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Application of Sodium Alginate-Carrageenan Coatings to PTFE Membranes for Protection Against Wet-Out by Surface-Active Agents

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Abstract: A technique has been developed for the application of sodium alginate-carrageenan coatings to PTFE membranes for protection against wet-out when used for the membrane distillation or osmotic distillation of feeds containing surface-active agents. The adhesive strength between the hydrophilic coating and the hydrophobic substrate was increased three-fold using an interfacial-bonding agent, myristyltrimethylammonium bromide. The coating afforded protection against wet-out by sodium dodecylbenzene sulfonate, which is a widely used industrial detergent, and orange oil. It was also found to reduce membrane fouling by the fat globules present in whole milk. The coating technique described in this work may provide the basis for the development of a simple in situ membrane modification method for use with existing commercially available modules.

Keywords: Membrane coating, PTFE membrane, Interfacial bonding, Osmotic distillation, Membrane distillation, Surface-active agents

INTRODUCTION

The successful application of membrane distillation (MD) and osmotic distillation (OD) to the dewatering of aqueous feeds depends on the

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maintenance of membrane hydrophobicity. In both processes water is removed as the vapor by diffusion through the air-filled membrane pores. However, a loss of hydrophobicity allows liquid water and solutes to pass freely through the membrane. This reduces the capacity of the process to form a concentrated product and, in the case of OD, allows the feed to become contaminated by the osmotic agent (inorganic salt) present in the strip solution (1).

Membrane wet-out occurs when surface-active components present in the feed reduce the liquid surface tension, γ_l, and the solid (membrane)-liquid contact angle, θ, sufficiently for the critical liquid entry pressure, ΔP, to fall to the level of the operating pressure in accordance with the Laplace equation (Eq. 1) (2).

$$\Delta P = \frac{-2B\gamma_l \cos\theta}{r_{\max}} \tag{1}$$

where $r_{\max}$ is the maximum value of the membrane pore radius distribution and B is the pore geometry factor (unity for cylindrical shape).

Membrane wet-out is usually not instantaneous. Rather, there is a progressive decrease in the contact angle as the increasing concentration of adsorbed surface-active material decreases the membrane-liquid interfacial tension, γ_{sl}, in accordance with the Young equation (2) (Eq. 2).

$$\gamma_l \cos\theta = \gamma_s - \gamma_{sl} \tag{2}$$

Applications of MD and OD have thus far been limited to the concentration of non-wetting feeds. However, there are several feed materials containing surface-active components that cannot be concentrated to the desired level by conventional processes without product damage or an unacceptable loss of solutes. The present work involved the modification of a PTFE membrane for use in the MD or OD of the latter feed materials.

An application of interest is the production of citrus juice concentrates, in particular that of orange juice extracted from fruit with a high peel-oil content. Orange juice concentrate is typically produced by thermal evaporation. However, the concentration of the product is limited to 59–63° Brix because of the rapid increase in viscosity above this concentration. Adherence of the viscous juice to evaporator heat transfer surfaces results in thermal degradation or "burn-on" of the product (3). MD and OD are not limited by this phenomenon and therefore have the potential to achieve higher product concentrations. Also, the ambient temperature operation of OD would be expected to reduce the loss of volatile organic flavor/fragrance components associated with thermal evaporation. However, the monoterpene limonene, which is the major constituent of orange oil (4), has a high affinity for hydrophobic membranes and leads to rapid wet-out even in relatively low concentration (5).

Another potential food industry application for OD is the concentration of whole milk. Initial concentration by OD prior to spray-drying in powdered-milk production would be expected to yield a superior product. However, the presence of relatively large hydrophobic fat globules (4–10 μm (6)) in whole milk may be expected to cause severe membrane fouling and possible wet-out of an unprotected membrane.

A potentially important application for MD/OD is the concentration of detergent-containing solutions for economic packaging and long-term storage after use in the decontamination of nuclear power plant facilities (7). Most radioactive contaminants are located in the primary cooling circuit as oxide deposits or sludge. These are removed using large volumes of detergent solutions that, together with contaminated cooling circuit water, are concentrated using a combination of several processes. There include distillation, ultrafiltration, reverse osmosis, electrodialysis and ion exchange. However, each of these processes is either restricted in the types of radionuclides that can be removed or facilitates some loss of radionuclides to the environment. MD has been successfully applied to the concentration of radioactive, non-detergent liquid wastes, with high retention and decontamination factors being obtained (8–10). However, the potential loss of radionuclides to the strip stream following membrane wet-out has precluded the use of MD/OD for the concentration of detergent-containing solutions.

Work undertaken in our laboratory on the preparation, structural characterization, optimization of crosslinking conditions, and durability against water of blended sodium alginate-carrageenan films has been reported previously (11). The crosslinking agent used was 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, or WSC. It was found that sodium alginate and carrageenan were totally miscible at 20 wt% carrageenan content and that this blend had lower crystallinity, and hence greater flexibility, and higher water absorption capacity than nascent sodium alginate hydrogel films. Films produced using these optimum parameters retained their integrity over a 29-day water-durability trial. It was suggested that these properties of the blend film could be expected to provide better water transfer characteristics and higher resistance to the transfer of other components such as surface-active agents than other hydrophilic materials such as poly(vinylalcohol) (PVA) when used as a pervaporation membrane or as a coating for MD/OD membranes.

The present work was undertaken to develop a technique for coating PTFE membranes with a sodium alginate-carrageenan blend film, labeled ALCG20 to signify 20 wt% carrageenan, and to test the coated membrane for OD performance and resistance to wet-out by surface-active agents. A cationic surfactant, myristyltrimethylammonium bromide (MTMA), was used as an interfacial-bonding agent in an attempt to increase the inherently low adhesion strength of the hydrophilic coating to the hydrophobic substrate. MTMA has a 14-hydrocarbon chain and a positively charged quaternary amine head. The hydrocarbon chain was expected to attach itself to the PTFE membrane, with the amine group being electrostatically attracted to alginate carboxylate and carrageenan sulfate groups (12, 13).

Previous work on the coating of hydrophobic membranes for protection against wet-out in OD applications involved etching of the polypropylene substrate with chromic acid to facilitate interfacial chemical bonding with the glutaraldehyde-crosslinked PVA coating (5). The physical interfacial bonding technique using MTMA was developed to avoid harsh chemical treatment and thereby facilitate future in situ coating of membranes in existing membrane modules. Also, unlike glutaraldehyde, WSC facilitates crosslinking without itself remaining part of the coating structure. This negates the potential for product contamination by crosslinking-agent release during coating degradation. The coated membranes were tested for their OD performance and resistance to wet-out using orange oil, sodium dodecylbenzene sulfonate (DBS) detergent, and full-cream milk.

EXPERIMENTAL PART

Materials

Sodium alginate (Manugel GMB) and carrageenan (Caragem AP, k type, mixed potassium and calcium salts) were donated by Germantown International Limited (Sydney, Australia). WSC (AR grade), DBS (AR grade), and MTMA (99% purity) were purchased from Sigma-Aldrich (Sydney, Australia). Ethanol (spectrophotometric grade) was purchased from Aldrich Chemical Co. (Sydney, Australia). Hydrochloric acid (32% content, AR grade) and calcium chloride dihydrate (AR grade) were purchased from BDH Chemicals (Melbourne, Australia). Potassium hydroxide (AR grade) was purchased from AJAX Chemicals (Sydney, Australia). Desal PTFE membranes (type KSK 150) with a nominal pore diameter of 0.1 μm were purchased from Desalination Systems Inc. (Vista, California). Pure orange oil (100% limonene) was purchased from Perfect Potion (Brisbane, Australia). Fresh full-cream milk was purchased locally. All chemicals were used without further purification.

Membrane Coating

The mixed polymer powder (0.45 g) was initially dispersed in ethanol (3.0 mL) in order to avoid lumping during solution preparation. Water (27 mL) was then added to the dispersion and the mixture heated at 60 ± 5°C with constant stirring until dissolution was complete (approximately 30 min). The resulting solution contained 1.5 wt% ALCG20 and 10 vol.% ethanol.

A small quantity (0.25 mL) of solution containing 0.2, 0.4, 0.6, or 0.8 wt% MTMA was spread evenly over the surface of a piece of PTFE membrane (4.5 cm × 4.5 cm) with the aid of a spatula. ALCG20 solution (1.5 or

3.0 mL) was then immediately cast evenly over the treated surface using a similar technique. The coated membrane was then allowed to dry in air for 24 h. Polysaccharide cross-linking was then carried out by immersing the membrane in a solution containing 60 vol% ethanol and 120 mM WSC at pH 4 (adjusted with hydrochloric acid). The cross-linking reaction was allowed to continue for 24 h at 24 ± 2°C. For comparison purposes, a coated membrane was prepared by the same procedure but without MTMA treatment.

Coating Characterization

Scanning electron microscopy (SEM)

Membrane surface and cross-sectional images were obtained using a FEI Quanta 200 environmental scanning electron microscope. Samples were gold-coated and examined in the high-vacuum mode.

Infrared Spectroscopy

Infrared spectra were recorded in the attenuated total reflectance mode using a Nexus 870 Fourier transform spectrophotometer. The spectra were used to monitor the nature of the membrane surface at each stage of the coating process.

Coating Adhesion Strength

The T-peel strength of membranes coated with and without the use of MTMA as a binding agent was determined using a Hounsfield Tensometer with a 500 N load cell in accordance with ASTM D1876-93.

Osmotic Distillation

The configuration of the experimental apparatus used for OD flux measurement is shown in Fig. 1. The membrane (surface area 10.2 cm^2) was held between identical feed and strip solution chambers (80 cm^3) of a stirred cell placed on a multiposition magnetic stirrer. A stirring rate of 300 rpm was used in all experiments. A pure water reservoir placed on a top-pan balance was connected to the feed chamber by flexible silicone tubing. This facilitated the maintenance of a constant feed composition and allowed the water flux to be monitored by observation of the weight loss from the reservoir. The precision of the balance was

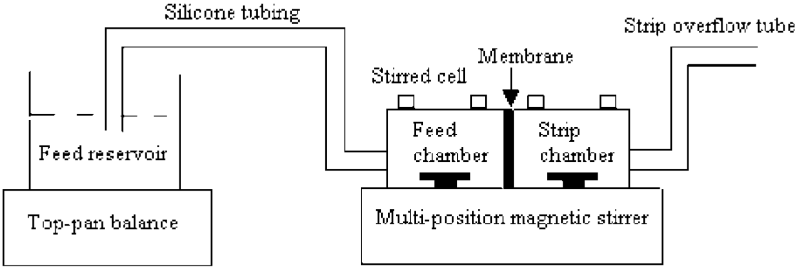

Figure 1. Apparatus used for OD flux measurements.

±0.01 g. The correction for the weight loss due to normal evaporation was determined using the weight loss from an identical water reservoir placed adjacent to the apparatus. The process was allowed to equilibrate for 20 min prior to the commencement of flux measurements. Flux measurements were made every 10 min for 360 min. Floating averages based on the weight lost during the preceding 20 min and the following 10 min were used for flux calculations in order to reduce the effect of the scatter that resulted from noise due to the use of a small membrane area and short measurement interval. OD feeds used were deionized water, 0.1, 0.3, and 0.5 wt% aqueous DBS solutions, 0.2, 0.4, and 0.8 wt% orange oil-water mixtures, and fresh full-cream milk. The strip solution used was 40 wt% $CaCl_2$. All flux measurements were carried out at 23 ± 1°C.

Durability Testing

Testing for durability against wet-out was conducted using a 0.5 wt% DBS aqueous solution and a 1.2 wt% orange oil-water mixture. The same stirred cell and conditions that were used for the flux trials were used, with the exception that the strip solution was absent. The appearance of membrane transparency was taken to be indicative of wet-out.

RESULTS AND DISCUSSION

SEM Images

SEM images of the surfaces of an uncoated membrane and a membrane coated using 0.2 wt% MTMA solution and 1.5 mL ALCG20 solution are shown in Fig. 2. The smooth coating completely covered the otherwise highly porous surface. SEM images of the cross-sectional structures of membranes coated

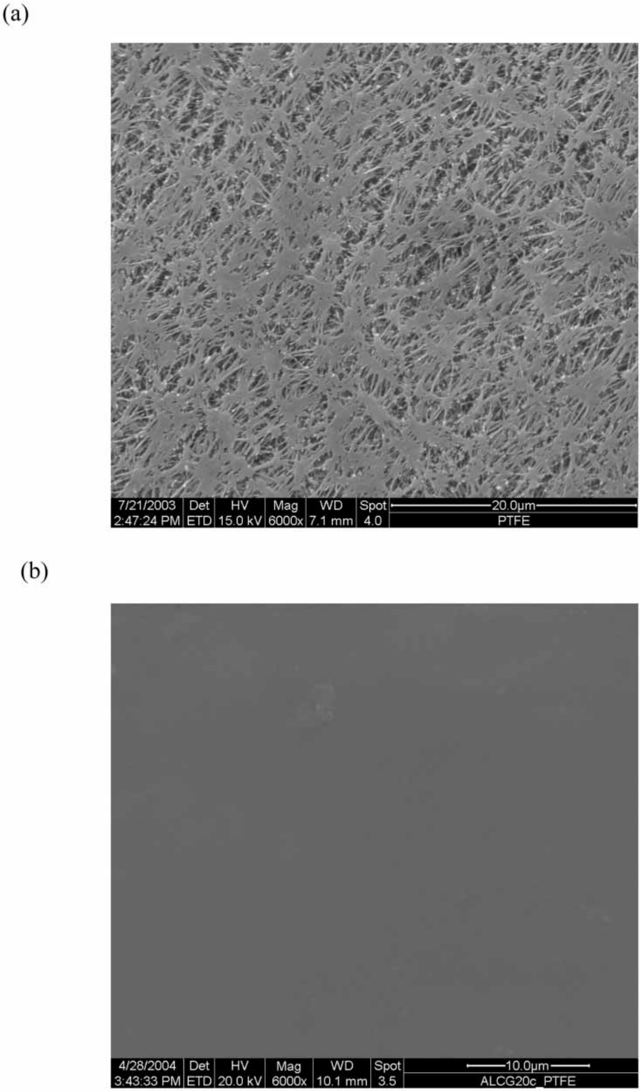

Figure 2. SEM images of (a) an uncoated membrane and (b) a membrane coated using 0.2 wt% MTMA solution and 1.5 mL ALCG20 solution (cross-linked).

using 1.5 mL ALCG20, with and without MTMA treatment, are shown in Fig. 3. The coating cast after MTMA treatment showed close contact with the PTFE structure. In contrast, the coating cast without MTMA treatment appeared as a loose laminate. The better contact in the former case was attributed to lowering of the membrane-liquid interfacial tension by MTMA.

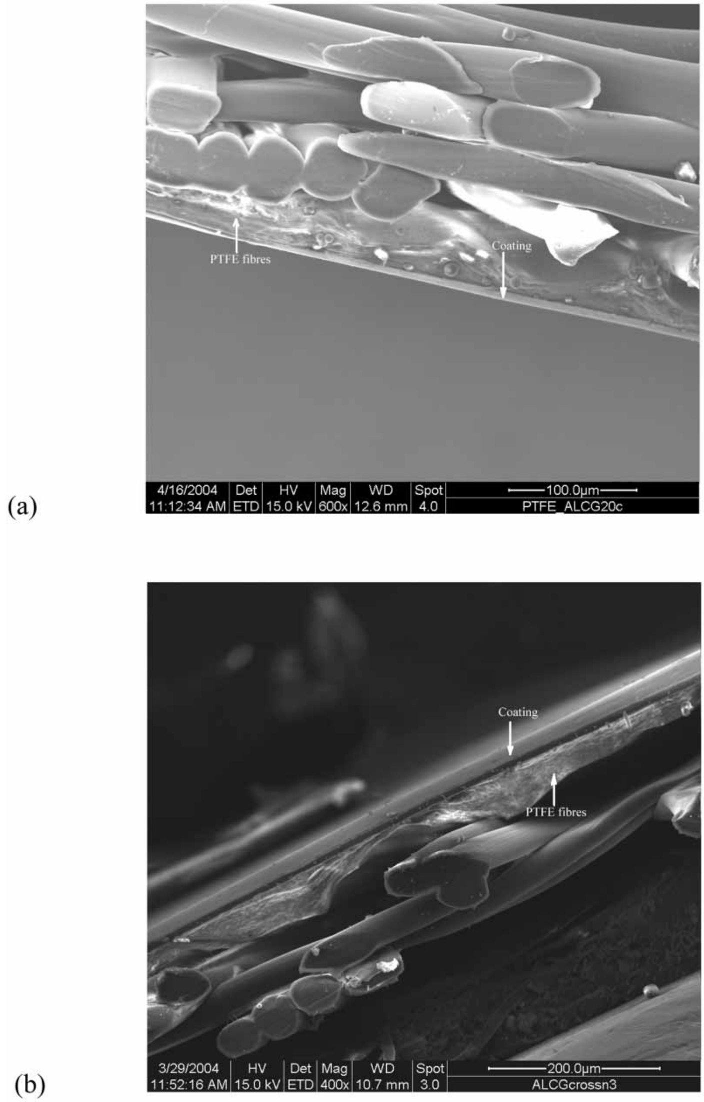

Figure 3. SEM images of the cross-sectional structures of coated membranes (cross-linked) (a) with MTMA treatment and (b) without MTMA treatment.

The thickness of the coating obtained with MTMA treatment was considerably less (8–10 μm) than that obtained without MTMA treatment (16–20 μm). The increased thickness in the latter case was attributed to beading of the coating solution with resulting incomplete coverage of the untreated membrane surface.

Infrared Spectra

Infrared spectra of a virgin PTFE membrane, an uncoated PTFE membrane treated with 0.6 wt% MTMA solution and dried in a desiccator, and non-cross-linked and cross-linked coated membranes prepared using 0.6 wt% MTMA and 1.5 mL of ALCG20 solution are shown in Fig. 4. The spectra of the uncoated membranes showed two groups of PTFE bands, at 1100–1250 and 500–650 cm^{-1}. The strong band at 1203 cm^{-1} was assigned to a CF_2 stretching mode while that at 1149 cm^{-1} was assigned to both CF_2 and CC stretching modes. The weaker bands at 638 and 554 cm^{-1} were assigned to CF_2 rocking modes (14). The very weak bands at 2919 and 2838 cm^{-1} in the spectrum of the uncoated membrane treated with MTMA have been assigned to C-H stretching modes of MTMA (15).

The PTFE and MTMA bands were not visible in the spectra of the coated membranes, confirming complete coverage of the surface by ALCG20. The spectra of both coated membranes showed bands due to alginate carboxylate C-O stretching modes at 1595 and 1410 cm^{-1} (16), and a carrageenan sulfate S-O stretching mode at 1256 cm^{-1} (17). The spectrum of the cross-linked ALCG20 coating contained a shoulder on the 1595 cm^{-1} band that corresponded to the characteristic C-O stretching mode band of a cross-linking ester group at 1698 cm^{-1} (11).

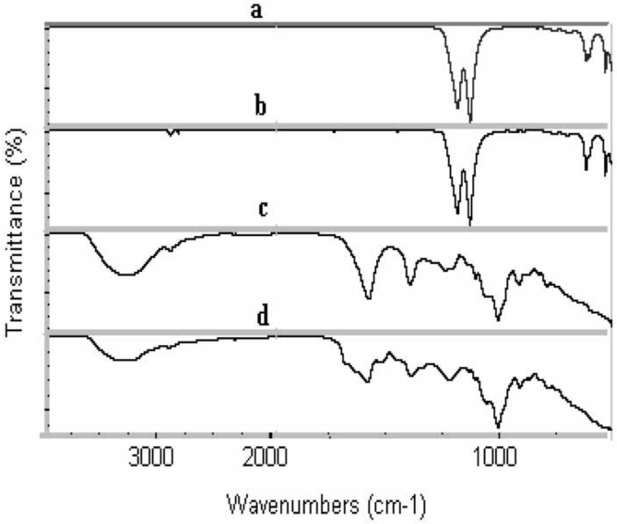

Figure 4. Infrared spectra of (a) a virgin membrane, (b) an uncoated membrane treated with MTMA, (c) a non-cross-linked coated membrane, and (d) a cross-linked coated membrane.

Determination of Optimum MTMA Concentration and Coating Solution Volume

OD flux data obtained using pure water feed with a virgin membrane, membranes coated using 1.5 mL ALCG20 solution after treatment with 0.2 or 0.6 wt% MTMA solution, and a membrane coated using 3.0 mL ALCG20 solution after treatment with 0.2 wt% MTMA solution are shown in Fig. 5. Membranes coated using 1.5 mL ALCG20 solution had similar overall mass transfer coefficients to that of the uncoated membrane ($1.7\,\mathrm{kg\,m^{-2}\,h^{-1}\,kPa^{-1}}$), whereas that coated using 3.0 mL had a significantly lower value ($1.5\,\mathrm{kg\,m^{-2}\,h^{-1}\,kPa^{-1}}$). The overall mass transfer coefficients were calculated using the method described previously (18). This suggested that the thinner coatings did not offer a significant resistance to mass transfer and that the lower mass transfer coefficient of the latter membrane was due to coating thickness rather than reduced pore size. Neither 0.2 nor 0.6 wt% MTMA solutions wet-out the membrane during the coating process or over the 6 h duration of the trial. However, a membrane coated using 1.5 mL ALCG20 solution and 0.8 wt% MTMA solution showed the significant high flux indicative of membrane wet-out at the commencement of the trial, which was discontinued. Based on the superior mass transfer of thinner coatings and the propensity for wet-out using higher MTMA concentrations, 1.5 mL ALCG20 solution and 0.2 wt% MTMA solution

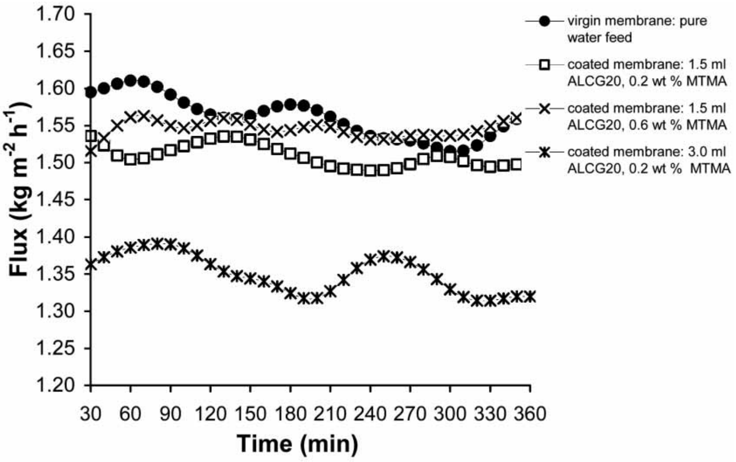

Figure 5. Variation of OD flux with time for water feed using an uncoated membrane, and membranes coated using 1.5 mL ALCG20 solution after treatment with 0.2 or 0.6 wt% MTMA solution, and a membrane coated using 3.0 mL ALCG20 solution and 0.2 wt% MTMA solution.

were adopted for use in the coating of membranes used in the OD, adhesion strength, and durability testing described next.

OD of Detergent-Containing Feeds

DBS detergent was chosen for membrane testing because of its widespread industrial applications (19, 20), including radionuclide removal in nuclear facilities (21). OD flux data for 0.1, 0.3, and 0.5 wt% DBS solution feeds are shown in Fig. 6. The results showed that the coated membranes had similar fluxes for 0.1 and 0.3 wt% DBS solutions, with that for the 0.5 wt% solution being slightly lower. All fluxes were lower than that of the uncoated membrane with pure water feed, indicating that membrane wet-out did not occur over the duration of the trial. The pure water plot shown in Fig. 5 has been reproduced in this and subsequent flux data figures for comparison purposes.

OD of Oily Feeds

OD flux data for 0.2, 0.4, and 0.8 wt% of orange oil-water mixtures are shown in Fig. 7. The results showed that the fluxes were similar for 0.2 and 0.4 wt% orange oil, with that for 0.8 wt% oil being 10–20% lower. This difference may have been indicative of partial breakdown of the oil-water emulsion and the subsequent deposition of coagulated oil on the coating

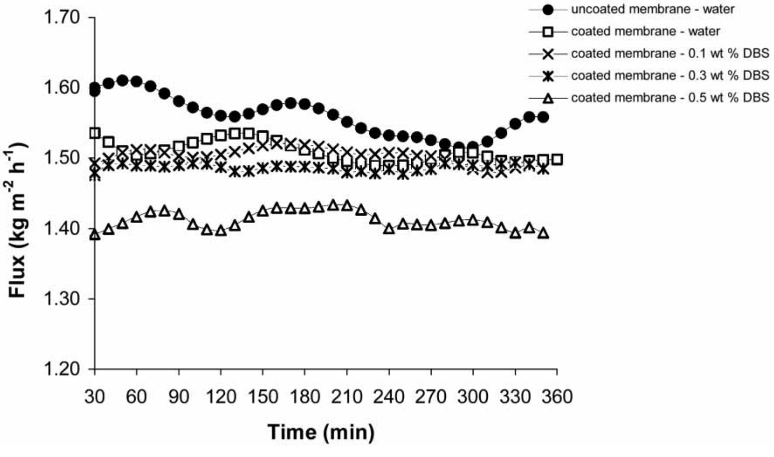

Figure 6. Variation of OD flux with time for 0.1, 0.3, and 0.5 wt% DBS solutions.

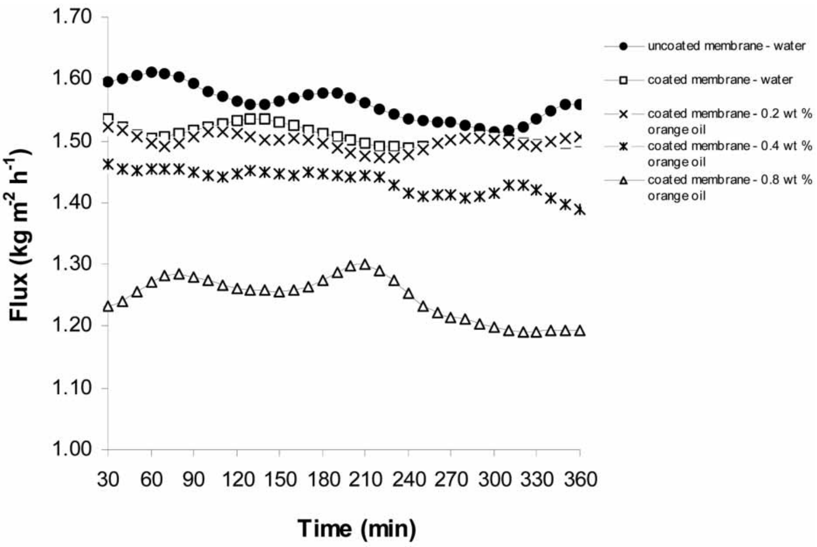

Figure 7. Variation of OD flux with time for 0.2, 0.4, and 0.8 wt% limonene-water mixtures.

surface. However, exposure of the membrane to pure water feed after each orange oil trial resulted in immediate restoration of the pure water flux to its original level. The lower fluxes of all orange oil feeds relative to that of pure water feed indicated that membrane wet-out did not occur. The 0.2 wt% orange oil feed wet-out an uncoated membrane within the first 2 min of operation.

OD of Milk Feeds

OD flux data for whole milk are shown in Fig. 8. Of particular significance in these trials was the attainment of a higher flux with a coated membrane than with an uncoated membrane. The flux of the coated membrane remained lower than that obtained with pure water feed, indicating that this flux enhancement was not the result of membrane wet-out. These observations were attributed to fouling of the uncoated membrane, possibly by colloidal milk fat. The hydrophilic coating on the other hand acted as a barrier to these globules. These observations were consistent with those of Kimura et al. (22) Long-term fouling of the coating, presumably by hydrophilic and amphiphilic solutes was, however, observed. Nevertheless, this fouling was found to be reversible by soaking the membrane in water with gentle ultrasonic vibration for 5–10 min followed by water-rinsing.

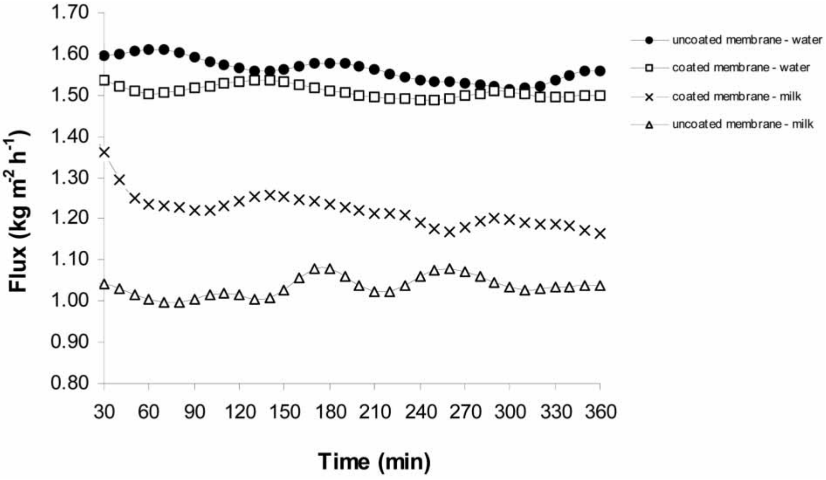

Figure 8. Variation of OD flux with time for whole milk.

Coating Adhesion Strength

Typical T-peel strength results for membranes coated with and without treatment with MTMA are shown in Fig. 9. The average adhesive forces for the tests shown were 0.1083 and 0.0345 N mm^{-1}, respectively, that is, a threefold increase when MTMA was used as a binding agent.

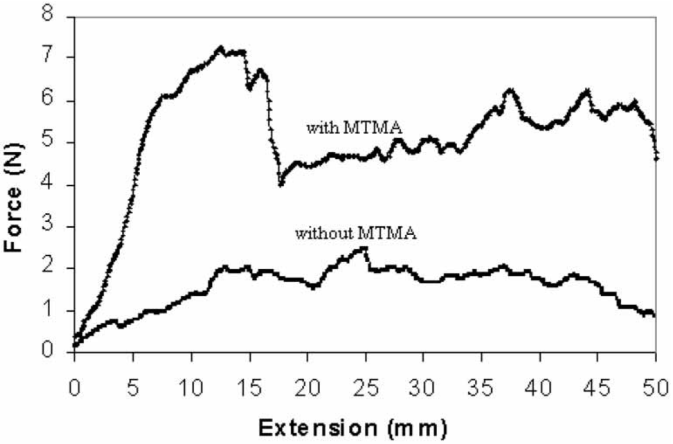

Figure 9. T-peel strength results for membranes coated with and without MTMA treatment.

Coating Durability

Coated membranes contacted with 0.5 wt% DBS solution retained their hydrophobicity for 22–28 h. Those contacted with a 1.2 wt% orange oil-water mixture retained their hydrophobicity until the trial was abandoned after 3 days when the oil became severely discolored through oxidative deterioration (6). Uncoated membranes wet-out immediately on exposure to both solutions.

CONCLUSION

The present work has shown that the cationic surfactant MTMA can act as an interfacial bonding agent to provide a threefold increase in the adhesion strength of a hydrophilic sodium alginate-carrageenan coating to a hydrophobic PTFE OD membrane. This coating afforded protection against wet-out by DBS for 22–28 h and against orange oil for a minimum of 3 days. It was also found to assist in protecting the membrane against fouling by components of whole milk.

The coating technique described in this work may provide the basis for the development of a simple in situ membrane modification method for use with existing commercially available modules. However, further work to determine the effect of cleaning solutions on the membrane coating, durability of the cross-link, and the feasibility of coating replacement as required on the same substrate will be necessary before possible appliance.

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