

Alginate-silica hydrogel coatings for the protection of osmotic distillation membranes against wet-out by surface-active agents

J.B. Xu[†], D.A. Spittler[‡], J.P. Bartley[†], R.A. Johnson^{†*}

[†]*School of Physical and Chemical Sciences, Queensland University of Technology, 2 George St. Brisbane 4001, Australia*

[‡]*Department of Material Sciences and Chemical Engineering, University of Applied Sciences Osnabrueck, Germany*

Introduction

Previous work in our laboratory has shown that crosslinked sodium alginate and 4:1 sodium alginate-carrageenan blend coatings on PTFE osmotic distillation (OD) membranes act to protect the hydrophobic membrane against wet-out by surface-active agents [1,2]. However, these coatings have several properties that may reduce their effectiveness in an industrial plant. These include susceptibility of the biological polymers to microbial attack, low melting points with softening when contacted by hot cleaning solutions, and poor mechanical strength with possible damage during membrane stretching under pressure.

The objective of the present work was to produce protective alginate acid-polymerised silicic acid (silica gel) blends with suitable properties for coating PTFE OD membranes. Silica gel is chemically inert and resistant to microbial attack [3]. It is also known for its good water sorption capability and high melting point (1610 °C). Adhesion of the hydrophilic coating to the hydrophobic membrane surface was achieved using a cationic surfactant, myristyltrimethylammonium bromide (MTMA) as an interfacial bonding agent. In order to create a homogeneous dispersion of silica in the alginate matrix and thereby control the degree of silica polymerisation, films were also prepared with the addition of glycerol (10 wt %) to the sodium alginate-sodium silicate mixture because of its dispersing [4], plasticizing [5] and moisturizing [6] properties.

Blend films were characterized using SEM, XRD, DSC, swelling measurements, mechanical strength measurements and durability testing. Coated films were tested for OD performance and resistance to surface-active agents using pure water, limonene (orange oil)-water mixtures, and sodium dodecylbenzene sulfonate (DBS) detergent solutions.

Experimental

A sodium silicate solution (2.0 wt % as SiO₂) was prepared by the addition of 13 g NaOH and 8 g SiO₂ to 400 ml water. Aliquots (1.5, 3.0, 4.5 or 6.0 ml) of this solution were diluted to 30 ml with water, with and without the prior addition of 3 ml glycerol. The diluted solutions were then heated at 45 °C and added to sodium alginate powder (0.6 g). The solution was then cast onto a Petri dish (diameter 5 cm) and air-dried for two days. The silicate content of the blend films corresponding to the above aliquots was 5, 10, 15 and 20 wt % (as SiO₂) respectively. The film was then immersed for 10 min in a 1:1 ethanol-water solution adjusted to pH 1.5 by HCl addition to form the water-insoluble alginate-silica hydrogel.

Membrane coating was effected by the method described above. In this case however the blend solution was cast directly onto a PTFE membrane (4.5 cm x 4.5 cm) that had been evenly coated with 0.25 ml of 0.3 ± 0.1 wt % MTMA solution.

Results and discussion

SEM images of blend films prepared without glycerol addition showed lumps of aggregated crystalline material (mainly silica) on a continuous background. This was consistent with the occurrence of non-moderated silicic acid polymerisation. SEM images of films prepared with glycerol addition generally showed uniform, albeit rough surfaces.

The XRD of an alginate acid film and films prepared without glycerol addition showed a sharp peak at a 2θ value of 13.6° attributable to alginate acid, with the intensity of this peak decreasing with increasing silica content. A second, broad peak at about 23° attributable to polymerized salicylic acid was present in all diffractograms. The XRD of alginate acid film and the blend films prepared with glycerol addition showed a sharp peak at 2θ of 13.6° for the alginate acid film and a broad peak at 22.5° for the blend films. The marked intensity reduction or absence of the 13.6° peak in the blend films and the presence of a single blend peak indicated a single, uniform crystal structure at all silica concentrations used.

DSC showed a major endothermic peak attributable to the melting point, T_m, at 85 °C for alginate acid. This increased steadily with increasing silica content to 96 °C for the 20 wt % silica film. The heats of fusion of alginate acid and the 5 and 10 wt % silica films were similar, while the 15 and 20 wt % silica films were significantly larger. These larger values may have reflected increased silica polymerisation within the alginate acid matrix. DSC curves of films prepared with glycerol addition showed no peaks at temperatures below 250 °C. This observation indicated that the presence of glycerol resulted in a uniform, more thermally stable structure at all silica concentrations.

Swelling measurements on an alginate acid film and blend films prepared without glycerol addition showed that the blend films had similar water sorption characteristics (43-49 wt %) to alginate acid (49 wt %). However, those prepared with glycerol addition had markedly larger values (83-92 wt %).

Young's modulus for alginate acid was shown to be at least 3600 times greater than that of the blend films. The alginate film could only withstand 4.73 % displacement before breaking compared with greater than 100 % for the blend films.

The 10 % silica coating gave good protection against membrane wet-out during three six hour trials using the same membrane. Rapid membrane wet-out occurred when an uncoated membrane was contacted by 0.2 wt % orange oil feed. The flux for full-cream milk using a coated membrane was approximately one-half that for pure water. This was attributed to concentration polarization and fouling by hydrophilic and amphiphilic milk components.

Conclusions

Alginate acid-silica composite coatings on PTFE OD membranes have been shown to have the properties required of OD membranes and provide protection against wet-out by surface-active materials.

References

- [1] J.B. Xu, S. Lange, J.P. Bartley and R.A. Johnson, Alginate-coated microporous PTFE membranes for use in the osmotic distillation of oily feeds, *J. Membrane Sci.* In press.
- [2] J.B. Xu, J.P. Bartley and R.A. Johnson, Application of sodium alginate-carrageenan coatings to PTFE membranes for protection against wet-out by surface-active agents, *Separation Sci. and Tech.* In press.
- [3] A.Kros, M. Gerritsen, V.S.I. Sprakel, N.A.J.M. Sommerdijk, J.A. Jansen and R. J.M. Nolte, Silica-based hybrid materials as biocompatible coatings for glucose sensors. *Sensors and Actuators, B: Chemical*. B81(1) (2001) 68.
- [4] W. Yang, Z. Shao, C. You, G. Xiong. Oxygen-permeable film of perovskite-type composite oxide. Chinese patent 1277072, 2000.
- [5] F. El-Tantawy and Y.K. Sung. A novel ultrasonic transducer backing from porous epoxy resin-titanium-silane coupling agent and plasticizer composites. *Materials letters*. 58 (2003) 154-158.
- [6] P.M. Elias, K.R. Feingold, and C.R. Thornfeldt. Lipids for epidermal moisturization and repair of barrier function. US patent 5643899, 1997.