

FINAL REPORT
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**Novel Ceramic-Polymer Composite Membranes
for the Separation of Liquid Waste**

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1. EXECUTIVE SUMMARY

Membrane separation processes are especially suited for removal of colloids from colloidal dispersions and emulsions by ultrafiltration and nanofiltration and removal of volatile organic solutes from dilute solutions by pervaporation. Membranes have the advantage of requiring less energy relative to conventional separation technologies (e.g., distillation, extraction and even adsorption processes). The major difficulty with current filtration membranes is their tendency to foul. Polymeric pervaporation membranes often suffer from poor longevity under harsh conditions (high temperature, harsh solvents and pH conditions) while ceramic membranes usually lack of selectivity.

In the present project ceramic-supported polymer (CSP) membranes were developed combining the positive attributes of polymeric and ceramic membranes. The polymer imparts the desired membrane selectivity while the ceramic support provides structural integrity. The CSP membranes are fabricated via a free-radical surface-graft polymerization process. This method results in a molecular layer of polymer chains that are terminally and covalently anchored to the porous membrane support. The CSP membrane retains its structural integrity and performance even when the polymer phase is exposed to harsh solvent conditions since the polymer chains are covalently bonded to the ceramic support surface. This research resulted in the development of CSP membranes for two different membrane separation processes: (a) pervaporation removal of organics from aqueous systems; and (b) ultrafiltration of oil-in-water emulsions. Pervaporation CSP membranes, based on polyvinylacetate and polyvinylpyrrolidone, were demonstrated for the removal of selected organics (TCE and chloroform) from aqueous solutions and for separation of methanol-MTBE solutions. Permeate could be concentrated by factors of 10-1000 relative to the feed solution. The present ceramic-polymer membrane technology was also demonstrated to be

successful for the preparation of an effective fouling-resistant zirconia-PVP ultrafiltration (UF) membrane for the treatment of oil-in-water emulsions.

The CSP membranes represent a class of commercially viable membranes based on a chemical surface modification technology suitable for "tailor designing" and optimizing selective and robust pervaporation and low-resistant polymer-ceramic (CSP) membranes. The present CSP technology has been explored for commercial utilization and a U.S. patent is pending for the CSP pervaporation membrane.

The research project has provided a unique opportunity for graduate student training. Three Ph.D. students and three M.S. students who contributed to the present project have graduated with one additional Ph.D. dissertation in progress. The uniqueness of the CSP membrane was recognized in two student awards: (a) The 1997 Outstanding Research Paper Award given to Robert Castro from the AIChE Separations Division and a 2000 Presentation Award given to Ron S. Faibish by the North American Membrane Society. It is also noted that highlights of our research accomplishments were published in *Initiatives in Environmental Technology Investment* (Volume 6, Winter 1999; <http://www.wpi.org/initiatives>). Finally, it is noted that in the course of the study use was made of analytical equipment the DOE William R. Wiley Environmental Molecular Sciences Laboratory (Richland, WA) during three-week visit to the laboratory. Surface imaging by atomic force microscopy was also conducted at the AFM Facility at the University of California at Santa Barbara. In addition, dynamic light scattering (DSL) measurements were made at the Department of Chemical Engineering at Yale University (New Haven, CT).

2. SYNOPSIS

The present project was conceived to address the need for robust yet selective membranes suitable for operating in harsh pH, solvent, and temperature environments. An important goal of the project was to develop a membrane chemical modification technology that would allow one to tailor-design membranes for targeted separation tasks. The method developed in the present study is based on the process of surface graft polymerization. Using essentially the same base technology of surface modification the research was aimed at demonstrating that improved membranes can be designed for both pervaporation separation and ultrafiltration. In the case of pervaporation, the present study was the first to demonstrate that pervaporation can be achieved with ceramic support membranes modified with an essentially molecular layer of terminally anchored polymer chains. The main advantage of the above approach, relative to other proposed membranes, is that the separating polymer layer is covalently attached to the ceramic support. Therefore, such membranes have a potential use in organic-organic separations where the polymer can swell significantly yet membrane robustness is maintained due to the chemical linkage of the chains to the inorganic support. The above membrane technology was also useful in developing fouling resistant ultrafiltration membranes. The prototype membrane developed in the project was evaluated for the treatment of oil-in-water microemulsions, demonstrating lack of irreversible fouling common with commercial membranes.

In the preceding sections an overview is provided of the basis for the development of ceramic-supported polymer membranes, followed by a description of research methodology, summary of the relevant results and an assessment of the significance of the CSP membrane technology and technology transfer potential.

3. BACKGROUND

Environmental remediation and pollution prevention applications require processes capable of selectively separating and concentrating target organic species from aqueous and organic liquid mixtures. In recent years, membrane processes have been developed for both ultrafiltration removal of colloidal organics matter and pervaporation separation of volatile organics from hazardous aqueous waste. Ultrafiltration separation is accomplished by pore size exclusion (i.e., rejection by size) of given solutes from the membrane. Solute rejection is improved if the membrane exhibits specific rejection of the target solute due to geometrical exclusion or the chemical nature of the membrane. Pervaporation is a separation process whereby a liquid mixture is contacted with a membrane and the solute to be removed preferentially permeates through the membrane and undergoes a transition to a vapor phase as it emerges at the permeate side. In pervaporation the solute partial pressure on the permeate side is maintained well below its feed value.

Since the early 1990's it has been suggested that selective pervaporation membranes could be effectively employed for the separation of organics from contaminated water supplies and industrial aqueous streams (Fig. 3.1; Lipski and Cote, 1990; Wijmans et al., 1990; Baker et al., 1999). Polymeric pervaporation membranes have shown a great deal of promise for applications in the recovery of volatile solvents, alcohol-water streams, separation of close boiling point and azeotropic mixtures and separation of organic mixtures (Aptel et al., 1976; Acharya et al., 1988; Redman, 1990; Fleming, 1993; Lai et al., 1994; Lu et al., 1997; Ray et al., 1997; Yamasaki et al., 1997; Cao et al., 1999; Sun et al., 1999; Wang et al., 1999; Wynn, 2001).

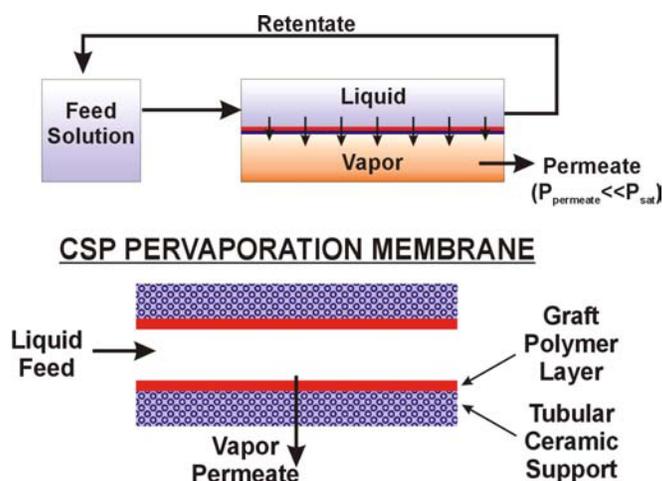


Figure 3.1. Schematic illustration of membrane pervaporation

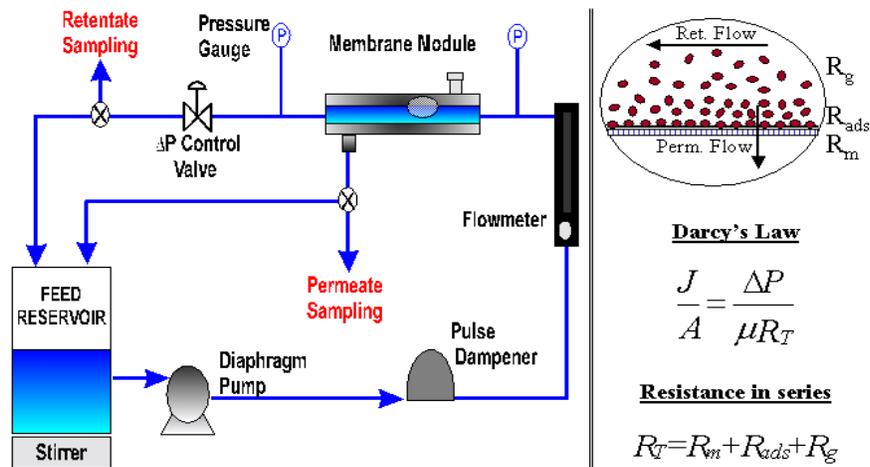


Figure 3.2. Typical ultrafiltration setup. Resistances are due to the membrane, cake formed on the membrane surface and due to fouling.

The treatment of aqueous colloidal systems and emulsions by ultrafiltration membranes (Fig. 3.2) has long been used as an efficient and cost-effective alternative to conventional separation techniques in order to separate inorganic, organic and biotic colloids and dispersions (Seungkwan et al., 1997; Faibish et al., 1998; Belfort et al., 1994; Zeman and Zydney, 1996). At present, two types of commercial ultrafiltration and pervaporation membranes are available, polymeric and inorganic (ceramic). One major disadvantage of polymeric membranes, however, is their low mechanical, chemical and thermal resistance. This has inhibited their use where harsh process conditions such as, high temperatures, extreme solution pH, high pressures, and corrosive chemicals exist. Polymeric membranes are also known to degrade in the presence of aggressive solvents. Ceramic membranes, on the other hand, present superb mechanical, thermal, and chemical stability. However, their chemical selectivity and the available pore size range are rather limited. Nevertheless, these membranes have found increasing use in separation applications where polymeric membranes cannot be used. These applications include filtration of hot oily streams and various aqueous and organic streams of corrosive nature as well as detergent-containing wastewater (Holdich et al., 1998; Bhattacharyya, 1997; Cheryan and Rajagopalan, 1998; and references therein).

Over the past two decades, increased interest in improving membrane performance (i.e., reducing membrane fouling and enhancing membrane selectivity) and longevity (i.e., chemical, mechanical, and thermal long-term stability) has encouraged the development of new classes of membranes by introducing various chemical and physical modifications to exiting membranes (Aptel et al., 1972, 1974; Randon et al., 1995; Ulbricht and Belfort, 1996; Krasemann and Tieke, 1998; Chen and Belfort, 1999; Wang et al., 1998, 1999; and references therein). Typical

modification procedures have involved physical adsorption or chemical attachment of polymers and other compounds onto the surface of the membrane to improve membrane selectivity (affinity) or rejection of specific solute and/or reduce membrane fouling by deposition of solutes onto the membrane surface. Although modified polymeric membranes have demonstrated increased selectivity, and in some cases improved fouling resistance, their poor thermal stability and longevity in harsh solvent conditions hampered their commercial acceptance.

In order to overcome the above shortcomings, this research project focused on developing a class of ceramic-supported polymer (CSP) membranes that combine the positive attributes of the two conventional types of polymer and ceramic membranes to produce robust and selective membranes. The approach is based on targeted chemical surface modification of robust ceramic support membranes, with a covalently bonded (grafted) and terminally anchored polymer, to control and optimize membrane performance for both pervaporation applications and for fouling minimization in UF. The CSP membrane is created by a two-step process consisting of surface activation by silylation followed by free-radical surface graft polymerization resulting in a macromolecular phase of polymer chains that are terminally-anchored and covalently attached (grafted) onto the surface of a ceramic support membrane.

Graft polymerization is the process of growing polymer chains from reactive surface sites (e.g., reactive surface-bonded monomer or initiator). The popular method of growing polymer chains from reactive surface sites of inorganic supports such as silica, alumina and zirconia are free-radical polymerization and anionically-initiated polymerization (Cohen et al., 1999, 2000; Nguyen et al., 2001). Graft polymerization via free-radical polymerization from reactive vinylsilane surface sites has been shown to be an efficient and controllable method of obtaining a high polymer graft yield in the dense “brush” regime (Cohen et al., 1992; Castro et al., 1993; Cohen et al., 1999, 2000) which is desirable for effective CSP membranes. The first step in the graft polymerization process is to activate the ceramic (e.g., silica, alumina, and zirconia) surface. As an illustration, the silylation of silica with an active organic group is shown below

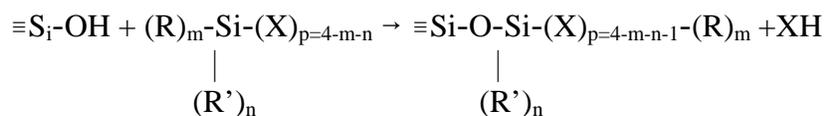


Figure 3.3. Silylation of Silica Surface

where R is an organic group, R' is a non-hydrolyzable group with the desired functionality to be imparted to the silica surface, X represents a hydrolyzable group such as alkoxy, acyloxy, amine, or chlorine which are able to react with the inorganic substrate and $m+n \leq 3$. When the organosilane contains two or more hydrolyzable groups, surface-bonded polysilanes can form.

The CSP membrane is created by introducing terminally-anchored and covalently attached (grafted) polymer chains onto the surface of a ceramic membrane. For pervaporation, the polymer surface layer has to be of sufficient surface graft density and chain length to reduce the passage of the majority component while allowing the dissolution and permeation of the solute to be removed through the membrane. Since the polymer chains are covalently bonded to the membrane support, integrity and performance of the membrane are retained even upon swelling of the anchored surface chains. For UF applications the polymer layer acts as a dynamic polymer “brush” capable of stretching and aligning along the flow direction, when subjected to shear flow, while effectively rejecting colloidal particles from depositing and/or adsorbing onto the membrane surface and pores; thus, minimizing/eliminating irreversible fouling of the membrane. Using the above technology, a major goal of the proposed project was to demonstrate the technical viability of the CSP membranes and the feasibility of the approach to tailor-design these membranes for specific applications.

4. EXPERIMENTAL METHODS

4.1 Analysis of Modified Surfaces and Identification of Chemical Groups

The graft polymerization process was first optimized using surrogate zirconia or silica particles (Table 4.1). Identification of chemical groups on the surface of the unmodified, silylated and PVP-grafted particles was made by diffuse reflectance infrared-Fourier transform (DRIFT) spectroscopy using a Bio-Rad FTS-40 FTIR (Digilab Division, Cambridge, MA) with a diffuse reflectance accessory. Quantitative measurements of the yield ($\mu\text{mol}/\text{m}^2$ or mg/m^2) of vinyltrimethoxy silane (VTSM) and poly(vinylpyrrolidone) (PVP) grafted onto the ceramic substrate were determined by thermogravimetric (TGA) analysis conducted with a Perkin-Elmer TGS-2 thermogravimetric analyzer. References for the above measurements were taken with respect to the cleaned unmodified substrate and hydrolyzed particles.

Table 4.1 Physical and chemical properties of zirconia and silica particles^(a)

	Zirconia	Silica
Particle size (μm)	< 5	< 5
Specific surface area (m^2/g)	6.1	2.2
Surface hydroxyl groups concentration ($\mu\text{mol}/\text{m}^2$)	9.8	7.6
Density ($10^3 \text{ kg}/\text{m}^3$)	5.8	2.3
pI (isoelectric point)	5.8	2
pH stability	<10	≤ 14

^(a) Source: Rovira et al. (2001)

4.2 Emulsions

Oil-in-water microemulsions were prepared by mixing the dispersed oil phase, n-decane, in ultra-pure DI water with varying proportions of the emulsifying agents to yield a range of nanodroplet sizes. Sodium octanoate was used as the anionic surfactant, while octanoic acid and isobutanol were utilized as co-surfactants. The resultant microemulsions contained nanodroplets in the size range of 18 ~ 66 nm with standard deviation range of 20–39%, as determined by Dynamic Light Scattering (DLS) measurements (Submicron Particle Sizer, Nicomp Model 370, Santa Barbara, CA) and ranged in oil concentration (C_{oil}) from 3.33×10^4 to 3.64×10^4 ppm. The low-shear Newtonian viscosity of the microemulsions was determined using an Ubbelohde viscometer (Cannon Instrument Co., State College, PA). The dependence of microemulsion viscosity on shear rate was subsequently evaluated using a parallel plate rheometer (Fluid Dynamics, Flemington, NJ). All of the microemulsions were found to be Newtonian (i.e., shear-

independent viscosity) over a shear rate range up to 1500 s^{-1} (which correspond to the shear rate range in the membrane experiments) with viscosity ranging from 5.38 to 12.6 mPa•s. Finally, interfacial tension measurements of various combinations of microemulsions components (Faibish, 2001) were obtained using a DuNouy tensiometer (Model 70545, CSC Scientific Co., Inc., Fairfax, VA). A summary of the physical properties of the microemulsions used in the study is given in Table 4.2.

Table 4.2 Physical properties of microemulsions^(a)

d [nm]	Standard deviation of size [%]	Viscosity [mPa s]	Density [kg/m ³]	Surface tension [mJ/m ²]
18	39	5.38	893	25.3
35	28	12.6	893	25.3
66	20	12.6	916	25.2

^(a) Source: Faibish et al. (2001a)

A commercial cutting oil emulsion was prepared by mixing 4.5 g Castrol water-soluble cutting oil with 1.5 L (i.e., 3000 mg/L) ultra-pure DI water using a homogenizer (Powergen 700, Fisher Scientific, Pittsburgh, PA) at a constant speed of 2500 rpm for 2 minutes. The composition of the cutting oil is given in Table 4.3. The viscosity of the emulsion at 20°C, determined using an Ubbelohde viscometer (Cannon Instrument Co., State College, PA), was 1.03 mPa•s. The average oil droplet sizes in the feed and permeate solutions were measured by DLS and found to be in the range of 98 – 105 nm and 110 – 120 nm, respectively, with a standard deviation range of 30 – 60%.

Table 4.3. Composition of Castrol 329 oil

Component	wt %	CAS number
Distillates (petroleum), hydrotreated heavy naphthenic	5-10	64742-52-5
Alkanes, C12-18, ethoxylated propoxylated	1-5	69227-21-0
Chloro-alkanes	15-20	61788-21-0
Distillates (petroleum), solvent-refined heavy naphthenic	45-50	64741-96-4

Note: Manufacturer also reported presence of sulfonate surfactants.

4.3 Chemical Analysis

Decane and isobutanol components of the oil-in-water microemulsions were monitored by sol methylene chloride extraction followed by gas chromatographic analysis (HP 5890A GC with FID detector and a Carbowax 1500 packed column). For the oil-in-water microemulsions,

octanoic acid and sodium octanoate concentrations were determined by titrating grab samples diluted in methanol to the equivalence point using 0.1 N NaOH and 0.1 N HCl solutions, respectively. Permeate and feed analysis of the oil-in-water emulsions was also conducted by total organic analysis (TOC; EPA Method 415.1). Lysozyme, used to probe the effectiveness of the surface density of PVP chains, was monitored in the permeate and feed streams by UV spectroscopy. Analysis of trichloroethylene and chloroform for the pervaporation studies was accomplished by gas chromatography (GC) using a Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector and a 6' x 1/8" stainless steel column packed with Carbograph Graphitized Carbon Black 2AC (Alltech, Deerfield, IL). MTBE and methanol were also analyzed by GC using a SRI 8610C gas chromatograph equipped with a flame ionization detector (FID) and a 10' x 1/8" stainless steel GC column packed with 80/120 Carbopack B (Supelco, Bellefonte, PA).

4.4 Surface Hydroxyl Masking and Surface Charge

The effectiveness of surface hydroxyl replacement and masking by graft polymerized PVP surface phase was evaluated by both the surface charge density and zeta potential measurements for native and polymer-modified inorganic-oxide particles (5 μm size and 6.13 m^2/g). The surface charge density (C/m^2) was determined by a potentiometric acid-base titration (Rovira et al., 2001). Zeta potential measurements were performed with a Laser Zee MeterTM 501 (Pen Kem Inc., Bedford Hills, NY). The measurements were conducted by dispersing about 0.5 g of particles (native or modified) in a 1 liter solution of 0.1 M NaCl solution with pH adjustment using aqueous NaOH or HCl solutions.

4.5 Surface Adsorption

Batch adsorption experiments, with solutions of the emulsion species were carried out using native surrogate zirconia or silica particles Adsorption experiments were carried out by standard batch equilibrium adsorption studies at 25°C. Carefully weighed quantities of unmodified, silylated, or grafted ceramic particles were added to 10 ml glass vials with Teflon-lined screw-cap tops. The vials were filled with previously prepared solutions of containing one or more of the emulsion components or aqueous protein solutions. Solute adsorption vials and blanks containing water and water with grafted-ceramic particles were prepared in triplicates. The vials were agitated using a 3 ft-long rack (capacity of 66 adsorption vials) that rotated the

tubes end-over-end at 12 rpm. An equilibration time of about 30 hours was determined to be sufficient for the adsorption study. At the end of the adsorption period the particles were removed from the solution by filtration using a 0.8 μm cellulose acetate membrane. The supernatant solutions were then analyzed in triplicate by UV spectrophotometry, total carbon analysis or GC analysis.

4.6 Surface Topology

Direct observation of the topology of the grafted PVP surface phase was accomplished by atomic force microscopy (AFM) imaging of the PVP-modified silicon <100> prime-grade wafers (Wafernet, San Jose). The wafers were first soaked in acetone and subsequently methanol to remove soluble organic contaminants. The wafer was cleaned using a 7:3 (by volume) solution of sulfuric acid (Certified ACS grade, Fisher Scientific) and 30% hydrogen peroxide in water (Certified ACS grade, Fisher Scientific). Drying of the wafers was accomplished by oven drying, under vacuum at 110°C. Subsequently, the wafers were silylated and graft polymerized under the same reaction conditions as for the particles. AFM images were obtained using a Digital Instruments (Santa Barbara, CA) multimode atomic force microscope with a Nanoscope IIIa SPM controller, operating in tapping mode.

4.7 Contact Angle

Variations in surface wetting of the polymer-modified surfaces, as a function of surface polymer graft yield, were examined by water contact angle measurements using surrogate native and polymer-modified silicon wafers. In addition, contact angle measurements were performed for the microemulsion solution and several combinations of the microemulsion ingredients on the native and PVP-grafted silicon wafers. The polymer-modified wafers were cleaned by immersion in DI water, followed by several rinses with ethanol and water. Contact angle measurements were performed using the advancing/receding sessile drop method (Good, 1993) with a Kruss Model G-23 (Hamburg, Germany) contact angle instrument. Each of the reported contact angles represents average values (with a standard deviation of $\sim 4\text{--}5^\circ$) based on at least 4 separate drops for different areas of a given wafer.

4.8 Pervaporation

The tubular porous inorganic substrates for the CSP pervaporation membranes were made of either silica or alumina. The membranes supports were polymer-modified by graft polymerizing vinyl acetate or vinyl pyrrolidone onto the membrane tube-side surface (Figure 4.1) following a two-step graft polymerization process (Section 5). The polymer-modified membrane was then inserted into a stainless steel pervaporation module (Figure 4.1). Tubular silica membrane supports, used for trichloroethylene/Water, chloroform/water and MTBE/water pervaporation were 19-20 cm in length and 0.4 mm in thickness, with a pore size of either 100 Å or 500 Å (Industrial Research Institute of Miyazaki, Tsunehisa, Japan). Pervaporation of MTBE/methanol studies were conducted with native and modified porous tubular alumina support membranes (US Filter, Filtration and Separations Group) 25 cm in length, 1 cm outer diameter and 0.7 cm inner diameter. These membranes were asymmetric in construction and consisted of a sintered layered structure with a 5 micron thick layer of average pore size 50Å on

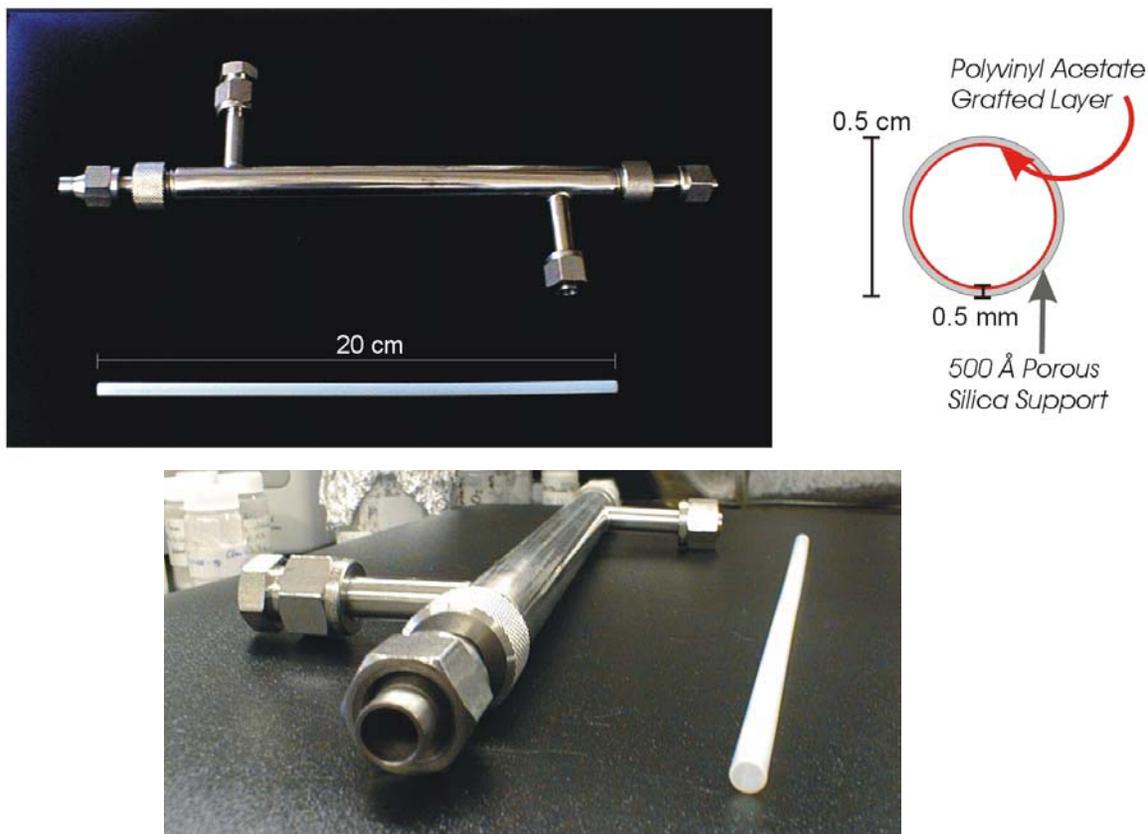


Figure 4. 1. Native silica support membrane and membrane module. The active polymer separation layer is graft polymerized onto the inner surface of the porous membrane support (top: top view; top right: dimensions and location of active polymer layer; bottom: side view)

top a series of increasing pore size substrates. The final separating layer was a 50Å gamma-alumina layer with three succeeding alpha-alumina support layers of pore sizes of 0.2 μm , 0.8 μm and 10-12 μm .

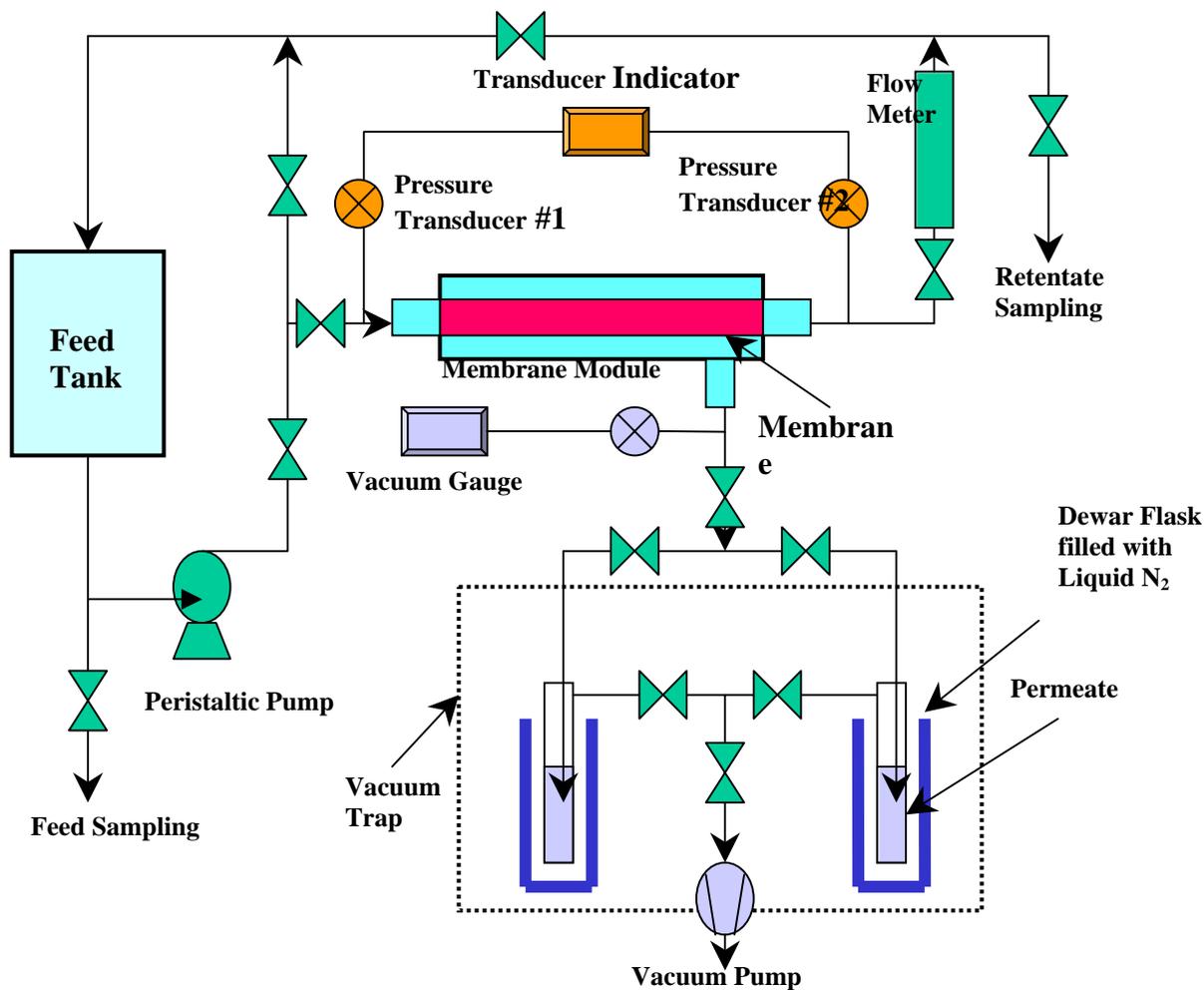


Figure 4.2. Schematic diagram of laboratory pervaporation test unit

Pervaporation of dilute aqueous solutions of organic solutes (TCE, chloroform or MTBE) and MTBE/methanol mixtures with polymer-modified silica and alumina membranes was carried out experimentally using a bench-scale pervaporation system (Figure 4.2). A tedlar bag (Chromatography Research Supplies, Addison, IL) containing approximately 1000 ml of feed solution was used as a reservoir in order to eliminate chemical losses by volatilization. The feed solution was pumped through the tube-side of the module and the retentate was recycled back to

the feed tank with the flow rate measured by an on-line flow meter. The gaseous permeate was condensed and collected by means of two vacuum traps immersed in liquid nitrogen. Low pressure, approximately 2 Torr on the permeate side, was maintained by a vacuum pump (Model M8C, Fisher Scientific, Pittsburgh, PA). Transmembrane pressure was measured by pressure transducers (Model CD 223, Validyne, Northridge, CA) and a vacuum gauge (Pirani Vacuum Gauges, Edwards, Wilmington, MA) placed on the feed and permeate sides of the membrane, respectively. All pervaporation experiments were conducted at room temperature. The permeation rate was then determined by monitoring the volume of condensed permeate in the dewar flasks, throughout the course of the experiment. Prior to pervaporation tests, the native, silylated and polymer-modified ceramic membranes were characterized by hydraulic permeability measurements with water. A series of pervaporation measurements were then performed with the unmodified, silylated and grafted silica membranes.

4.9 Membrane Filtration

Tubular ceramic-supported polymer ultrafiltration membranes were produced by graft polymerization of vinyl pyrrolidone onto the inner membrane tube-side. The support membrane (Figure 4.3) was a tubular porous carbon-supported zirconia membrane (Carbosep membrane; Rhodia Oreilis, Miribel, France) with a manufacturer reported MW cutoff of 15 kDa (average pore size of approximately 4 nm) and an overall thickness of 0.247 cm. The average thickness of

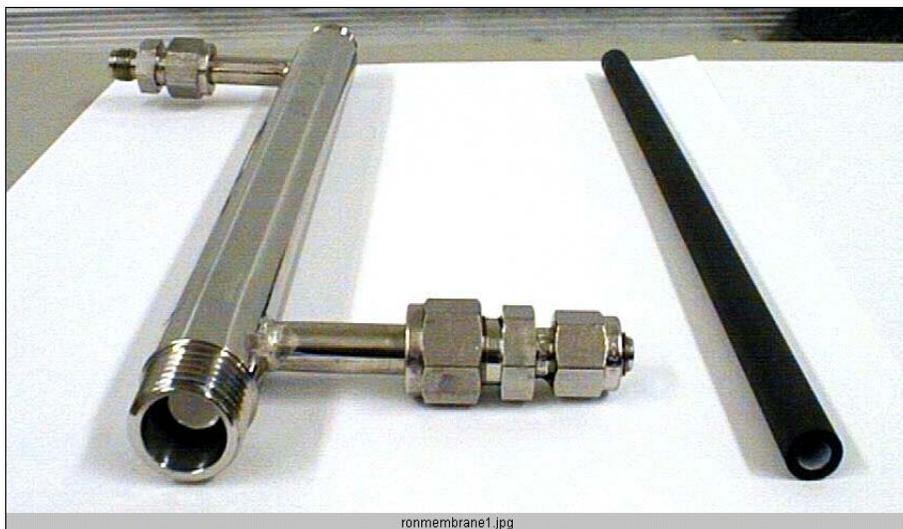


Figure 4.3. Carbosep support membrane (Length = 24 cm; I.D. = 6 mm; Water flux = 400 - 600 l/h/m² @ 1 bar and 25°C). The inner layer is the zirconia support layer). The active polymer layer is grafted onto the inside surface of the membrane.

the active zirconia layer was 2.75 μm (Faibish and Cohen, 2001). The measured membrane with inner and outer diameters of 3.00 and 5.29 mm, respectively, was rated by the manufacturer for use over a pH range of 0–14, temperatures exceeding 100°C, and a maximum operating pressure of 10 bars (1.01 MPa). The measured specific hydraulic water permeability of the membranes ranged from 1.71×10^{-7} to $3.78 \times 10^{-7} \text{ m s}^{-1} \text{ Pa}^{-1}$ at 20°C.

The zirconia membranes were modified to form a polyvinylpyrrolidone layer (Section 5). Prior to graft polymerization, the membranes were silylated with VTMS and subsequently hydrolyzed using a KOH solution (pH=12) to convert unreacted surface methoxy groups to silanols. The graft polymerization process resulted in a surface consisting of poly(vinylpyrrolidone) chains that were terminally anchored to the ceramic substrate. The ultrafiltration performance of the above CSP membranes was evaluated using oil-in-water emulsions (micro- and macroemulsions) with the crossflow filtration system shown schematically in Fig. 3.2. The temperature-controlled feed solution was fed through a flow damper to the inlet port of the membrane module using a diaphragm pump. Transmembrane pressure was controlled by a needle valve at the outlet side of the membrane module. The transmembrane pressure was monitored by variable reluctant differential pressure transducers (Model DP15-44, Validyne Engineering Corp., Northridge, CA) of full-scale error of $\pm 0.5\%$, connected to the outlet and inlet sides of the membrane module. Permeate flux and feed flow rate were measured gravimetrically and/or volumetrically.

After each filtration experiment the membrane was cleaned by rinsing it at the maximum allowable flow rate (in a crossflow operation) with DI water and subsequently submerging it in a stirred aqueous solution of NaOH (pH 12) for about an hour. The membrane was then thoroughly rinsed with DI water. The hydraulic permeability was calculated for the membranes before and after the filtration experiments and membrane cleaning to assess the impact of irreversible membrane fouling. The hydraulic permeability, k_i [m^2], of the membranes was determined by measuring permeate flux as a function of transmembrane pressure and using Darcy's equation (Castro et al., 2001). For the tubular membranes, the hydraulic permeability was determined from (Faibish and Cohen, 2001)

$$k_i = \frac{J_w \mu_w R_i \ln(R_o / R_i)}{\Delta P_m}$$

in which R_i and R_o are the inside and outside membrane tube radius (m), respectively, and ΔP_m is the transmembrane pressure (Pa).

5. SURFACE MODIFICATION

Surface density of vinyl silane groups is controlled by: (a) initial concentration of surface hydroxyls which in turn can be affected by surface hydroxylation, surface water and heat treatment; and (b) silylation reaction conditions (e.g. vinyl silane concentration in the reaction mixture, temperature and reaction time (Cohen et al., 2001). The present study revealed that surface water has a profound effect on the resulting level of surface silylation (Fig. 5.1). It is believed that bonding of the first silane layer to the inorganic oxide substrate requires the presence of surface water which is not consumed in this reaction (Fig. 5.2a). However, subsequent attachments of alkoxy silanes to surface bonded silanes result in a net loss of water surface water (Fig. 5.2b). Therefore, a silane network can form (Fig. 5.2c) when sufficient surface water is available (Fig. 5.2c); this leads to a high surface coverage by the desired functional groups (vinyl groups in the present study), thereby increasing the efficiency of the subsequent surface graft polymerization step.

Through careful control of surface water coverage, in the silylation of VTMS from xylenes (Fig. 5.1), it is possible to attain vinyl silane surface densities as high as 6.5 mg/m^2 (about $55 \text{ } \mu\text{mol/m}^2$) and 3 mg/m^2 (about $26 \text{ } \mu\text{mol/m}^2$) for silica and zirconia, respectively (Rovira et al., 2001; Chaimberg and Cohen, 1991; Yoshida et al., 2001). The upper bound of the surface hydroxyl concentration for silica and zirconia have been reported at $4.6 \text{ hydroxyls/nm}^2$ and $5.9 \text{ hydroxyls/nm}^2$ (Rovira et al; and references therein), respectively; therefore, a higher surface silane coverage is indicative of the formation of polysilanes.

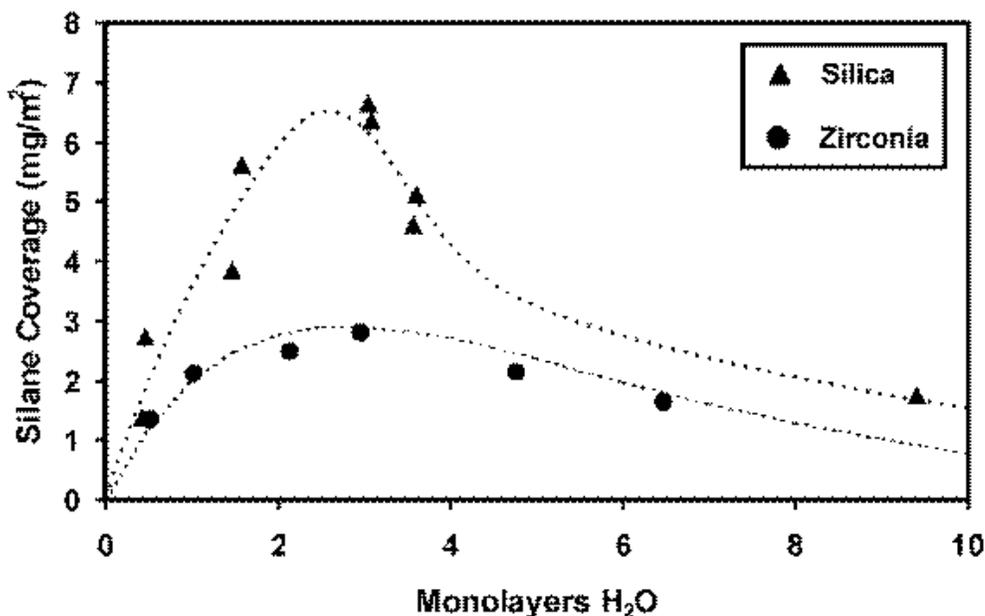


Figure 5.1. Effect of surface water on surface silylation coverage for trimethyl vinyl alkoxy silane (VTMS).

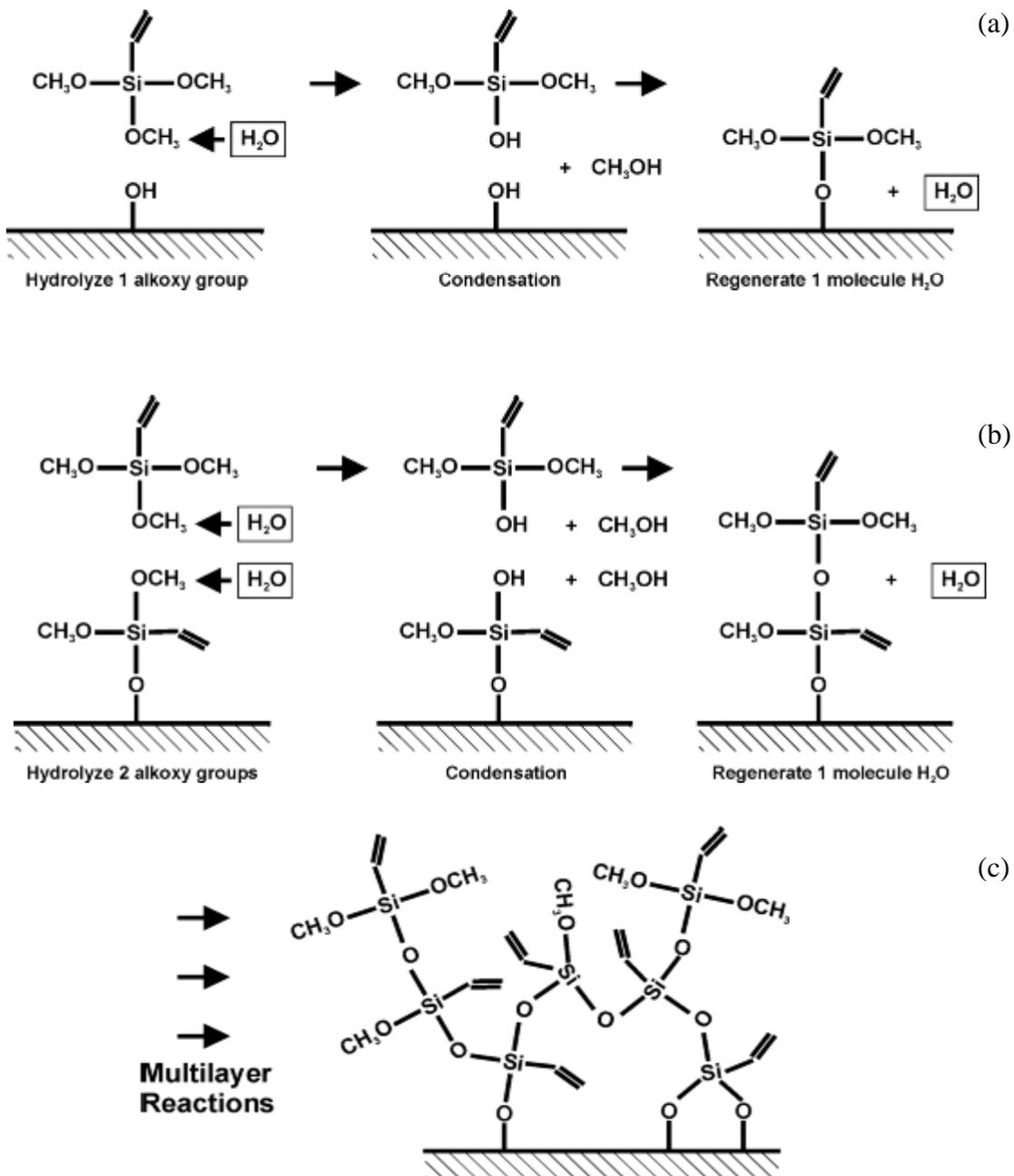


Figure 5.2. Surface Silylation with trimethylalkoxy vinyl silane (VTMS). a) reaction for initial VTMS coverage (hydroxyl/alkoxy). b) reaction for multilayer VTMS coverage (alkoxy/alkoxy); c) surface-bonded polysilane resulting from initial and multilayer reactions.

The topology of the vinyl silylated surface was examined by atomic force microscopy (AFM) on surrogate silicon wafer surfaces (Yoshida et al., 2001) revealing surface clusters with well-defined boundaries (Fig. 5.3). These structures have smooth edges and do not appear to be the result of aggregation of smaller clusters. The two-dimensional fractal dimension of 2.16 for these structures suggested that the clusters are distributed randomly without ordered aggregation. The cluster surface topology is believed to result from the formation of chemically attached polysilane networks grown on the surface during silylation and/or the attachment of solution-formed polysilanes by condensation reactions. Inspection of the regions between the clusters, using a 200 x 200 nm scan, revealed that the majority of the surface was covered with surface-bonded VTMS clusters with a continuous size distribution (Yoshida et al., 2001). The heterogeneous distribution of cluster sizes (heights and projected area) as seen in Fig. 5.3 contributes to the resultant uneven surface topology of the grafted polymer phase.

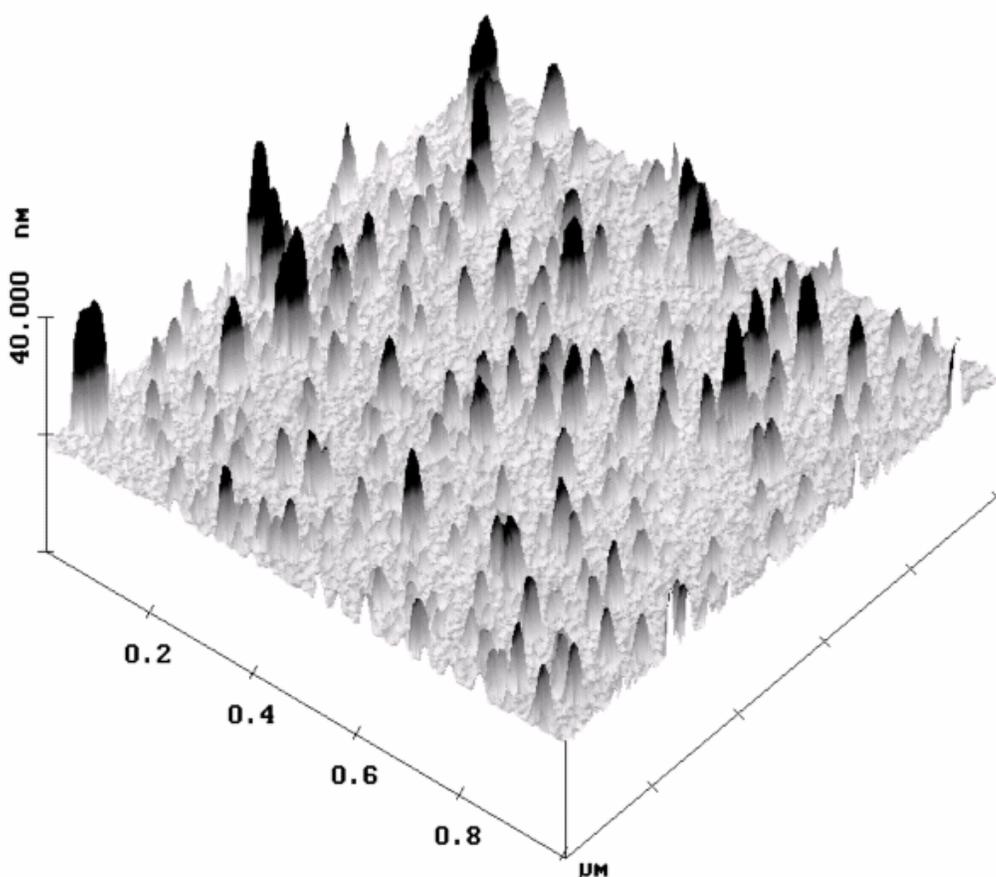


Figure 5.3. 1x1 μ m AFM image of CTMS silylated silicon wafer. (Vertical scale= 40 nm)

The step subsequent to vinyl silylation is graft polymerization of a suitable vinyl monomer onto the support surface such that polymer chains are grown from activated (i.e., vinyl) surface sites. The polymer graft yield (mg polymer/m^2), obtained in the present study, for vinyl acetate and vinyl pyrrolidone graft polymerization onto inorganic oxide surfaces, increased with reaction time, temperature and initial monomer concentration (Figs. 5.4a and 5.4b). A schematic illustration of the steps of graft polymerization of vinylpyrrolidone onto a silica surface is shown in Figure 5.5. It is noted that the Si-O-Si-C coupling to silica (Fig.5.5) was shown to be stable over a pH range of 1.0 to 9.5. Moreover, since the polymer chains are covalently bonded to the solid substrate, polymer attrition is virtually eliminated (Chaimberg and Cohen, 1991).

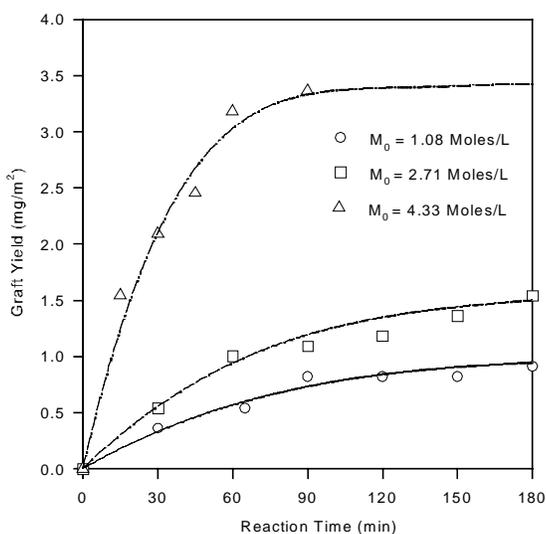


Figure 5.4a. Polymer graft yield for graft polymerization of vinyl acetate onto silica (70°C).

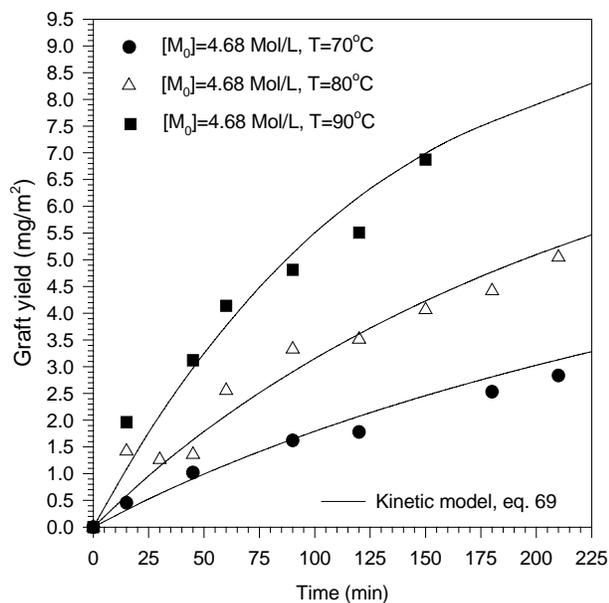
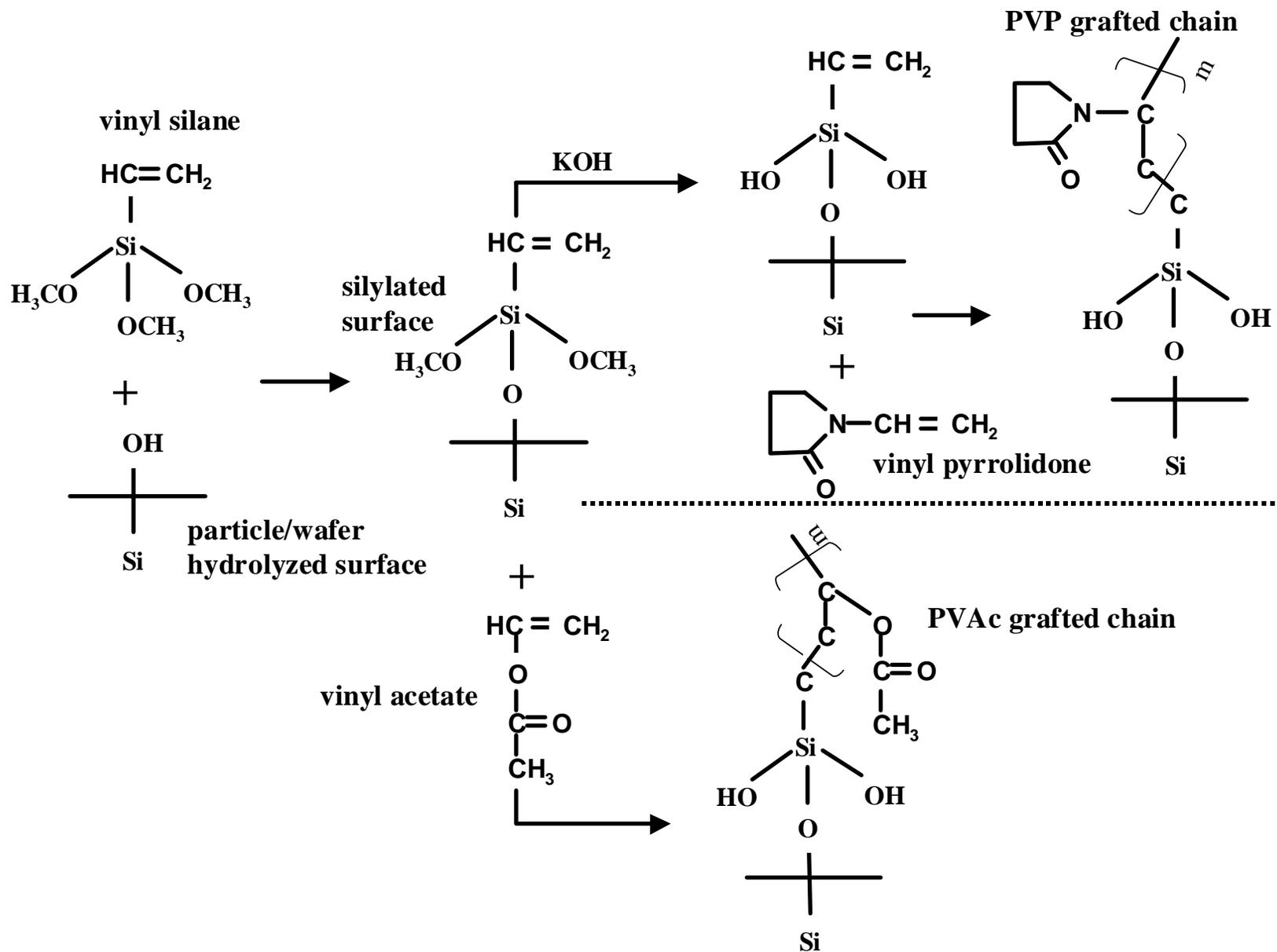


Figure 5.4b. Polymer graft yield for graft polymerization of vinylpyrrolidone onto silica.



The active polymer layer, obtained by the present graft polymerization method, is a molecular layer. Therefore, the polymer surface graft yield (e.g., mg polymer/m²), for modified membranes surfaces will be lower, on a surface area basis, relative to grafted polymer surfaces obtained by pore-filling methods (including graft-polymerization pore-filling); the latter methods results in significantly thicker membranes. Notwithstanding, the present approach results in a polymer surface coverage (i.e., surface chain density) that is significantly higher than possible by previous methods. For example, surface chain density up to about 3 $\mu\text{mol/m}^2$ can be achieved with an average chain MW in the range of 1000-90,000 and a polymer graft yield as high as 7 mg/m² (Nguyen et al., 2001; Cohen et al., 1999, 2001; and references therein).

Surface density of the grafted chains is a function of the initial spacing between the surface vinyl silane groups (Figure 5.6) and polymerization reaction conditions. Reasonably high surface graft densities can be obtained by graft polymerization (i.e., sequential addition of monomers to a growing chain) to produce effective membranes with a polymer layer in the dense “brush regime” (Faibish and Cohen, 2001a; Cohen et al., 2001; Castro et al., 2001). In a good solvent, surface chains in the “brush” regime extend away from the surface. In contrast, when the surface chains are far apart they are more likely to be in a random configuration resembling a “mushroom” shape. It is also known that when the chains are exposed to a poor solvent cluster of chains (or surface micelles) may form on the surface.

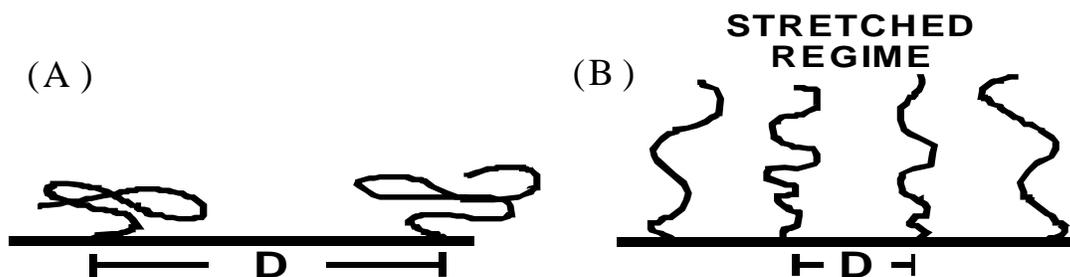


Figure 5.6. Schematic representation of terminally grafted chains. (A) chains are in a random coil (mushroom) configuration. (B) chains are in the “brush” regime which exists when $(a/D)^2 > N^{-6/5}$, D is the chain spacing given as $D = (f n_s)^{-0.5}$, N is the number of monomers per chain, $N = G/[f n_s MW_{pvp}]$, where G is the graft yield (g/m^2), f is the grafting efficiency, n_s is the silylation coverage, and MW_{pvp} is the molecular weight of the monomer.

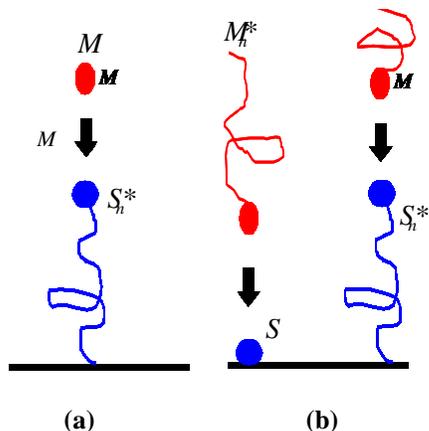


Figure 5.7. (a) Monomer addition to a growing chain (graft polymerization) and (b) Attachment of a growing chain from the bulk to the surface (polymer grafting).

In graft polymerization (Figure 5.5), surface chain formation occurs due to both graft polymerization and polymer grafting as shown schematically in Figure 5.7; the latter process leads to reduced surface chain density (due to steric hindrance associated with chain crowding as the homopolymer chains approach the surface). Therefore, to increase the density of surface-bonded chains, the contribution of graft polymerization has to dominate relative to polymer grafting (Fig. 5.8).

Control over the relative importance of polymer grafting and graft polymerization is possible by adjusting the reaction conditions (Nguyen et al., 2001; Chaimberg and Cohen, 1994). For example, for the poly(vinylpyrrolidone)-silica system (Figure 5.8), it was demonstrated that carrying the polymerization reaction at moderate temperatures and moderate initial monomer concentrations is desirable so as to minimize the contribution of polymer grafting to the total polymer graft yield. Examples of surface polymer graft yield, root-mean-square roughness and chain spacing are provided in Table 5.1 for PVP and PVAc graft polymerized onto a silicon

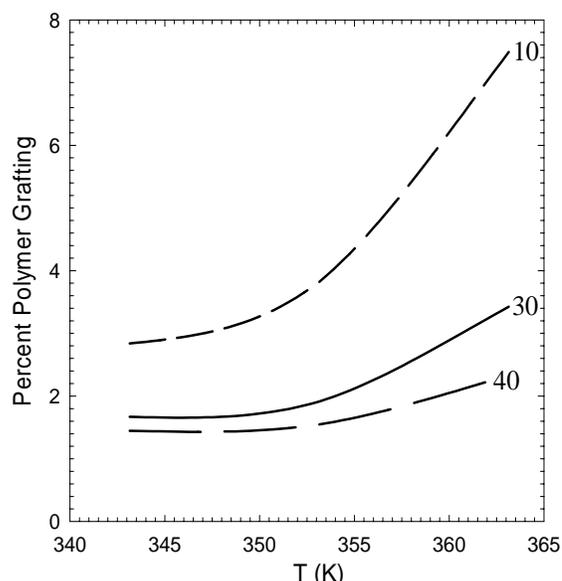


Figure 5.8. Contribution of polymer grafting to the total polymer graft yield for vinyl pyrrolidone graft polymerization onto silica with a hydrogen peroxide initiator.

Figure 5.1 Properties of PVP and PVAc Grafted Silicon Wafers

Grafting conditions		R_{RMS} [nm]	σ [nm]	Graft yield [mg/m ²]
Native wafer		0.21	0.04	N/A
PVP	M10T70	3.55	0.69	1.27
	M30T70	0.82	0.04	1.52
	M30T80	1.14	0.02	2.63
PVAc	M10T60	3.89	0.22	0.80
	M40T50	3.32	0.29	2.52
	M40T60	3.62	0.04	3.54

wafer. These results demonstrate that it is possible to obtain a range of surface arrangement of the grafted polymer.

Through careful control of the polymerization conditions, given a detailed description of the polymerization kinetics (Nguyen et al., 2001; Chaimberg and Cohen, 1994), one can attain higher polymer graft yield than previously possible. The resulting polymer phase is of a broad molecular weight distribution (Nguyen et al., 2001; and references therein) as expected for free radical polymerization; the surface topology (Fig. 5.9) is consistent with the broad range of chain sizes as well as the topology of the underlying vinyl silane structure. It is noted that, with the present approach, graft yields are sufficiently high to produce polymer separation layers that are in the dense “brush regime” (Faibish and Cohen, 2001a,b; Cohen et al., 2001; Rovira et al., 2001). Moreover, kinetic data and models developed for the present systems can be used to determine the polymerization reaction conditions needed to achieve a surface polymer phase of the desired properties (e.g., molecular weight and surface density).

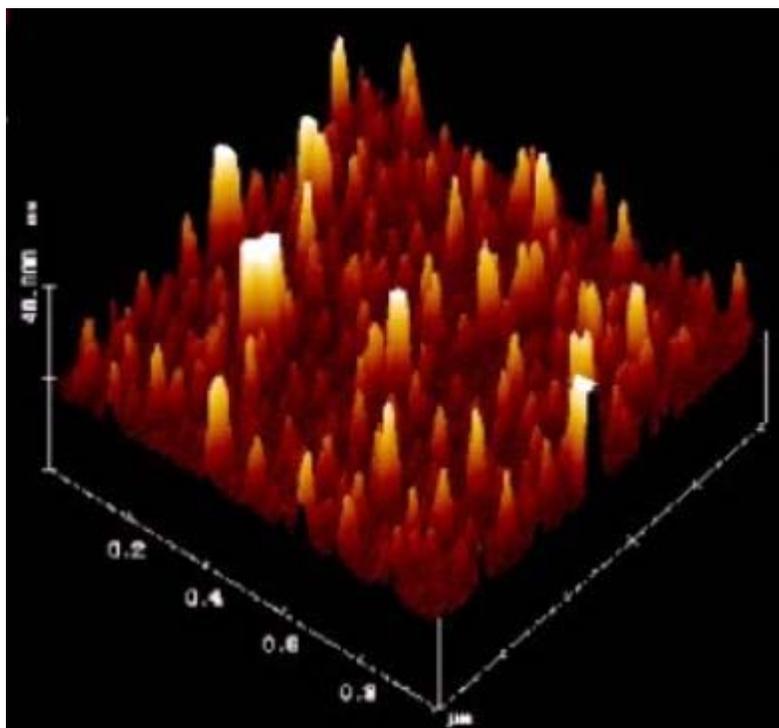


Figure 5.9. PVAc-Modified Silicon Wafer. (1x1 μm area, 40 nm vertical full scale. RMS=4.15 nm)

6. CSP PERVAPORATION MEMBRANES

Silica membrane supports were modified with the goal of attaining a selective polymer separation layer and a level of pore reduction sufficient for pervaporation. The selection of the separating polymer phase for specific separations was made based on simple solubility considerations utilizing a 2-D Hansen solubility parameter map (Jou et al., 1999) shown in Fig.6.1. Solvent (or solute)-polymer compatibility is indicated by the distance between the polymer and organic points on the map; increased compatibility (or solubility of polymer in the organic liquid) is depicted by smaller distances between a selected chemical pair. For example, Poly(vinyl acetate) (PVAc) is completely soluble in trichloroethylene and insoluble in water;

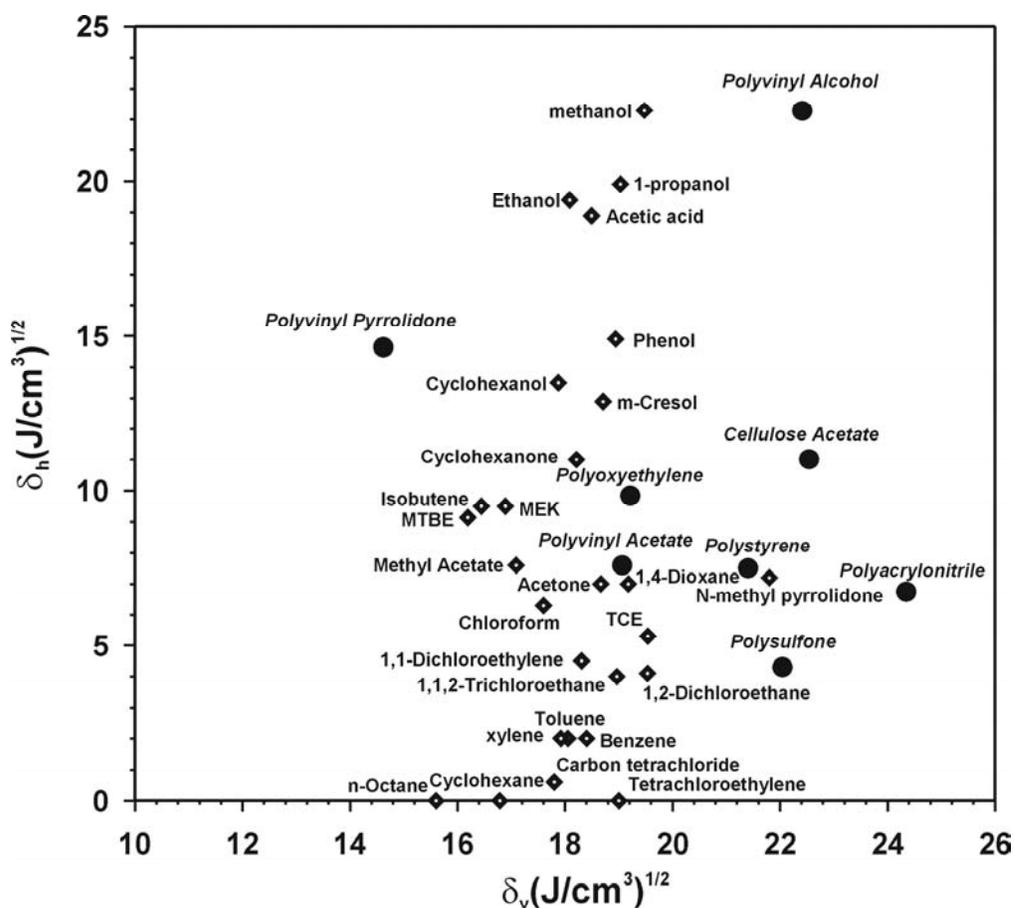


Figure 6.1. Hansen Space Solubility Parameter Map. The Hansen space solubility parameters δ_d , δ_p , and δ_h represent nonpolar, polar, and hydrogen bonding interactions and $\delta_v=(\delta_d^2+\delta_p^2)^{1/2}$. The large circles indicate a polymer and the diamonds indicate solvent (or solute).

thus, PVAc is a suitable polymer for pervaporation removal of trichloroethylene from water and also for the separation of MTBE from water. Selections of suitable polymer based on solubility parameter considerations should always be checked against experimental solubility data. For

example, solubility parameter considerations suggest that MTBE is more compatible with PVAc than with PVP, while PVP is more compatible with methanol. Therefore, one may be led to conclude that a PVP-modified membrane would be suitable for removal of methanol from methanol/MTBE mixtures while a PVAc-based membrane would be suitable for removal of MTBE. However, actual solubility tests proved that PVP and PVAc are soluble in methanol, while PVP is insoluble in MTBE and PVAc swells in MTBE. Therefore, it was surmised that both PVAc and PVP-modified ceramic membranes would lead to preferential permeation of methanol from methanol/NTBE mixtures.

Based on the above considerations a number of PVAc and PVP-modified silica (Figure 6.2) and alumina membranes were prepared. It is important to note that the presence modification method resulted in a very thin modification zone. As illustrated in the SEM images of Fig. 6.2, the modified region extended to a depth of about 100-200 nm and clearly appears to have reduced the pore openings. The average hydraulic permeability of the silica membranes,

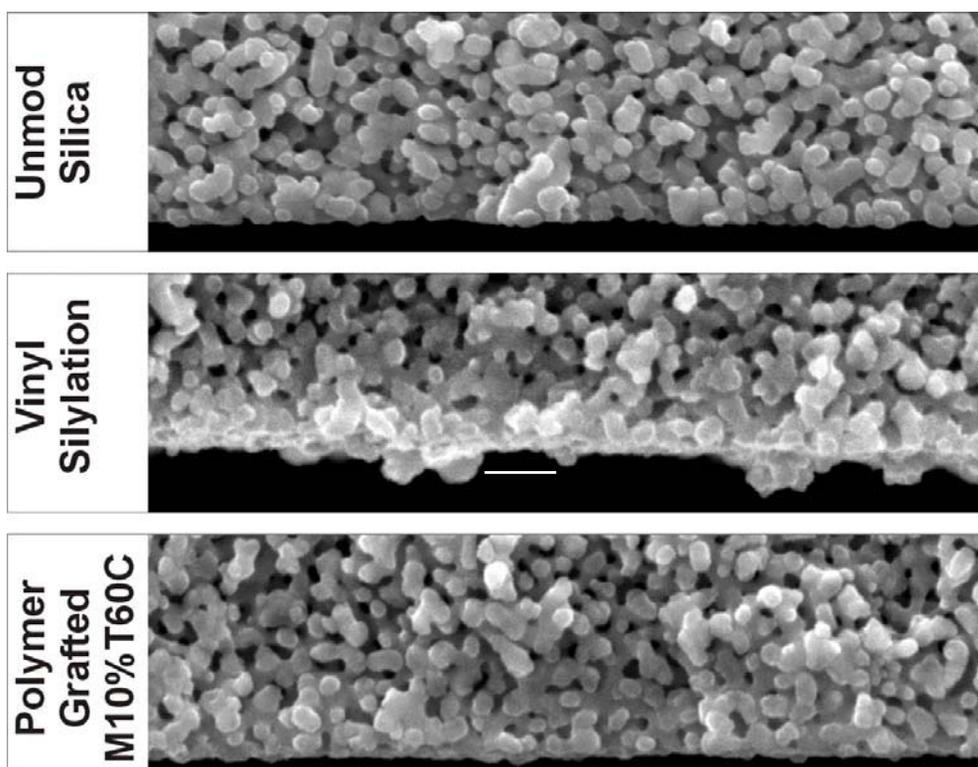


Figure 6.2. SEM cross-sections of native (top), silylated (middle) and PVAc (bottom) modified silica membranes. Native pore size= 500 Å. The bottom in each photo is the active layer side (i.e., tube feed-side). The horizontal white line in the middle photograph represents a distance of 200 nm.

based on dead-end filtration measurements, for seven different unmodified 500 Å, was about $1.2 \times 10^{-15} \text{ cm}^2$ with less than 15% deviation. The silylated and PVAc-modified silica membranes were impermeable to water up to a transmembrane pressure of 12 psia, indicating that the membrane had become hydrophobic. Negligible hydraulic water permeability for the CSP membrane, as our experience has shown, is a prerequisite for a suitable pervaporation membrane. It was also found that, with the present surface modification method, the starting native membrane pore size had to be no larger than 500 Å in order to produce a functioning pervaporation membrane

The PVAc-grafted silica membranes were shown to be capable of removing volatile chlorinated organic solvents from water by pervaporation, while PVP-based membranes were useful for polar/non-polar organic/organic separation and dehydration of organic solvents. The performance of a tubular silica-poly(vinyl acetate) membrane for the removal of methyl t-butyl ether (MTBE) from a 1 liter feed solution. The permeate side was set at vacuum of 2 torr with total permeate removal and total recycle of the retentate stream to the feed reservoir (up to 740 ppm initial MTBE concentration). An illustrative set of results MTBE removal from water is shown in Fig. 6.3. The corresponding theoretical predictions, denoted by the solid curves (Fig. 6.3), are based on the assumption that mass transfer resistance is only due to the tube-side

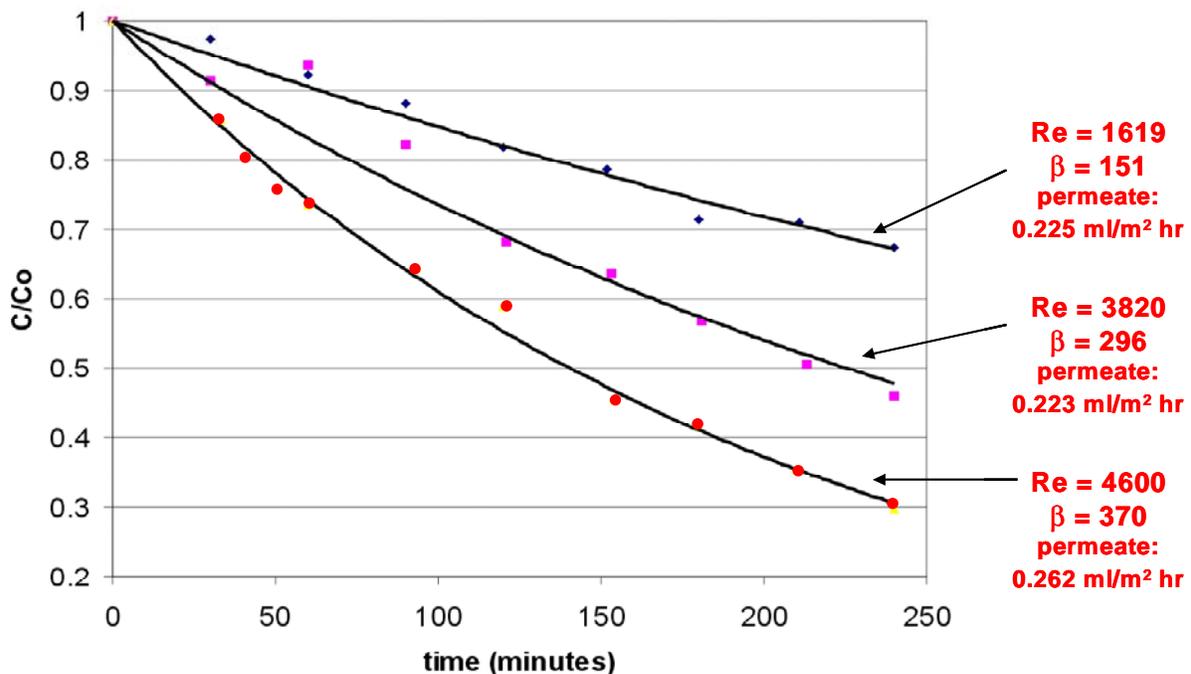


Figure 6.3. Removal of MTBE from a water/MTBE solution using a tubular silica/PVAc pervaporation membrane (Initial MTBE concentration= 740 ppm; polymer graft yield=0.22 mg/m²; solid lines represent theoretical predictions based on tube-side concentration boundary layer resistance.)

concentration boundary layer. The excellent agreement between the predictions and the experimental data suggest that membrane resistance is negligible for the range of tube-side Reynolds numbers and polymer graft density in the present study. The enrichment factors for MTBE (i.e., permeate concentration/feed concentration) increased, as expected, with tube-side Reynolds numbers owing to the corresponding increase in the tube-side mass transfer coefficient.

The performance of the silica-PVAc pervaporation membrane for the removal of trichloroethylene (TCE) from a 1 liter water/TCE solution also revealed negligible membrane resistance. The TCE concentration in the feed reservoir (Fig. 6.4) is seen to decrease rapidly with the rate of removal increasing with the tube-side Reynolds number, as predicted based on the tube-side mass transfer coefficient. Clearly, the CSP pervaporation membrane has negligible mass transfer resistance, relative to the feed-side (i.e., tube-side) mass transfer resistance.

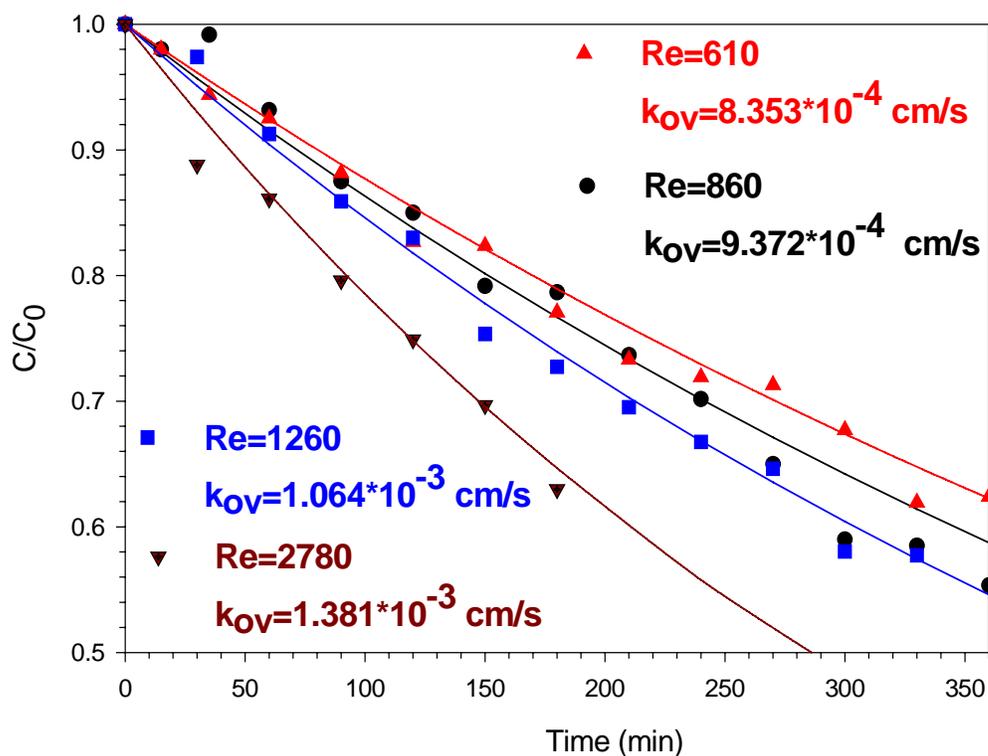


Figure 6.4. Relative concentration-time data for pervaporation removal of TCE from water/TCE solutions. (PVAc-grafted silica membrane: graft polymer density=0.17 mg/m², C₀- initial feed concentration= 500-700 ppm).

The enrichment factors (solute concentration in permeate/solute concentration in feed) for the removal of trichloroethylene (TCE) and chloroform and MTBE, using poly(vinylacetate)-silica membrane, was sufficiently high (with permeate enrichment factors ranging from about 100-370) to create a functional pervaporation membrane suitable for practical applications. For example, the enrichment factor for TCE (for TCE/water pervaporation) increased from a value of about 70 to 110 as the polymer graft density increased from about 0.17 mg/m² to 0.43 mg/m², at Re=610. For the MTBE/water system, the enrichment factor for MTBE was more sensitive to the polymer graft density as illustrated in Fig. 6.5 when using an alumina based support membrane with native pore size of 50 Å. We note that, as the enrichment factor increased with increasing polymer graft yield, the permeate flux decreased due to a decreased membrane permeability with increased volume of grafted polymer in the membrane pore space.

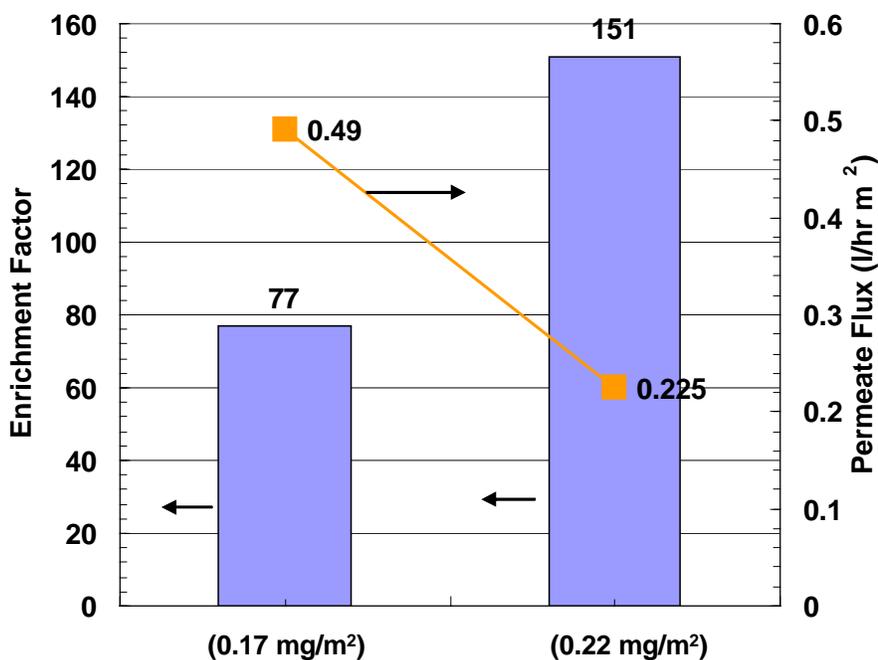


Figure 6.5. MTBE Enrichment Factor and permeate flux variation with polymer graft density for a silica-PVAc membrane (Re=1620, initial MTBE concentration in feed=740 ppm).

Membrane resistance for the present class of CSP membranes is negligible, for the Reynolds number range studied; therefore, permeate flux is dictated by the hydrodynamics on the feed-side of the membrane. Consequently, for the current membranes, the target solute flux is

already at its possible maximum with respect to the membrane separation power. Therefore, one is led to conclude that enrichment of the permeate beyond the level achieved in the present study would require greater reduction of the water permeation flux. The above improvement in performance could be achieved by increasing the polymer graft density as illustrated in a design calculation for TCE pervaporation shown in Figure 6.6 (Jou et al., 1999). The shaded region to the right shows a region of polymer graft density and water pervaporation flux (for a water/TCE system) and the corresponding range of enrichment factor values (shaded area to the left). As the calculations demonstrate, high enrichment factors that approach 1000 are possible; however, to achieve this target separation performance, an alternate surface activation may be required so as to increase the initial surface concentration of active sites for graft polymerization.

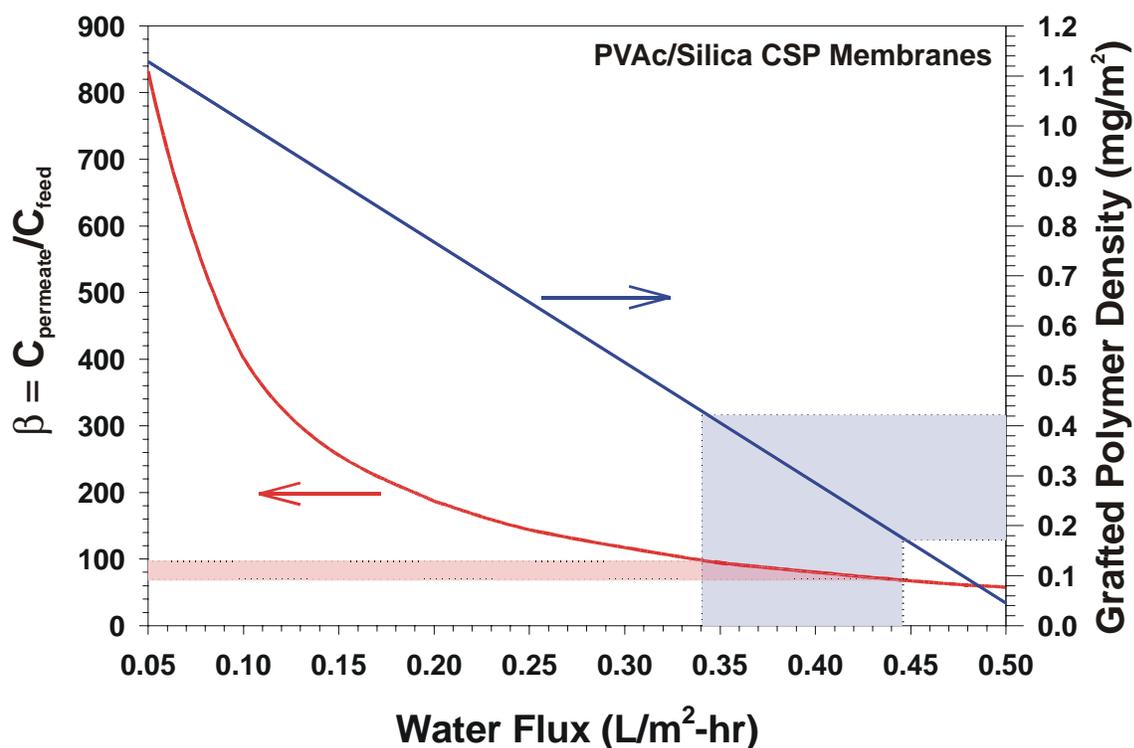


Figure 6.6. Design curves for a silica-PVAc pervaporation membrane for TCE/water pervaporation. The required grafted polymer density is obtained as follows: (a) an enrichment factor is specified and a horizontal line is drawn to intersect the enrichment curve; (b) a vertical line is then drawn to intersect the curve for the grafted polymer density and the required graft density is then read from the right vertical axis.

The performance of two alumina-based CSP membranes, based on polyvinyl acetate and poly (vinylpyrrolidone) was also evaluated for the separation of mixtures of methanol/MTBE. The PVAc-modified membrane was produced by graft polymerizing vinyl acetate from a 40% by

volume vinyl acetate solution at 60°C. The silica-PVP membrane was produced by graft polymerization of 30% by volume vinyl pyrrolidone monomer solution at 80°C. The resulting polymer graft densities for the silica-PVAc and silica-PVP membranes were 3.54 mg/m² and 2.63 mg/m², respectively. Both membrane supports were alumina-based with a native pore size of 50 Å for the upper γ -alumina layer. A set of pervaporation performance studies, with the above two membranes, revealed that the enrichment factor (EF) increased with decreasing methanol feed concentration. The total permeation flux increased with increasing methanol feed concentration a fact that is attributed, in part, to the higher permeation concentration driving force as methanol concentration in the feed-side increases. In general, as the enrichment factor increases the permeation flux decreases. Clearly, selection of optimal performance is a balance between separation and flux. For example, the PVAc membrane displayed a higher enrichment factor for MTBE compared to the PVP membrane, albeit at a lower pervaporation flux.

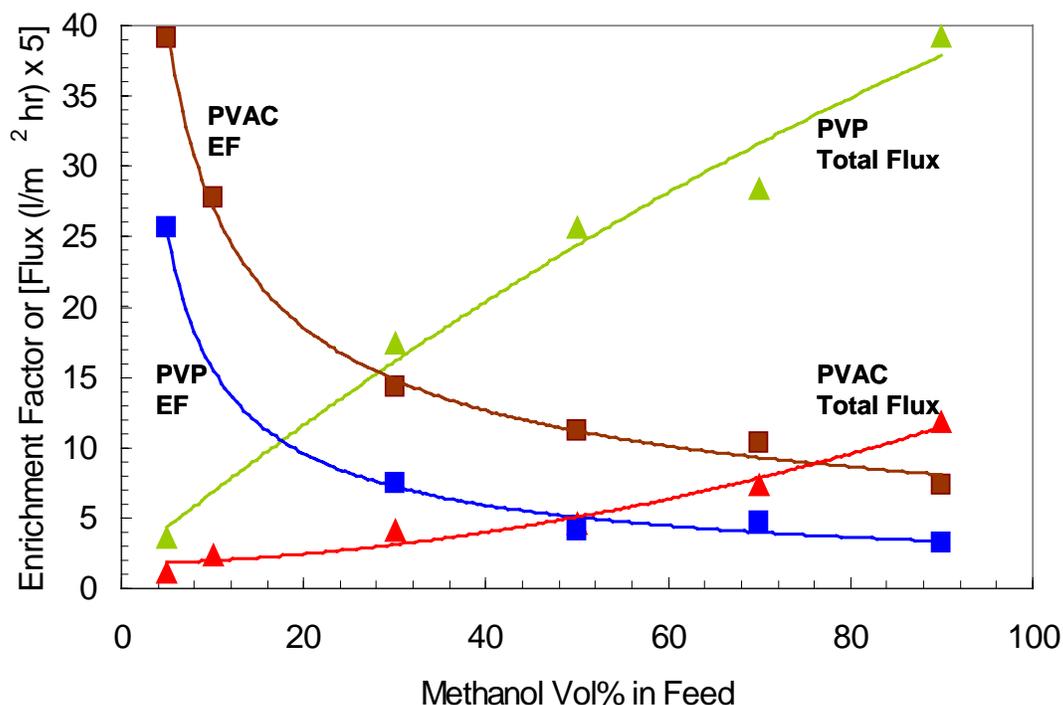


Figure 6.7. Permeate enrichment factor for MTBE and total pervaporation flux for pervaporation of MTBE/Methanol mixture using tubular PVP and PVAc grafted alumina membranes.

7. FOULING-RESISTANT ULTRAFILTRATION MEMBRANE

7.1 Masking of Surface Hydroxyls for Fouling Resistant Membranes

Surface hydroxyl groups on the surface of inorganic oxides were effectively masked by surface modification via graft polymerization. For example, terminally grafted poly(vinyl pyrrolidone) chains on a zirconia surface significantly reduced surface charge (Fig. 7.1), relative to the native surface, and the interaction of solutes with surface hydroxyls. Such a surface should be useful in reducing the adsorption of negatively charged solutes. It is also believed that the greater local partial mobility of terminally anchored polymer chains, relative to casted or cross-

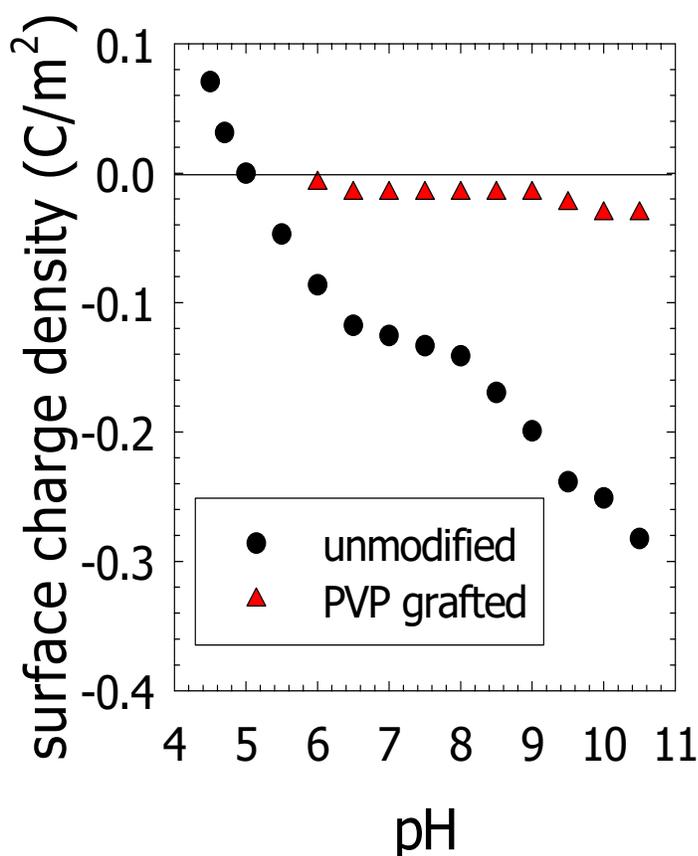


Figure 7.1. Surface charge density for native and PVP-modified zirconia particles in aqueous dispersion (0.1 M NaCl). Source: Rovira et al. (2001).

linked polymer layers, is also effective in reducing surface adsorption.

Irreversible fouling was reduced by terminally anchored PVP surface chains (section 7.3) when treating oil-in-water microemulsions (which are typically negatively charged). An additional benefit of the grafted polymer phase is that membrane rejection for UF can be increased (section 7.3).

A companion study on the lysozyme adsorption on PVP-grafted zirconia demonstrated the effectiveness of the resultant brush layer in screening lysozyme-surface interactions. The relatively small size of LYS (45x30x30 Å) allowed testing of relationship between surface graft density and exclusion of lysozyme from direct

interaction with the native surface. Adsorption reduction (up to 76%), due to protein exclusion from the surface by the tethered polymer layer, increased significantly when the distance between surface chains was less than the large axis of LYS (i.e., 45 Å).

7.2 Surface Wettability

Hydrophilic surface chains can serve as an effective fouling-resistant layer for UF treatment of aqueous streams provided that they are selected so as to minimize solute-polymer affinity (Rovira et al., 2001; Faibish and Cohen, 2001a,b; Cohen et al., 1999). The hydrophobicity/hydrophilicity of grafted surfaces can be evaluated via contact angle measurements. An illustration of contact angle measurements for native and modified silica surfaces is shown in Figure 7.2. For the hydrophilic PVP brush layer the contact angle for water decreased with increasing polymer graft yield indicating the formation of a more hydrophilic surface layer. Spreading of water on the PVP grafted layer is possible since the surface chains can absorb water and swell. In contrast, the PVAc layer is more hydrophobic and sufficiently dense, even at the lowest graft yield; thus, little variation in contact angle was observed.

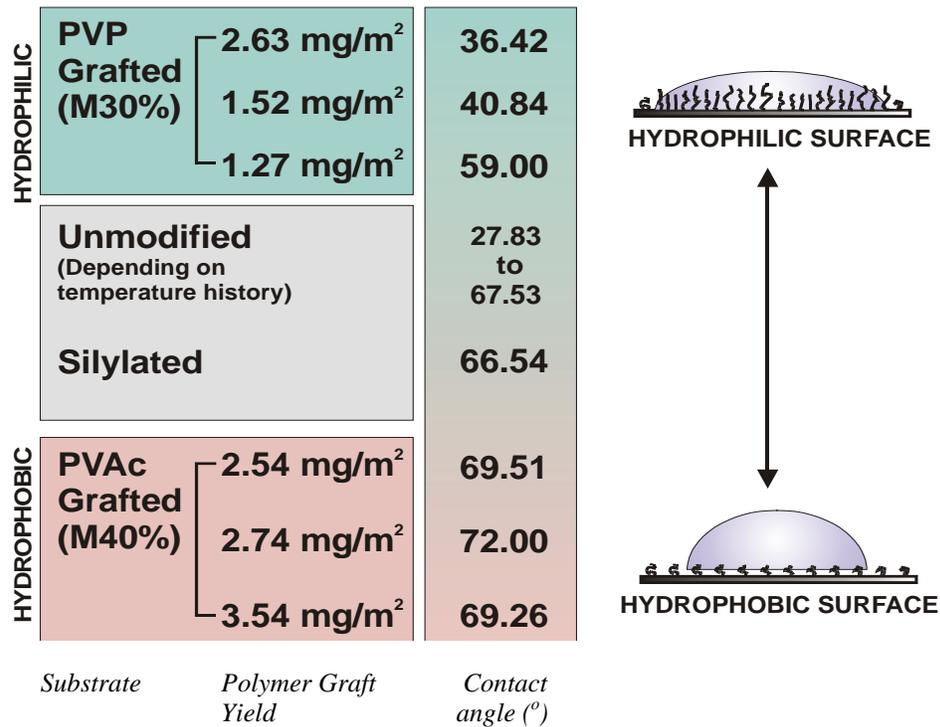


Figure 7.2. Contact angles for PVP and PVAc grafted onto a silicon wafer surface. Also shown are contact angles for unmodified and silylated surfaces.

The hydrophilicity of the surface is best illustrated by the free energy of hydration as a function of the contact angle as shown in Fig. 7.3. The results were obtained based on independent contact angle measurements using three different liquids (water, formamide and

diiodomethane). The results demonstrate that the degree of hydrophilicity for the two grafted polymer surfaces (PVAc and PVP) depends on the chain density and length obtained at the different surface preparation conditions (Faibish, 2001). For example, a PVP layer formed at initial monomer concentration of 10% (vinyl pyrrolidone) at 70°C has a similar hydrophilic character as a PVAc layer formed at 40% initial monomer concentration (vinyl acetate) at 60°C. This result clearly demonstrates that both the chemical character of the polymer as well as the surface arrangement of the chains (density and length) are important factors affecting the wettability of the modified surface.

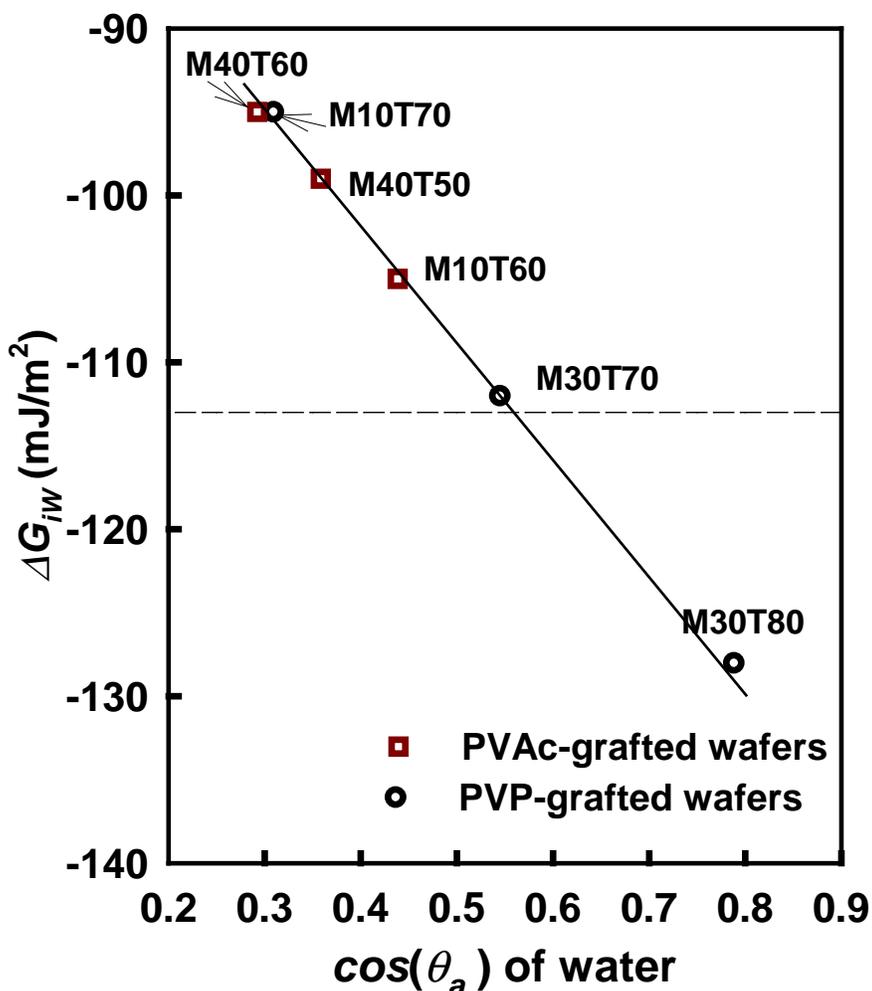


Figure 7.3. Relative hydrophilicity of the PVP- and PVAc-grafted wafers as determined from surface wettability and free energy of hydration (ΔG_{iw}) results. The nomenclature of M#T# denotes initial percent monomer concentration (by volume) by the first number and the reaction temperature in °C indicated by the second number.

7.3 Fouling-Resistant UF Membranes

Fouling resistant ultrafiltration (UF) ceramic-supported polymer (CSP) ultrafiltration membrane was developed for the treatment of oil-in-water (o/w) microemulsions. The CSP membrane was prepared by free-radical graft polymerization of vinylpyrrolidone onto the surface of a zirconia-based membrane support. The potential use of the UF CSP membranes was demonstrated using a well-characterized synthetic oil-in-water (o/w) microemulsions (water/decane (oil)/sodium octanoate (surfactant)/octanoic acid (co-surfactant)/isobutanol (co-surfactant)) and a commercial cutting oil fluid (Section 4.2). The properties of the modified membranes are shown in Table 7.1.

Table 7.1. Properties of native and PVP-modified zirconia membranes^(a)

Membrane	Permeability [10 ⁻¹⁶ m ²]	\overline{M}_n [kDa] ^(b)	Average brush height, L_c [nm]	Polymer graft yield, G [mg/m ²]	Degree of polymerization N ^(b)	Average chain spacing, D [nm]
Native30	4.70	--	--	--	--	--
Native10	5.60	--	--	--	--	--
CSP30	2.67	10.3	7.9	1.09	92	4.0
CSP10	2.89	4.9	4.4	0.807	44	3.2

^(a) Adapted Faibish and Cohen (2001), Note: The grafted polymer chain average molecular weight (\overline{M}_n), degree of polymerization (N), chain length and density were obtained using the surrogate zirconia particles (see Sec. 2.2); ^(b) $N = \overline{M}_n / (\text{MW of vinyl pyrrolidone monomer})$.

Table 7.2 Hydraulic permeability of the native and CSP membranes

Membrane	Hydraulic Permeability [10 ⁻¹⁶ m ²]	
	Before oil filtration experiment	After oil filtration experiment ^(a)
Native	4.70 ± 0.24	3.47 ± 0.17
CSP30	2.67 ± 0.13	2.60 ± 0.13
CSP10	2.89 ± 0.14	2.89 ± 0.14

^(a) Followed by mild caustic (NaOH solution pH ~11) cleaning. T = 20°C

Ultrafiltration studies revealed that after filtration of the decane-based o/w microemulsions, and despite chemical cleaning, the hydraulic permeability of the native zirconia membrane was irreversibly reduced by about 26% (Table 7.2). The permeability reduction was attributed to irreversible adsorption of octanoate onto the zirconia surface, which is expected at the high ionic strength in the present study (>0.3 M) (Faibish and Cohen, 2001a). Adsorption experiments revealed significant adsorption of octanoate (4.0 x 10⁻⁴ mol octanoate/g particles or 5.8 mg/m²) onto the surface of surrogate zirconia particles. In contrast, no measurable adsorption of octanoic acid or

isobutanol onto the native zirconia particles was detected. The adsorption of octanoate (anionic surfactant) was linked to possible association of the surfactant's carboxyl functional group with hydroxyls and negatively-charged surface sites, which were screened by high concentration of counterions. In contrast, adsorption studies with zirconia particles, grafted with PVP (which provides effective screening of surface hydroxyls, Section 7.1), did not reveal any detectable adsorption of isobutanol, octanoic acid or sodium octanoate.

It is noted that the native zirconia membrane was also irreversibly fouled (i.e., 17% irreversible decrease in hydraulic permeability) when used to treat a commercial cutting oil/water emulsion for a brief period. In contrast, the PVP-modified zirconia membrane maintained its pre-filtration hydraulic permeability, for the treatment of both the diagnostic microemulsion and the commercial cutting oil/water emulsion, even after many filtration runs.

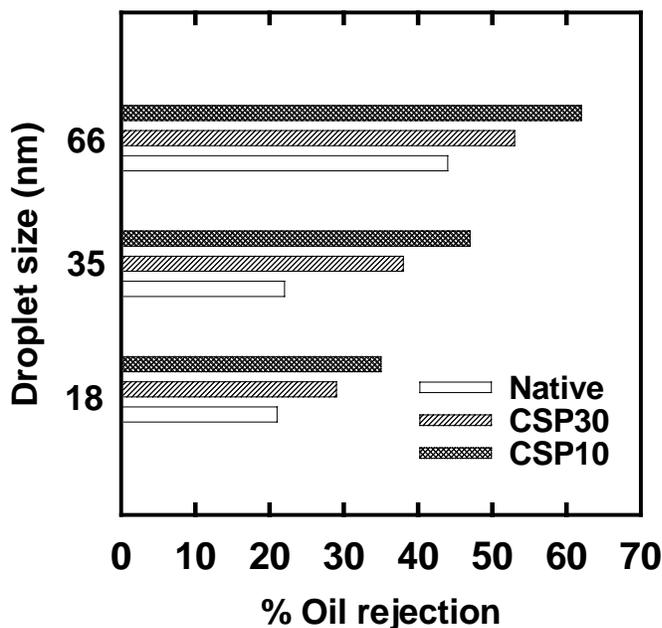


Figure 7.4. Comparison of oil rejection for native, CSP30, and CSP10 membranes for three different microemulsion droplet sizes. $\Delta P_m = 68.9$ kPa; $\overline{NRe} = 571$, average permeate flux for the native, CSP30, and CSP10 membranes = 1.10×10^{-6} , 8.85×10^{-7} , and 8.47×10^{-7} m/s, respectively. Average feed oil concentration, $C_{oil} = 3.43 \times 10^4$ ppm.

Relative to the native membrane, oil rejection of the CSP membrane (Fig. 7.4), for the diagnostic microemulsion, increased more than 2-fold for the range of studied oil droplet size (18 – 66 nm). This behavior was, in part, due a decrease in the average membrane pore size upon grafting, as suggested by the reduction in membrane hydraulic permeability. The slightly greater effective pore size reduction for the CSP10 can be understood by noting that the clean Native10 membrane had a higher hydraulic permeability than the Native30 membrane prior to modification. Given that both membranes (CSP10 and CSP30) had a zirconia layer of essentially the same thickness, higher initial hydraulic

permeability of the Native10 membrane may indicate the presence of larger pores compared to the Native30 membrane. Larger pores can facilitate greater penetration of the reacting species during free-radical polymerization into the zirconia layer resulting in increased grafting inside

the membrane pores (i.e., a thicker grafted polymer layer). It is also possible that “pin holes” in the membrane were repaired as a result of the graft polymerization process

Improvement in oil rejection was noticeable for the treatment of the commercial cutting oil emulsion as shown in Figure 7.5. Oil rejection for this cutting oil/water emulsion with droplets size of 98 – 105 nm) was higher than for the diagnostic microemulsion with micelle size

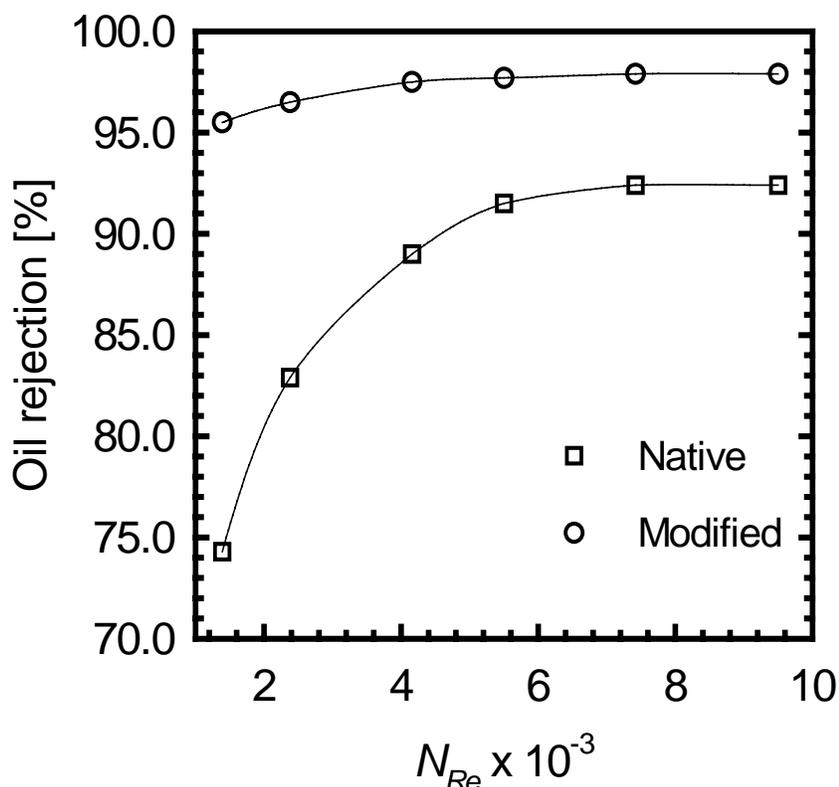


Figure 7.5. Effect of Reynolds number on rejection of cutting oil emulsion droplets. Experimental conditions: $T = 20^{\circ}\text{C}$; $\Delta P = 68.9 \text{ kPa}$; oil concentration = 3000 mg/L.

of 18 ~ 66 nm. Incomplete oil rejection was encountered for both the microemulsion and the cutting oil macroemulsion even when the droplet size was larger than the average membrane pore size. Such a behavior is consistent with previous studies on membrane treatment of oil-in-water emulsions (Hlavacek, 1995; Scott et al., 1994; Lipp et al., 1988). One possible explanation for the incomplete rejection is that coalescence of oil droplets at the surface of the membrane; as the droplet are being concentrated due to concentration polarization, a continuous dispersed phase is formed that can then permeate through the membrane. Incomplete oil rejection can also be attributed to the very low interfacial tension ($\ll 1 \text{ mJ/m}^2$) between the coalesced organic

layer (which is composed mainly of decane and the dissolved co-surfactant isobutanol), at the surface of the membrane, and the solution continuous phase (i.e., water or water and surfactant).

Rejections of the main anionic surfactant (sodium octanoate) and the non-ionic co-surfactant (isobutanol) components of the diagnostic microemulsion, for both the CSP and the native membranes, were typically lower than for oil (i.e., decane) rejection as shown in the illustration in Table 7.3. This behavior suggests that, for both the modified and native zirconia membranes, it is possible to recycle a significant portion of the detergents (i.e., surfactant species) and thus reduce the total volume and cost of the treatment process. Rejection of the co-surfactant octanoic acid, on the other hand, was lower, and essentially at the same oil rejection level. This result is not surprising since the octanoic acid molecules are expected to be present mainly in the dispersed hydrophobic oil phase; therefore, very similar rejection values to that of the oil (i.e., decane) were obtained for the octanoic acid. Clearly, such a performance could be desirable in applications in which spent detergent cleaning solutions containing various amphiphilic species (e.g., various surfactants) are to be recycled, as for example, in cleaning of various oil-contaminated materials (e.g., machine parts and finished products in the metal fabrication, automotive, and railroad industries).

Table 7.3. Typical rejection values (%) of the various microemulsion components. $\Delta P_m = 68.9$ kPa; $T = 20^\circ\text{C}$; laminar flow conditions ($\bar{N}_{Re} = 453$).

membrane	decane	sodium octanoate	octanoic acid	isobutanol
Native	20	14	22	20
CSP30	44	20	45	26

Finally, it is noted that although the water contact angle for the grafted surfaces decreased (i.e., the polymer-modified wafers became more hydrophilic and water wetting) with increasing polymer graft yield (Table 7.4), the fouling-resistant character of the CSP10 and CSP30 membranes was unchanged. Presumably, in both cases there was sufficient screening of the surface hydroxyl groups. Rejection for the CSP10 membrane, however, was greater due to the longer grafted PVP chains.

Table 7.4. Water contact angle measurements on grafted silicon wafers.

Grafting conditions	Contact angle ($^\circ$)	Average chain spacing, D [nm]	\bar{M}_n [kDa]	Graft yield, G [mg/m^2]
CSP10	72	3.0	7.0	1.25
CSP30	57	3.8	13.6	1.56

8. SUMMARY

A technology of tailor-designing selective ceramic-supported polymer (CSP) membranes was developed. The approach is based on surface modification of porous ceramic support substrates possessing surface hydroxyls. The technology was demonstrated for the synthesis of pervaporation CSP membranes. Pervaporation studies showed that the CSP membranes could be designed to achieve separation levels that are of commercial viability. The surface modification method was also used to develop a class of fouling-resistant ultrafiltration membranes. The utility of such membranes was demonstrated for the treatment of oil-in-water emulsions.

9. RELEVANCE, IMPACT, and TECHNOLOGY TRANSFER

Pervaporation has finally come of age (Wynn, 2001) and holds a great potential for replacing or augmenting certain distillations processes thereby reducing energy costs while at the same time aiding in reducing fugitive emissions. Pervaporation processes can also be used in conjunction with some reactor configurations to increase product yield and selectivity. The present technology is now in a sufficiently progressive state to enable the tailor-design of ceramic-supported polymer membranes for a variety of pervaporation tasks. The present CSP membrane technology has also proved suitable for creating fouling-resistant filtration membranes. However, large-scale deployment of CSP membranes will require optimization of the membrane preparation process to multi-channel (monolithic) membrane module and/or a module containing an array of single tubular membranes.

The present study is the first to provide a detailed characterization of polymer-modified inorganic surfaces with respect to the density and chain size distribution. The study also resulted in fundamental reaction models for graft polymerization and surface silylation that allow one to formulate, a priori, the desired modification conditions required to achieve a targeted level of polymer graft yield and surface chain density surface.

10. PROJECT PRODUCTIVITY AND PERSONNEL SUPPORTED

A total of five graduate students were supported in whole or to a significant degree by the present research project. Three Ph.D. students (Robert Castro, Jeng-Dung Jou and Ron S. Faibish) have contributed to the project with one additional Ph.D. student (Wyane H. Yoshida) whose research work is in progress. Two M.S. students were also involved in the project (Niangjiong Bei, Ron S. Faibish and Hiroyoshi Ohya) and three undergraduate students. Robert Castro received the 1997 Outstanding Paper award from the AIChE Separations Division for the UF/CSP membrane development work (Castro et al., *J. Membrane Sci.*, 115, 179-190, 1996). Ron Faibish received a Presentation Award from the North American Membrane Society (NAMS) at the 2000 Annual Meeting of NAMS, for his work on Fouling-Resistant Membranes. Wayne Yoshida received the 1999 First Place Poster Presentation Award from the Southern California Society for Risk Analysis for his work on pervaporation removal of toxic solvents. In addition, a U.S. Patent is pending (with the major claims already approved) for a ceramic-supported polymer pervaporation membrane. The project resulted in the publication of 12 journal articles and book chapters and 29 conference presentations and invited seminars. Highlights of some of the research accomplishments were published in the DOE *Initiatives in Environmental Technology Investment* newsletter (Volume 6, Winter 1999; <http://www.wpi.org/initiatives>).

11. PUBLICATIONS

11.1 Papers and Book Chapters:

1. Nguyen, V., H. W. Yoshida, J-D. Jou and Y. Cohen, "Kinetics of Free-Radical Graft Polymerization of 1-vinyl-2-pyrrolidone onto Silica," *Journal of Polymer Science Part A: Polymer Chemistry*, Volume 40, Number 1, 26-42 (2001).
2. Cohen, Y., J-D, Jou, H. W. Yoshida and N. Bei, "Surface Modification of Oxide Surfaces by Graft Polymerization," in "Oxide Surfaces", J. A. Wingrave (Editor), Marcel Dekker, New York, 2001.
3. Yoshida, H. W., Castro, R. P., Jou, J-D. and Cohen, Y., "Multilayer alkoxy silane silylation of oxide surfaces," *Langmuir*, 17, 5882-5888 (2001).
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12. Josep, Font, R. P. Castro and Y. Cohen, "A Note on the Loss of Hydraulic Permeability in Ceramic Membranes, " *J. Colloid Interface Sci.*, 181, 347-350 (1996).

11.2 Conference and Invited Presentations

1. Cohen, Y., R. P. Castro, J-D Jou and H. G. Monbouquette, "Ceramic-Supported Polymer Membranes for Ultrafiltration," AICHE Annual Meeting, November 10-15, 1996, Chicago, IL.
2. Cohen, Y., R. S. Faibish and M. Elimelech, "Flux Decline in Cross-Flow Filtration of Colloidal Silica", North America Membrane Society, Annual Meeting, Baltimore, Maryland, March 1997.
3. Cohen, Y., "Graft Polymerized Ceramic Membranes", Gordon Research Conference on Membrane: Materials and Synthesis, New Hampshire, July 1997.

4. Cohen, Y., invited seminar, "Polymer Surfaces and Separation Processes, California Institute of Technology, Department of Chemical Engineering, March, 1997.
5. Faibish, R. S. and Y. Cohen, "Particle-Particle Interactions and Cake Formation in Cross-Flow Filtration of Colloidal Particles", Gordon Research Conference on Membrane: Materials and Synthesis, New Hampshire, July, 1997.
6. Yoshida, H. W., Y. Cohen and Jeng-Deng J., "Graft Polymerization and Application to ceramic Supported Polymer Pervaporation membranes for VOC Removal", AIChE Annual Meeting, Miami Beach, FL, November 15-20, 1998.
7. Rovira, M., F. Giralt and Y. Cohen, "Protein Fouling Reduction on ceramic Membranes via Graft Polymerization", AIChE Annual Meeting, Miami Beach, FL, November 15-20, 1998.
8. Cohen, Y. and J-D. Jou, "Ceramic-Supported Polymer Pervaporation Membranes for VOC Removal," 10th Annual Meeting of the North American Membrane Society, May 19-20, 1998, Cleveland, OH.
9. Cohen, Y., H. W. Yoshida and J-D, Jou, "CSP Membranes", invited poster presentation, DOE First Annual Environmental Management Science Program Scientific (EMSP) Workshop, Rosemont, IL, July 27-30, 1998.
10. Cohen, Y., National Institute of Standards and Technology, invited seminar, "Polymer Surfaces in Separation Processes", Gaithersburg, Maryland, May 15, 1998.
11. Cohen, Y., NSF/EPRI, Advanced Polymer Initiative Workshop, *invited presentation*, "Ceramic-Supported Polymer Membranes," April 15, 1998, Arlington, VA.
12. Cohen, Y., invited seminar, United States Environmental Protection Agency, National Risk Management Research Laboratory "Polymer Surfaces and Separation Processes", July, 1998, Cincinnati, OH.
13. Faibish, R. and Y. Cohen, Crossflow Ultrafiltration of Oil-in-Water Microemulsions with Polymer-Modified Ceramic Membranes, 1999 AIChE Annual Meeting, October 31-November 5, 1999, Dallas, TX
14. Cohen, Y., DOE, Environmental Molecular Surface Laboratory (EMSL), invited seminar, "Polymer Surfaces for Selective Separations", February 9, 1999.
15. Yoshida, H. W., J-D Jou, Y. Liang (EMSL) and Y. Cohen, Graft Polymerized Poly (vinyl acetate) and Poly(vinylpyrrolidone) Layers on Inorganic Substrates for Membrane Separations, 1999 AIChE Annual Meeting, October 31-November 5, 1999, Dallas, TX.

16. Yoshida, H. W. and Y. Cohen, "Characterization of Ceramic-Supported Polymer (CSP) Pervaporation Membranes using Atomic Force Microscopy", Poster Presentation at the EMSL Workshop, William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), Richland, Washington, July 19-24 (1999).
17. Cohen, Y., invited presentation, Polymer at Solid Surfaces for Novel Membranes, invited presentation, Chemistry For a Cleaner Environment (January 29-February 2, 2000), Santa Fe New Mexico.
18. Cohen, Y., Gordon Research Conference, "Surface Engineering for Membrane Synthesis", invited lecture, 2000 Gordon Research Conference on Membrane Materials and Processes, July 29-August 3, 2000, New London, Connecticut.
19. Faibish, R. S. and Y. Cohen, Novel Polymer-Modified Ceramic Membrane for the Treatment of Oily Aqueous Waste, Poster Presentation, North American Membrane Society (NAMS) Annual Meeting, Boulder, CO, USA, May 2000.
20. Cohen, Y., invited seminar, Michigan State University, "Surface Engineering of Membranes for Pollution Prevention", November 8, 2000.
21. Yoshida, H. W. and Y. Cohen, Characterization of Polymer-Modified Ceramic Membranes, American Membrane Society (NAMS) Annual Meeting, Boulder, CO, USA, May 2000.
22. Faibish, R. S. and Y. Cohen, Novel Polymer-Modified Ceramic (PMC) Membranes for the Filtration of Stable Oil-in-Water (O/W) Microemulsions, Poster Presentation, 74th Colloid and Surface Science Symposium, Lehigh University, Bethlehem, PA, USA, June 2000.
23. Faibish, R. S. and Y. Cohen, Fouling-Resistant Polymer-Modified Ceramic Membranes for Ultrafiltration of Oil-In-Water Microemulsions, Poster Presentation, Euromembrane 2000, September 2000, Israel.
24. Nguyen, N. V. and Y. Cohen, "Kinetics of Graft Polymerization of Vinylpyrrolidone onto Vinyl Silane-Modified Silica Surface," AIChE Annual Meeting, November 11-17, 2000, Los Angeles, CA.
25. Yoshida, H. W. and Y. Cohen, "Characterization of Graft Polymerized Layers on Inorganic Substrates," AIChE Annual Meeting, November 11-17, 2000, Los Angeles, CA.
26. Yoshida, H. W. and Y. Cohen, "Pervaporation Removal of MTBE from Aqueous Solutions Using Ceramic Supported Polymer (CSP) Pervaporation Membranes", AIChE Annual Meeting, November 11-17, 2000, Los Angeles, CA.

27. Faibish, R. S., H. W. Yoshida and Y. Cohen, Topology and Wetting Characteristics of Terminally Grafted Polymer Chains on Ceramic Surfaces," AIChE Annual Meeting, November 11-17, 2000, Los Angeles, CA.
28. Faibish, R. S. and Y. Cohen, Fouling-Resistant Polymer-Modified Ceramic Membranes for Ultrafiltration of Oil-In-Water Microemulsions, AIChE Annual Meeting, November 11-17, 2000, Los Angeles, CA.
29. Cohen, Y. and H. W. Yoshida, "Ceramic-Supported Polymer Membranes for Separation of Organics", Poster Presentation, DOE, Environmental Management Science Program (EMSP), April 24-28, Atlanta, Georgia.

11.3 Student Awards

1. Faibish, R. S. and Cohen, Y., Student Paper Award: "Novel Polymer-Modified Ceramic Membrane for the Treatment of Oily Aqueous Waste", North American Membrane Society (NAMS) Annual Meeting, Boulder, CO, USA, May 2000.
2. Yoshida, Y. and Y. Cohen, 2nd Place Student Poster Award: Separations and Recovery of Organics using Novel Polymer Grafted Ceramic Membranes", Southern California Society for Risk Assessment (SCSRA), 2000 Annual Meeting, May 18, 2000, Los Angeles, California.
3. Doherty, S., R. Faibish and Y. Cohen, 3rd Place Student Poster Award, "Surface Characterization of Polymer-Modified Ceramics by Contact Angle Measurements", AIChE Western Regional Student Conference, Los Angeles, 2000
4. Faibish, R. was a Finalist in the competition for the Zenon Membrane Technology Prize, Zenon Environmental Inc., Canada, 2000.

11.4 Student Theses

1. Faibish, R. S., *Fouling-Resistant Polymer-Modified Ceramic Membranes*, Ph.D. Dissertation, University of California, Los Angeles (2001).
2. Jou, Jeng-Dung, *Graft Polymerization and Application to Membrane Pervaporation*, Ph.D. Dissertation, University of California, Los Angeles (1998).
3. Castro, R. P., *Development of Ceramic-Supported Polymeric Membrane for Filtration of Oil Emulsions*, Ph.D. Dissertation, University of California, Los Angeles (1997).

4. Faibish, R. S., *Effect of Interparticle Interactions on Permeate Flux Decline in Membrane Crossflow Filtration of Colloidal Suspensions*, M.S. Thesis, Chemical Engineering Department, University of California, Los Angeles, California (1997).
5. Bei, Nianjiong, *Graft Polymerization of Polyvinyl Acetate: Surface Morphology and Reaction Mechanism*, M.S. Thesis, Chemical Engineering Department, University of California, Los Angeles, California (1997).
6. Ohya, Hiroyoshi, *PVAc Grafted Silica Pervaporation Membrane*, Chemical Engineering Department, University of California, Los Angeles, California (1999).

13. INTERACTIONS

Results of the project, at its various stages, were presented in a total of 24 scientific meetings, workshops and invited seminars (Section 11.2). The PI was invited to give a presentation on ceramic membrane modification at a meeting organized by the Los Alamos National Laboratory Environment (January 29-February 2, 2000, 2000). The PI also gave an invited seminar at the DOE Environmental Molecular Surface Laboratory (February 9, 1999) and participated in two three EMSP workshops as well as serve as a reviewer for the EMSP program. During the month of February 1998 one of the PI's Ph.D. students, Wayne Yoshida, was a visiting researcher at the DOE EMSL facility. During the above period he conducted a detailed AFM characterization of grafted surfaces in collaboration with Dr. Liang Young of the EMSL laboratory. Finally, it is worth noting that as a result of the rich experience gained in the present work, the PI's research program in the area of membranes has expanded to include reverse osmosis. Finally, as a result of the growth of the research program the PI has taken a lead role in the membrane community by organizing the 2002 Annual Meeting of the North American Membrane Society.

13. PATENTS

A patent application was submitted for the invention of a ceramic-supported polymer membrane (Application/Control Number: 09/573,599; Filing Date: 05/17/2000). The major claims have been approved and the final patent assignment is pending. A brief description of the patent is provided below.

Patent Abstract: A ceramic-supported polymer membrane is disclosed where a porous ceramic membrane support of average pore size no larger than 500 Å is activated by attaching a vinyl terminated lower alkoxy silane to the surface of the ceramic membrane pores. The resulting membrane retains at least 10 micromoles of the vinyl terminated loweralkoxy silane per square meter of the ceramic membrane surface. A method for optimizing the amount of vinyl loweralkoxy silane reacted with the ceramic support surface is also disclosed. The large amount of vinyl terminated loweralkoxy silane which is chemically bonded to the surface of the ceramic porous support produces activated ceramic membrane support surface which is useful for graft polymerization of vinyl monomers onto the porous ceramic membrane support surface. A vinyl monomer is then graft polymerized onto the activated membrane. The resulting ceramic-supported polymer membrane is useful for pervaporation separation of liquids mixtures that are sufficiently different in their vapor pressure.

The invention broadly relates to three areas:

- (1) A method for producing ceramic membranes that are surface activated with vinyl lower alkoxy silane, the amount of vinyl lower alkoxy silane on the surface of the said ceramic membrane support greatly exceeding that is known in the art.
- (2) A pervaporation membrane comprising of said surface activated ceramic membrane support that have graft polymerized on the surface vinyl polymer, the amount of the vinyl polymer greatly exceeding that which is known in the art.
- (3) A method of making said ceramic-supported polymer pervaporation membrane. The ceramic-supported polymer membrane is very useful for pervaporation separation of volatile liquids from both organic-aqueous and organic-organic liquid solutions

14. FUTURE WORK

Current efforts are focused on developing a graft polymerization method to create a higher density polymer surface separation layer. The methods under investigation include plasma graft polymerization and “living” free radical graft polymerization. The application of the present membrane technology to organic-organic pervaporation separation is also being considered. The present technology of producing fouling-resistant membranes is ready for technology transfer and industrial collaboration.

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