistance to water transport.

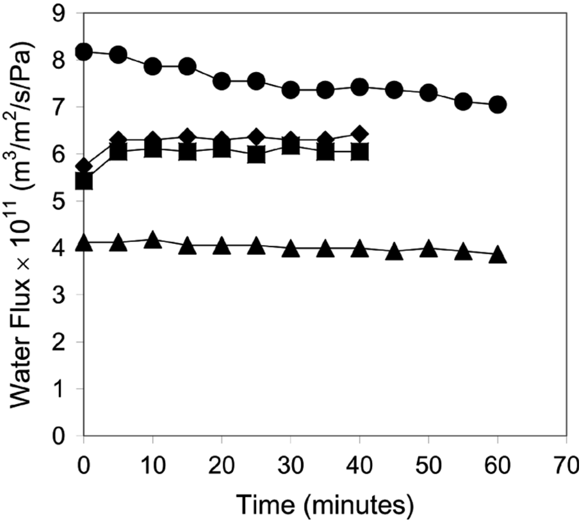


***Figure 5.*** Water flux during yeast filtration with first (1, 9, 100,000) layer-wise modified membrane. The order of the experiments was: 1) constant T = 24°C run (triangles), 2) constant T = 60°C run (circles), 3) fluctuating temperature run (diamonds), and 4) fluctuating temperature run (squares). The initial pure water hydraulic permeability was 7.39E-11 $m^3/m^2/s/Pa$. The permeability after the first run was 7.18E-11 $m^3/m^2/s/Pa$ and that after the final run was 7.12E-11 $m^3/m^2/s/Pa$.

Water fluxes decreased significantly during the constant temperature filtration run at 60°C. However, flux changes were small or nonexistent during the 24°C and fluctuating temperature runs. These results suggest that the expanded, hydrophilic gel increased the fouling resistance of the membrane. Moreover, the constant flux observed during the fluctuating temperature runs, in contrast to the small decline observed at 24°C, suggests that the movement of the gel may have increased the fouling resistance of the hydrophilic state over that in the equilibrium, expanded configuration.

However, attempts to reproduce the results in Fig. 5 were unsuccessful. Figure 6 illustrates the results of one duplicate experiment; a second duplicate experiment gave similar results. Although the initial hydraulic permeability at 24°C is similar to that in Fig. 4, the permeation rate decreases with time in all of the filtration runs. The pure water hydraulic permeability decreased to approximately one-half of its initial value due to irreversible fouling. Attempts to produce membranes with other

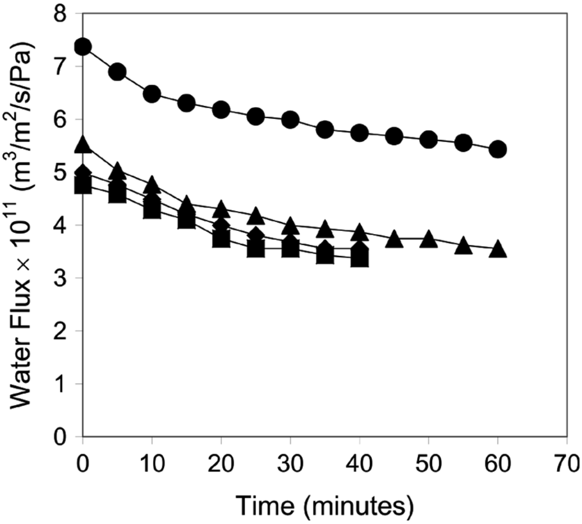


***Figure 6.*** Water flux during yeast filtration with second (1, 9, 100,000) layer-wise modified membrane. The order of the experiments was: 1) constant T = 24°C run (triangles), 2) constant T = 60°C run (circles), 3) fluctuating temperature run (diamonds), and 4) fluctuating temperature run (squares). The initial pure water hydraulic permeability was 7.59E-11 $m^3/m^2/s/Pa$. Subsequent permeability measurements made after each run were: 4.23E-11, 3.98E-11, and 4.06E-11 $m^3/m^2/s/Pa$. A final measurement was not made.

DVS and HPC solution concentrations led to similar problems with reproducibility.

Because of the difficulties encountered preparing uniform membranes, the layer-wise technique was not pursued further. It is speculated that subtle differences in the DVS pre-coating step led to non-uniform surface modification.

## Membranes Modified Mixture-Wise

Three (1, 9, 100,000) membranes were modified mixture-wise and all displayed similar behavior. This set of concentrations corresponds to the lowest concentrations used for layer-wise modification which showed some signs of fouling resistance. The results for one membrane are illustrated in Fig. 7.

Water fluxes remained constant during filtration runs at a constant temperature of 24°C or with temperature fluctuations between 24 and 60°C. However, the flux declined severely during the constant

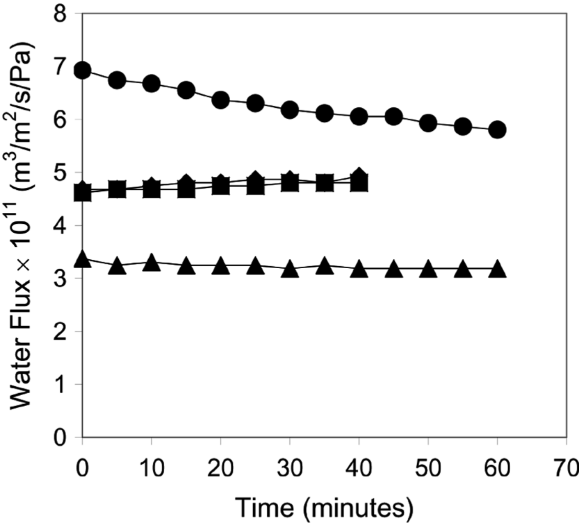


***Figure 7.*** Water flux during yeast filtration with (1, 9, 100,000) mixture-wise modified membrane. The order of the experiments was: 1) constant T = 24°C run (triangles), 2) constant T = 60°C run (circles), 3) fluctuating temperature run (diamonds), and 4) fluctuating temperature run (squares). The initial pure water hydraulic permeability was 4.78E-11 $m^3/m^2/s/Pa$. Subsequent permeability measurements made after each run were: 4.69E-11, 3.73E-11, and 3.63E-11 $m^3/m^2/s/Pa$. A final measurement was not made.

temperature run at 60°C. The slight increase in flux observed during the fluctuating temperature run is attributed to the slight temperature increase in the cold feed tank.

The pure water hydraulic permeability measurements before and after the filtration experiments confirm the lack of fouling in the low temperature and fluctuating temperature runs. The hydraulic permeability changed by less than 2% after these runs. However, the permeability decreased by more than 20% after the high temperature run indicating irreversible fouling had occurred.

## HPC Filtration

### Uncoated Membrane

Figure 8 illustrates the results obtained for the HPC filtration with the unmodified membrane. The flux decline during the first filtration run at a constant temperature of 24°C appears small. However, the pure

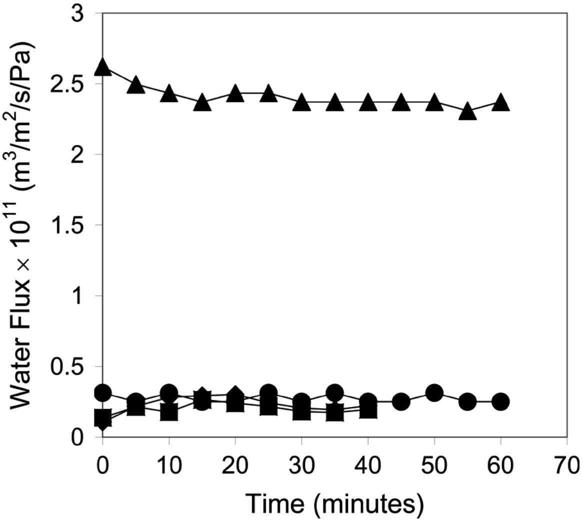


***Figure 8.*** Water flux during HPC filtration with an unmodified membrane. The order of the experiments was: 1) constant T = 24°C run (triangles), 2) constant T = 60°C run (circles), 3) fluctuating temperature run (diamonds), and 4) fluctuating temperature run (squares). The initial pure water hydraulic permeability was 1.47E-10 $m^3/m^2/s/Pa$. Subsequent permeability measurements made after each run were: 5.20E-12, 4.93E-12, and 4.58E-12 $m^3/m^2/s/Pa$. A final measurement was not made.

water hydraulic permeability decreased by more than 95% after the run indicating severe irreversible fouling. This fouling must have occurred immediately since little flux decline is observed after the first permeation measurement.

The pure water hydraulic permeability decreased slightly after subsequent filtration runs at constant temperature (60°C) and with temperature fluctuations. The flux decline during the filtration runs was minimal indicating that the fouling had reached a steady state level.

### Membranes Modified Mixture-Wise

A flux decline was observed for the (1, 9, 100,000) modified membranes during all of the filtration runs as illustrated in Fig. 9. The decrease in flux was greatest for the fluctuating temperature runs.

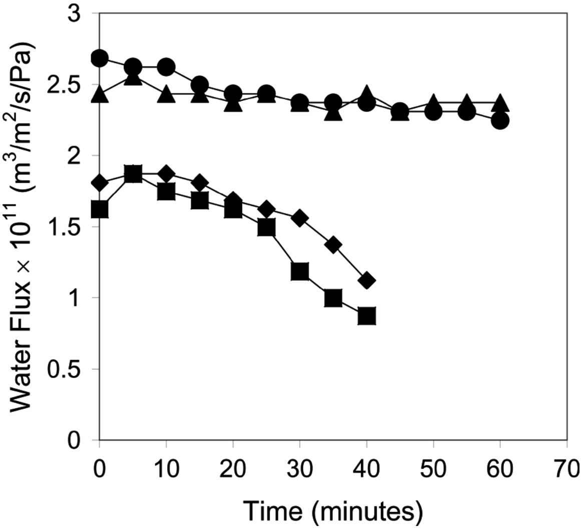


***Figure 9.*** Water flux during HPC filtration with (1, 9, 100,000) mixture-wise modified membrane. The order of the experiments was: 1) constant T = 24°C run (triangles), 2) constant T = 60°C run (circles), 3) fluctuating temperature run (diamonds), and 4) fluctuating temperature run (squares). The initial pure water hydraulic permeability was 6.84E-11 $m^3/m^2/s/Pa$. Subsequent permeability measurements made after each run were: 5.21E-11, 4.30E-11, and 4.18E-11 $m^3/m^2/s/Pa$. A final measurement was not made.

The pure water hydraulic permeability decreased by 25% after the first constant temperature run at 24°C but by smaller amounts in subsequent filtration runs. The final hydraulic permeability measurement is ~60% of its initial value.

Although significant changes in water flux occurred during the fluctuating temperature run (the flux decreased from 1.78E-11 to

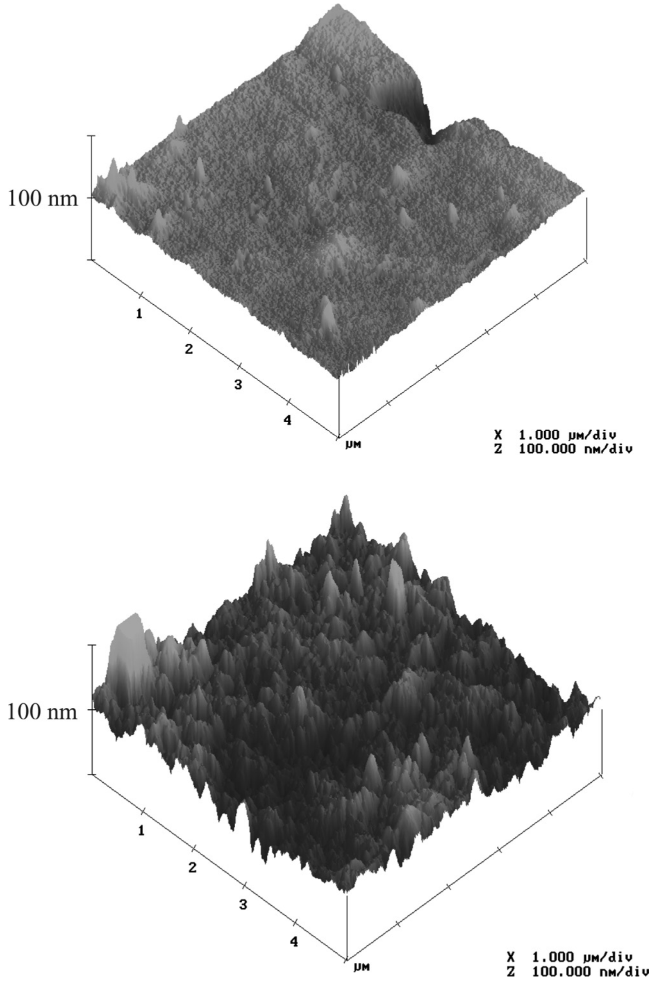


***Figure 10.*** AFM images of an unmodified membrane before use (top) and after a fluctuating temperature run (bottom). The surface roughness increased from 4.78 nm to 23.0 nm after the run.

1.16E-11 $m^3/m^2/s/Pa$), the pure water hydraulic permeability decreased only slightly (from 4.31E-11 to 4.17E-11 $m^3/m^2/s/Pa$). This suggests that the flux decline during filtration was primarily due to reversible fouling that was removed upon flushing and backwashing.

We attribute the severe fouling of the unmodified membrane to penetration of the HPC into the membrane porosity and irreversible adsorption. This fouling is greatly reduced after surface modification. We believe the surface layer itself does not foul the membrane during manufacture due to light cross-linking when the polymer and the cross-linker are mixed prior to deposition. Additionally, the surface layer is not dense enough to eliminate fouling by HPC—it reduces fouling but does not eliminate it.

## AFM Images

AFM images were obtained for four membranes including:

1. an unmodified membrane prior to filtration,
2. an unmodified membrane after a fluctuating temperature yeast filtration run,
3. a mixture-wise modified membrane prior to filtration, and
4. a mixture-wise modified membrane after a fluctuating temperature yeast filtration run.

These four allow visualization of the changes in fouling that occur with surface modification.

Figure 10 illustrates the surface of an unmodified membrane prior to use and after a fluctuating temperature yeast filtration run, respectively. The surface roughness increased by a factor of 5 after the filtration run. The significant increase in the surface roughness provides evidence of severe external fouling.

Figure 11 illustrates the surface of a (1, 9, 100,000) mixture-wise modified membrane prior to use and after a fluctuating temperature yeast filtration run, respectively. In comparison to the unmodified membrane (Fig. 9), surface modification did not have an impact on the surface roughness. However, after filtration a significant difference exits. The increase in surface roughness was a factor of 3 for the modified membrane compared to a factor of 5 for the unmodified membrane. This reduction in roughness indicates that fouling was less severe. Furthermore, the hydraulic permeability measurements suggest that the fouling layer did not have a detrimental impact on water flux.

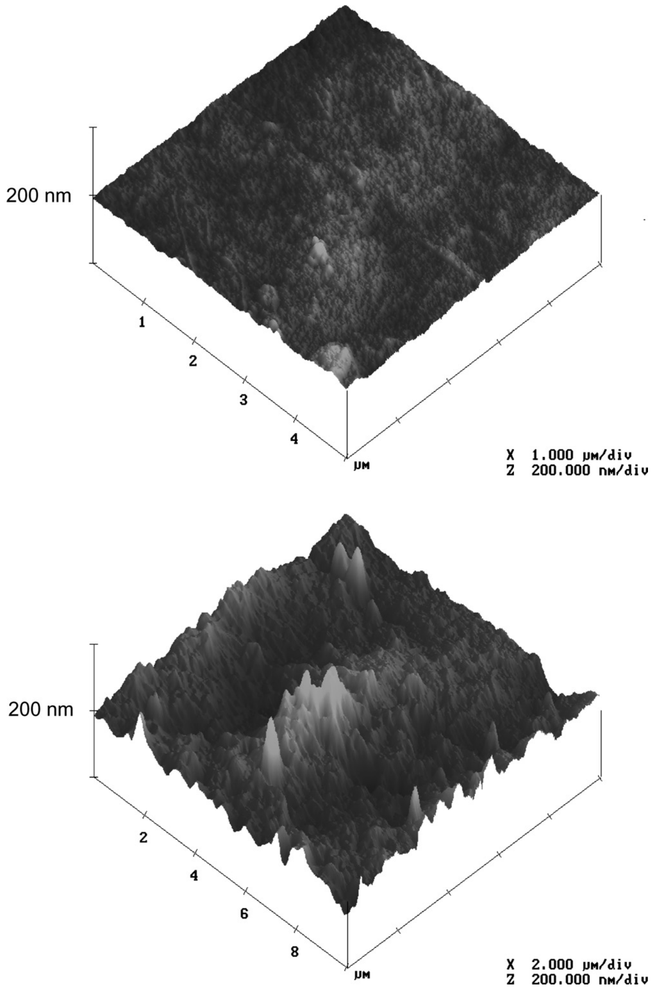


***Figure 11.*** AFM images of a (1, 9, 100,000) mixture-wise modified membrane before use (top) and after a fluctuating temperature run (bottom). The surface roughness increased from 4.24 nm to 12.6 nm after the run.

## CONCLUSIONS

The performance of an ultrafiltration membrane modified with a thermally responsive surface gel layer is reported. At temperatures below the LCST of the gel, it exists in an expanded, hydrophilic, fouling resistant state. Raising the temperature above the LCST causes the gel to collapse into a hydrophobic, fouling prone state.

The modified membranes were tested in filtration runs with yeast and HPC suspensions. The operating temperature during a run was changed by using two different temperature feeds. The membranes modified by coating with the crosslinker and then with the gel material (layer-wise) were highly variable. The fouling-resistant membranes could not be reproducibly prepared using this technique. However, membranes modified by pre-mixing the crosslinker and gel material (mixture-wise) before coating could be prepared reproducibly with enhanced fouling resistance.

The mixture-wise modified membranes showed little to no change in the permeate flux during yeast filtration runs at temperatures below the LCST but fouled severely above the LCST as expected. The fouling resistance of the membrane below the LCST was retained in filtration runs where the temperature fluctuated from below to above the LCST. The unmodified membrane fouled severely under all operating conditions.

At temperatures above the LCST, the modified membrane possesses a higher hydraulic permeability than below the LCST due to the collapse of the gel. Therefore, by fluctuating the temperature above and below the LCST, the membrane flux can be increased without sacrificing the fouling resistance.

The unmodified and modified membranes fouled under all filtration conditions for HPC solutions. For the modified membrane, significant irreversible fouling occurred during the first filtration run but fouling in subsequent fluctuating temperature runs was reversible.

AFM images of membranes before and after filtration confirmed the filtration measurements. Unmodified membranes possessed significantly greater surface accumulation than modified membranes.

The procedure used here to fluctuate the membrane temperature (i.e., changing the feed temperature) is not a viable commercial option. However, one can envision a number of configurations that would be viable including using a fine metal mesh as a support for the membrane or using a conductive polymer support which would heat upon the passage of electric current. The results provide motivation for pursuing the development of such materials which have the added benefit of only heating the membrane and the adjacent fluid boundary layers.

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