Characteristics of water and salt transport, free volume and their relationship with the functional groups of novel cellulose esters

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ARTICLE INFO

ABSTRACT

Fundamental transport properties including salt and water partition coefficients, permeability and diffusivity of various newly synthesized cellulose esters were evaluated in this study in order to investigate the relationship among them as a function of molecular structure. Dense flat cellulose ester films were prepared and studied so that the influence of membrane fabrication, morphology and processing history on transport properties can be minimized. Positron annihilation lifetime spectroscopy (PALS) was employed to characterize the free volume of these cellulose esters. It was found that the transport and free volume properties can be correlated with the functional groups and their content in cellulose esters. High hydroxyl content leads to a high hydrophilicity hence resulting in a high water and salt partition coefficient. Hydrophilic cellulose esters suffer from low water/salt selectivity. On the other hand, an increase in bulky and hydrophobic propionyl or butyryl groups generally enhances cellulose esters' selectivity but brings down the permeability. However, a very high content of bulky functional group causes a drop in selectivity due to poor chain packing and the enlarged free volume as confirmed by PALS. Experimental results suggest that cellulose esters with moderate content of both hydroxyl and bulky side groups have the best diffusivity selectivity and may be suitable as membrane materials for salty water separation. An upper bound relationship between solubility selectivity and water partition coefficient was also observed in these cellulose esters as suggested in previous literature for other polymers.

1. Introduction

Cellulose esters have been one of the most studied materials for reverse osmosis (RO) and forward osmosis (FO) membranes in the membrane history [1–6]. Since the invention of non-solvent induced phase-inversion asymmetric membranes made of cellulose acetate (CA) [1,2], membrane technologies have gained much attention as less energy is consumed comparing to conventional thermal distillation processes for water reuse and desalination [3]. CA gains further attention due to the recent surge in FO research and development that aim to compete or replace RO for water production [7–18]. Among many cellulose esters, CA received most attention as an FO membrane material because of its availability, low cost, high hydrophilicity, easy fabrication and superior chlorine resistance. However, CA has problems such as intolerance to harsh pH environments which leads to hydrolyzation and vulnerability

towards biodegradation [3,4,7–9]. Therefore, cellulose triacetate (CTA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) FO membranes with better stability have been fabricated and studied [6,19–23]. Interestingly, distinctive FO performance in terms of water flux and salt rejection has been reported for each of these cellulose esters where some showed higher water flux or salt rejection than the other. A slight deviation in the degree of substitution of functional groups in cellulose ester polymers may result in membranes with quite different FO performance [19–23]. This phenomenon may be attributed to the changes in hydrophilicity and fractional free volume (FFV) because different functional groups have different sizes and physicochemical properties. In addition, it has been observed that selectivity increases with increasing acetyl content due to the decrease in salt solubility and diffusivity [23]. However, no in-depth studies have been reported on the examination of the effect of different ester functional groups on water and salt transport properties across cellulose ester membranes at the molecular level yet.

In FO, movement of water molecules across the semi-permeable membrane is induced by the chemical potential difference of the two

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solutions contacting each side of the membrane. The solution possessing a higher osmotic pressure is considered as the draw solution because it accepts water transport from a water source having a lower osmotic pressure while the semi-permeable membrane is in charge of rejecting unwanted solutes. Similar to RO, the solution diffusion mechanism has been used to describe the water and solute transport in FO since a non-porous/dense selective layer is required for FO membranes [24–28]. According to the mechanism, water and solutes first dissolve into the surface of the selective layer, then diffuse across the polymer matrix along their concentration gradients, and lastly leave the polymer layer into the bulk permeate solution through desorption. Therefore, the characteristics of membrane's transport properties in terms of water flux and solute rejection are largely determined by the relative solubility and diffusivity of water and solutes in the polymer matrix.

Many factors such as material chemistry, hydrophilicity, charge and free volume determine the water and solute solubility and diffusivity in a polymer. Quantitatively, one has to measure the individual partition coefficient (i.e., solubility) and individual diffusivity of salt and water in order to predict the suitability of a membrane material for RO and FO applications [29–31]. However, the underlying science between water and salt solubility and diffusivity as well as between the microscopic free volume of cellulose esters and the polymer chemistry has to be explored in order to determine the best polymer chemistry for FO membranes [27,32,33]. Positron annihilation lifetime spectroscopy (PALS) is employed in this work for free volume evaluation.

PALS has been widely used as a probe for the measurements of free volume, size and distribution in polymers and polymeric membranes [27,34–40]. By analyzing the orthopositronium (o-Ps) lifetime and intensity in a material, one can translate the measured information into free volume size and intensity of the material. In order to obtain the inherent free volume and transport properties of cellulose esters, dense flat films were specially prepared in this study so that the influence of membrane fabrication, morphology and processing history on transport properties can be minimized. In other words, extensive studies have reported that the internal concentration polarization (ICP) plays a significant role on the FO performance of asymmetric membranes due to transport resistance in the supporting layer. As a result, the measured water flux deviates severely from the theoretical prediction [41–43]. Therefore, it would be difficult to accurately correlate the water and salt transport characteristics and the free volume properties to the different functional groups in cellulose esters based on the results from asymmetric membranes.

To our best knowledge, this is the first effort (1) that involves a systematic study of synthesized cellulose esters comprising various functional group such as hydroxyl (OH), acetyl (Ac), propionyl (Pr) and butyryl (Bu) with different content, (2) to measure their water uptake, salt partition coefficient, water and salt diffusivity, wet and dry free volume size and fractional free volume, and (3) to examine the relationship between physicochemical properties and transport properties of cellulose esters. In addition to identifying the optimal cellulose esters with high FO potential, this study may reveal the fundamental science to molecularly design advanced cellulose esters with suitable degrees of substitution and functional groups for various FO applications.

2. Experimental

2.1. Chemicals

11 Proprietary CAPs (CAP_A, CAP_C, CAP_D, CAP_E, CAP_F, CAP_I, CAP_K, CAP_L, CAP_O, CAP_P, CAP_Q) and 2 proprietary CABs (CAB_M, CAB_N) with different degrees of substitution (hereafter referred to as DS) of functional groups were synthesized by Eastman Chemical Company (USA). Their DS of different functional groups, densities and glass transition temperatures is summarized in Table 1. The polymer structure of cellulose ester is illustrated in Fig. 1. There are three sites available for functional group substitution on each cellulose ester repeating unit. Therefore, the maximum degree of substitution for a functional group on cellulose ester is three. These polymers were dried at 120 °C in a vacuum oven overnight prior to usage. Acetone ($\geq$99.5%), N,N-dimethyl formamide (DMF, $\geq$99.5%), ethanol ($\geq$99.5), NaCl ($\geq$99.5) and N-methyl-2-pyrrolidone (NMP, $\geq$99.5%) were purchased from Merck, Singapore. The deionized (DI) water used in experiments was produced by a Milli-Q unit (Millipore, USA) at a resistivity of 18 MΩ cm.

The density ρ of each cellulose ester was determined by a Mettler Toledo balance and a density kit according to the Archimedean principle by measuring the weights of a cellulose ester dense film in air (w_{air}) and ethanol liquid (w_{liq}) and using Eq. (1).

$$\rho = \frac{w_{air}}{w_{air} - w_{liq}} \rho_0 \tag{1}$$

where ρ_0 denotes the density of ethanol.

2.2. Dense film preparation

For better accuracy, thick films of 100–150 μm were used for PALS, water uptake and salt partition coefficient measurements. Except CAP_E and CAP_F which are insoluble in acetone, all other films were prepared by dissolving cellulose esters in acetone to form 5 wt% solutions. DMF was used for the preparation of CAP_E and CAP_F films. All polymer solutions were filtered through 5 μm syringe filters, cast into clean Petri dishes and then the Petri dishes were kept in ovens at 45 °C for 2 days for solvent evaporation to obtain the thick films. When DMF is used as the solvent, the oven temperature is set at 85 °C. The thick films were then further dried in vacuum ovens at 120 °C overnight.

Thin films of 15–20 μm were prepared for the measurements of water and salt permeability. All cellulose esters were dissolved in DMF at 10 wt% concentration. The polymer solutions were cast on clean glass plates using a 250 μm casting knife. The as-cast films with glass plates were placed in ovens at 80 °C overnight for solvent evaporation. Then thin cellulose ester films were peeled off from glass plates and placed into a vacuum oven at 80 °C with a heat-up rate of 12.5 °C/h until 120 °C. The films were then kept at 120 °C in the vacuum oven for overnight. Before characterizations, the thick and thin dense films were heated 20 °C above their respective T_g for 10 min and immediately quenched to room temperature. The thick films were used immediately for PALS, water uptake and salt

Table 1
Degrees of substitution (DS) of hydroxyl (OH), acetyl (Ac), propionyl (Pr) or butyryl (Bu) functional groups, glass transition temperatures (T_g) and densities of cellulose esters used in this study.

Polymer	DS(OH)	DS(Ac)	DS(Pr)	DS(Bu)	T_g (°C)	Density (g/cm^3)
CAP_A	0.82	1.64	0.54	–	187	1.31
CAP_C	0.89	1.00	1.11	–	176	1.31
CAP_D	1.14	0.87	0.99	–	173	1.30
CAP_E	1.29	1.22	0.48	–	178	1.30
CAP_F	1.30	1.51	0.19	–	180	1.29
CAP_I	0.63	1.68	0.69	–	186	1.30
CAP_K	0.65	0.65	1.69	–	169	1.28
CAP_L	0.84	0.62	1.54	–	174	1.29
CAP_O	1.10	1.31	0.59	–	187	1.28
CAP_P	0.35	1.31	1.34	–	162	1.27
CAP_Q	0.09	1.47	1.44	–	162	1.24
CAB_M	0.83	1.49	–	0.68	180	1.28
CAB_N	0.82	0.73	–	1.45	157	1.27