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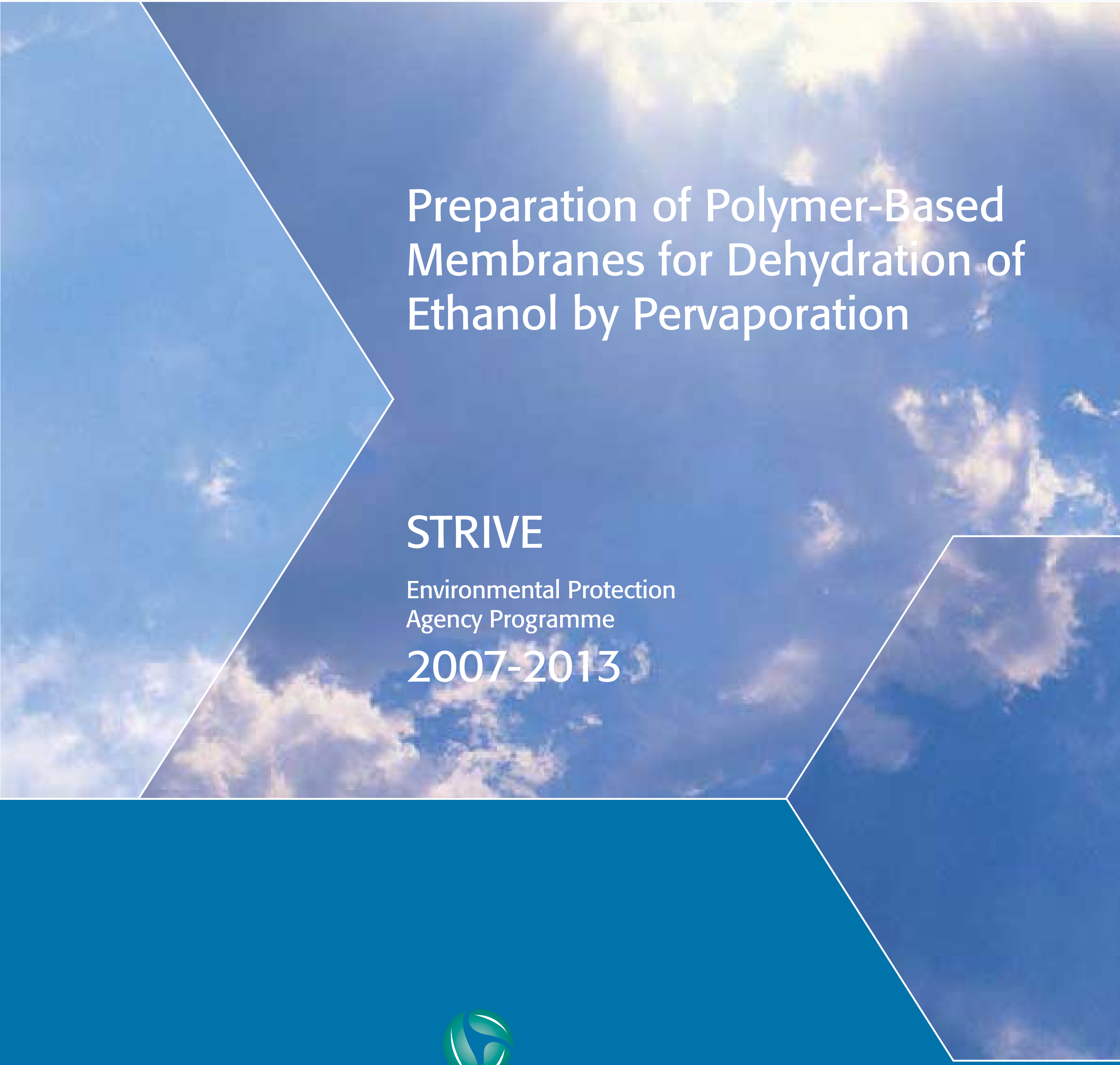

Preparation of Polymer-Based Membranes for Dehydration of Ethanol by Pervaporation

STRIVE

Environmental Protection
Agency Programme
2007-2013

SSTI
Strategy for Science, Technology and Innovation

Comhshaol, Oidhreacht agus Rialtas Áitiúil
Environment, Heritage and Local Government

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EPA STRIVE Programme 2007–2013

Preparation of Polymer-Based Membranes for Dehydration of Ethanol by Pervaporation

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STRIVE Report

Prepared for the Environmental Protection Agency

by

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DISCLAIMER

The EPA STRIVE Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Executive Summary

Pervaporation is a membrane separation process involving partial vaporisation of a liquid mixture through a membrane whose downstream side is held under vacuum. The main industrial application of pervaporation is organic solvent dehydration. The most common example still remains the production of anhydrous ethanol for the pharmaceutical industry. This clean technology avoids ethanol contamination by toxic species as typically encountered with the former azeotropic distillation process.

Ethanol produced from renewable energy sources has received recent interest as a future biofuel. At present, anhydrous ethanol is added to petrol to improve efficiency and reduce emission of exhaust. This report describes the preparation of supported polymeric membranes for dehydration of ethanol by pervaporation.

The concept of pervaporation and its historical development in the 20th century is first described. The different types of membrane used in pervaporation today, both industrially and academically, are outlined, namely: polymeric, inorganic, mixed matrix and hybrid organic–inorganic membranes. The polymers used in this study are focused on sodium alginate (NaAlg) and polyvinyl alcohol (PVA). The inorganic filler particles used to prepare mixed matrix membranes were zeolite 4A and spherical mesoporous silica. Procedures for preparing supported and unsupported membranes are provided. Special attention is paid to supported membranes as this is the norm industrially to achieve a high transmembrane flux. The setup and operation of the laboratory-scale pervaporation unit (Sulzer Chemtech) are also described in detail.

The results comprise chiefly of the comparison of flux and selectivity data of the various types of membrane prepared in this work, under similar pervaporation conditions. Sodium alginate was found to be a super-selective membrane superior to that of PVA. However, as a membrane material it was found to be too brittle for practical use, i.e. it could not be supported, reused or used as a polymer for mixed matrix membranes as it curled or cracked. By blending with PVA or the addition of the plasticiser glycerol, supported modified NaAlg membranes could be prepared. Glycerol was found to improve the miscibility of the NaAlg–PVA blend, and at a certain weight per cent resulted in an increase in the selectivity of the membrane. The supported NaAlg-based membranes showed a decline in flux over time whereas the unsupported membranes did not. This phenomenon is discussed in terms of polymer-chain relaxation across the membrane. As expected, supported membranes showed an increase in flux in comparison to unsupported membranes.

Future work could include cross-linking NaAlg, embedding novel filler particles and preparation of the new class of ceramic and molecular hybrid membranes which are described in the Introduction. Other applications of pervaporation include the removal of small amounts of volatile organic compounds (VOCs) from contaminated water and separation of organic–organic mixtures.

1 Introduction

1.1 Concept and History of Pervaporation

Pervaporation is a membrane technology for liquid separation in which a polymeric or ceramic membrane serves as a separating barrier for the process. When a membrane (held under vacuum) is in contact with a liquid mixture, one of the components in the mixture can be preferentially removed as a vapour from the mixture due to its higher affinity with and/or quicker diffusivity in the membrane. In the laboratory, a vacuum pump is usually used to draw a vacuum on the permeate side of the membrane and the permeate vapour is condensed in a liquid-nitrogen trap.

Membrane separation performance is usually reported by flux and separation factor data. Flux and separation factors are calculated using the formulae:

$$J = \frac{m}{St} \text{ and } \alpha_i = \left(\frac{y_i / y_j}{x_i / x_j} \right),$$

where J is the permeate flux, m the mass of permeate, S the membrane surface area, t the permeation time, y_i the weight of component i in the permeate, y_j the weight of component j in the permeate, x_i the weight of component i in the retentate, x_j the weight of component j in the retentate and α_i is the separation factor for component i with respect to component j. As α_i approaches infinity, the membrane tends towards being super-selective. As the separation factor is a ratio of ratios, small composition changes can lead to large changes in separation factors, especially at low feed concentrations and high permeate concentrations.

Baker (2004) and Pereira Nunes et al. (2006) have described the history of pervaporation. Baker highlights the significant milestones and Pereira Nunes et al. record the number of US patents each year. The word ‘pervaporation’ itself was coined by Kober (1995) in 1917 after observing spontaneous evaporation of a liquid in a closed colloidon bag. The first systematic studies were not performed until the 1950s at American Oil by Binning (1961) and co-workers. The process, however, did not go beyond the laboratory and the programme was abandoned by American Oil after a few years. Through the rest of the 1960s and into the 1970s a low level of interest was maintained in Monsanto, Exxon and Standard Oil, although again commercialisation was not achieved. The reason for this was that high-performance membranes and modules were not available at the time to make the process competitive. The breakthrough came in 1982 when GFT (now owned by Sulzer) installed the first pilot plant for the removal of water from concentrated ethanol. After this, interest in the process surged and it was thought that it would only be a matter of time before pervaporation replaced distillation industrially. The potential of pervaporation has not, however, been realised. Jonquieres et al. (2002) reviewed in detail the trends in industrial pervaporation in the USA and Europe since 1995. They concluded that the great majority of pervaporation applications are still limited to organic solvent dehydration using PVA membranes. They found that several industrial companies have given up their pervaporation activity despite satisfactory progression. This is due to difficulty in industrialising the process profitably and in being competitive with distillation.

1.2 Notes on Membrane Transport Mechanisms

There are two types of separation membrane used today: (1) pore-flow microporous membranes, and (2) dense solution diffusion membranes, which are classified according to the mechanism of separation. Simplistically, pore-flow membranes separate by molecular sieving in which one of the permeates with a smaller molecular size moves through some pores, whereas some larger molecules are excluded. In solution-diffusion membranes one of the permeates has a larger solubility and diffusivity across the membrane.

According to Baker (2004), both models were proposed in the 19th century but the pore-flow model was more popular as it is more in line with normal physical experience. With the development of reverse osmosis dense polymeric membranes, the solution-diffusion mechanism became more accepted although some pore-flow modellers still remain.

The controversy may be due to the definition of a pore, which calls into question the distinction between porous and non-porous membranes. Bruschke (1995) drew attention to a previous observation that ‘there exists an unresolved question as to whether any membrane, so-called porous or non-porous will act to some extent as a microporous medium. Even so-called non-porous membranes may have pores in the 5–10 Å region’. These pores would arise from free volume microcavities between polymer chains, which fluctuate according to thermal energy. Computer simulation has allowed modelling of molecular motion within such polymeric matrices (Baker, 2004). It is clear how one could classify these matrices as porous, with the pores being temporal as opposed to fixed in certain ceramics such as zeolites. However, the ‘non-porous’ description has remained as the behaviour (solution-diffusion) of such dense membranes has supported the solution-diffusion theory. Detailed theory of solution-diffusion and pore-flow mechanisms are beyond the scope of this study but can be found elsewhere (Shao and Huang, 2007; Bowen et al., 2004; Baker, 2004).

1.3 Membrane Types

1.3.1 Polymeric Membranes

Shao and Huang (2007) have reviewed polymeric-membrane pervaporation with emphasis on the fundamental understanding of the membranes. Chapman et al. (2008) have reviewed hydrophilic polymeric (and inorganic) membranes for dehydrating solvents, and compared flux and separation factor data from literature. The two polymers used in this study are polyvinyl alcohol (PVA) and sodium alginate (NaAlg). The structure, properties and application of NaAlg as a pervaporation membrane material will be discussed in more detail. The aforementioned reviews should be consulted for publications on other polymers used in pervaporation.

1.3.1.1 Algin/Alginte/Alginic Acid

Alginate is a hydrophilic carbohydrate extracted with dilute alkali from various species of brown seaweeds. In molecular terms, it is a family of unbranched binary copolymers of (1-4)-linked β-d-mannuronic acid and α-l-guluronic acid residues. The structure of alginic acid is the only polysaccharide which naturally contains carboxyl groups in each constituent residue. Alginic acid is not very soluble in commercial solvents but its sodium salt is well soluble in water.

1.3.1.2 Alginate as a Pervaporation Membrane

Research into the use of sodium alginate membranes for alcohol dehydration was first reported in the late 1980s (Shao and Huang, 2007). The membrane has since been shown to be the highest performing membrane for dewatering solvents, exceeding that of PVA and other polysaccharides such as chitosan and cellulose. Bhat and Aminabhavi (2007) have recently reviewed NaAlg-based membranes, compiling and comparing literature J and α data. A similar comparison of data can also be found in the review by Chapman et al. (2008).

However, as a pervaporation membrane material NaAlg has a number of disadvantages:

1. As an ionic hydrophilic polymer, NaAlg is water soluble and unstable in aqueous environments, which is not feasible for membrane production or application. As Shi et al. (1996) pointed out, when using pristine NaAlg, the water content in the feed should not exceed 50% by weight in pervaporation experiments or the membrane will resolve into the feed;
2. As a film or membrane NaAlg is brittle and not practical for many applications including pervaporation. Russo et al. (2005) have carried out tensile tests on NaAlg and PVA films cast from 2% by weight solutions, the data of which is shown in Table 1.1. In comparison to PVA, NaAlg has a very high Young’s modulus and very low strain at break. These properties make it unsuitable as a membrane material as any wrinkles or cracks on the micron scale would affect both selectivity and the vacuum. Rupture would render the membrane useless. Although functional NaAlg pervaporation membranes can be prepared at small scale, modification is necessary to go beyond the laboratory;

Table 1.1. Mechanical parameters of NaAlg and PVA (from Russo et al., 2005).

Film	Young’s modulus (MPa)	Stress at break (MPa)	Strain at break (%)
NaAlg	5551 ± 307	147 ± 17	2.6 ± 0.3
PVA	1697 ± 46	47 ± 3	220 ± 30

3. NaAlg pervaporation membranes have shown a significant decline in flux over time and in repeated use. Yeom et al. (1996) suggested polymeric chain relaxation was the cause. This is discussed in more

detail in Section 3.2.4.1. Shi et al. (1998) suggested that this phenomenon may also be due to loss of sodium ions to the permeate during pervaporation operation.

The three disadvantages described here can be addressed by: (1) cross-linking treatments to render the membrane insoluble in water and prevent polymer-chain relaxation, and (2) addition of plasticisers to decrease the fragility of the membrane for practical use. Cross-linking can be achieved using glutaraldehyde (Yeom and Lee, 1998b) or by exchange of sodium ions with certain multivalent metal ions (Shi et al., 1998; Huang et al., 1999). The degree of cross-linking, however, needs to be controlled as pervaporation performance is decreased and the membrane may become too brittle for use, even at the laboratory scale (Shao and Huang, 2007). The addition of plasticisers miscible with NaAlg and water such as glycerol can impart further softening and flexibility (Whistler and BeMiller, 1993; Russo et al., 2005). The addition of plasticisers is not incompatible with insolubilisation of NaAlg by ion exchange with metal cations such as calcium (Rhim, 2004).

1.3.2 Inorganic Membranes

The advantages of inorganic/ceramic membranes (in comparison to polymeric) are greater thermal, mechanical and chemical stability, which means the membranes can be used at higher temperatures, resulting in flux increase and in harsher chemical environments in which polymeric membranes would fail. On the other hand, inorganic membranes have been reported as being ‘brittle’ and difficult and expensive to process. Chapman et al. (2008) divided inorganic membranes into two types: ceramic and zeolitic. These ceramic membranes may be best described as inorganic non-zeolitic membrane active layers, as zeolitic membranes are the only commercial pervaporation membranes available at present. The ceramic membranes are typically microporous amorphous silica prepared by the sol-gel method and have been applied for other membrane separation processes, but studies have also been done on pervaporation. Other ceramic pervaporation membranes studied have been doped silica and non-siliceous classes. However, the majority of research in inorganic pervaporation membranes has been on zeolites.

Zeolites are microporous crystalline alumina silicates with well-defined pore structures. Due to their excellent adsorption properties and molecular-sieving ability (pore size in Å scale), these pore-flow type membranes have been researched and commercialised as pervaporation membranes. In academic literature the membranes are typically in tubular form and the membranes are grown hydrothermally on porous substrates (asymmetric type). Type A zeolite has been the most investigated zeolite membrane for ethanol dewatering, due to its high hydrophilicity and its possessing a pore diameter of 0.4 nm, which results in an efficient molecular-sieving effect (molecular diameter of H_2O = 0.296 nm and EtOH = 0.430 nm). Use of zeolite membranes in large-scale pervaporation is challenging and this is reflected in the lack of commercialisation. According to Bowen (2004), the only large-scale use is by Mitsui Engineering and Shipbuilding in Japan using Type A zeolite for ethanol dehydration. The difficulties of commercialisation are highlighted by the failure of Smart Chemical Co. in the UK to transfer their successful zeolite membranes (laboratory scale) to large-scale production. The company that was referenced in Bowen’s review has ceased to exist and the reasons (internet source) given are scale-up and processing difficulties.

1.3.2.1 Mesoporous Silica Membranes and Pervaporation

The use of mesoporous silica for pervaporation application was first reported by Cot et al. (2000) using membranes prepared using alkyltrimethylammonium bromide templated silica. They carried out tests on a polar–non-polar binary, ethanol–cyclohexane, and observed a pervaporation effect. The mechanism of separation differs from both the solution-diffusion model in dense polymers and the pore-flow (molecular-sieving) model in microporous zeolites. According to the authors, in this mesoporous membrane the selectivity of ethanol over cyclohexane is due to preferential adsorption and the flux is governed by surface diffusion. As the pore size (~1 nm measured by nitrogen sorption) is larger than both the ethanol (0.43 nm) and the cyclohexane (0.60 nm) molecular diameters, a classical pore-sieving mechanism as in the case of zeolites cannot be occurring. However, the difference in polarity causes a preferential adsorption of ethanol on the hydroxylated silica surface (pore walls) and also there exists a steric hindrance to cyclohexane.

The use of polarity data has been used in polymeric membrane material selection for pervaporation (Jonquieres (1996)). It has been proposed that the polar groups in the membrane matrix, responsible for the membrane hydrophilicity, act as the fixed carriers for mass transport in the membrane (Shao and Huang, 2007). In the case of dehydration of organic solvents, it is believed that water transport in the membrane proceeds in a special manner. Unlike the random walk of the less polar species, the water molecule jumps from one polar site to another. The fixed-carrier theory implies that water and the less polar species in the liquid mixture take different paths while diffusing through the membrane. This theory can be applied to the ethanol–cyclohexane system in the mesoporous silica membrane described above. In this case the fixed carriers are silanol groups along a siloxane pore wall, as opposed to hydrophilic groups along a polymer backbone. Dimroth and Reichardt's solvent polarity $E_T(30)$ values (Reichardt, 1998) can be used to empirically predict a separation (Jonquieres et al., 1996). In this case the less polar cyclohexane has a polarity ($E_T(30)$) of 30.9 kcal mol^{-1} and the more polar ethanol has a polarity of 51.9 kcal mol^{-1}. This suggests that the mesoporous silica membrane could potentially be used to separate water from ethanol, considering water has a polarity ($E_T(30)$) of 63.1 kcal mol^{-1}.

The ability to control the connectivity and tortuosity of ordered mesoporous silica-type membranes would be expected to result in improved permeability (Beck et al., 1992). Ideally the pore channels would be orientated perpendicular to the substrate. One method of achieving this is using a modified Stöber sol. In 1997 Grun et al. (1997) synthesised ordered mesoporous silica microspheres by a modified method in which a quaternary ammonium salt was used as the pore template (Stöber, 1968). Microscopy investigations (Van Tendeloo et al., 2003) have shown the hexagonal pore system to radiate from the centre of the particle. Yoon et al. (2007) have subsequently shown that silica spheres with a solid core and a porous shell with a perpendicular pore orientation can be grown.

The direction of the mesochannels in mesoporous/mesostructured films is typically parallel to the substrate. Pores have been successfully oriented perpendicular by methods such as growth in anodic aluminium oxide (AAO) and application of an external magnetic field. Using a modified Stober sol, Ogawa et al. (Shimura and Ogawa, 2006; Ogawa et al., 2006) have shown that a porous thin film can be formed by simply placing a substrate perpendicular to the base in the reaction vessel. The pore direction of these films was not characterised. The sol used in this case results in a disordered pore network due to the large methanol content. However, if the same approach is applied to the sol used by Grun et al. (1997) a thin film with perpendicular pores is expected. The surface of the substrate in the sol should act in a similar way to the surface of the growing sphere, resulting in perpendicular growth of the silica-surfactant array. The pore size of this membrane would be in the region of 2–4 nm. This pore size would be too large to take advantage of the molecular sieving separation mechanism in ethanol dehydration by pervaporation, as demonstrated by zeolitic membranes. For this reason a membrane of this type may be better suited for the larger-pore membrane separation processes such as nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF), or as an intermediate supporting layer for zeolitic or dense polymeric selective layers. However, use of structure directing agents (SDAs) with shorter alkyl chain length and/or increasing the sol alcohol content (Anderson et al., 1998) may result in a pore size in the desirable microporous region for pervaporation.

Chung and co-workers (2009) have used a static pervaporation system to test membrane performance at room temperature and a Sulzer bench-top unit (see Section 2.2) to test performance at higher temperatures. The static cell would be suitable for initial trials of novel membranes that are difficult to prepare, such as the mesoporous membranes described above. The membrane selective layer should be directly deposited onto the porous support used in the cell, i.e. the porous support would be used as the substrate. The deposited film should plug the pores and coat both sides of the support. Porous stainless steel at this scale has been successfully used as supports for zeolite coatings (Chau et al., 2000; Fankhanel et al., 2009), including pervaporation membranes (Holmes et al., 2000). As pointed out by Holmes (1999), stainless steel has a number of attractive properties such as mechanical strength, thermal stability and resistance to chemical attack. Other inorganic substrates such as porous alumina or porous glass frits could also be investigated (Cot et al., 2000; Holmes et al., 1999).

1.3.3 Mixed Matrix Membranes

The ceramic and zeolitic membranes described above have shown superior performance in membrane separations, but the advantages are offset by the costs in manufacturing the membranes and the membrane holders (modules). One approach to solving this problem is to prepare membranes consisting of inorganic (in particular zeolitic) particles dispersed in the polymeric matrix. These so-called 'mixed matrix' membranes would be expected to combine the selectivity of the zeolitic membranes with the low cost and ease of manufacture of polymer membranes (Baker, 2004). Ideally, zeolite particles increase the mobility of the component that is more permeable in the polymer, while decreasing the mobility of the component that is less permeable. Zeolite incorporation often increases pervaporation flux with little or no decrease in separation factor, or increases separation factor with little or no decrease in flux (Bowen et al., 2004).

Mesoporous silica has also been used in mixed matrix membranes as a filler particulate in pervaporation and gas separation. Aminabhavi et al. (2006) reported an increase in both flux and selectivity when MCM-41 particles were embedded in a cross-linked NaAlg membrane for dewatering isopropanol by pervaporation. MCM-41 nanoparticles have also been used in polysulfone membranes for gas separation and have been found to increase gas permeability without a loss in selectivity (Reid et al. 2001; Kim and Marand, 2008).

1.3.4 Hybrid Membranes

Silsesquioxanes/ormosils are organically modified silicates in which the organic groups are bonded to the silica framework and have the general formula $[R_2Si_2O_3]_n$. These hybrid materials have been described as molecular composites, in comparison to other inorganic–organic composites that have the organic moiety interaction at a larger scale.

This decrease in length scale to the molecular scale offers novel properties. As regards pervaporation membranes, the potential of this nanocomposite lies in the properties rendered by the molecular inorganic–organic interaction, which allows the advantages of both classes of materials to be shown.

Organic–inorganic hybrid materials are viewed as next-generation materials in many applications because they have both the functionality of organic compounds and the stability of inorganic compounds. There has been recent interest in pervaporation to control the organic–inorganic interaction at the molecular level by sol-gel methods. Uragami et al. (2007) have used liquid silica precursors to react with polymers to form hybrid membranes for ethanol dehydration. This results in a silica network bonded to the polymer chains, which has resulted in improved selectivity and hydrothermal stability. Another potential hybrid membrane could consist of the silica phase condensed around the water-soluble polymer as a hard glass (Sato et al., 1990).

Castricum et al. (2008) have recently shown remarkable hydrothermal stability in a sol-gel synthesised ormosil membrane. The hydrothermal stability was achieved by the introduction of hydrophobic CH_3 groups into silica, which lowered the siloxane hydrolysis, thus maintaining the microporosity which otherwise tends to be lost in aqueous solution due to silica dissolution or 'leaching'. A CH_x:Si ratio of unity was achieved. The introduced hydrophobicity did not decrease the flux or selectivity. Indeed, the authors have claimed this membrane to be in this next-generation category and their study over such a timescale (two years) suggests this to be true. This is the type of membrane that experienced pervaporation reviewers conclude is needed for pervaporation to become more competitive industrially with distillation.

Polyhedral oligomeric silsesquioxane (POSS) polymers are a relatively new class of materials that are generating a large research interest (Phillips et al., 2004) due to the improved properties, such as thermal and mechanical, in comparison to pristine polymers. Although the first oligomeric polysilsesquioxanes were synthesised in 1945, it is only since 1991 that POSS polymers have been reported (Li et al., 2001). The distinction between POSS and silsesquioxane (SS) is that the POSS materials are classified by having the cage structures. The materials are compatible with polymers due to the organic end groups (tethers), which may be covalently or non-covalently bonded to the organic molecular chains. The molecular precursors are now commercially available in which a range of cage sizes is available and also non-siliceous materials.

1.4 Membrane Preparation

Baker (2004) has described the preparation of dense non-porous unsupported polymeric membranes. This class of membrane is rarely used in membrane separation processes because the transmembrane flux through these relatively thick membranes is too low for practical separation processes. However, they are widely used in laboratory and academic work to characterise membrane properties, and, in the case of pervaporation, J and α can be measured. Solution casting is the most common method of preparing dense membranes in the laboratory.

In many literature pervaporation experiments, the membrane area is small (~5 cm diameter) and the membrane is prepared by casting a dissolved polymeric solution onto glass and allowing the solvent to evaporate. The dried membrane is relatively thick and the thickness is uncontrolled. A hand-casting knife can be used to control the thickness of the membrane. The casting knife consists of a steel blade resting on two runners arranged to form a precise gap between the blade and the plate onto which the film is cast. Such hand-casting knives and simple casting machines are used for producing uniform films of paints and varnishes (ASTM D823-95(2007) Standard Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels), but work well also for laboratory membrane preparation.

1.4.1 Supported/Anisotropic Membranes

Supported membranes are layered structures in which the porosity, pore size and membrane composition change from the top to the bottom surfaces of the membrane. They usually consist of a thin selective layer supported on a much thicker highly permeable porous substrate. The thin selective layer results in a high flux and the porous support provides the strength required for handling the membrane. The breakthrough in commercial pervaporation (see Section 1.2) arose due to the large-scale production of polyacrylonitrile (PAN) membranes reinforced on a fabric backing layer which acted as a porous support for the selective PVA layer. The fabrication of such multilayer membranes is always considered a trade secret. There are only a very few academic reports on this subject for the alcohol dehydration by pervaporation. Although methods can be found in patent literature, they are not described in detail and use large-scale membrane casting machines for mass production. Recently, Huang et al. (2006) reported a method of producing supported pervaporation membrane sheets using a simple casting machine.

1.5 Alternative Membrane Configurations

As well as investigating new higher-performing materials for the selective layer membrane, scientists and engineers have also researched membrane and module design. For example, following the first anisotropic membranes made by Loeb-Sourirajan, processes membrane thickness has been reduced to ~0.1 μm, which has resulted in today's membranes having 5–10 times more flux than 30 years ago (Baker, 2004). This has been essential for making membrane processes competitive commercially.

It has been shown recently (Sabottke, 2008; Jiang et al., 2009) that an improved pervaporation separation performance can be achieved by inverting an anisotropic membrane so that the support (e.g. fabric) is facing the feed and the selective layer is facing the vacuum. Jiang et al. (2009) found that inverting their polyimide membranes resulted in an increase in selectivity and only a slight decrease in flux. Sabottke included an additional polymer layer at the permeate side to provide stability, and found an increase in both flux and selectivity.

1.6 Objectives

The main objectives of this project were to:

1. Install a pervaporation unit and develop a method for permeate analysis;
2. Prepare unsupported PVA membranes;
3. Prepare unsupported mixed matrix PVA with porous silica filler particles and investigate if pore size results in an increase in J and α;
4. Prepare supported cross-linked PVA membranes according to a recent literature procedure (Huang, 2006) which reported superior performance to commercial cross-linked PVA membranes;
5. Prepare supported NaAlg and modified NaAlg membranes.

2 Experimental

2.1 Materials and Methods

Dimethyl sulfoxide (DMSO), NaAlg, glycerol and zeolite 4A were purchased from Sigma Aldrich. Polyvinyl alcohol 88% hydrolysed was purchased from Polysciences. Polyacrylonitrile was purchased from Scientific Polymer Products. A large quantity (50 yard × 40 inch roll) of polyester non-woven fabric (CU 414) was kindly donated by Mr Ralph Di Palma of Crane Nonwovens (www.cranenonwovens.com). The K control coater K202 was purchased from RK Paint. The Mettler Toledo density meter (DE40) was purchased from Mason Technology. The Sulzer Chemtech bench-top pervaporation unit was kindly loaned by the Irish National Centre for Membrane Technology (INCMT) located in Cork Institute of Technology (CIT).

The preparation of mesoporous silica particles can be found elsewhere (Keane et al., 2010; Hanrahan et al., 2009).

2.2 Membrane Preparation

Polyvinyl alcohol and NaAlg precasting solutions were prepared by dissolving X g of solid polymer in 100 + X g of deionised water to give a solution of X%. For example, to prepare a 12% wt/wt PVA solution, 12 g of solid PVA were dissolved in 88 g of deionised water. Polyvinyl alcohol was typically dissolved at 90°C for two hours, whereas NaAlg was dissolved at room temperature. The solid polymer was dispersed by mechanical stirring. Undissolved solids or foam could be removed by filtering through the non-woven fabric.

2.2.1 Unsupported Membranes

Unsupported PVA and NaAlg membranes were prepared by pouring the dissolved polymeric solution onto glass disc plates until the surface of the plate was completely covered. Care was taken so that the solution did not flow over the edge, which would result in an uneven membrane thickness and membrane rupture after drying. The membranes were allowed to dry at room temperature for 24–72 hours depending on the composition. The plates were cut slightly larger than the membrane area. Once dry, an incision was made in the edge of the membrane and peeled back to facilitate easy removal of the membrane from the plate. After removal from the plate, the membrane was cut to fit the pervaporation unit cell using a scalpel.

2.2.2 Supported Membranes

Supported membranes were prepared in a method similar to that reported by Huang et al. (2006), also taking some steps employed by Hirata et al. (1992) and patent literature. First it was ensured that the glass plates (25 cm × 25 cm × 3 cm) were clean and free of dust or dirt, which could cause defects in the coating and resulting membrane. The non-woven fabric was cut to 25 cm × 23 cm. The fabric was then taped to the glass plate using duck tape. The tape was in contact with both the fabric and the surface of the glass plate. The fabric was then saturated with DMSO so that it was flat against the plate, ensuring no air bubbles formed beneath the fabric. The plate was then mounted on the coating machine. (Note: The casting machine was modified for preparing phase-inversion membranes as it is necessary to immerse a *flat* PAN membrane in water. The machine originally had a large fixed glass plate. In this study the plate is removable and placed on a rubber mat to prevent movement when casting.) The height is calibrated using the calibration rod and a rod of chosen thickness (typically 40 µm) is attached. The speed is adjusted (typically 3 m/min). A puddle of 7% wt/wt PAN in DMSO is poured in front of the rod and the machine is switched on, resulting in a uniform coating. The plate is immediately removed and immersed in a basin of water for 20 minutes. The plate is removed and dried in an air stream, which takes approximately 30 minutes. The tape at this stage may become loose due to the presence of DMSO or water in which case it is re-taped. The plate is again placed on the coating machine for casting the selective skin layer. Typically a 150 µm rod is used and the layer is cast similar to previously. The plate is put in an oven at 40°C overnight to dry. (Note: Duck tape is stable only to 60°C.) In the case of cross-linking the PVA membrane, the sheet is removed from the plate and placed between two sheets of non-woven fabric and two glass plates and placed in the oven at

160°C. When dry, the membranes are cut carefully to size (158 mm) and checked for leaks (by reading the vacuum) in the permeation cell before carrying out a pervaporation experiment.

2.3 Pervaporation Unit

The pervaporator installed is a bench-scale Sulzer Chemtech unit designed for testing the performance of flat sheet membranes for the removal of minor components from feed mixtures. The unit can be used for process demonstration for special applications and optimisation of parameters. All parts in contact with the feed mixture are either stainless steel, PTFE, the membrane, or appropriate elastomers (O-ring) such as Kalrez or Viton. Figure 2.1 shows a schematic diagram of the unit.

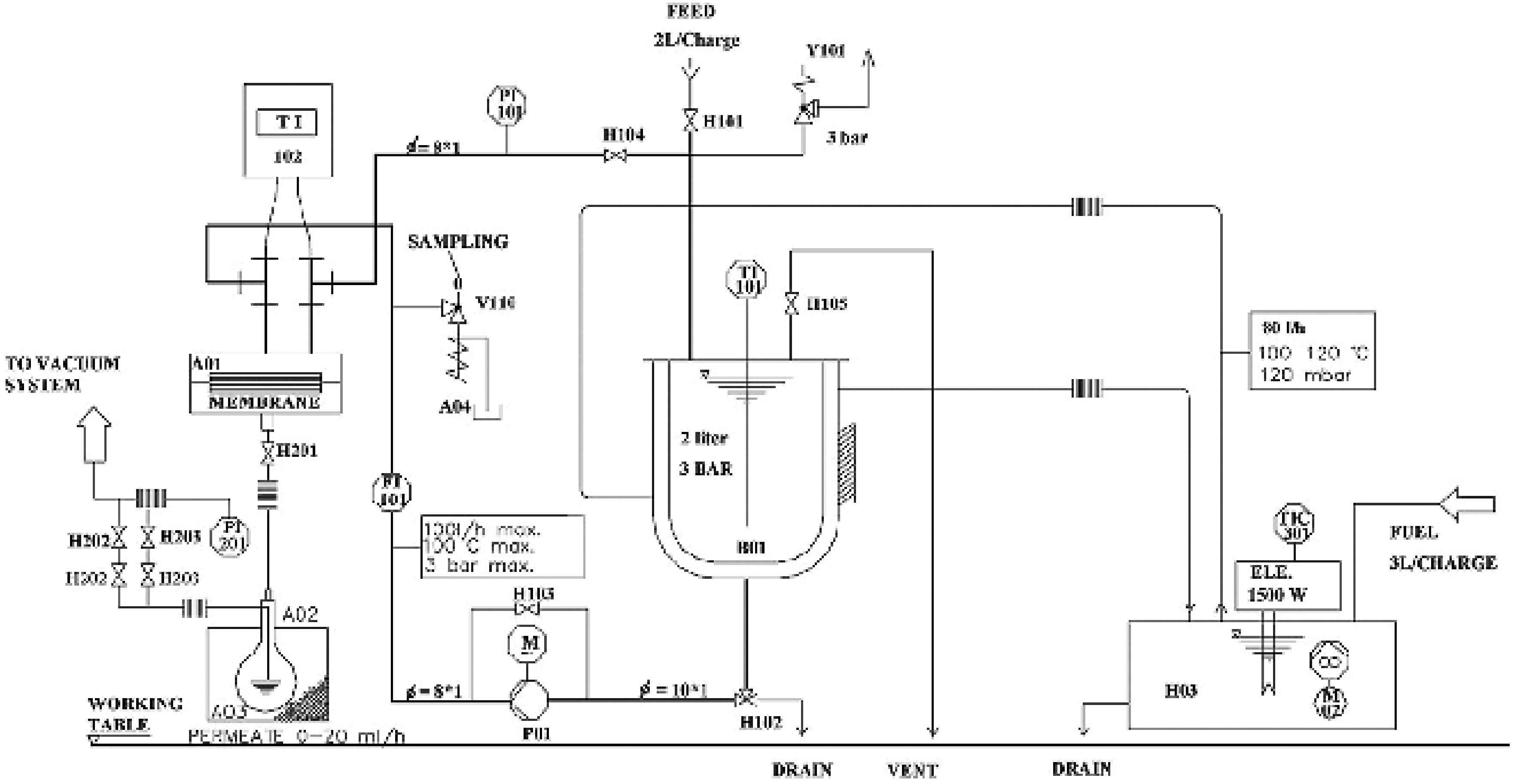
2.3.1 *Description of Main Features of the Pervaporator (Adapted from Operating Instruction Manual)*

The unit comprises a heating bath (H03, Haake PC30) with a temperature control (TIC301) and recycling pump. The heating bath is equipped with safety switches that will shut off the heating bath at high temperature (130°C) and a low level of heat-transfer liquid. The double-jacketed closed feed tank (B01) is heated by circulation of the heat-transfer liquid (glycol) from the heating bath through a double jacket. The maximum pressure in the feed tank is 3 bar measured by a pressure gauge (PI101). A safety valve (Y101) will open if this pressure is exceeded in order to protect the feed tank and the unit. The feed pump (P01, Speck Pumpen pump) circulates the feed from the feed tank through the test cell (A01), over the membrane and back to the tank. The test cell (A01) has an inner diameter of 15.8 cm in which the membrane under test is housed. (Note: A smaller test cell has been manufactured by Sulzer, which has an inner diameter of 4.4 cm. This is not their standard size but has been used in academic research (Huang et al., 2006).) It has an upper part with the connection for inlet and outlet of the feed mixture, and a bottom part that can be removed from the upper part. During operation, the upper and lower parts are held together by four clamps. The membrane sample is supported by a porous steel plate in the bottom part through which the permeate vapours can pass. Sealing between the feed side and the permeate side is effected by means of an O-ring around the circumference of the membrane at the inner side of the bottom part of the test cell. The temperature of the test cell is constantly monitored by a Greisinger Electronic GTH 1100/2 DIF digital thermometer (TI102). An Edwards RV3 two-stage rotary-vane vacuum pump provided the vacuum to be applied at the permeate side to maintain the pressure at around 0 mbar which is measured by a vacuum meter (PI201). The vapour permeate is collected in a 250 ml round-bottom flask cold trap (A03) using liquid nitrogen. The glass cold trap is connected to the vacuum system with appropriate tubing (e.g. Tygon).

2.4 Pervaporation Experiments

2.4.1 *Membrane Installation*

The Sulzer PERVAP 2200 membranes were provided as a disk cut to the correct size (158 mm). Supported membranes prepared in this study were cut to size carefully using scissors. The membrane must be cut as close to the correct size as possible. If it is cut too large, wrinkles could develop which would cause a loss of selectivity. Also the O-ring could be pushed up, leading to a loss in vacuum pressure. If it is cut too small, a full vacuum would not be achieved due to leakage at the O-ring, which would again result in loss of selectivity. The membranes must be handled with gloves to avoid getting grease or dirt on the selective layer. The cold trap is first weighed prior to starting the vacuum system. It is then connected to the vacuum system. Valves H203 and H202 are closed and the vacuum pump is switched on. The vacuum meter should read 0 mbar if the pump is operating properly. Valve H201 is closed at the permeate side of the test cell and H202 is opened to check that the system is free of leakages. The vacuum meter should read 0–1 mbar. H104, H101 and H103 are opened prior to closing the cell to avoid back pressure. The cell is closed by lifting the lower part housing the membrane and inserting it into the upper part, the bolts are fixed and hand tightened. The vacuum pressure is observed at this stage also to ensure the O-ring is not displaced by the upper part of the cell. The feed tank is filled by ensuring H102 is closed and both H101 and H105 are open. A beaker is placed at the outlet of H105.



Key: A01, test cell; A02, cold trap; A03, cold trap; A04, retentate sampling coil; B01, double-jacketed closed feed tank; ELE., electronic stirrer; FI101, flowmeter; H03, heating bath; Hxxx, valves; M~, feed pump motor; M02, electric stirrer motor (heating unit); P01, feed pump; PI101, pressure gauge; PI201, vacuum meter; TI101, feed tank temperature indicator gauge; TIC301, temperature controller; V110, sampling valve; Y101, safety release valve; TI102, thermometer.

Figure 2.1. Schematic diagram of the Sulzer pervaporation unit.

The feed mixture to be tested (max. 2.5 L, min. 1.5 L) is poured slowly through a funnel into the feed tank. Air and any overfill will leave through venting valve H105. When filled, H101 and H105 are closed. The thermostat is filled with heat-carrier liquid (e.g. glycol) and the thermostat pump is started. The temperature is typically set 3–5°C higher than the target temperature.

2.4.2 Cold Trap Installation

The liquid nitrogen dewar is placed on a lowered laboratory jack and filled. The dewar is then raised until the cold trap is immersed about 2/3 in the liquid nitrogen. In operation, cotton wool can be placed around the cold trap to minimise evaporation.

2.4.3 Starting the Feed Pump

Before starting the feed pump, it is checked that feed sampling valve V110 is closed and H104 and H103 are half open. The feed pump is started and H104 and H103 are adjusted together so that the flow rate reading on flowmeter FI101 is in the target range (typically 75–85 L/hr).

2.4.4 Collecting Samples

In our experiments the cold trap consists of two pieces, a 250 ml round-bottom flask and a cold finger connection which fits into the flask. As permeate ice can form in the finger itself, the entire trap is weighed and removed when permeate sampling rather than just the round-bottom flask.

To collect permeate, H201 is first closed, followed by H202. The vacuum is broken by slowly opening valve H203. The cold trap is removed and replaced with one of known weight and immersed again in the dewar. Cryogloves should be worn in the changeover. H203 is closed and H202 is opened. When full vacuum is achieved, H201 is opened and again full vacuum should be reached in seconds. The whole procedure should not last longer than a minute. The cold trap is sealed and the permeate is allowed to melt before composition measurement.

At any collection of permeate sample, a feed sample should also be taken. If the feed temperature is above atmospheric boiling temperature, a beaker of ice water should be placed around the spiral capillary of the feed sample needle valve V110. The valve is opened slowly and carefully, the first few millilitres are discarded (already present in the spiral capillary), followed by collecting 5–10 ml of the feed mixture.

2.4.5 Membrane Performance

By measuring the mass of the permeate and the composition of the permeate and retentate, the flux and separation factor can be calculated, which establish membrane performance (see the equations in Section 1.1).

The composition of the permeate and retentate are measured by density. A standard relationship exists between the weight per cent of the ethanol content in water and the density of the binary at 20°C (*Handbook of Chemistry and Physics* 64th edition). The density is measured using a Mettler-Toledo DE40 density meter, which has an accuracy of 0.0001 g/ml and a built-in thermostat. The minimum sample volume is 1.2 ml and the measurement time is about 50 seconds. Samples are measured in duplicate.

3 Results and Discussion

3.1 Unsupported Membranes

Although unsupported membranes are commonly used for laboratory studies they have a number of disadvantages for practical application. Firstly, it was not always possible to successfully cut a membrane in which vacuum is achieved, in particular with NaAlg due to its brittle nature. It was not possible to prepare a mixed matrix NaAlg membrane due to crinkling and curling. The PVA and NaAlg membranes prepared in this study could be used only once due to shrinkage and curling when the vacuum is released, and the membrane is removed from the cell after a pervaporation experiment.

3.1.1 Sodium Alginate

Unsupported NaAlg membranes were prepared according to the simple procedure of Shi et al. (1996). The membrane area in their membranes was 25 cm^2 as opposed to 177 cm^2 in our study. Figure 3.1 shows a photograph of the membrane after peeling from the glass plate. Table 3.1 compares flux and selectivity data under similar conditions from both studies. As shown, the results are similar, showing the high separation performance of NaAlg membranes. The difference may be accounted for by temperature, membrane thickness, source of NaAlg (Shi et al. used a mannuronic acid-rich polymer) and inherent pervaporation errors.

The flux and selectivity of the unsupported NaAlg membrane was measured over an eight-hour period.

Over this time period the water content in the feed was reduced from 78% to 86% as shown in Fig. 3.2(a). The water content in the permeate increased further to as high as 99.2% and remained consistently higher than 98% for the duration of the experiment, as shown in Fig. 3.2(b). The flux decreased over the eight hours as expected (Fig. 3.2(c)), due to the decreased water content in the feed (Kalyani et al., 2008). The significant loss of flux over time due to polymer-chain relaxation, a characteristic property of NaAlg, was not observed in this membrane (discussed later in Section 3.2.4.1).

Figure 3.1. Photograph of pristine unsupported sodium alginate (NaAlg) membrane.

3.1.2 Polyvinyl Alcohol

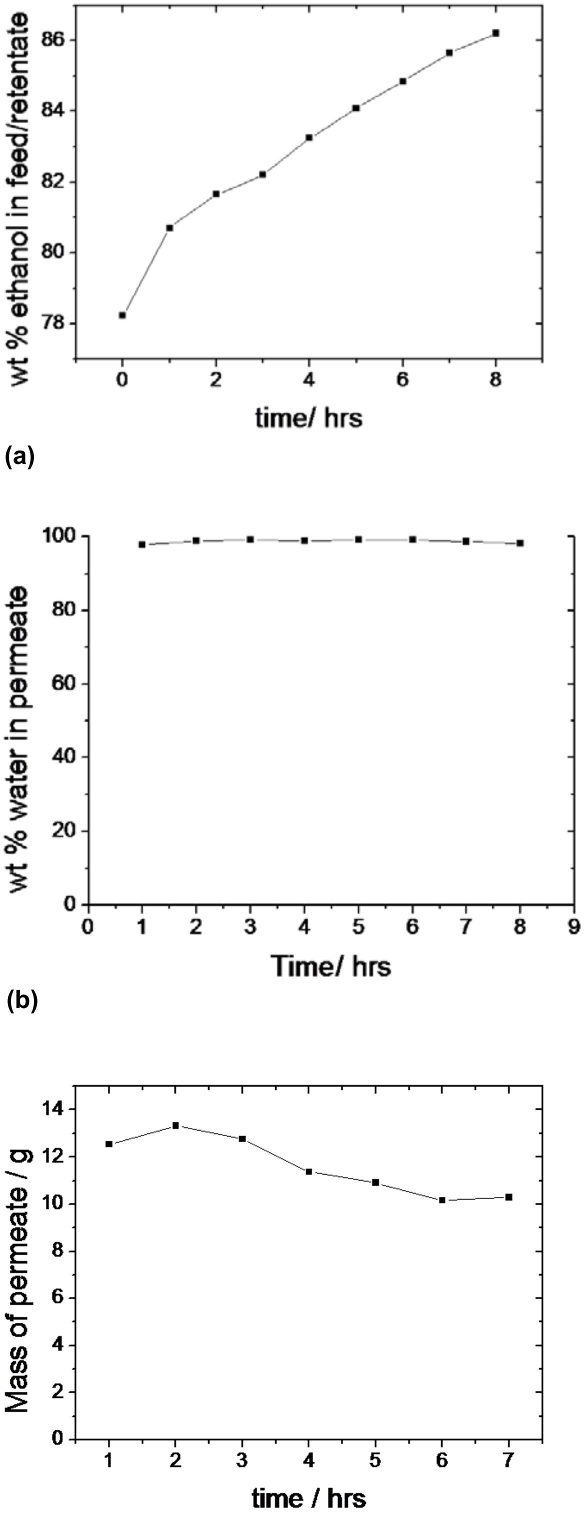
Unsupported PVA membranes were cast from a 10% wt/wt casting solution. Flux and selectivity data in comparison to NaAlg are shown in Table 3.1. As shown, the separation factor is low and for this reason cross-linking in typically employed (Chapman, 2008). In pristine form, the superiority of NaAlg is evident in this table.

3.1.3 Mixed Matrix PVA–Silica Membranes

Efforts to prepare unsupported mixed matrix membranes using mesoporous and zeolitic filler particles in a NaAlg polymeric matrix similar to Bhat et al. (2006) were

Table 3.1. Unsupported pristine membrane pervaporation data.

Membrane	T/°C	Flux (g/m^{2}hr)	EtOH wt% (feed)	EtOH wt% (permeate)	α
NaAlg (this study)	60	708	80.71	2.12	192
NaAlg (Shi et al., 1996)	70	703	80.00	0	∞
PVA (this study)	60	467	76.09	29.91	7.5



(a)

(b)

(c)

Figure 3.2. Pervaporation performance of unsupported sodium alginate (NaAlg) membrane over an eight-hour period.

unsuccessful as the membranes were too brittle. For this reason PVA was used as the polymeric matrix as it possesses a much greater strain at break (Russo et al., 2005). Three different porous silicas were used as filler particles: a commercial zeolite A, small-pore mesoporous microspheres and large-pore mesoporous microspheres. The porosity and particle size data of the mesoporous particles can be found elsewhere (Keane et al., 2009). Figure 3.3 shows an SEM image of the zeolitic sample. Flux and separation factor data using each mixed matrix membrane and the pristine PVA membrane are shown in Table 3.2.

The separation factor showed the expected trend according to the pore size of the SiO_2 filler. There was an increase in the separation factor from 7.5 to 21.4 in the zeolite membrane compared to the pristine PVA membrane. This is due to the efficient molecular sieving action of the zeolite particles as they possess pore diameters (~0.4 nm) intermediate between the approximate kinetic diameters of water (0.296 nm) and ethanol (0.43 nm) (Bowen et al., 2004). The flux remains about the same, thus utilising the applicability of mixed matrix zeolitic membranes (Bowen et al., 2004). When small-pore mesoporous silica particles are incorporated in the polymeric matrix, α is similar, although the flux is increased slightly due to the pore-flow separation mechanism. The α is not increased in the zeolitic membrane as there is no molecular sieving due to the larger pore size of the mesoporous particles (~2 nm). When large-pore (10–15 nm) mesoporous

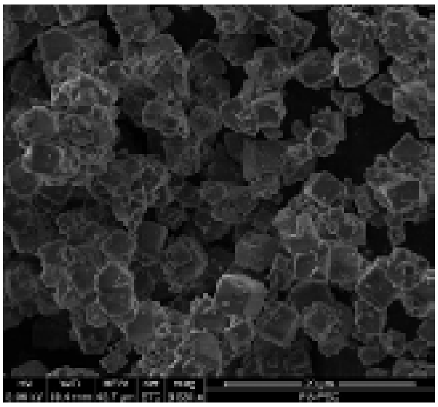


Figure 3.3. Scanning electron microscopy (SEM) image of zeolite 4A particles.

Table 3.2. Unsupported polyvinyl alcohol (PVA) and mixed matrix polyvinyl alcohol–silica (PVA–SiO_2) membranes.

Membrane	T/°C	Flux (g/m²hr)	EtOH wt% (feed)	EtOH wt% (permeate)	α
PVA	60	467	76.09	29.91	7.5
PVA–zeolite	60	487	75.23	12.45	21.4
PVA–M41S (small)	60	591	76.84	27.83	8.6
PVA–M41S (large)	60	832	76.38	41.93	4.5

particles are incorporated there is a significant decrease in *α* and an increase in flux due to greater transport of ethanol molecules through the larger pores. The increase in both *α* and *J* observed by Bhat et al. (2006) using mesoporous silica was not observed in the current study, although this may be explained by a number of differences in the membranes. Bhat et al. (2006) were dewatering the isopropanol binary using cross-linked NaAlg membranes, which already showed a high *α*. Furthermore, the mesoporous silica particles had a different synthesis history (acid catalysed, sodium silicate precursor), which is well known to result in a different final porosity (pore size, size distribution, structural order) and particle size (Barton et al., 1999).

3.1.4 PVA–NaAlg Blend

Unsupported PVA–NaAlg blend membranes were prepared for the purpose of improving the flexibility of the membrane whilst utilising the separation properties of NaAlg. *J* and *α* data (Table 3.3) show that the selectivity of NaAlg is utilised. Figure 3.4 shows a photograph of an unsupported pristine NaAlg and the NaAlg–PVA blend after a pervaporation experiment. The blend does not crinkle, curl or shrink to the same degree as the pristine NaAlg, due to the plasticising effect of PVA. The effect of plasticisation can be measured by tensile testing (Young's moduli and stress–strain). Russo et al. (2005) have carried out tensile tests on the effect of PVA and glycerol as plasticisers on NaAlg films, as discussed in the Introduction.

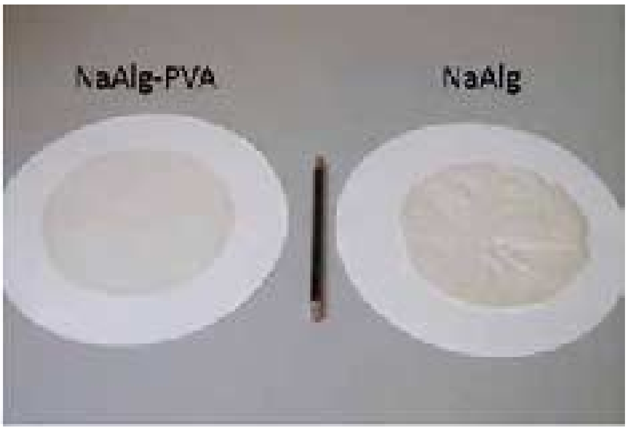


Figure 3.4. Photograph of unsupported sodium alginate–polyvinyl alcohol (NaAlg–PVA) blend and NaAlg.

3.2 Supported Membranes

Supported membranes were successfully prepared in a method similar to that of Huang et al. (2006), as described in Section 2.2.2. Figure 3.5 shows a cross-sectional SEM image of a typical supported membrane with three layers: (1) non-woven fabric backing layer, (2) PAN microporous support layer, and (3) selective skin layer.

The method of preparation of the PAN support layer also incorporated procedures of Hirata et al. (1992). The non-woven fabric is first saturated with DMSO solvent. The purpose of this is to keep the fabric flat on the glass plate but this may also allow the PAN to penetrate further into the fabric layer. Figure 3.6 shows a SEM image of the PAN layer peeling from the fabric support.

Table 3.3. Pervaporation results for unsupported sodium alginate–polyvinyl alcohol (NaAlg–PVA) blend membrane.

Membrane	T/°C	Flux (g/m²hr)	EtOH wt% (feed)	EtOH wt% (permeate)	α
PVA–NaAlg blend	60	783	76.79	0.12	2753

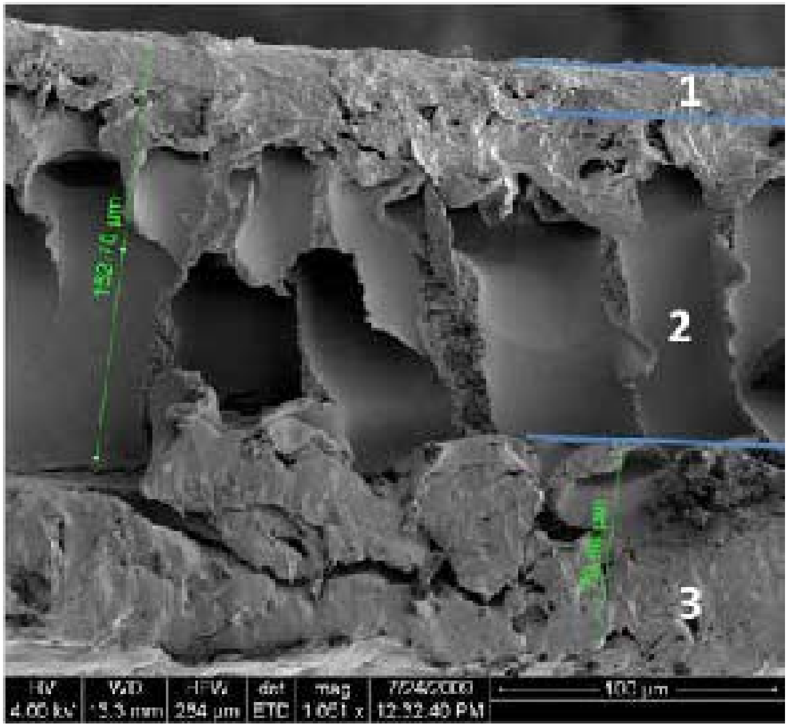


Figure 3.5. Cross-sectional scanning electron microscopy (SEM) showing the three layers of the composite supported membrane.

The PAN supports are pore-flow microporous membranes formed by phase inversion of the DMSO solvent into water. Figure 3.7 shows cross-sectional SEM images of the formed pores. The membrane consists of two types of pore: large ~50 µm pores and smaller pores ranging from about 0.1–1 µm. It is these smaller pores that do not permit the cast selective layer solution to pass due to surface tension.

It has been shown that the microporous support can influence pervaporation performance. Shi et al. (1998) and Wang (2000) have both demonstrated that hydrolysing the PAN support (converting cyano groups to carboxyl groups) can influence *J* and *α*. Wang has also discussed the effect of the porosity of the support layer on *J* and *α*. If the pore diameter is large enough (such as the large pores in Fig. 3.7) the selective skin layer can

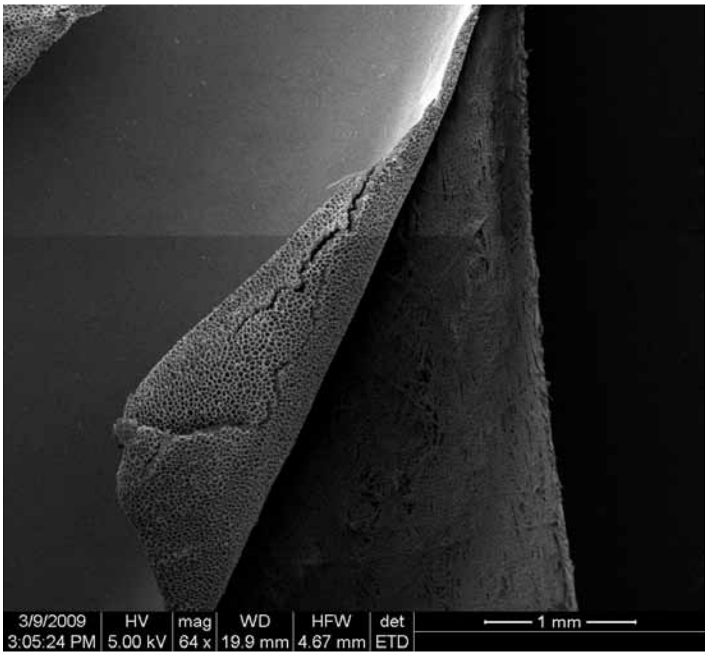


Figure 3.6. Polyacryonitrile (PAN) layer on non-woven fabric support.

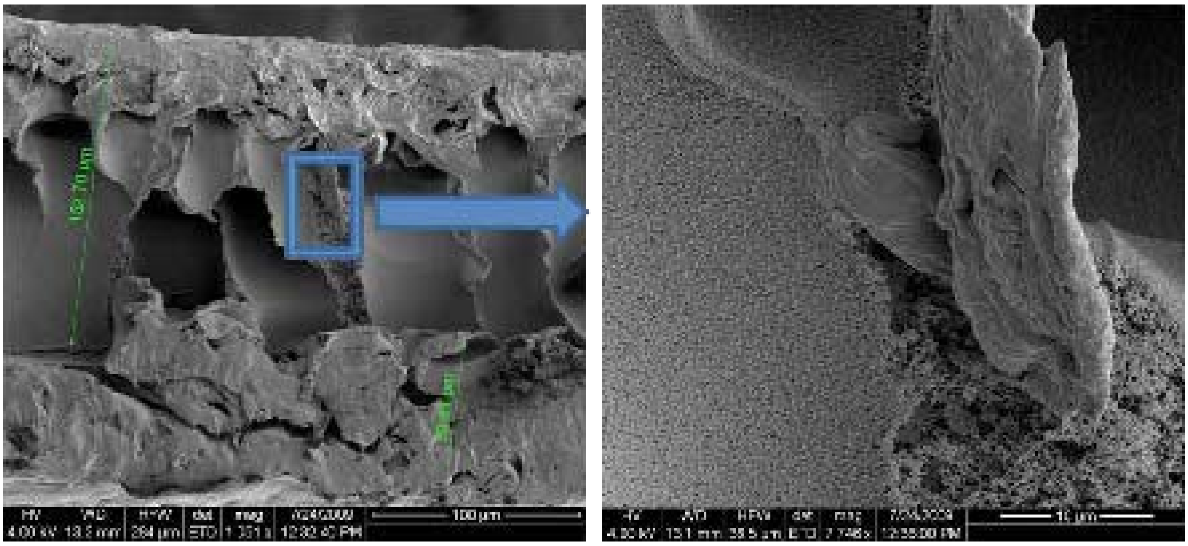


Figure 3.7. Cross-sectional image showing pore sizes of polyacrylonitrile (PAN) layer.

penetrate further into the pores, resulting in regions of greater thickness that would increase *α* and decrease *J*.

Initially the PAN was cast using a 150 µm casting rod similar to Huang et al. (2006). In this study, however, the supports at this thickness were found to curl and crack. When cast using the 40 µm rod the membranes did not curl as much, were easier to handle and remained functional as pervaporation membrane supports.

3.2.1 PVA

First, attempts were made to reproduce the cross-linked supported PVA membranes reported by Huang et al. (2006) using similar chemicals, materials and instrumentation. Although the same bench-top Sulzer pervaporator was used, the cell housing the membrane was smaller in their study. They used a membrane area of 15.2 cm^2 as opposed to the standard 177 cm^2 used in this study. Attempts to achieve the high flux and selectivity reported in this paper were unsuccessful. Table 3.4 shows *α* and *J* data from their study and the best-performing equivalent from the current study. The membranes had a lower separation factor but larger flux. Subtle differences in the membrane preparation and source of PVA (different degree of hydrolysis) may have contributed to this. We found the reproducibility and degree of cross-linking difficult to control. For this reason, when porous silica particles were incorporated into these membranes the results were for the most part inconclusive.

3.2.2 Sodium Alginate

Supported pristine NaAlg membranes could not be cast successfully as a functional pervaporation membrane. Typically full vacuum was not achieved due to leaks which would have been caused by cracks in the membrane due to the brittle nature of NaAlg. Even when vacuum was achieved, a poor selectivity uncharacteristic of NaAlg was often observed. The pervaporator manual suggests that mechanical damage or 'wrinkles' in the membrane could be a source of poor selectivity. If the selective layer is too brittle, excessive curling or wrinkling may cause microscale cracks (see Fig. 3.8) not visible to the naked eye and may not influence the vacuum significantly but would result in a loss of selectivity.

Table 3.4. Pervaporation results for supported cross-linked polyvinyl alcohol (PVA) membranes.

Membrane	T/°C	Flux (g/m^{2}hr)	EtOH wt% (feed)	EtOH wt% (permeate)	*α*
PVA (this study)	60	1051	77.00	8.04	38
PVA (Huang et al.)	60	538	76.41	0.49	658

Table 3.5. Pervaporation results for supported and unsupported sodium alginate–polyvinyl alcohol (NaAlg–PVA) blend membranes.

Membrane	T/°C	Flux (g/m²hr)	EtOH wt% (feed)	EtOH wt% (permeate)	α
Unsupported blend	60	783	76.79	0.12	2753
Supported blend	60	1331	78.80	1.56	235

3.2.3 NaAlg–PVA Blend

Following the encouraging effects of blending PVA with NaAlg on the flexibility of the unsupported membrane and the good separation performance (Section 3.1.4), a supported membrane with the same selective layer composition was prepared. *J* and *α* data of the supported membrane in comparison to the unsupported form are shown in Table 3.5. As shown, the supported membrane resulted in a greater flux but reduced separation factor, which is expected due to the thinner selective layer. The supported membrane is superior, however, as the selectivity remains very high (>98% H_2O in permeate) due to the presence of NaAlg, and the flux is significantly greater. Furthermore the supported membrane could be reused.

Despite greater flexibility, the NaAlg–PVA blend was not sufficiently flexible as a polymeric matrix to prepare mixed matrix membranes consistently. Although functional pervaporation mixed matrix membranes in supported form could be prepared, the aforementioned problems with leaks and loss of selectivity (Section 3.2.2) were observed. Similar to pristine NaAlg, this made the blend unsuitable for systematic studies on the effect of filler particle porosity. Figure 3.8 shows an SEM image of a cut supported NaAlg–PVA blend membrane in which small microcracks are observed.

3.2.4 NaAlg–PVA–Glycerol Blend

To increase the flexibility of the membranes for pervaporation application, the plasticiser glycerol was added to NaAlg and also the NaAlg–PVA blend. Before casting the glycerol blends on the supports, initial trials were conducted to investigate the flexibility and drying behaviour of the blends. The polymers were dissolved in water at a small scale and varying amounts of glycerol were added and mixed before dropping on a glass slide and allowing to dry in an oven. Although these tests are simple and rather crude they are useful due to the 'black art' nature of membrane preparation (Baker, 2004), and save time by optimising the weight ratio prior to casting on the larger scale in supported form which

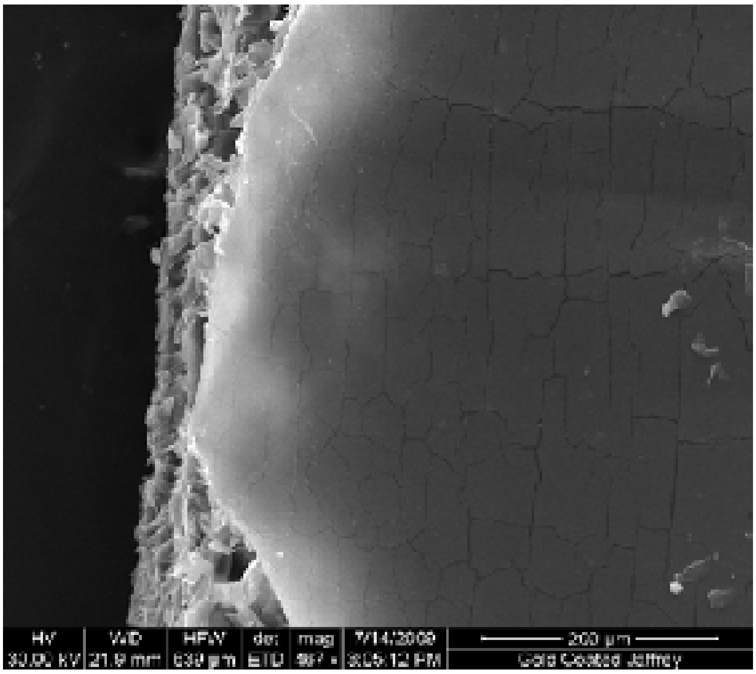


Figure 3.8. Scanning electron microscopy (SEM) image of micron-scale cracks in a cut supported sodium alginate–polyvinyl alcohol (NaAlg–PVA) membrane.

takes 24 hours. The flexibility of the dried membranes could be tested (by hand) as glycerol has a significant effect (Russo et al., 2005). It can also be checked whether the films dried, which is not the case with larger glycerol content due to its high boiling point (182°C). Furthermore, the blend films could be examined under an optical microscope for phase separation.

3.2.4.1 NaAlg–Glycerol

When glycerol is added to NaAlg prior to casting, a functional supported membrane could be prepared due to the increased flexibility of the selective layer. J and α data of a three-hour pervaporation experiment are shown in Table 3.6.

The membrane shows the high separation factor characteristic of NaAlg over the three hours. However, there is a significant loss of flux after each hour. This is due to polymer-chain relaxation, another property of NaAlg pervaporation membranes first identified by Yeom et al. (1996). They stated that glassy polymers have a rigid structure that tends to be stressed or relaxed depending on their thermal condition. When a polymer in a rubbery state is cooled, its molecular mobility decreases. At the glass transition temperature, T_g, the structural changes needed to maintain equilibrium cannot occur in the timescale of cooling and, instead, stress is created in the material, which becomes a thermodynamically unstable glass (hence 'glass transition temperature'). Since a glass is not in a state of thermodynamic equilibrium, its physical and mechanical properties change with time as the material attempts to achieve equilibrium through changes in its molecular configuration, which can induce the release of the formed stress. In the relaxation process, equilibrium is approached asymptotically. This relaxation process can make the membrane structure denser by the configurational rearrangement of polymeric chains so that the flux can be decreased.

However, this theory does not seem to hold for the unsupported membrane described in Section 3.1.1. A membrane under pervaporation conditions experiences a change in state across the membrane; from the feed side to the permeate side. The solubility of a permeant is at its maximum at the feed side and decreases across the membrane to zero at the permeate side. The more permeant absorbed in the membrane the greater the plasticisation effect exerted on the polymer-chain mobility, resulting in the T_g being reduced. It follows that there is a change in state across the membrane, ranging from a rubbery state at the feed side to a glassy state at the permeate side. This means that there is also a change in Young's modulus across the membrane; this ranges from extremely low on the rubbery feed side, meaning that the relaxation process outlined above would occur almost instantly, to extremely high on the glassy permeate side, where relaxation would occur over an almost infinite period due to the lack of mobility of the side groups of the polymer chains.

The most overt difference between the unsupported and supported membranes described above is the thickness. The selective layer of the unsupported membrane is extremely thick relative to that of the supported membrane. This would mean that while the feed side of the membrane would reach equilibrium with the permeate instantly and attain its rubbery state as with the unsupported, a greater percentage of the membrane remains glassy than in the supported membrane. Thus, the portion of the membrane that undergoes a relaxation process resulting in a loss of flux is a smaller percentage of the overall membrane than it would be in the thinner supported membrane. This means the effect is outweighed by the swelling that occurs throughout the membrane over a faster timescale, increasing the overall flux.

Despite, the loss of flux after three hours, it still remained much larger than the unsupported membrane (Figs 3.9 and 3.10). Further studies over a larger timescale would be needed to establish the extent of chain relaxation and the time needed for equilibrium. However, as this phenomenon is undesirable for pervaporation application, blending with PVA (Yeom and Lee, 1998a)

Table 3.6. Pervaporation results for a supported sodium alginate (NaAlg) membrane.

Time/hr	T/°C	Flux (g/m²hr)	EtOH wt% (feed)	EtOH wt% (permeate)	α
1	60	2197	76.18	0.80	397
2	60	1871	77.94	0.70	502
3	60	1467	79.46	0.54	712

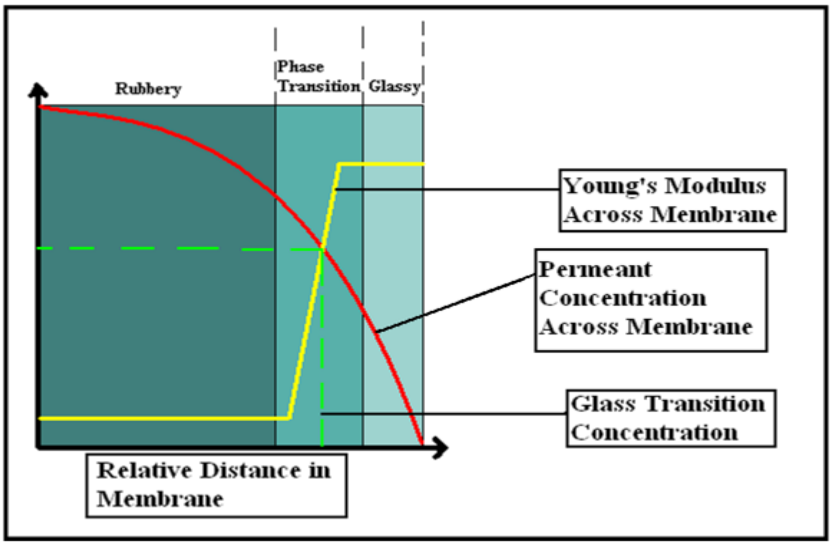


Figure 3.9. Transitions across supported (thin) membrane.

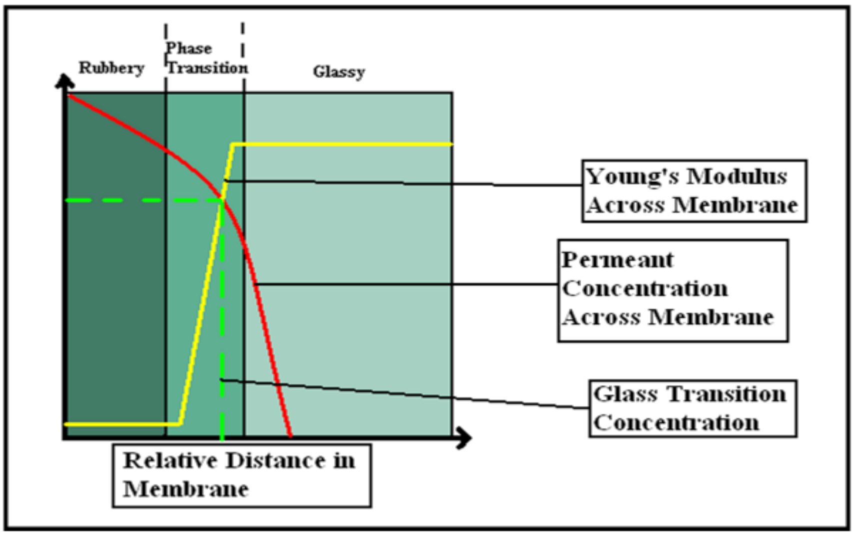


Figure 3.10. Transitions across unsupported (thick) membrane.

and/or various cross-linking treatments (Shi et al., 1998; Kalyani et al., 2008) would prevent its occurrence albeit with a slight loss in separation performance.

3.2.4.2 NaAlg–PVA–Glycerol

A 1:1 PVA–NaAlg blend when cast on a glass slide and dried at 40˚C was too brittle to be peeled from the glass. When viewed under an optical microscope, phase separation is clearly visible, with large spherical globules of PVA dispersed throughout the NaAlg layer (Fig. 3.11). This was also found by Yeom et al. (1998a) and they could not continue pervaporation experiments with a membrane of this composition. In fact, Yeom et al. observed phase separation in all blend membranes by SEM.

Figure 3.11. Optical microscope image of 1:1 sodium alginate–polyvinyl alcohol (NaAlg–PVA) blend film.

When supported, however, we found that a leak-free functional membrane could be prepared; the pervaporation performance is shown in Table 3.7. When glycerol is added a homogeneous layer is formed and no phase separation is observed (Fig. 3.12). The membrane was ductile and could be peeled from the glass plate.

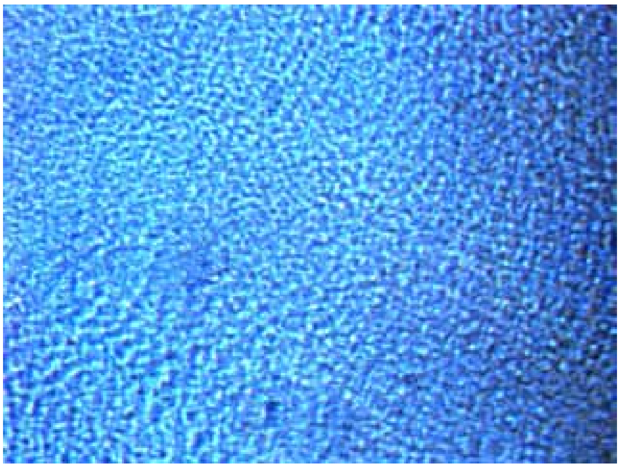


Figure 3.12. Optical microscope image of a sodium alginate–polyvinylalcohol–glycerol (NaAlg–PVA–glycerol) blend film.

Glycerol plasticised blend membranes were then prepared to investigate the effect of glycerol content on pervaporation performance. *J* and *α* data of these blends are shown in Table 3.7. The presence of glycerol increased *α* in the blend membranes due to its plasticising effect, resulting in greater miscibility between the two polymers. When there is no glycerol present, *α* is reduced due to permeation through the less selective PVA globules, visible in Fig. 3.11. The *J* was comparable in all membranes. Experiments over time were not conducted to investigate the loss of flux due to chain relaxation. The short-chain polymer, PVA, would be expected to reduce chain relaxation (Yeom and Lee, 1998a), however, the presence of the plasticiser glycerol could serve to negate this effect. The optimum glycerol–water ratio was 90:5 in this investigation, which resulted in the highest separation factor. Above 80:10 the membrane did not dry completely.

The glycerol plasticised membrane was also compared to Sulzer PERVAP 2200 under conditions used to install the pervaporator (80°C, 90–95% ethanol feed). *J* and *α* data of these membranes are shown in Tables 3.8 and 3.9. The experiment was run over two hours to allow the feed to reach test temperature and to allow for conditioning. In this respect the data from the second hour is more accurate. The typical test performance for PERVAP 2200 under the above conditions is ~450 g/m^{2}hr with less than 5% ethanol in the permeate. Table 3.8 shows that the pervaporator and membrane class PERVAP 2200 is performing according to the manufacturer's specifications. There is an increase in *J* and *α* from the first hour to the second, indicating that there was conditioning of the membrane. The NaAlg–PVA blend had a larger *J* and a decreased *α* over the two hours. As observed previously, the NaAlg membranes do not require a conditioning period. It should be noted that this blend did not contain the optimum amount of glycerol and that the *α* could potentially be further improved.

Table 3.7. Pervaporation results for a supported sodium alginate–polyvinylalcohol–glycerol (NaAlg–PVA–glycerol) blend membrane.

Glycerol wt%	T/°C	Flux (g/m^{2}hr)	EtOH wt% (feed)	EtOH wt% (permeate)	α
0	60	1784	76.51	6.33	48
2.5	60	1458	77.49	2.40	140
5	60	1961	76.96	1.84	178
10	60	1828	77.37	3.73	88

Table 3.8. Pervaporation results for a supported Sulzer PERVAP 2200 membrane.

Time	Mass/g	Flux (g/m^{2}hr)	EtOH wt% (feed)	EtOH wt% (permeate)	α
1	5.718	323	90.36	3.26	278
2	9.263	523	90.85	1.89	515

Table 3.9. Pervaporation results for a supported sodium alginate–polyvinylalcohol–glycerol (NaAlg–PVA–glycerol) blend.

Time	Mass/g	Flux (g/m^{2}hr)	EtOH wt% (feed)	EtOH wt% (permeate)	α
1	12.084	683	90.25	6.65	130
2	12.076	682	90.85	4.70	201

3.3 Alternative Membrane Configurations

Investigations were made into alternative membrane configurations for pervaporation as outlined in Section 1.5. All experiments, however, proved unsuccessful when using the Sulzer pervaporation unit. When membranes were inverted a full vacuum was not achieved, suggesting leaks are unavoidable when the selective layer is not in contact with the O-ring. When the round-bottom flask is immersed in liquid nitrogen a vacuum is achievable and a pervaporation experiment can be carried out. The flux and selectivity are, however, extremely low. Similar results are obtained when one membrane is placed on top of another. Using PVA as a protective coating on top of a NaAlg layer was also unsuccessful as the PVA layer peeled off after the experiment.

4 Conclusions and Future Work

- A Sulzer bench-top pervaporator was installed and a method was developed for simple ethanol–water composition measurements (density). Materials, chemicals and an automated coating machine were purchased to prepare supported polymeric pervaporation membranes. In this respect all necessary equipment and materials are present for future pervaporation membrane research.
- Polyvinyl alcohol, NaAlg, polymeric blends and mixed matrix membranes in supported and unsupported form were prepared. Unsupported pristine NaAlg membranes showed greater flux and selectivity in comparison to PVA. Sodium alginate membranes were, however, brittle and an unsuitable polymer for mixed matrix membranes. Due to the greater flexibility of PVA, mixed matrix membranes were successfully prepared. Zeolite 4A showed an increase in separation factor and a slight increase in flux. Mesoporous silica particles showed a comparable separation factor with an increase in flux. Large-pore silica particles showed a decrease in separation factor and an increase in flux.
- Cross-linked PVA membranes were prepared according to Huang et al. (2006) but the high flux and separation factor reported could not be reproduced. This study found the degree of cross-linking difficult to control, which led to inconclusive data with regard to the mixed matrix membranes.
- NaAlg was found to be too brittle as a membrane or film to prepare in supported form. Functional supported pervaporation membranes could be formed by the addition of PVA or glycerol as plasticisers. The supported membranes showed greater flux than the unsupported membranes due to the reduced thickness of the selective layer. Glycerol plasticised supported NaAlg membranes showed a significant decline in flux over time due to polymer-chain relaxation, a characteristic property of NaAlg membranes. Interestingly the unsupported NaAlg membranes did not show this decline in flux, which is discussed in terms of transitions in state across both thick and thin pervaporation membranes.
- By adding glycerol to the NaAlg–PVA blend the miscibility of the blend increased, resulting in homogeneous films and membranes that can otherwise phase separate. This increase in miscibility resulted in an increase in separation factor in pervaporation, highlighting the applicability of glycerol as a plasticiser. Furthermore the flexibility of the membrane is increased.
- The NaAlg blend membranes show greater flux and slightly lower separation factor in comparison to Sulzer PERVAP 2200 membranes under standard conditions. By optimising the NaAlg–PVA–glycerol blend ratio, the separation factor could be further improved by utilising the known super-selective properties of NaAlg.
- The problem of NaAlg chain relaxation in pervaporation and stability in aqueous environments has not been addressed in this study. These issues can be overcome by a cross-linking treatment with agents such as glutaraldehyde or exchange of sodium ions with calcium ions. Such modifications should be the focus of future research on alginate-based pervaporation membranes. The insertion of novel filler particles into the polymeric matrix or the preparation of molecular hybrid membranes should also be considered for future projects.
- A static pervaporation test cell with smaller diameter could be used for expensive or difficult to prepare membranes such as zeolite, mesoporous silica and certain polymers. A smaller test cell could be fitted to the Sulzer pervaporation unit. In this case gas chromatography or refractive index measurements may be necessary to measure the smaller quantity of permeate.
- Alternative membrane configurations such as inverting the membrane so that the selective layer faced the permeate proved unsuccessful (very low flux and selectivity) due to loss of vacuum.

Acronyms and Annotations

AAO	Anodic aluminium oxide
CIT	Cork Institute of Technology
DMSO	Dimethyl sulphoxide
NaAlg	Sodium alginate
INCMT	Irish National Centre for Membrane Technology
PAN	Polyacrylonitrile
POSS	Polyhedral oligomeric silsesquioxane
PVA	Polyvinyl alcohol
SEM	Scanning electron microscopy
SS	Silsesquioxane
VOC	Volatile organic compound

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An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomh-nithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil agus Rialtais Áitiúil a dhéanann urraíocht uirthi.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail.
- Scardadh dramhuisce

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce.
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.

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