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The effect of aging on thermomechanical and metal extraction properties of poly (vinyl chloride)/Aliquat 336 polymer inclusion membranes

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ABSTRACT

The impact of aging PVC/Aliquat 336 polymer inclusion membranes (PIMs) on their thermomechanical properties and heavy metal extraction performance was investigated. The results show that freshly prepared PIMs contain residual tetrahydrofuran (THF) which was used as the solvent for membrane manufacture. Removal of some residual THF by membrane aging resulted in notable changes in the thermomechanical properties of the PIMs. By aging the membrane for 1 week at 40˚C, the glass transition increased from 42 to 55˚C. In addition, while the melting temperature (T_m) of the Aliquat 336 component could not be determined for freshly prepared PIMs, the aged membrane showed a clear T_m value of –19˚C. Metal extraction capacity was not affected by membrane aging.

Keywords: Polymer inclusion membrane (PIMs); Membrane aging; Metal extraction; Poly (vinyl chloride) (PVC); Aliquat 336

1. Introduction

Polymer inclusion membranes (PIMs) have emerged as a promising material for extracting metal ions from aqueous and solvent solutions. Compared to all other forms of liquid membranes, PIMs have superior mechanical and chemical stability properties, while their capacity for metal extraction is either slightly lower or similar [1]. PIMs can be formed from poly (vinyl chloride) (PVC) or cellulose triacetate (CTA) as a base polymer (which provides mechanical strength to the film), an extractant that acts as ion exchanger and a plasticizer [1].

Aliquat 336 is a good extractant for selective and efficient transport of numerous metal ions [2–7]. Aliquat 336, a commercial name for tricaprylmethylammonium chloride, is a quaternary ammonium salt which is insoluble in water. It is composed of a large quaternary ammonium cation associated with a chloride anion. Aliquat 336 is not only an anion extractant but can also function as a plasticizer for PVC. Our previous study [8] showed that Aliquat 336 addition to PVC could substantially reduce the modulus relative to that of a neat PVC solid film with the product being transparent flexible membranes. However, it was also shown that Aliquat 336 does not plasticize PVC by an increase of its segmental mobility, since

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the glass transition (T_g) of PVC-type PIMs is independent of Aliquat 336 content.

The preparation of PVC/Aliquat 336 PIMs involves the use of tetrahydrofuran (THF) as the casting solvent. After dissolving both PVC and Aliquat 336 into THF and casting the solution over a glass plate, THF is allowed to evaporate over 24–48 h forming flexible and transparent thin film PIMs. It is feasible that PIMs formed via this route contain some residual THF which can be reduced by membrane aging. However, it is unclear whether the presence of THF in PIMs affects their physical properties or metal extraction performance.

While the potential of PVC/Aliquat 336 PIMs has been widely demonstrated, no previous work has been conducted to study the process of membrane aging PIMs on the impact of membrane properties and extraction performance. This study aims to examine impact of membrane aging on polymeric properties and subsequently the extraction of Cd(II) as a representative heavy metal by PVC/Aliquat 336 PIMs. Changes in PIMs properties and chemical composition were also evaluated using dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Reagents

All reagents were obtained from Sigma-Aldrich, Australia. High molar mass PVC (M_w 80,000 g/mol) and Aliquat 336 were used as the base polymer and extractant, respectively. HPLC grade THF was used without further purification. Cadmium was used as a representative heavy metal. Cadmium is widely used in various applications such as nickel–cadmium batteries, metallurgy, pigmenting, and other industries. In fact, the extraction of cadmium from other metallic elements is the focus for many recent studies [2,3,9]. Being a heavy metal, cadmium is highly toxic. Thus, cadmium removal from industrial wastewater is also important in many industries [10]. Cd(II) solution used in the membrane extraction experiments and for calibration purposes was prepared from analytical grade $Cd(NO_3)_2$. Milli-Q grade water (Milipore, Australia) was used for the preparation of all aqueous solutions.

2.2. Preparation of PVC/Aliquat 336 PIMs

PVC/Aliquat 336 PIMs were prepared by dissolving 360 mg Aliquat 336 and 240 mg PVC in 5 mL of THF [8]. The mixture was stirred in a beaker vigorously for 1 h forming a clear solution. The solution was then poured into a 70-mm-diameter glass petri dish and covered with a filter paper (Advantec, Toyo. 0.45 μm). Petri dishes containing the solution are placed inside a fume extraction cupboard for 48 h at room temperature (~25˚C) where most of the THF evaporates PIMs are formed. The membranes were peeled from the petri dish and were immediately used for further experiments as freshly prepared PIMs. Membrane aging was simulated by placing freshly prepared PVC/Aliquat 336 PIMs in an enclosed oven at 40˚C for one week. Note that aging at temperatures higher than ~40˚C [11] is not feasible without PIMs composition modification due to oxidation of PVC as evidenced by discoloration [12].

2.3. FTIR analysis

FTIR analysis of freshly prepared and aged PVC/Aliquat 336 PIMs was conducted using an IRAffinity-1 (Shimadzu, Kyoto, Japan). The instrument was equipped with a diamond crystal. The measured spectrum was between 500 and 3,500 cm^{-1}.

2.4. Dynamic mechanical analysis

A Q800 dynamic mechanical analyser (TA Instrument, USA) was used to characterize the thermal transitions of the PVC/Aliquat 336 PIMs. A film clamp was used with a heating rate of 4˚C/min over the temperature range of −100 to 100˚C at a frequency of 1 Hz. The temperatures associated with transitions were identified by local maximums in the tan delta response. The thermal transitions are labeled chronologically from the highest to lowest temperature at which they occur.

2.5. Mass loss during aging

An initial weight of PVC/Aliquat 336 PIMs was measured immediately following PIMs formation (i.e. after 48 h of drying in a fume extraction cupboard), and a final weight of the membrane was measured after aging at 40˚C for one week. Both samples were measured without the petri dish. THF reduction as a percentage due to aging was determined by dividing the weight change due to aging into the initial weight.

2.6. Extraction protocol

Extraction experiments were conducted in bath mode at room temperature [5,6]. Each membrane was cut into small pieces and was placed in beakers containing 100 mL of extraction solution. The extraction solution contained 35 mg/L of Cd(II). The solution was continuously stirred, and 1-mL aliquots were taken at specific time intervals for analysis. Cd(II) concentrations were determined by atomic adsorption spectrometry analysis (Varian SpectrAA 300 AAS, Australia). Calibration using standard Cd(II) solutions was conducted prior to each batch of analysis. The linear regression coefficient for all calibration curves was greater than 0.98.

3. Results and discussion

3.1. Changes in membrane morphology and composition due to aging

Thin, flexible, and transparent PIMs were obtained from the casting method described in Section 2.2. No discernible changes in the appearance and morphology of PIMs before and after aging could be visually identified. The FTIR spectra of freshly prepared and aged PIMs are shown in Fig. 1. The peaks observed from the FTIR spectra of both freshly prepared and aged PIMs can be assigned to individual constituents of the membranes. No significant changes in peaks assigned to PVC or Aliquat 336 could be attributed to the aging process. Results reported in Fig. 1 also show that no chemical interaction has occurred during the membrane preparation process, and thus, only weak interaction between constituents such as van der Waals and hydrogen bonds exists.

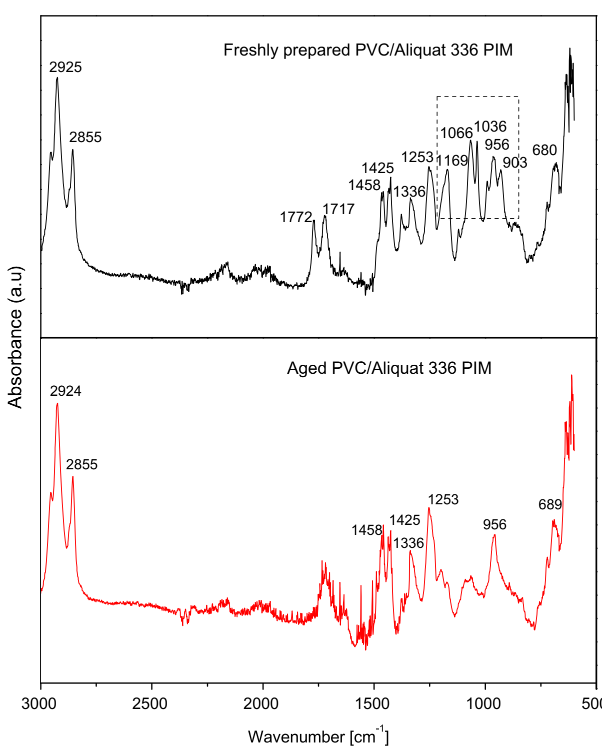

Fig. 1. FTIR spectra of freshly prepared and aged PVC/Aliquat 336 (60/40) PIMs.

PVC shows strong absorption bands at 2,924, 2,855, 1,772, 1,717, 1,458, 1,425, and 1,253 cm^{-1} [13–15] which can be attributed to the specific chemical groups such as carbon–hydrogen (C–H) bond, carbon–oxygen (C=O) bond, or carbon–chlorine (C–Cl) bond (Table 1). The spectra of Aliquat 336 show strong bands at 2,926, 2,871, and 2,855 cm^{-1} [13]. The spectra of the PVC also have absorption bands in this region but usually they are much less intense. FTIR of freshly prepared PIMs exhibited adsorption peaks in addition to those noted for PVC and Aliquat 336. Specifically, substantial adsorption peaks at 903, 1,036, 1,066, and 1,169 cm^{-1} which coincide with the THF coordinated bands [16]. The highest intensity adsorption bands of THF result from C–O–C stretching which generally appear as a strong bands at 1,071 and 909 cm^{-1} [16] consistent with the peaks observed at 1,066 and 903 cm^{-1} observed here. In this study, THF was used as a solvent for membrane preparation. Results shown in Fig. 1 indicate that THF was still present in freshly prepared PVC/Aliquat 336 PIMs. Furthermore, the THF component was significantly reduced by aging for one week at 40°C relative to that in freshly prepared PIMs.

3.2. Storage modulus and glass transition temperature

The storage modulus and the tan δ of freshly prepared and aged PVC/Aliquat 336 PIMs as a function of temperature are shown in Figs. 2 and 3, respectively. The freshly prepared PVC/Aliquat 336 PIMs have a broad α transition at 42°C, while the aged PVC/Aliquat 336 PIMs exhibit an α transition at 55°C and a β transition at −19°C. The α transitions are assigned to the glass transition (T_g) of PVC, since they coincide with the reduction of storage modulus from greater than 100 MPa to less than 10 MPa. On the other hand, the β transition is assigned to the melting temperature (T_m) of Aliquat 336 [8,17]. Note that the T_g of the freshly prepared PIMs was lower than the aged PIMs. In a previous study [8], we reported that the T_g of PVC cast from THF without Aliquat 336 is also lower than the T_g of neat PVC. It is likely that the T_g depression relative to that for neat PVC of all PIMs membranes observed here results from a small amount of residual THF in the PVC. For example, 1 wt.% residual THF is sufficient to achieve a depression of 4°C [18]. A T_g depressed below that for neat PVC is consistent for PVC cast from THF [19].

Table 1
Assignments of FTIR peaks

Constituent	Wavenumber (cm^{-1})	Chemical group	Reference
PVC	2,800–3,000	C–H	[13]
	1,717	C=O	[14]
	1,426	CH_2	[14]
	1,339	CH_2	[14]
	1,250	C–H near Cl.	[15]
	956	CH	[14]
	669	C–Cl.	[15]
Aliquat 336	2,926	C–H (CH_2)	[13]
	2,871	C–H (CH_3)	[13]
	2,856	C–H (CH_2)	[13]
THF	1,044, 1,118, 1,169, 1,250, 1,308, and 1,348	C–O–C	[16]
	840, 846, 922, 956, and 993	C–O–C	[16]

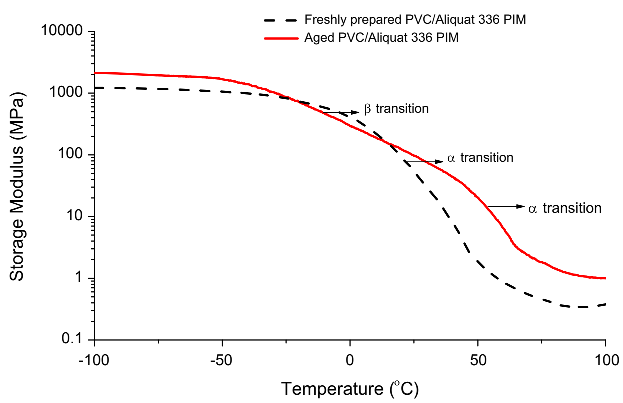

Fig. 2. Storage modulus curves of freshly prepared and aged PVC/Aliquat 336 PIMs.

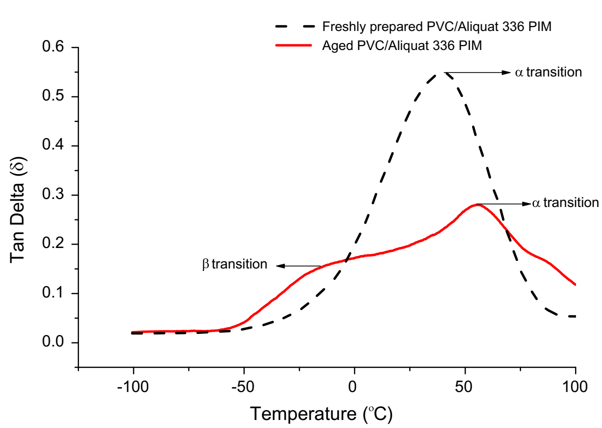

Fig. 3. Tan δ of freshly prepared and aged PVC/Aliquat 336 PIMs versus temperature.

The increase in T_g value of PIMs due to aging is most likely attributed to a decrease in the residual THF that was identified by FTIR. All polymer solvents will function as a plasticizer for the same polymer when the concentration is sufficiently low. The T_g of THF was predicted to be in the range from −158 to −143°C [20]. Application of the Fox equation predicts a reduction of THF in the PVC phase from 7 to 4 wt.% due to the aging process [21]. Similarly, interpolation of the experimental T_g measurements presented by Adachi and Ishida [18] for PVC–THF systems estimates a reduction in THF from 9 to 6 wt.% by aging. Indeed, the experimentally observed mass loss of PVC/Aliquat PIMs after the aging process was 10% (from an initial mass of 618 mg), which was slightly higher than that predicted by changes in the T_g.

The DMA results also indicate that aged PIMs exhibit a β transition, which can be assigned to the melting of Aliquat 336, whilst the freshly prepared PIMs do not. It is feasible that a residual amount of THF depresses the melting temperature of Aliquat 336 and hence prevents its detection. Note that the T_g of the freshly prepared PIMs is much higher than what it would be expected for an Aliquat 336–PVC solid solution. Hence, it is likely that the Aliquat 336 is phase separated from the PVC in both the freshly prepared and aged PIMs.

3.3. Extraction of cadmium

In general, the extraction of Cd(II) ions by Aliquat 336 is based on an ion exchange mechanism. Aliquat 336 reacts as an ion exchanger forming an ion pair with a metal anion complex from the aqueous solution. Consequently, in a chloride matrix, the availability of a metal chloride complex carrying one negative charge is crucial for the extraction of the metal ion to the membrane. However, Upitis et al. [3] suggested that only trichloro metal complexes could be extracted by PVC/Aliquat 336 PIMs. This hypothesis was supported by Adelung et al. [2] who predicted the distribution of metallic ions in 0.05, 0.1, and 3 M of NaCl solution using the ChemEQL (version 3.1) thermodynamic modeling software. They found that at below 0.1 M of chloride solution, the trichloro zinc complex does not exist, thus, the extraction of Zn(II) to PVC/Aliquat 336 PIMs could not occur. But as they increased the chloride solution to 3 M, the trichloro zinc complex was formed and significant extraction of Zn(II) was observed. Meanwhile, both trichloro and tetrachloro cadmium complexes exist over the same chloride concentration (0.05, 1, and 3 M) and the molar fraction of the trichloro cadmium complex increased dramatically as the chloride concentration increased [2]. Therefore, the extraction of Cd(II) to PVC/Aliquat 336 PIMs can be described as below:

$$CdCl_3^- + CH_3(C_8H_{17})_3N^+Cl^- \leftrightarrow CH_3(C_8H_{17})_3N^+CdCl_3^- + Cl^-$$

Fig. 4 shows the extraction kinetics of Cd(II) from 1 M HCl solution into aged and freshly prepared PVC/Aliquat 336 PIMs. There is no difference on the extraction rate between both membranes. After 5 h, more than 95% of Cd(II) was extracted by both PIMs indicating that aging process has not affected the membrane performance even though the membrane characteristics has somewhat changed.

As described in our previous study [8], the presence of an Aliquat 336 melting transition in the aged PIMs is consistent with a phase separated membrane mesostructure. Similar Cd(II) extraction profiles were observed here for both the freshly prepared and aged PIMs. The Aliquat 336:PVC weight ratio used here was 3:2, which is well above the threshold ratio of 3:7 [8] where Aliquat 336 far from the membrane surface starts to participate in the extraction process. The experimental design that Aliquat 336 far from the membrane surface participates in the extraction process is validated by the substantial extraction of Cd(II) ions observed. Furthermore, within experimental error, the same extraction profiles were observed for both aged and fresh PIMs. Hence, it is concluded that the access to the Aliquat 336 component is the same for each membrane which infers that the mesostructure of both the aged and fresh membranes is the same.

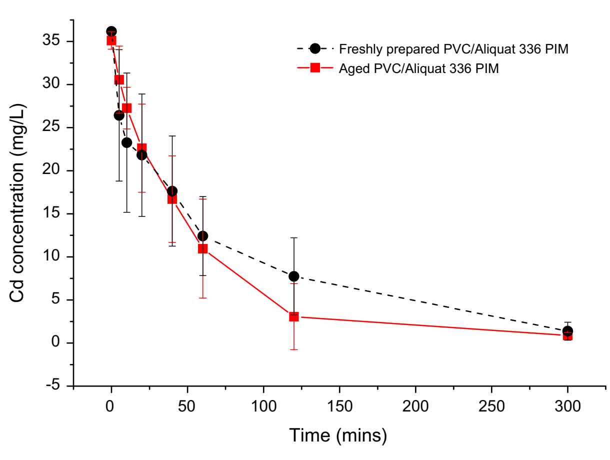

Fig. 4. The extraction of Cd(II) in 1-M HCl solution into freshly prepared and aged PVC/Aliquat 336 (60/40) PIMs. Error bars show the standard deviation of three replicate experiments.

4. Conclusion

In this study, the aging effects on the polymeric and metal extraction properties PVC/Aliquat 336 PIMs were investigated. Freshly prepared PVC/Aliquat 336 PIMs exhibit a single thermal transition within the temperature range of −100 to 100˚C formed. This transition was attributed to the glass transition of PVC with the melting transition of the Aliquat 336 masked by residual THF. However, after the aging process, THF residual has decreased and the PIMs exhibit two thermal transitions over the same temperature range. Although there is a clear impact of aging on membrane properties, there is no significant impact on the extraction of Cd(II) by PVC/Aliquat 336 PIMs.

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