

# Permeability of N, P, K-fertilizer nutrient and water vapor through PLA, PLA/PS, and PLA/HA membranes

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To collect permeability data and establish its database of fertilizer nutrients and water vapor through different polymer membranes for the development of polymer-coated fertilizer, the permeabilities of N-, P-, and K-nutrient from saturated aqueous of urea, NaH<sub>2</sub>PO<sub>4</sub> and KCl solution and the permeability of water vapor through the membranes of poly lactic acid (PLA), its blends with polystyrene (PS), and its composites with humic acid (HA) particles were determined experimentally at the temperatures of 288, 298, and 308 K, respectively. The effects of the addition of PS and HA particles, temperature, and coating thickness on the permeability of fertilizer nutrient and water vapor were investigated. It was found that the addition of PS and HA increased the permeability for both the fertilizer nutrients and water vapor. The increase in temperature raised the permeability of N-, P-, and K-nutrient while decrease the permeability of water vapor in the range studied.

**Keywords:** Permeability, polymer-coated fertilizer, mathematical model, poly lactic acid, membrane.

## INTRODUCTION

The permeability, also called permeation coefficient, of nitrogen- (N-), phosphorus- (P-), potassium-(K-) nutrient and water vapor through polymer membrane are key parameters governing the release kinetics of these nutrients out of the polymer-coated fertilizers (PCFs). Even though the PCFs have been commercialized for more than 50 years, the permeability data of N-, P-, K-nutrient through polymer membrane are still in serious shortage which has been a great hinder to apply the mathematical models to predict the release of nutrient and to help to select and screening the coating materials.

Watanabe and coworkers<sup>1</sup> reported the permeability of urea through various polyurethane membranes they synthesized from the urea solution in water. Lan and coworkers<sup>2</sup> measured the permeability of urea through membranes of polyacrylic acid from saturated urea aqueous solution 298 K. However, the permeability data reported were not sufficient and enough for mathematical models to predict the release of N-, P-, and K-nutrient out of the polymer coated NPK compound fertilizer granules since most of the permeability data were for N-nutrient only. A series of studies were launched since 2015 in our group to measure the permeability data of N-, P-, and K-nutrient through polymer membranes such as polystyrene (PS) and poly ( $\epsilon$ -caprolactone) (PCL) from

different aqueous solutions of nutrients with a variety of target fertilizers, as shown in Table 1.

It is worth noting that all the data listed in this table are permeability data from saturated aqueous fertilizer nutrient solutions since they are required for the calculations of mathematical model and the influence of nutrient concentration in the feed solution on its permeability is pronounced<sup>3</sup>.

In this study, to collect systematical permeability data of N-, P-, and K- fertilizer nutrient through different polymer membranes and enrich the current database, the permeability of N-, P-, K-nutrient and water vapor were determined experimentally with the polymer membranes of PLA, PLA/PS blends, and PLA/humic acid (HA) composites and with the saturated solution of urea, NaH<sub>2</sub>PO<sub>4</sub> and KCl in water as feed solution, which corresponded to the scenario for nutrient release of polymer-coated NPK compound fertilizer. Recently, the PLA had become one of the cheapest commercial synthetic biodegradable polymers due to the fast development of corn-based chemical industry, which made it an ideal candidate as a coating material of PCFs. The addition of PS and HA could not only reduce the cost but also adjust the permeability of the membrane. Additionally, the HA particles would be helpful to improve the soil quality. Even though the PS is non-biodegradable, it has been used in gardening and horticulture.

**Table 1.** Systematical permeability data measured in our previous studies

Saturated aqueous solution	Membrane material	Permeability (cm <sup>2</sup> /d)			Target Fertilizer	Ref.
		N-(10 <sup>-5</sup> )	P-(10 <sup>-5</sup> )	K-(10 <sup>-5</sup> )		
Urea	PS	17.00	/	/	PS-coated urea	3
Urea + KCl		60.00	/	3.79	PS-coated urea and KCl	3
Urea +NaH <sub>2</sub> PO <sub>4</sub>		7.20	3.67	/	PS-coated urea and NaH <sub>2</sub> PO <sub>4</sub>	3
Urea + NaCl		51.10	/	/	PS-coated urea and NaCl	3
KH <sub>2</sub> PO <sub>4</sub>		/	/	1.60	PS-coated NaH <sub>2</sub> PO <sub>4</sub>	4
Urea +KH <sub>2</sub> PO <sub>4</sub>		21.00	3.50	4.12	PS-coated urea and KH <sub>2</sub> PO <sub>4</sub>	4
Urea+NaH <sub>2</sub> PO <sub>4</sub> +KCl		4.60	3.42	4.01	PS-coated NPK compound fertilizer	4
Urea	PCL	17.00	/	/	PCL-coated urea	4
Urea + KCl		54.00	/	3.45	PCL-coated urea and KCl	4
Urea +NaH <sub>2</sub> PO <sub>4</sub> +KCl		17.90	2.10	3.21	PCL-coated NPK compound fertilizer	4

The effects of temperature and membrane thickness on the N-, P-, and K-nutrient and water vapor permeability were also investigated.

## EXPERIMENTAL

### Chemicals and reagents

The urea ( $\text{CO}(\text{NH}_2)_2$ ,  $\geq 99.0\%$ ), monopotassium phosphate ( $\text{NaH}_2\text{PO}_4$ ,  $\geq 99.0\%$ ), and potassium chloride ( $\text{KCl}$ ,  $\geq 99.0\%$ ) purchased from Sigma-Aldrich (Shanghai, China) were used as sources of N, P, and K-nutrient, respectively. PLA ( $M_w = 30\,000$  g/mol,  $\text{PDI} = 1.0$ ), PS ( $M_w = 104\,000$  g/mol,  $\text{PDI} = 1.3$ ), HA (90%, particle size =  $20 \pm 5 \mu\text{m}$ ) obtained from Aladdin-e (Shanghai, China) were used as coating materials.

### Membrane preparation and characterization

The PLA, PS, and PLA/PS membranes were prepared using the solution casting method, in which typically 4.0 g of 5.0 wt.% their solutions in dichloromethane (DCM) were cast freely on a flat dish with a diameter of 9.0 cm. The PLA/HA membrane was prepared by dispersing HA particles in the PLA solution in DCM with a homogenizer (T18, IKA) before the solution casting. All the solution casting was carried out in a 50-liter homemade incubator with constant temperature, humidity, and air velocity of 303.2 K, 35.0%, and 1.0 m/s, respectively.

For the 5.0 wt.% solute in the casting solution, the mass ratio of PLA to PS was 1:0, 3:1, 1:1, 1:3, and 0:1 and the HA concentrations were 0.25, 0.50, 0.75, and 1.00 wt.%, respectively. The thickness of the membranes was controlled by using the casting solutions with different amounts and measured using a micrometer with a precision of  $0.1 \mu\text{m}$ . The thicknesses of the membranes prepared were in the range of 40–60  $\mu\text{m}$ .

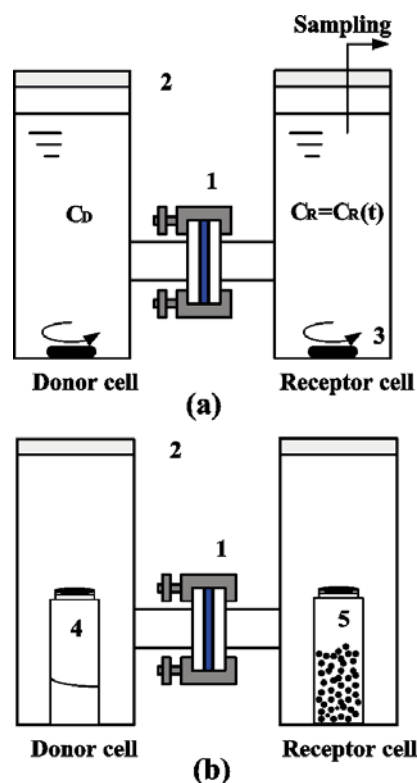
### Permeability measurement

The Ussing chamber method was adopted to measure the flux and the permeability of fertilizer nutrients through polymer membrane, which was discussed previously<sup>3,4</sup>. Briefly, after a piece of polymer membrane was mounted between the Ussing chambers, the feed solution and DI water with same volume were loaded into the donor cell and receptor cell, as shown in Figure 1(a). The samples were taken from the receptor cell every other day for analysis to determine the concentrations of urea,  $\text{NaH}_2\text{PO}_4$ , and KCl. Specifically, the urea concentration and  $\text{NaH}_2\text{PO}_4$  concentration were measured using a UV-Visible spectrometer with PDAB and molybdenum antimony as a chromogenic agent, respectively, while the KCl concentration was measured using a flame atomic absorption spectrometer. The permeability can be calculated using the equation of,

$$P_s = \frac{V}{A} \frac{l}{C_D - C_R} \frac{dC_R}{dt} = \frac{Vl}{AC_D} \frac{dC_R}{dt} \quad (1)$$

where  $V$  (mL) is the receptor volume,  $A$  ( $\text{cm}^2$ ) the membrane area,  $l$  (cm) the membrane thickness,  $P_s$  ( $\text{cm}^2/\text{d}$ ) the permeability coefficient,  $C_R$  and  $C_D$  ( $\text{g}/\text{cm}^3$ ) are receptor and donor concentration of the solute, respectively, and  $C_D \gg C_R \approx 0$ .

The permeability of water vapor through the polymer membrane were determined experimentally using the



**Figure 1.** Schematic diagram of the Ussing chamber method to measure the permeability of fertilizer nutrients (a) and water vapor (b). 1 – clamps to fix the polymer membrane, 2 – covers to prevent water evaporation, 3 – stirring bar, 4 – vial loaded with water, and 5 – vial loaded with silica gel granules

similar equipment in which a vial loaded with water was placed in the donor cell (4) and a vial loaded with dry silica gel granules (5) was placed in the receptor cell, as shown in Figure 1(b). The water vapor flux through the polymer membrane was accessed by weighing the vial in the receptor cell every 24 hours for 8 days and the water vapor permeability  $P_h$  ( $\text{cm}^2 \cdot \text{Pa}^{-1} \cdot \text{d}^{-1}$ ) was calculated by<sup>5-9</sup>,

$$P_h = \frac{dw(t)}{dt} \frac{l}{A \rho_w \Delta P} \quad (2)$$

where  $w(t)$  (g) is the mass of vial in receptor cell at time of  $t$  (d),  $A$  ( $\text{cm}^2$ ) and  $l$  (cm) are the area and thickness of the membrane, respectively.  $\rho_w$  ( $\text{g}/\text{cm}^3$ ) and  $\Delta P$  (Pa) are the density of the water vapor and pressure difference between the two cells which is closed to the vapor pressure of water at the temperature of measurement.

In this study, according to the tradition of the fertilizer industry, the permeability of N-, P-, and K-nutrient was shown in terms of urea,  $\text{P}_2\text{O}_5$ , and  $\text{K}_2\text{O}$ , respectively. The error analysis of the measurements for the permeability of N-, P-, K-nutrient and water vapor were conducted and the measurement accuracy for the permeability was within  $\pm 3\%$ , as discussed in a previous study<sup>4</sup>.

### Differential scanning calorimetric test of membrane

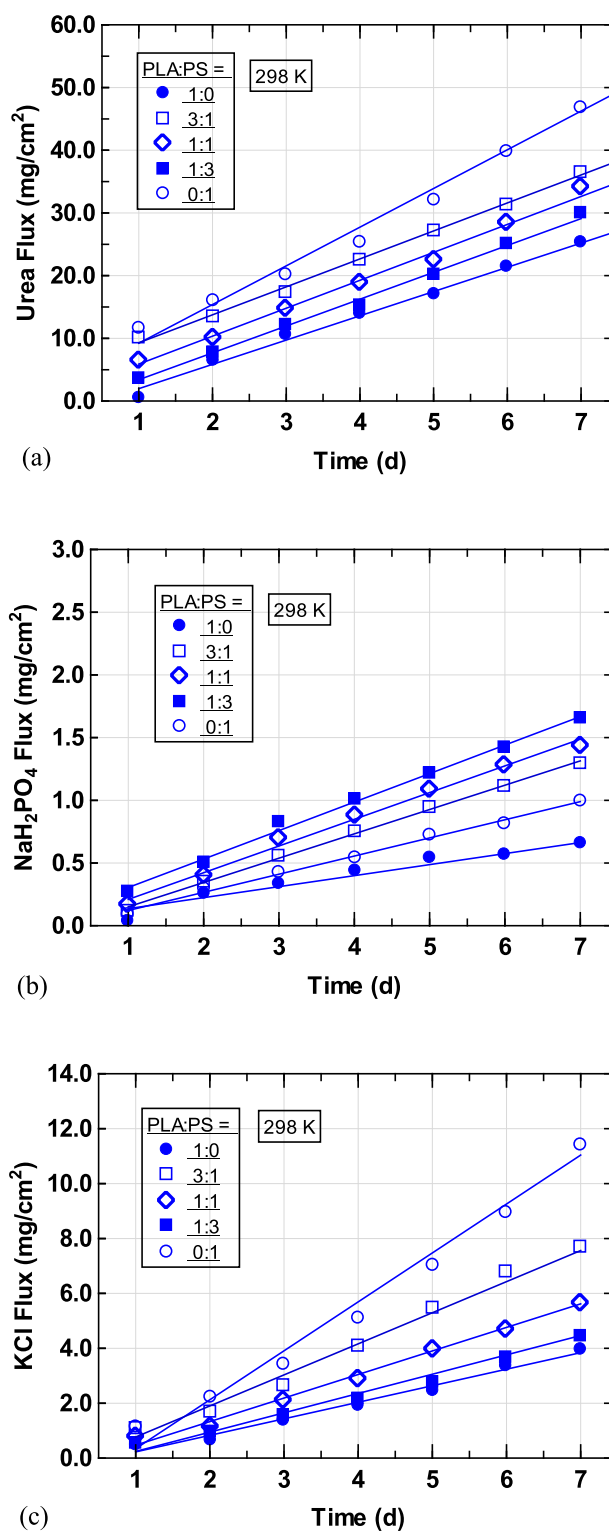
The thermal properties of the membranes were characterized by a differential scanning calorimetric (DSC, US TA instrument, Q2000) test, in which the temperature range was 0–180°C and the rate of temperature increase was 10 K/min.

## RESULTS AND DISCUSSION

In this study, the permeability of N-, P-, K-nutrient and water vapor through different membranes was determined experimentally at temperatures of 288, 298, and 308 K, respectively. The effects of PLA/PS mass ratio, HA concentration, temperature, and thickness of membrane on the permeability of N-, P-, K-nutrient, and water vapor were investigated. The initial concentration of urea was 0.38 g/mL, the initial concentration of  $\text{NaH}_2\text{PO}_4$  was 0.25 g/mL, and the initial concentration of KCl was 0.10 g/mL.

### Effect of PLA/PS mass ratio

The variation of flux for N-, K-, and P- nutrient with time up to 7 days through the membranes of PLA, PS, and PLA/PS blends with different mass ratios that were generated from the experiments were shown in the Figures 2 in terms of urea,  $\text{NaH}_2\text{PO}_4$ , and KCl, respectively. As expected, the flux demonstrated an increase with time in the range investigated. After fitting these curves with linear equations, the slopes of the plots were used to calculate the permeability of N-nutrient, which was shown in Figure 3 along with the permeability of P- and K-nutrient. The permeabilities for the three nutrients were at the same magnitude of  $10^{-5} \text{ cm}^2/\text{d}$ , while the N- and K-nutrient demonstrated higher permeability than P-nutrient for all the membranes tested. Since all the membranes used could be regarded as dense membrane, according to the “solution-diffusion” theory, the permeability of fertilizer nutrient could be attributed to its solubility and diffusion coefficient in the polymer membrane representing the intermolecular interactions of nutrient molecule or nutrient ion with polymer molecule and with solvent molecule, respectively. It seemed that even though the smaller size of  $\text{K}^+$  ion compared to the urea molecule suggested a larger diffusion coefficient, its lower permeability might result from lower solubility in the membranes made of PLA, PS, and PLA/PS blends compared to urea molecule, which was confirmed in our previous study<sup>4</sup>. Additionally, the permeability of water vapor through the polymer membranes was also included in the figure. The water vapor permeability through the PLA/PS membranes also demonstrated an increase upon the addition of amorphous polymer PS, which was similar to the permeability of fertilizer nutrients. The increases of N-, P-, K-nutrient and water vapor permeability with the addition of PS could be attributed to the decreases in the crystallinity degree of the membranes. Figure 4 displayed the first heating scans of DSC tests for the PLA, PLA/PS (1:1, mass ratio), and PLA/HA (200:1, mass ratio) membranes. The glass transition temperature was slightly increased and the area of crystalline peak was slightly decreased upon the addition of PS and HA into the PLA membrane. The latter suggested a slight decrease in the crystallinity degree of the membrane. Therefore, the results of the DSC tests were consistent with the permeability of N-, P-, and K-nutrient through the PLA, PS, and PLA/PS membranes, which had been observed in other studies for the permeation of liquid through membranes made of polymer blends<sup>10</sup>.



**Figure 2.** The variation of flux for N- (a), P- (b), and K-nutrients (c) with time through the membranes made of PLA, PS, and PLA/PS blends with the mass ratio of PLA/PS = 3:1, 1:1, and 1:3

### Effect of HA concentration

As shown in Figure 5, the permeability of N-, P-, K-nutrient and water vapor through the PLA/HA membranes demonstrated increases with the addition of HA particle into the PLA membrane, which could be explained by the decreases in the crystallinity of the membranes and was consistent with the results of DSC tests in section 3.1. Meanwhile, similar to the PLA/PS membranes as shown in Figure 3, the urea demonstrated the highest permeability while the  $\text{NaH}_2\text{PO}_4$  showed the lowest ones.

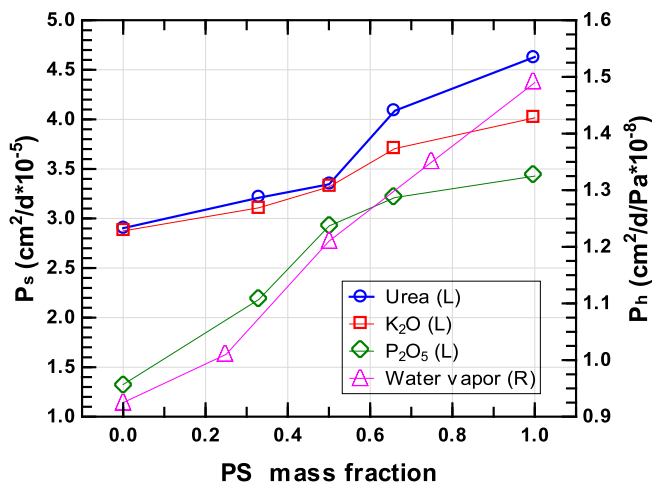


Figure 3. Variation of permeability for N-, P-, and K-fertilizer nutrients and water vapor through membrane of PLA, PLA/PS blends, and PS with the PS mass fractions of 0, 0.33, 0.50, 0.66, and 1.00, respectively

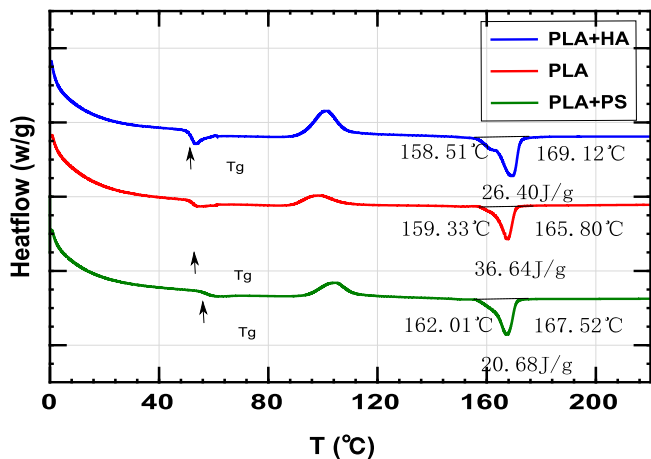


Figure 4. The first heating DSC scan of PLA, PLA/PS, and PLA/HA membrane

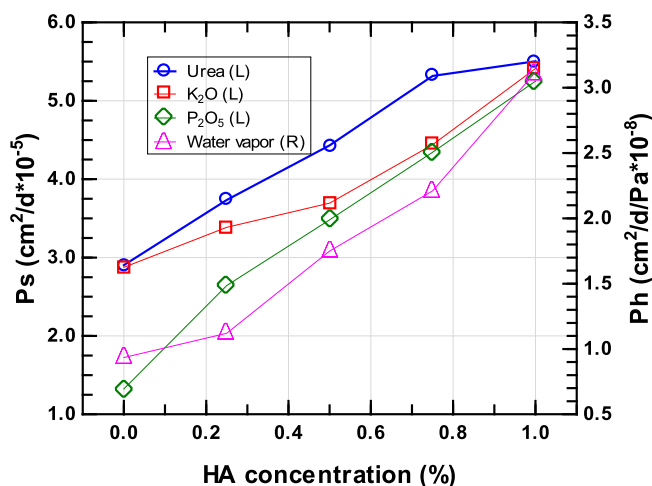


Figure 5. Variations of permeability for N-, P-, K-fertilizer nutrient and water vapor through membrane of PLA and PLA/HA composites with the HA mass concentration of 0.25, 0.50, 0.75, and 1.00 wt.%, respectively

### Effect of temperature

One of the most important features of the PCFs was the dependence of fertilizer nutrients release kinetics on the permeability and thickness of the coating membrane, moisture and temperature of the environment rather than the soil condition including its porosity,

structure, texture, pH value<sup>1, 2</sup>. Therefore, the effect of temperature on permeability was of great importance in selecting the proper coating material. Figure 6 showed the variations of permeability for N-, P-, K-nutrient and water vapor with temperature for the PLA membrane at nominal temperatures of 288, 298, and 308 K from feed solution of saturated urea-KCl-NaH<sub>2</sub>PO<sub>4</sub> in water, respectively. The permeability of the nutrients displayed increases with temperature which could be attributed to the increase in solubility and/or diffusion coefficient of nutrients in the polymer membrane with temperature<sup>11</sup>.

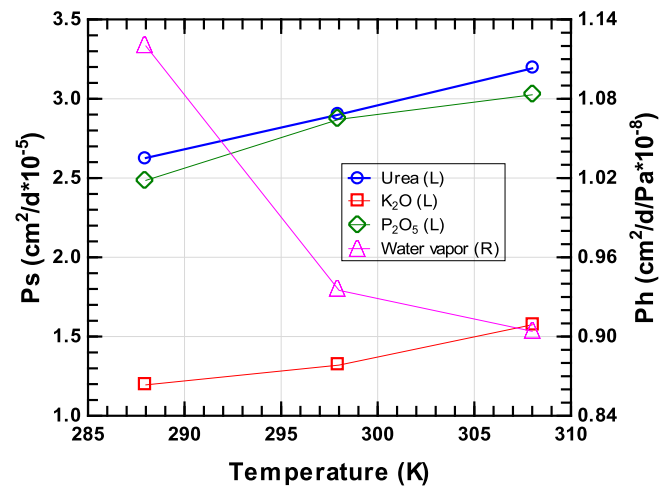


Figure 6. The variation of permeability with temperature for N-, P-, K-nutrient and water vapor through PLA membrane

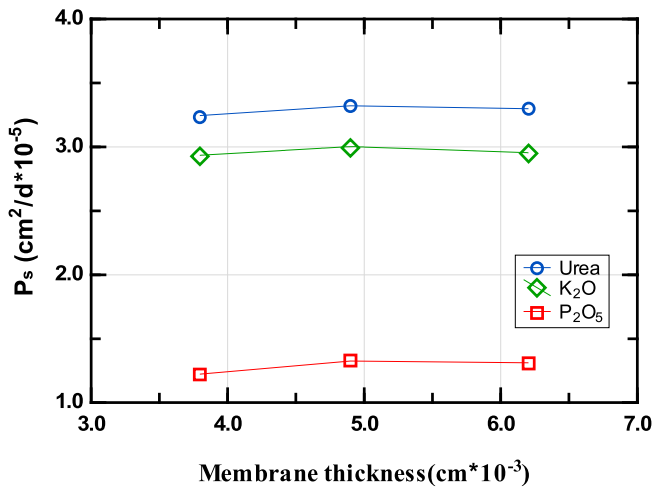
The effects of temperature on the permeability of water vapor through the PLA membrane were also included in this figure. Even though the increase in temperature could weaken the hydrogen bonding interaction between water molecules, reduce the size of the permeate molecule thus raise the diffusion coefficient, it also might lead to a decrease in water solubility in polymer membrane. It was the outcome of the two factors that decide the variation of water vapor permeability with temperature. Besides, the viscosity reduction of water vapor upon temperature increase could be another factor promoting the permeation with temperature<sup>12</sup>. Additionally, some studies reported the rearrangements of polymer chain and the formation of denser polymer membrane structure at higher temperatures. However, the glass transition temperature ( $T_g$ ) of PLA was determined at about 57°C as shown in section 3.1. The highest temperature investigated in this study was about 35°C, suggesting the effects of the rearrangements of polymer chain and the formation of denser polymer membrane structure could be neglected.

### Effect of membrane thickness

To investigate the effect of membrane thickness on the permeability of nutrients through polymer membrane, the PLA membrane with different thickness were prepared and the permeability of N-, P-, and K-nutrient were measured and shown in Figure 7.

The permeability of fertilizer nutrients demonstrated a very slight increase with the membrane thickness through the PLA membrane in the range of thickness studied, which was the theoretical basis for applying





**Figure 7.** The variation of permeability for N-, P-, and K-nutrient through PLA membrane with different membrane thickness

the permeability data to predict the release of nutrients from PCF granule that was coated with the same polymer material but different coating thickness. It should be pointed out that the range of membrane thickness corresponded to the about 7.7–12.7% mass ratio of PLA to urea for the PLA-coated urea granule with a diameter of 0.3 cm, which covered most of the polymer addition range for commercial PCFs.

In a permeation process, the flux of solute  $J$  (mg/cm<sup>2</sup>/d) through the polymer membrane at a pseudo-steady state can be described as<sup>13</sup>,

$$J = P_s \frac{C_D - C_R}{l} \approx P_s \frac{C_D}{l} \quad (3)$$

According to our previous studies<sup>4</sup>, the permeability  $P_s$  displayed significant “increase-decrease” variations with the nutrient concentration  $C_D$ . It was slightly increased with the membrane thickness  $l$ , as discussed above. Therefore, the permeability of nutrients  $P_s$  was a strong function of  $C_D/l$ , suggesting the non-Fickian diffusion.

The permeability data of N-, P-, and K-nutrient generated in the current study was summarized in Table 2 with the same format of Table 1 including the saturated aqueous solution, membrane material, permeability of N-, P-, and K-nutrient, and target fertilizer. It was worth noting that the permeability of water vapor through the membranes was also measured and listed.

**Table 2.** Permeability data generated in the current study

Saturated aqueous solution	Membrane material	Permeability (cm <sup>2</sup> ·d <sup>-1</sup> )			Permeability (cm <sup>2</sup> ·Pa <sup>-1</sup> ·d <sup>-1</sup> )	Target Fertilizer
		N-(10 <sup>-5</sup> )	P-(10 <sup>-5</sup> )	K-(10 <sup>-5</sup> )		
Urea +NaH <sub>2</sub> PO <sub>4</sub> +KCl	PLA	1.12	0.99	1.06	0.94	PLA-coated NPK compound fertilizer
	PLA/PS (3:1)	3.21	2.18	3.21	1.01	
	PLA/PS (1:1)	3.34	2.92	3.31	1.21	
	PLA/PS (1:3)	4.08	3.21	3.70	1.35	PLA/PS-coated NPK compound fertilizer
	PLA/HA (0.25wt.%)	3.70	2.64	3.38	1.12	
	PLA/HA (0.5 wt.%)	4.43	3.48	3.70	1.75	
	PLA/HA (0.75 wt.%)	5.30	4.31	4.44	2.21	
PLA/HA (1.00 wt.%)	5.55	5.25	5.41	3.12	PLA/HA-coated NPK compound fertilizer	

## Mathematical model

As one of the most important mathematical models based on dense membrane, the model proposed by Shaviv and coworkers<sup>14</sup> in 2003 has been applied to predict the release kinetics of fertilizer nutrient from PCF granule and satisfactory agreements have been reached. According to the model, the release process of fertilizer nutrients could be divided into lag stage, constant-release stage, and decaying release stage. In the lag stage, the fractional release of nutrient

$$g(r, l, t) = 0, \quad t < t' \quad (4)$$

$$t' = \frac{\gamma l}{3P_h \Delta P} \quad (5)$$

In the constant-release stage,

$$g(r, l, t) = \frac{3P_s C_{sat}}{rl\rho_s} (t - t'), \quad t' \leq t \leq t'' \quad (6)$$

$$t'' = t' + \left(1 - \frac{C_{sat}}{\rho_s}\right) \frac{rl\rho_s}{3P_s C_{sat}} \quad (7)$$

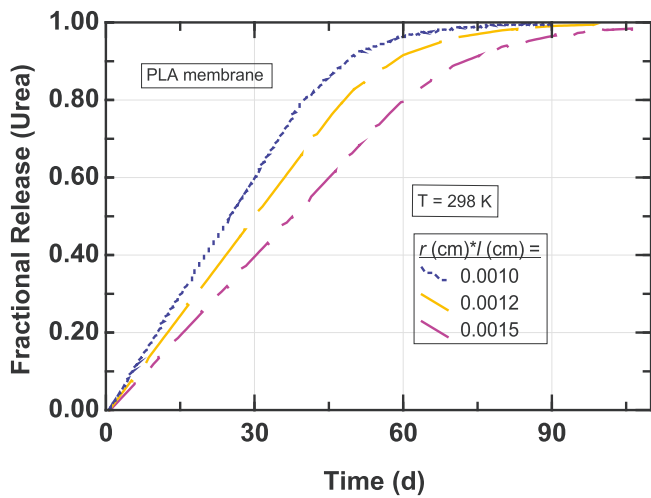
In the decaying stage,

$$g(r, l, t) = 1 - \frac{C_{sat}}{\rho_s} \exp\left[-\frac{3P_s}{rl}(t - t'')\right], \quad t > t'' \quad (8)$$

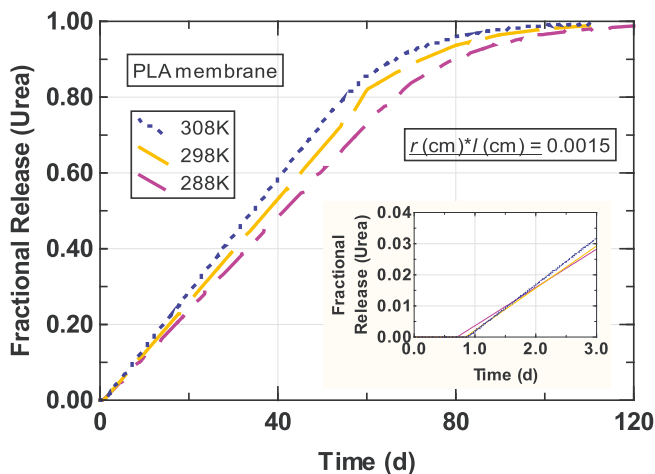
where  $P_s$  and  $P_h$  were the permeability of fertilizer nutrient and water vapor through the polymer membrane, respectively.  $C_{sat}$  was the nutrient concentration of the saturated solution,  $\rho_s$  was the density of fertilizer,  $r$  was the radius of the PCF granules,  $l$  was the thickness of the polymer coating.  $\Delta P$  was the difference between the vapor pressure of water and saturated fertilizer solution, and  $\gamma$  was the critical volume fraction of voids filled with water which was generally estimated at around 0.05–0.1.

The release kinetics of N-, P-, and K-nutrient from a PCF granule that was coated with the PLA, PS, PLA/PS, and PLA/HA materials were predicted using the permeability data generated in this study as listed in Table 2 along with the properties of the saturated compound fertilizer solution in water such as  $\rho_s = 1.71$  g/cm<sup>3</sup>,  $C_{sat} = 1.09$  g/cm<sup>3</sup> that was reported in our previous study<sup>4</sup>. The results of the predictions were shown in Figure 8 through 11 with the focus of the effects of granule size, coating thickness, and temperature, respectively.

According to the model (Eq-4, 6, 8), the granule size  $r$  and coating thickness  $l$  were functioned as their product, suggesting the same effects. From Figure 8, the increases in  $r$  and  $l$  prolonged the release of urea. Meanwhile, the increase in temperature accelerated the release of urea as shown in Figure 9. Figures 10 and 11 displayed the release of N-, P-, and K-nutrient from the granule of PCFs with coating materials of PLA/PS blends and PLA/HA composites. It was obvious that the release kinetics of nutrient could be adjusted by varying the granule size, coating thickness temperature, and coating material, which could be used to match the specific demand of fertilizer nutrient for crops over their life cycles.



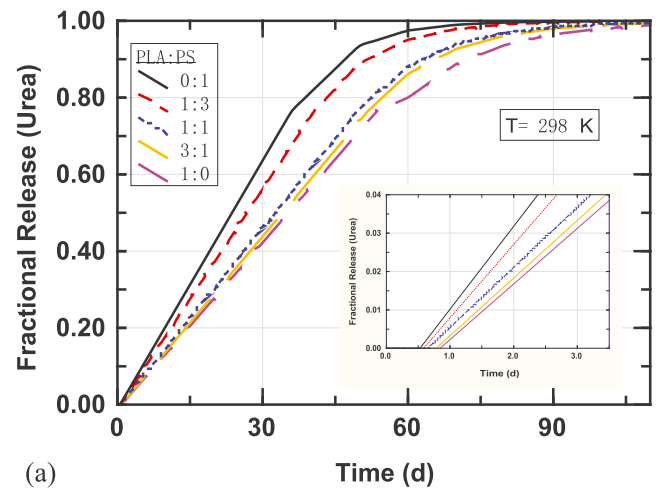
**Figure 8.** The predictions for variations of urea fractional release with time for PLA-coated NPK compound fertilizer granule with various product values of granule size  $r$  and coating thickness  $l$  at nominal temperature of 298 K



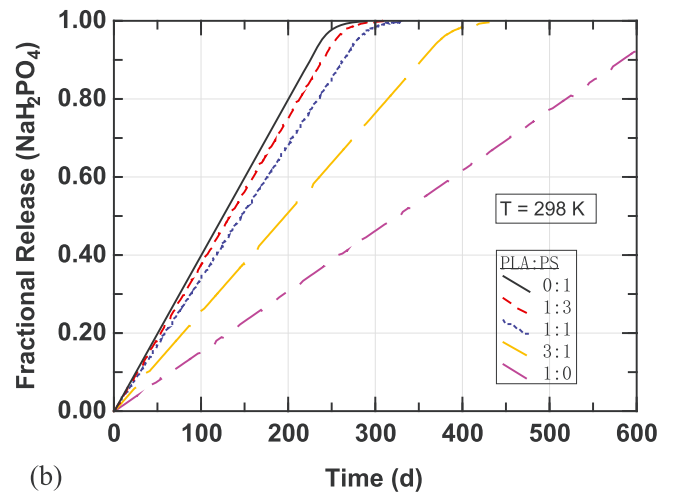
**Figure 9.** The predictions for variations of urea fractional releases with time for PLA-coated NPK compound fertilizer granule with granule size  $r$  of 0.3 cm and coating thickness  $l$  of 50  $\mu\text{m}$  at the temperature of 288, 298, and 308 K, respectively

## CONCLUSION

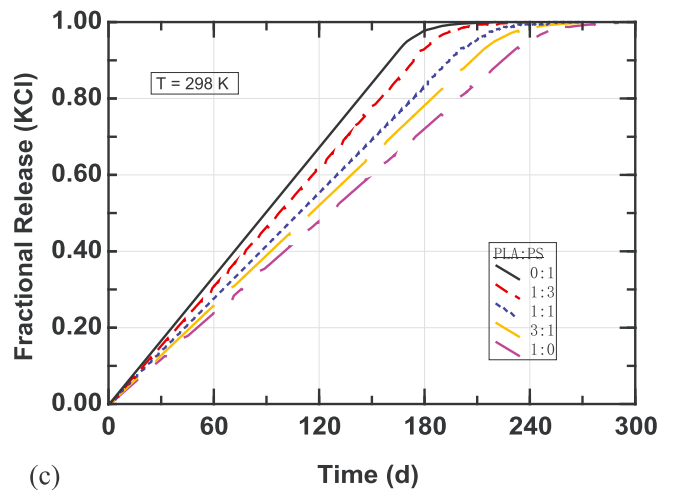
The permeability of N-, P-, and K-nutrient from saturated aqueous solutions of urea,  $\text{NaH}_2\text{PO}_4$  and KCl and water vapor through the membranes of PLA, PLA/PS blends, and PLA/HA composites was measured at temperatures of 288, 298, and 308 K to enrich the database of fertilizer nutrient



(a)



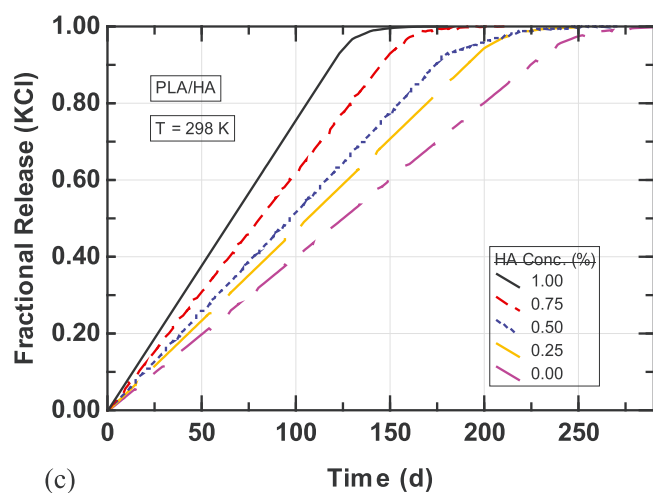
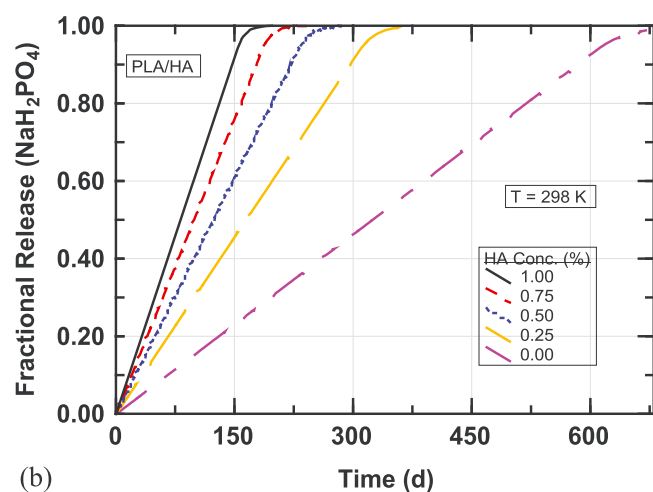
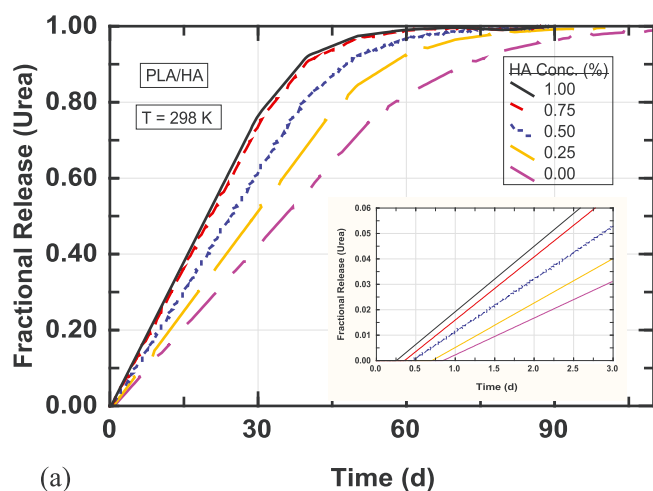
(b)



(c)

**Figure 10.** The predictions for variations of urea (a),  $\text{NaH}_2\text{PO}_4$  (b), and KCl (c) fractional releases with time for PLA/PS blend-coated NPK compound fertilizer granule with granule size  $r$  of 0.3 cm and coating thickness  $l$  of 0.005 cm at nominal temperature of 298 K. The mass ratios of PLA to PS were 0:1, 1:3, 1:1, 3:1, and 1:0, respectively

permeability for design, screening, and selecting of proper polymer coating material for the development of PCFs. In addition, both the nutrient permeability and water vapor permeability showed increases with the addition of PS and HA into the PLA membrane, which was due to the decrease in the crystallinity and crystalline region of the PLA membrane.



**Figure 11.** The predictions for variations of urea (a),  $\text{NaH}_2\text{PO}_4$  (b), and KCl (c) fractional releases with time for PLA/HA composite-coated NPK compound fertilizer granule with granule size  $r$  of 0.3 cm and coating thickness  $l$  of 0.005 cm at nominal temperature of 298 K. The mass concentration of HA in PLA/HA composite were 0, 0.25, 0.50, 0.75, and 1.00 wt.%, respectively

The nutrient permeability increased with temperature while the water vapor permeability decreased with temperature. In the range of membrane thickness studied (40–60  $\mu\text{m}$ ), the permeability of N-, K-, and K-nutrient showed a minor increase with membrane thickness.

## FUNDING DETAILS

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## DISCLOSURE STATEMENT

The authors declare no conflict of interest.

## SYMBOL DESCRIPTION

- $A$  – Mass transfer area,  $\text{cm}^2$
- $P_s$  – Solute permeability coefficient,  $\text{cm}^2/\text{d}$
- $C_{sat}$  – concentration of saturated solution inside fertilizer granules,  $\text{g}/\text{cm}^3$
- $r$  – Fertilizer particle radius, cm
- $l$  – Film thickness, cm
- $\rho_s$  – Particle density,  $\text{g}/\text{cm}^3$
- $\Delta P$  – Differential pressure, Pa
- $\rho_w$  – Water density,  $\text{g}/\text{cm}^3$
- $P_h$  – Water vapor permeability coefficient,  $\text{cm}^2 \cdot \text{Pa}^{-1} \cdot \text{d}^{-1}$
- $\gamma$  – Particle porosity

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