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# Estimation of resistance of starch/polyvinyl alcohol blends to permeation by organic solvents

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ABSTRACT

The chemical resistance of chlorinated hydrocarbons in starch/polyvinyl alcohol (PVA) blends has been investigated using a permeation cell with an in-cell solid phase microextraction (SPME) sampling device. The chlorinated hydrocarbon with a large molecule size or lower polarity was found to be less permeable through the starch/PVA blends. The tensile strength and chemical resistance of chlorinated hydrocarbons decreased with an increase in the starch content of blends. For the starch/PVA blends, the solubility of chlorinated hydrocarbons was inversely proportional to their molecular weight, molar volume and $\log K_{ow}$. The diffusion coefficients and solubility of permeants were proportional to the content of starch in the starch/PVA blends. It is plausible that the blends will be inclined to the starch characteristics as the plasticizer (i.e. glycerin) disrupts the rigidity arrangements of the starch and PVA. The present work provides information on the extent of organic compound permeation through starch/PVA blends for the practical application.

## 1. Introduction

Most synthetic polymers are difficult to degrade in a natural environment and may contribute to severe pollution. In the past few years, attempts have been made to solve these problems in the development of biodegradable polymers. Griffin (1974) proposed a method to increase the biodegradability of plastics by blending. Several researchers have focused on the production of starch-based polymers in which starch is blended with biodegradable synthetic polymers such as polyvinyl alcohol (PVA) and polylactide (PLA) (Imam, Cinelli, Gordon, & Chiellini, 2005; Park & Im, 2000; Zhao et al., 2006).

PVA is a water soluble polymer with excellent properties, such as low permeability and high water absorption capability. The PVA film has been used in a wide range of industrial and agricultural applications. However, PVA is relatively expensive and has a low biodegradation rate (Mao, Imam, Gordon, Cinelli, & Chiellini, 2000). Starch is a cheap and fully biodegradable polymer. A small amount of starch (6–30%) is blended with PVA to reduce the cost and enhance the biodegradability of PVA (Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004; Tang & Alavi, 2011).

Starch lacks the physico-mechanical characteristics of traditional plastics such as strength, water resistibility, processability and thermal stability (Tang & Alavi, 2011). In addition, the starch/PVA blends are compounded using a number of plasticizers, e.g. water and glycerol, to increase their flexibility and workability (Chai, Chow, Chen, Chuang, & Lu, 2009; Liu, Feng, & Yi, 1999). Several studies have been conducted to understand the biodegradability, processability and mechanical properties of starch/PVA blends (Mao et al., 2000; Tudorachi, Cascaval, Rusu, & Pruteanu, 2000; Zhao et al., 2006). Although PVA exhibits chemical resistance to solvent, oil and grease, it is doubtful that the blending of starch to PVA with the plasticizer, glycerin, may result in a degradation of chemical resistance with faster breakthrough of the chemical as compared to the permeation of PVA material only. Since the packaging and containers for organic chemicals are made of starch/PVC blends, it is critical to assess the resistance of the starch/PVA blends to permeation by these chemicals.

In this study, the permeability of chlorinated hydrocarbons through the starch/PVA blends was estimated using a 1-in. permeation cell. The corn starch was grafted with sodium trimetaphosphate (STMP) and then blended with the plasticizer (i.e. glycerin) and PVA. The diffusion coefficients and solubility of chlorinated hydrocarbons in the starch/PVA blends were determined using the diffusion equation of Fick's law. Finally, correlations between the diffusion coefficients or solubilities and several physical and chemical properties of the chlorinated hydrocarbons were investigated. The correlation analysis may provide an

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understanding in the permeation process of organic compounds in the PVA/starch blends.

## 2. Materials and methods

### 2.1. Chemicals and starch/PVA membrane

Chlorinated hydrocarbons used for this study were dichloromethane, 1,2-dichloroethane, trichloroethylene and carbon tetrachloride. These organic solvents were selected as they are commonly used in industry. As shown in Table 1, these organic solvents exhibit a wide range of physical and chemical properties, i.e. molecular weight and octanol–water partition coefficient. The tested solvents were of reagent grade or higher purity (>98%) and were used without further purification.

The starch was first modified to increase the surface roughness because of its poor processability and incompatibility with PVA. For the modification process, 40% (weight) of corn starch (African Products Limited) was mixed with 2% $Na_2SO_4$ and 0.1% STMP in the aqueous solution at 45 °C for 3 h. The solution was adjusted to pH = 5.5 by adding $H_3PO_4$, and then the precipitated sample, i.e. modified starch, was collected.

The modified starch was added into PVA (BF-17, Chang-Chun Petrochemical Co., Taiwan) at different ratios of 10, 20 and 30%, i.e. samples SP19, SP28 and SP37. The starch/PVA was blended with 20% glycerin (Nihon Shiyaku Industries, Japan) and 1% magnesium stearate (Nihon Shiyaku Industries, Japan) using a Brabender plastograph at 220 °C and 90 rpm for 2 min (Chai et al., 2009). The starch/PVA blends were then thermally compressed into films with a thickness of $0.047 \pm 0.009$ cm. The average thickness of each sample was determined by measuring at four random locations on the sample surface using a dial thickness gauge (Teclock Co., Japan) to an accuracy of 0.001 cm.

The tension test for the membrane samples was performed according to ASTM D638 (1994) in a Servohydraulic Material Testing System (Model MTS 810, Eden Prairie, MN) at a draw rate of 50 mm/min. The tensile strength of PVA membrane was 34.9 MPa. After blending starch in PVA, the tensile strength was 33.5, 32.4, and 30.4 MPa for samples SP19, SP28, and SP37, respectively. This result indicated that the tensile strength decreased with an increase in the starch content of the starch/PVA blends.

### 2.2. Permeation experiment

Permeation experiments were conducted using a 1″ cell with in-cell solid-phase microextraction (SPME) sampling. As shown in Fig. 1, the test membrane was vertically mounted in the permeation cell, dividing the cell into two chambers, i.e. the challenge chamber and the collection chamber. In the challenge chamber, the volume of the organic solvent was 10 mL, which covered the entire surface area of the test membrane. The collection chamber was completely filled with 11 mL of deionized water, i.e. collection medium. The organic solvent, if permeating through the test membrane, was mixed with deionized water for sampling purposes.

The assembled test cell was agitated at 200 rpm in an orbital shaking incubator (LB-BOD-300, Taiwan) and maintained at a temperature of $25 \pm 1$ °C. During the experimental run, SPME with the polydimethylsiloxane fiber (PDMS, 57300-U, Supelco, Bellefonte, PA) was directly injected into the inlet port of the collection chamber at 30 min intervals. The samples of collection medium were extracted using SPME for 20 min and then analyzed by a gas chromatography equipped with flame ionization detector (GC-FID, AutoSystem XL, Perkin Elmer, Norwalk, CT) to determine the concentration of the organic solvent.

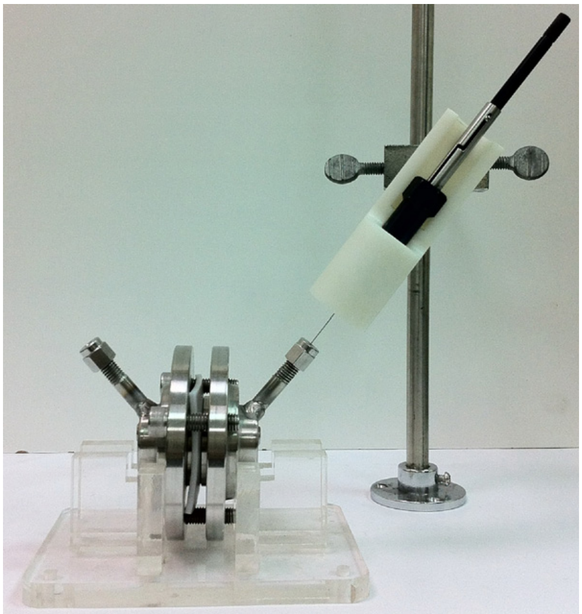

**Fig. 1.** Photo of the in-cell SPME permeation cell.

The capillary column used for GC-FID was DB-5 (J&W, USA). The column oven temperature was held at 60 °C for 1 min and then programmed to 150 °C at a rate of 8 °C/min with a final hold of 1 min. The temperatures of the injection port and detector were kept at 200 °C and 250 °C, respectively. Desorption time of the PDMS fiber was 7 min for the SPME device in GC-FID.

The GC calibration was performed using an in-cell SPME method. A PTFE membrane that is non-reactive with organic solvents was mounted in the test cell. Standard solutions of different solvent concentrations were loaded into the collection chamber of the assembled cell that was maintained in the orbital shaking incubator at a temperature of $25 \pm 1$ °C. The challenge chamber of the assembled cell was emptied of chemicals. SPME was inserted into the collection chamber to extract the aqueous sample and then analyzed by GC-FID. The linear regression coefficients for all calibration curves were $R^2 > 0.997$. The Limit Detection Levels (LDL) of test solvents are given in Table 1.

## 3. Results and discussion

### 3.1. Permeability coefficient

A minimum of three permeation tests was performed for each organic solvent and starch/PVA membrane, respectively. Fig. 2 shows the permeation results for the experiments conducted. Once breakthrough occurred, the cumulative mass of organic solvents in the collection medium was found to increase linearly. The steady state permeation rate, $J_s$ ($ML^{-2}T^{-1}$), was estimated using the rate of increase of the permeated mass in the collection medium as follows:

$$J_s = \frac{\alpha}{A} \tag{1}$$

where $\alpha$ is the slope of the linear portion, i.e. steady state permeation, of the cumulative permeant mass in deionized water ($MT^{-1}$), as shown in Fig. 2; and $A$ is the sample area exposed to the permeant, i.e. 5.06 $cm^2$.

The steady state permeation rate is known to be inversely proportional to the thickness, $L$ (L), of test samples (Crank & Park, 1968). To account for the effect of sample thickness, the resistance of the

**Table 1**
Physical and chemical properties of test solvents.

| Organic solvent | Grade | Dn[a] (g/cm$^3$) | Mw[b] (g/mole) | MV[c] (cm$^3$) | WS[d] (mg/L) | $H$[e] | log $K_{ow}$[f] | LDL (mg/L) |
|---|---|---|---|---|---|---|---|---|
| Dichloromethane (DCM) | LC grade | 1.327 | 84.93 | 63.98 | 20,000 | 0.085 | 1.25 | 0.481 |
| 1,2-Dichloroethane (DCE) | GR grade | 1.253 | 98.97 | 79.01 | 8690 | 0.063 | 1.45 | 0.353 |
| Trichloroethylene (TCE) | GC grade | 1.464 | 131.79 | 89.75 | 1100 | 0.397 | 2.53 | 0.332 |
| Carbon tetrachloride (CT) | GR grade | 1.594 | 153.84 | 96.51 | 800 | 0.029 | 2.64 | 0.626 |

[a] Dn, density at 25 °C.
[b] Mw, molecular weight (Lide, 1994).
[c] MV, molar volume = Mw/Dn at 25 °C.
[d] WS, water solubility at 20 °C (LaGrega, Buckingham, & Evans, 1994).
[e] $H$, Henry's constant (dimensionless) at 25 °C (LaGrega et al., 1994).
[f] $K_{ow}$, octanol–water partition coefficient at 25 °C (LaGrega et al., 1994).

test membrane was quantified using the permeability coefficient, $P$ (ML$^{-1}$ T$^{-1}$), as follows (Chao, Lai, & Lin, 2007):

$$P = J_s L \quad (2)$$

Table 2 presents the permeability coefficients of the test solvents in the starch/PVA membranes. In general, the order of permeability coefficients from highest to lowest were dichloromethane > 1,2-dichloroethane > TCE > carbon tetrachloride for starch/PVA blends of the same composition. Permeation of organic solvents through the polymeric membrane is dependent on the molecular interactions between the solvent and polymer. Table 3 shows that the permeability coefficients decreased with increasing molecular weight ($R^2 \geq 0.803$, $p < 0.05$) as well as molar volume ($R^2 \geq 0.753$, $p < 0.05$) of organic solvents. Therefore, the permeability of starch/PVA blends is dependent on the molecule size of chlorinated hydrocarbons. Also indicated in Table 3, the permeability coefficients in the starch/PVA membranes were inversely proportional to the octanol–water partition coefficient (log $K_{ow}$) of the test solvents ($R^2 \geq 0.746$, $p < 0.05$). This result may imply that chlorinated hydrocarbons of lower polarity (i.e. solvents with large values of log $K_{ow}$) are less permeable through the starch/PVA membranes.

As shown in Table 2, the permeability coefficients in the starch/PVA blends were higher than those in the PVA membrane for the same test solvent. For instance, the permeability coefficients of test solvents in SP19 were increased by 171–355% compared with the PVA membrane. This was as expected since the addition of glycerin weakened the physical bonding between starch and PVA (Rahman, Sin, Rahmat, & Samad, 2010). The glycerin disrupted the rigidity arrangements of starch and PVA, which enhanced the molecules of the test solvents permeation through the starch/PVA blends.

Table 3 indicates that the permeability coefficients of test solvents in the starch/PVA blends were significantly increased by their starch content ($R^2 = 0.725$, $p < 0.05$). In a study of biodegradability of starch/PVA blends, Chai et al. (2009) found that the degradability was enhanced with the addition of starch. Therefore, it is speculated that the higher the permeability coefficient, the larger the degradation rate of the starch/PVA blend.

In this study, the tensile strength of the test sample was found to be inversely proportional to the content of starch in the starch/PVA blend. Fig. 3 shows that the permeability coefficients of test solvents in the starch/PVA blends were significantly correlated to their starch contents ($R^2 > 0.808$). Therefore, an increase in the starch content resulted in a decrease in the tensile strength and chemical resistance of the starch/PVA blend.

In addition, multiple regression analyses of permeability coefficients were performed using stepwise regression with 95% confidence limits. For the test samples of PVA membranes and starch/PVA blends, the best fitting correlation ($R^2 = 0.968$, $p < 0.05$) for the permeability coefficient was:

$$P = 10^{11.901}\ \mathrm{Mw}^{-6.308}(1 - \mathrm{starch})^{-7.753} \quad (3)$$

The results of correlation analysis can provide a fundamental to evaluate the resistance of starch/PVA blends to permeation by chlorinated hydrocarbon. It should be emphasized that the correlation,

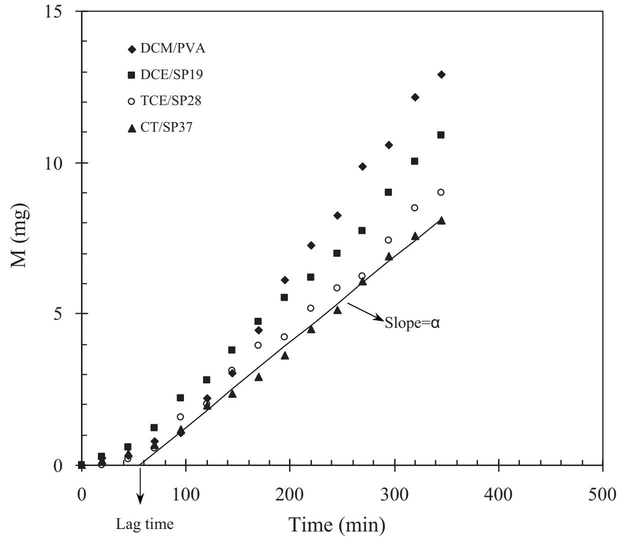

**Fig. 2.** The cumulative permeant mass in collection medium.

**Table 2**
Permeability, solubility and diffusion coefficients of test solvents in PVA and starch/PVA blends.

| Organic solvent | $P$[a] (μg/cm/min) | $D$[a] (10$^{-6}$ cm$^2$/min) | $S$[a] (10$^5$ mg/L) |
|---|---|---|---|
| *Dichloromethane* | | | |
| PVA | 0.57 ± 0.01 | 6.71 ± 1.69 | 0.91 ± 0.27 |
| SP19 (10% starch/PVA) | 1.55 ± 0.07 | 7.95 ± 2.04 | 2.07 ± 0.67 |
| SP28 (20% starch/PVA) | 4.89 ± 0.36 | 8.10 ± 1.49 | 6.22 ± 1.49 |
| SP37 (30% starch/PVA) | 5.44 ± 0.43 | 9.26 ± 1.80 | 6.61 ± 1.25 |
| *1,2-Dichloroethane* | | | |
| PVA | 0.16 ± 0.04 | 5.94 ± 0.93 | 0.27 ± 0.04 |
| SP19 (10% starch/PVA) | 0.47 ± 0.07 | 6.45 ± 0.65 | 0.76 ± 0.21 |
| SP28 (20% starch/PVA) | 1.30 ± 0.28 | 7.49 ± 1.48 | 1.75 ± 0.39 |
| SP37 (30% starch/PVA) | 2.33 ± 0.27 | 8.68 ± 1.47 | 3.78 ± 0.23 |
| *Trichloroethylene* | | | |
| PVA | 0.02 ± 0.01 | 4.62 ± 0.64 | 0.04 ± 0.01 |
| SP19 (10% starch/PVA) | 0.09 ± 0.01 | 5.04 ± 0.65 | 0.18 ± 0.03 |
| SP28 (20% starch/PVA) | 0.34 ± 0.05 | 6.89 ± 0.39 | 0.51 ± 0.08 |
| SP37 (30% starch/PVA) | 0.50 ± 0.09 | 8.9 ± 1.50 | 0.56 ± 0.04 |
| *Carbon tetrachloride* | | | |
| PVA | 0.01 ± 0.01 | 3.73 ± 1.48 | 0.04 ± 0.02 |
| SP19 (10% starch/PVA) | 0.04 ± 0.01 | 6.02 ± 0.28 | 0.06 ± 0.01 |
| SP28 (20% starch/PVA) | 0.05 ± 0.01 | 7.01 ± 1.06 | 0.07 ± 0.02 |
| SP37 (30% starch/PVA) | 0.26 ± 0.06 | 8.68 ± 1.47 | 0.31 ± 0.12 |

[a] Mean ± SD.

**Table 3**
Relationship of permeability, solubility and diffusion coefficients to test solvents and starch contents.

| Variable | PVA membrane | Starch/PVA membrane |
|---|---|---|
| *Permeation coefficient* | | |
| Mw | $P = 10^{12.094}\ \mathrm{Mw}^{-6.427}$ ($R^2 = 0.97$, $p < 0.05$) | $P = 10^{12.424}\ \mathrm{Mw}^{-6.167}$ ($R^2 = 0.803$, $p < 0.05$) |
| MV | $P = 10^{17.874}\ \mathrm{MV}^{-9.958}$ ($R^2 = 0.943$, $p < 0.05$) | $P = 10^{17.655}\ \mathrm{MV}^{-9.39}$ ($R^2 = 0.753$, $p < 0.05$) |
| $\log K_{ow}$ | $P = 10^{0.088} \log K_{ow}{}^{-4.581}$ ($R^2 = 0.98$, $p < 0.05$) | $P = 10^{-0.867} \log K_{ow}{}^{-4.244}$ ($R^2 = 0.746$, $p < 0.05$) |
| Starch content (%) | | $P = 10^{4.082}\ \mathrm{starch}^{1.756}$ ($R^2 = 0.725$, $p < 0.05$) |
| *Diffusion coefficient* | | |
| Mw | $D = 10^{-3.61}\ \mathrm{Mw}^{-0.8}$ ($R^2 = 0.916$, $p < 0.05$) | $D = 10^{-4.478}\ \mathrm{Mw}^{-0.397}$ ($R^2 = 0.17$, $p > 0.05$) |
| MV | $D = 10^{-3.06}\ \mathrm{MV}^{-1.51}$ ($R^2 = 0.766$, $p < 0.05$) | $D = 10^{-4.103}\ \mathrm{MV}^{-0.538}$ ($R^2 = 0.198$, $p > 0.05$) |
| $\log K_{ow}$ | $D = 10^{-5.114} \log K_{ow}{}^{-0.531}$ ($R^2 = 0.79$, $p < 0.05$) | $D = 10^{-5.068} \log K_{ow}{}^{-0.233}$ ($R^2 = 0.18$, $p > 0.05$) |
| Starch content (%) | | $D = 10^{-4.904}\ \mathrm{starch}^{0.307}$ ($R^2 = 0.608$, $p < 0.05$) |
| *Solubility* | | |
| Mw | $S = 10^{15.392}\ \mathrm{Mw}^{-5.463}$ ($R^2 = 0.925$, $p < 0.05$) | $S = 10^{17.224}\ \mathrm{Mw}^{-5.949}$ ($R^2 = 0.844$, $p < 0.05$) |
| MV | $S = 10^{20.614}\ \mathrm{MV}^{-8.627}$ ($R^2 = 0.933$, $p < 0.05$) | $S = 10^{21.479}\ \mathrm{MV}^{-8.701}$ ($R^2 = 0.792$, $p < 0.05$) |
| $\log K_{ow}$ | $S = 10^{5.211} \log K_{ow}{}^{-3.976}$ ($R^2 = 0.96$, $p < 0.05$) | $S = 10^{5.994} \log K_{ow}{}^{-4.106}$ ($R^2 = 0.779$, $p < 0.05$) |
| Starch content (%) | | $S = 10^{5.833}\ \mathrm{starch}^{1.281}$ ($R^2 = 0.147$, $p > 0.05$) |

i.e. Eq. (3), developed herein is appropriate for chlorinated hydrocarbons and may be different for the other solvents.

### 3.2. Solubility and diffusion coefficient

Permeation of organic solvents through the polymeric membrane involves various mass transfer mechanisms (George & Thomas, 2001). First, the permeant dissolves or partitions onto the contact surface of the membrane. Subsequently, the permeant diffuses through the membrane and finally is desorbed from the opposite surface of the membrane. Permeation is mainly a function of solubility and diffusivity of solvents through the membrane, with desorption playing an insignificant role (Crank & Park, 1968; Habeych, Van der Goot, & Boom, 2007).

One-dimensional diffusion of the permeant into the polymeric membrane can be expressed by Fick's second law as follows:

$$\frac{\partial C_z}{\partial t} = D \frac{\partial^2 C_z}{\partial Z^2} \tag{4}$$

where $D$ is the diffusion coefficient of the permeant in the polymeric membrane ($L^2\,T^{-1}$); $C_Z$ is the permeant concentration at some point $Z$ in the membrane ($ML^{-3}$); and $Z$ is the distance along the direction of diffusion (L). It is generally assumed that the diffusion coefficient is independent of the concentration $C_Z$ and position (i.e. $Z$) in the membrane (Chao et al., 2007; Crank, 1975).

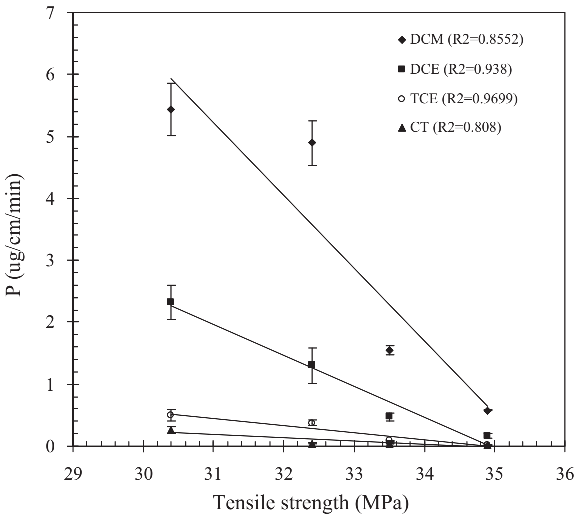

**Fig. 3.** Correlation of tensile strength and permeability coefficients for starch/PVA blends.

If the concentrations of permeants in the collection medium are significantly lower than the challenge chamber, i.e. density of permeant, then $C_{Z=L}$ can be assumed to be insignificant as compared to $C_{Z=0}$. In this study, the boundary and initial conditions of Eq. (4) were assumed to be:

$$C_z(0, t) = S$$
$$C_z(L, t) = 0$$
$$C_z(Z, 0) = 0$$

where $S$ is the solubility of the permeant in the test membrane ($ML^{-3}$).

By solving Eq. (4), the concentration profile $C_Z$ into the membrane was given as follows:

$$C_z(Z, t) = S\left(1 - \frac{Z}{L}\right) - \sum_{n=1}^{\infty} \frac{2S}{n\pi} \exp\left(-D\left(\frac{n\pi}{L}\right)^2 t\right) \sin\left(n\pi \frac{Z}{L}\right) \tag{5}$$

For the steady state, i.e. $t \to \infty$, the concentration profile $C_Z$ was described as follows:

$$C_z(Z, t) = S\left(1 - \frac{Z}{L}\right) \tag{6}$$

By taking the mass balance for the collection medium, the concentration of permeant, $C$ ($ML^{-3}$), in the collection chamber was determined as follows:

$$V \frac{dC}{dt} = -AD \left.\frac{\partial C_Z}{\partial Z}\right|_{Z=L} = -ADf(t) \tag{7}$$

where $V$ is the volume of collection medium, i.e. 11 mL for this study; and $f(t) = (\partial C_z / \partial Z)|_{Z=L}$.

The concentration of permeant in the collection chamber can be solved from Eq. (7) as follows:

$$C = -\frac{AD}{V} \int f(t)\,dt + C^* \tag{8}$$

With the initial condition of $C(0) = 0$ for Eq. (8), the integration constant $C^*$ can be determined.

According to the solutions of Eq. (5), the diffusion coefficient and solubility of permeant in the test membrane may be experimentally obtained by (Chao et al., 2007; Crank, 1975):

$$D = \frac{L^2}{6\,t_l} \tag{9}$$

$$S = \frac{P}{D} \tag{10}$$

where $t_l$ is the lag time (T) which is given by the extrapolation of the steady state portion of the permeation curve to the time axis,

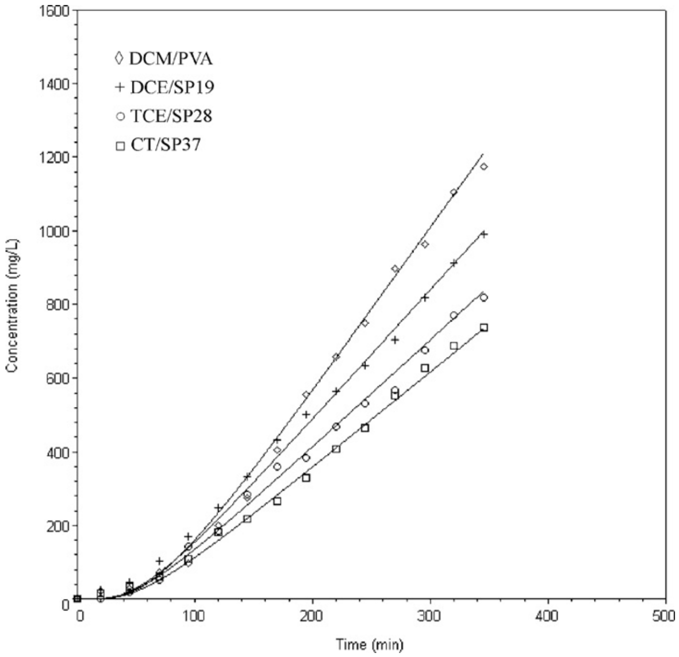

**Fig. 4.** Simulations for permeant concentrations in collection medium.

as shown in Fig. 2. In this study, the lag time was determined by the linear regression of experimental permeation data with $R^2 > 0.95$.

Table 2 shows the diffusion coefficients and solubility of test solvents in the starch/PVA membranes. The permeation concentration with respect to time in Eq. (8) can be solved using Maple software (Waterloo Maple Inc., Waterloo, Ontario, Canada). Fig. 4 indicates the simulation results of test solvents using diffusion coefficient $D$ and solubility $S$ for the permeation experiments. It can be seen that the diffusion coefficient $D$ estimated from Eq. (9) was able to approximately simulate the permeation results by Fick's second law with the assumptions of the boundary and initial conditions. However, Fig. 4 shows the simulated solvent concentrations were slightly lower than the experimental results during the initial period of permeation. This deviation may be the result of neglecting the effects of swelling of the test membranes in simulation equations. The thickness of starch/PVA blends increased by approximately 7–15% for the permeation experiments.

### 3.3. Correlation analysis of solubility and diffusion coefficient

In this study, the correlation analysis of the solubility and diffusion coefficient was conducted to comprehend the permeation process for organic compounds in the starch/PVA membranes. In general, chemicals with high molecular weights will have low diffusion coefficients. As shown in Table 3, the diffusion coefficients of test solvents in PVA membranes were inversely proportional to their molecular weight, molar volume and $\log K_{\mathrm{ow}}$ ($p < 0.05$). The diffusion coefficients were found to correlate best with the molecular weight of test solvents ($R^2 = 0.916$). Therefore, molecular weight can be a good basis to understand the diffusivity of chlorinated hydrocarbons in PVA membranes.

For the starch/PVA blends, the diffusion coefficients did not correlate well with the molecular weight, molar volume or $\log K_{\mathrm{ow}}$ of the test solvents ($p > 0.05$). This may be due to the blending interactions of PVA, starch and glycerin. On the other hand, it is interesting to note that the diffusion coefficients were significantly proportional to the content of starch in the starch/PVA blends. As discussed previously, the blending interactions may have weakened when starch was plasticized with glycerin. By increasing the content of starch, the characteristics of the blend such as chemical resistance will be inclined towards that of the starch. Therefore, the molecules of test solvents were found to diffuse easily in the starch/PVA blends. For the PVA and starch/PVA samples, the best fitting correlation for the diffusion coefficient using stepwise regression with 95% confidence limits ($R^2 = 0.851$, $p < 0.05$) was:

$$D = 10^{-3.949}\mathrm{Mv}^{-0.698}(1 - \mathrm{starch})^{-1.517} \tag{11}$$

Table 3 shows the correlation of the estimated solubility with the different physical-chemical properties. For the PVA membrane, the solubilities of chlorinated hydrocarbons were significantly correlated to their molecular weight, molar volume and $\log K_{\mathrm{ow}}$ ($R^2 \geq 0.925$, $p < 0.05$). The potential solvent solubility is related to solvent polarity, which is the so-called "like dissolves like" (Hansen, 2004). In general, the lower the octanol–water partition coefficient of a chemical, the higher the polarity. As PVA is a polar material, the chemical with a lower $K_{\mathrm{ow}}$ will have a stronger attraction to the PVA membrane. Therefore, the solubility was found to be inversely proportional to $\log K_{\mathrm{ow}}$ of the test solvents for PVA.

As indicated in Table 3, the solubility was inversely correlated to the $\log K_{\mathrm{ow}}$ of the test solvents ($R^2 = 0.779$, $p < 0.05$) for the starch/PVA blends. It was speculated that the starch/PVA blends of this study were polar materials. Also presented in Table 3, the solubility of the test solvents was increased with the content of starch in the starch/PVA blends. This result may imply that the more starch is in the blends, the stronger the sorption of the chlorinated hydrocarbons onto the starch/PVA samples. It should be noted that starch in the blends was gelatinized by glycerin. This may be a possible reason that the solubility of test solvents was correlated to the content of starch only with a regression coefficient $R^2 = 0.147$ for the starch/PVA blends. Based on the multiple regression analyses, the best fitting correlation ($R^2 = 0.961$, $p < 0.05$) for the solubility of PVA and starch/PVA samples was:

$$S = 10^{16.33}\mathrm{Mw}^{-5.888}(1 - \mathrm{starch})^{-6.27} \tag{12}$$

## 4. Conclusions

In this study, modified corn starch, glycerin and PVA were blended using a Brabender plastograph to prepare the starch/PVA membranes. The addition of starch may result in enhancing the degradation rate of the starch/PVA blends, while their tensile strength as well as chemical resistance to chlorinated hydrocarbons was found to decrease with an increase in the starch content. The chlorinated hydrocarbon with a large molecule size or lower polarity may be less permeable through the starch/PVA blends.

Based on Fick's second law, the diffusion coefficients, estimated by Crank's equation, were found to be simulated well the results of the permeation experiments using a solubility boundary condition. For the starch/PVA blends, the solubilities of chlorinated hydrocarbons were inversely proportional to their molecular weight, molar volume and $\log K_{\mathrm{ow}}$. The diffusion coefficients and solubility of permeants were proportional to the contents of starch in the starch/PVA blends. It is plausible that the blends will be inclined to the starch characteristics as glycerin has disrupted the rigidity arrangements of starch and PVA. The results of correlation analysis can provide a fundamental to evaluate the resistance of starch/PVA to permeation by organic compounds.

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