

Nanoscaled Free Volume Holes and Slow Release of Urea for Poly(vinyl alcohol)/urea Composite Films

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Poly(vinyl alcohol) coated urea films were prepared by simple tape casting. The crystallinity of the films decreased with increasing urea weight content, and hydrogen bonds were formed between PVA and urea. The size of nanoscaled free volume holes in the amorphous region were measured by positron annihilation lifetime spectroscopy, and it was found that the mean size of the free volume increased with increasing urea content. About 80 % of the urea was released from the composite film after 25 h in liquid water. The increased free volume holes supplied diffusion channels for water and urea molecules, ensuring efficient urea release from the PVA coating.

1. Introduction

Nitrogen is a basic requirement for plant growth and is needed in greater amounts than other nutrients and is essential for forming chlorophyll, proteides, proteins, and some other vital compounds like phytohormones [1]. Urea has a high nitrogen content of 46 %, and is the most widely used nitrogen fertilizer in agriculture. However, about 20 % to 70 % of urea escapes to the environment through nitrification leaching, and volatilization in the practical use of conventional urea [1–5], resulting in large economic and resource losses and very serious environmental pollution.

In recent years, slow release fertilizer has become one potential way to solve these problems in the agriculture industry, and the study of slow release nitrogen has received much attention. Generally, in order to obtain slow release urea fertilizer, the granules or tablets of conventional urea are typically coated in polymer or mineral based inorganic coating materials [1–3, 6–9], with polymer coated fertilizers among the most promising [10]. The key feature of the coatings is to slow down the diffusion of urea into the soil, in addition, coatings are required to be low cost, biodegradable, and non-toxic. In recent years, a large number of polymers were reported as coatings for slow release urea, such as poly(vinyl alcohol), 2,4,9 chitosan [11, 12], poly(acrylic acid) [13–15], polyurethane [16], natural rubber [17] and other polymers and their composites [4, 18, 19]. Most papers have studied the preparation of polymer coatings, water absorption, biodegradation, the release amount and release time of urea, and have provided valuable references to later researchers and the urea fertilizer industry.

Researchers have also discussed the mechanisms of the release process, for instance the kinetics of urea diffusion [12, 19], the coating structure and the permeability coefficient of urea [13, 20], but the nanoscaled free volume holes in polymer coating has rarely been taken into account during the release process. Actually, the free volume holes of polymer coatings play a very important role in the water and urea molecules diffusion in coatings. The free volume, defined as the “elbow room” of polymer chains, was firstly used to explain the permeability of small molecules in polymers by Cohen and Turnbull in 1959, and is considered to be closely related to many physical properties, such as mechanical properties [21, 22], thermal conductivity [22, 23], permeability [24, 25] and so on. Positron annihilation lifetime spectroscopy (PALS) is a unique method to measure the free volume

Table I Contents of PVA and urea used in the PVA/U composite films.

Film label	PVA [g]	Urea [g]	Weight content of urea [wt%]
PVA/U0	12	0	0
PVA/U2	12	2	14.29
PVA/U3	12	3	20.00
PVA/U4	12	4	25.00

holes directly [26–34].

In this work, we have chosen the poly(vinyl alcohol) (PVA) as the coating polymer of urea. PVA, a typical water-soluble semi-crystalline polymer, is considered to be non-toxic, biodegradable and biocompatible, and has been widely used in food, pharmaceutical and agricultural applications [4,35]. Most importantly, PVA coated urea (PVA/U) films can not only control the release manner of urea, but also can be used as a biodegradable mulch film [4,36–41] for crops, with good thermal insulation and water retention. PVA/U has the potential of optimal supply of nutrients during the growth period of crops, and its application will benefit the environmental and economy [42]. In this research, PVA/U films were prepared by simple tape casting, and the mean size and relative fraction of free volume holes in the amorphous region of the composite films were measured by PALS. The correlation of free volume holes and urea release ratio was discussed, which have rarely been reported in other works.

2. Experimental

2.1 Materials

Commercial poly(vinyl alcohol) (PVA) powder was purchased from Aladdin Industrial Incorporation (Shanghai, China), with a degree of polymerization of 1700 and a saponification degree larger than 99 %. Urea granules were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The PVA powder and Urea granules were used as received without any further purification. The distilled water used as solvent for PVA and urea was prepared in the laboratory.

2.2 Sample preparation

The PVA/urea (PVA/U) composite films were prepared by the tape casting method from an aqueous solution of PVA and urea. The PVA powder and Urea granules were dissolved into distilled water to prepare the aqueous casting solution, and the solution was then mixed uniformly by magnetic stirring and ultrasonic dispersion. The solution was cast on a fused silica plate and put in a natural convection oven at 45 °C to evaporate the water finally. The dry PVA/U composite films were peeled off from the fused silica plate and cut to pieces for the subsequent tests. All the samples were annealed at 120 °C before measurements. In this work, films with different mass ratio of PVA and Urea were prepared, and the masses in each film are listed in Table I.

2.3 X-Ray diffraction (XRD)

X-ray diffraction analysis of PVA/U samples was carried out using a XRD (Bruke D8-Focus, Germany) with Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$), fixing the voltage at 40 kV and the current at 40 mA. The data was recorded over the range of 5° to 45°, with a scanning rate of 0.05 s step⁻¹ and a step of 0.01°. The crystallinity (X_c) of PVA obtained from XRD can be defined using Eq. (1), where A_t is the area of the total XRD pattern, and A_a is the area of amorphous region.

$$X_c = \frac{A_t - A_a}{A_t} \quad (1)$$

2.4 Fourier-transform infrared (FTIR) spectroscopy

In order to characterize the chemical structure and interfacial interaction of PVA/U films, FTIR measurements were performed by a Bruker Vertex-70 FTIR spectrometer (Germany). Spectra for all samples were recorded over the range 4000 cm^{-1} to 400 cm^{-1} with the attenuated total reflectance (ATR) accessory. A total of 16 scans for each sample were collected at a resolution of 0.5 cm^{-1} . All spectra were baseline corrected.

2.5 Positron annihilation lifetime spectroscopy (PALS)

Positron lifetime measurements were performed at room temperature using a conventional fast-fast coincidence lifetime spectrometer with a time resolution of 250 ps full width at half maximum (FWHM). A 0.37-MBq ^{22}Na source was sandwiched between two identical samples. Analysis of positron lifetime spectra was performed using the finite-term lifetime analysis PATFIT program. All the measured spectra were resolved into three components (τ_1 , τ_2 and τ_3). The long-lived component τ_3 is attributed to the *o*-Ps pick-off annihilation in free volume holes in amorphous regions. The radius (R) and mean size (V) of free volume holes can be evaluated from τ_3 as Eqs. (2) and (3) [43]:

$$\tau_3 = 0.5 \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1} \quad (2)$$

$$V = \frac{4}{3}\pi R^3 \quad (3)$$

where $\Delta R = 0.1656\text{ nm}$ [44,45] is derived from fitting the observed *o*-Ps lifetimes in molecular solids with known hole sizes. The obtained relative intensity of *o*-Ps ($I_3 = 15\% - 17\%$) for the PVA/U samples should be affected by the introduction of carbonyl groups to urea, so that the change of I_3 becomes complicated and I_3 cannot be used to represent the free volume concentration. Therefore, the variation of I_3 is not discussed in detail here.

2.6 Swelling ratio (SR) and released ratio (RR) measurements

The SR is used to characterize the water absorption ability of the PVA/U films, and the RR is the ratio of urea release from PVA/U film into liquid water. SR and RR are defined using Eqs. (4) and (5), respectively:

$$\text{SR} = \frac{m_2 - m_1}{m_1} \times 100\% \quad (4)$$

$$\text{RR} = \frac{m_1 - m_3}{\text{Urea mass in the sample}} \times 100\% \quad (5)$$

where m_1 is the mass of a piece of dry PVA/U sample, and m_2 is the mass of the same sample after being steeped in liquid water for several hours at room temperature. The sample was then dried in oven at $45\text{ }^\circ\text{C}$ to constant mass, defined as m_3 .

3. Results and Discussion

3.1 Analysis of crystallinity

As a typical semi-crystalline polymer, the crystallinity of PVA was characterized by XRD. Fig. 1 shows XRD patterns of the PVA/U composite films. The characteristic peaks at $2\theta = 11.5^\circ$, 19.5° and 22.5° are attributed to the (100), (101/101) and (200) reflections, respectively. It is clear that the peaks of PVA/U films become lower and wider with the increase of urea weight content. In the spectrum of PVA/U0, A_a (the area marked by the red shadow) is attributed to the amorphous region, and $A_t - A_a$ (the area marked by the black shadow) is attributed to the crystalline region, respectively. The crystallinity of PVA/U films (X_c) calculated from Eq. (1) is shown in Fig. 2. X_c decreased significantly

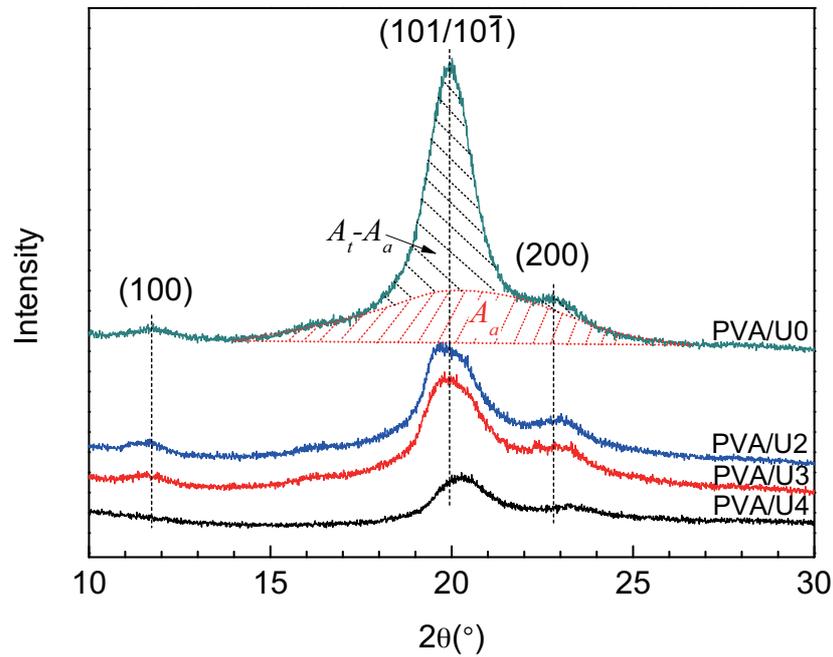


Fig. 1 XRD profiles for PVA/U composite films.

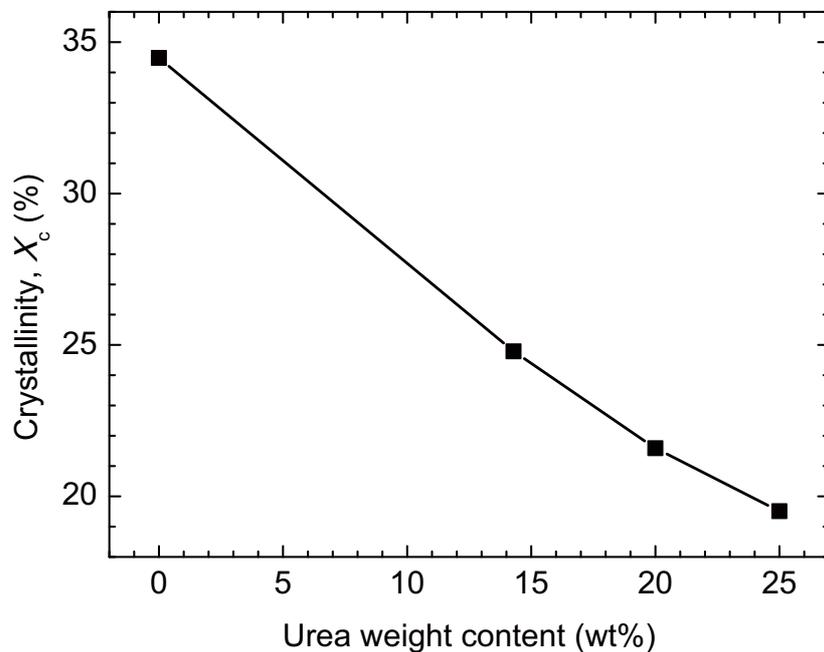


Fig. 2 Crystallinity of PVA/U composite films as a function of urea weight content. The line is drawn to guide the eyes.

from 34.48 % to 19.51 % as a function of urea weight content. This implies that the incorporation of urea can remarkably prevent the formation of crystalline regions in PVA/U films. When the urea granules were added into PVA coating, the motion of PVA chains were limited by the interfacial

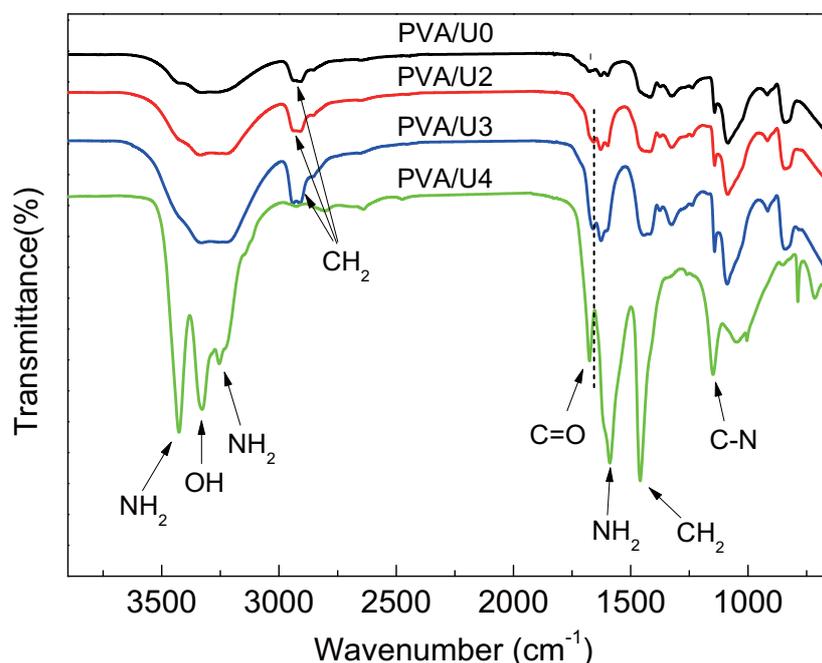


Fig. 3 FTIR spectra of PVA/U composite films.

interaction of PVA and urea, making it difficult for PVA chains to rearrange and form the crystalline regions in the films, resulting in decreasing crystallinity for PVA/U composite films.

3.2 Analysis of the interfacial interaction

FTIR spectra of the PVA/U composite films are shown in Fig. 3. For PVA/U0, PVA/U2 and PVA/U3 films, the absorption intensities of the peaks increase very slowly with increasing urea weight content and it is very difficult to distinguish the characteristic peaks of urea from the spectra of PVA/U composite films. In contrast, the characteristic peaks of urea are particularly evident in the spectrum of PVA/U4. The absorption peaks of the PVA/U4 film at 3426 cm^{-1} , 3255 cm^{-1} and 1589 cm^{-1} are attributed to antisymmetric stretching vibration, symmetric stretching vibration and bending vibration of amino groups (NH_2) in urea, respectively. The absorption peak at 1148 cm^{-1} is due to the stretching vibration of carbon-nitrogen (C–N) bonds. The stretching vibration of carbonyl groups (C=O) has a wavenumber of 1658 cm^{-1} , 1660 cm^{-1} and 1676 cm^{-1} for the PVA/U2, PVA/U3 and PVA/U4 films, respectively, which means that the peak position of C=O groups shifts to higher wavenumbers, implying the formation of hydrogen bonds between the hydroxyl groups of PVA and carbonyl groups of urea [46].

3.3 FTIR spectra of PVA/U composite films

The bending vibration of methylene (CH_2) groups for PVA chains can be observed at the absorption peaks of 1459 cm^{-1} for all PVA/U films in Fig. 3, and the intensities of the peaks increased with increasing urea weight content. However the stretching vibration of CH_2 groups at the peak of 2925 cm^{-1} was observed only for PVA/U0, PVA/U2 and PVA/U3 films and abruptly disappeared for PVA/U4 film. These results may be attributed to the lower absorption coefficient compared with those for the functional groups of urea, indicating that the hydrogen-bond formation between PVA and urea was partly suppressed with higher loading of urea, implying the aggregation of urea.

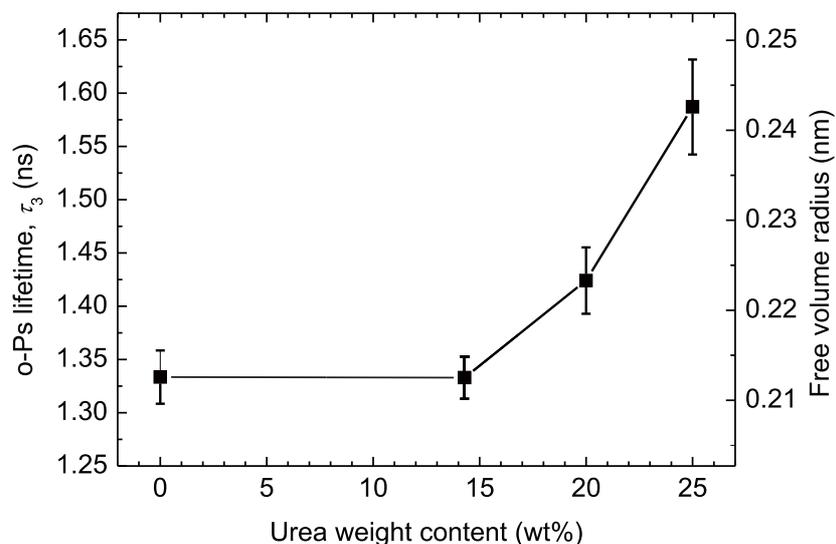


Fig. 4 *o*-Ps lifetime of PVA/U composite films as a function of urea weight content. The line is drawn to guide the eyes.

3.4 Analysis of free volume holes in amorphous region

Molecular chains of PVA are disordered in the amorphous region, movement requires free space of free volume in which the chains can move freely. PALS is a unique method to directly measure the size of free volume holes, based on the lifetime of ortho-positronium (*o*-Ps) as outlined above. Fig. 4 shows the *o*-Ps lifetime (τ_3) and free volume radius (R) as a function of urea weight content, representing the average size of free-volume holes in the amorphous region. Compared with the τ_3 of PVA/U0 (1.33 ns), the value of PVA/U2 (1.33 ns) did not change obviously, but for PVA/U3 (1.42 ns) and PVA/U4 (1.59 ns), τ_3 increased significantly. The free volume radius calculated from Eq. (2) increased from 0.21 nm for PVA/U0 to 0.24 nm for PVA/U4. It is worth mentioning that the mean free volume radius of PVA/U films is dramatically larger than the water molecule radius, 0.20 nm, which provides a movement path for the water molecules, they move from one side to the other side of the PVA coating by jumping from one free volume hole to an adjacent hole. After the urea was added into PVA, a large amount of interface was formed between them, and the free volume radius of PVA/U composite films was determined by two factors. The first one is that conformation changes of PVA molecular chains were induced, the packing modes of molecular segments were partly disarranged and a great deal of segmental chains were exposed on the interface, leading to an increase in motility of PVA molecules. The second one is that the hydrogen bonds on the interface limit the motion of PVA chains. The variation of free volume radius for PVA/U composite films is then an equilibrium of the above two factors. For PVA/U2, the effect of hydrogen bonds limitation is similar with the segmental chains exposure, resulting in no significant change of τ_3 . But for PVA/U3 and PVA/U4, with the increase of urea weight content, more and more segmental chains are exposed, the effect of which is much stronger than that of the hydrogen bonds limitation, so τ_3 is significantly increased. A similar phenomenon was observed in other polymer/inorganic composites [34, 47]. Furthermore, the τ_3 of pure urea, with a value of 2.07 ns reported by Shi [48], is much larger than that of the pure PVA, 1.33 ns. Taking into account the urea weight content of up to 25 %, the enlargement of τ_3 for PUA/U films by urea itself cannot be ignored. The increase in *o*-Ps lifetime of PVA/U is probably attributable to an influence of lifetime of the aggregated-urea domain, even if the aggregation of urea was not detected by XRD.

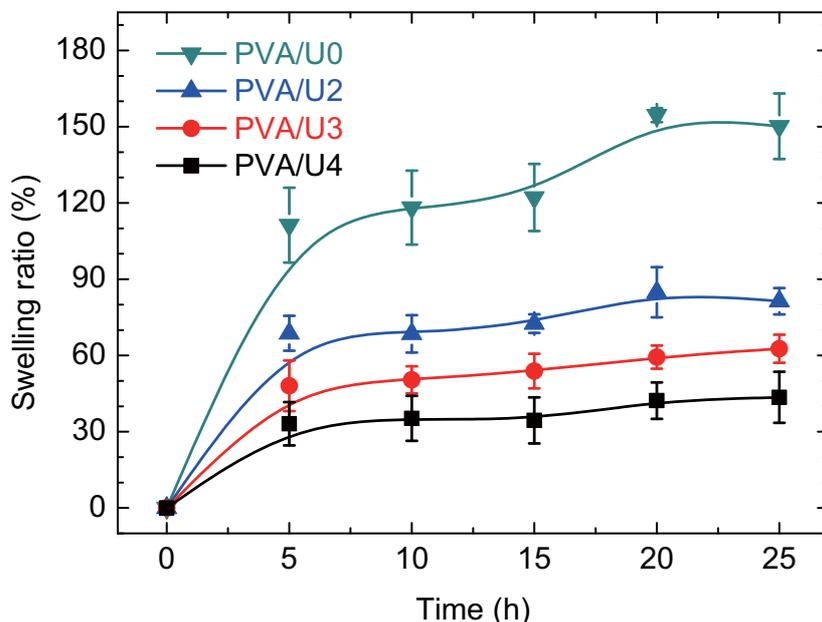


Fig. 5 The swelling ratio of PVA/U composite films as a function of swelling time and urea weight content. Lines are drawn to guide the eyes.

3.5 Analysis of water absorption

The swelling ratio (SR) was measured to characterize the ability to absorb liquid water, and is defined by Eq. (4). The urea weight content and swelling time dependence of SR for PVA/U films is shown in Fig. 5. The SR data was tested every five hours, and the average of five samples was calculated for each data point to reduce the error. Results show that the SR increased with increasing swelling time for all the PVA/U films. Pure PVA has the largest SR after 25 h, and the SR of other PVA/U films decreased with increasing urea weight content, declining rapidly from 150.2 % for PVA/U0 to 43.5 % for PVA/U4. It is well known that PVA is a typical water soluble polymer, it has large amount of hydrophilic hydroxyl groups on the molecular chain. The networks of cross-linked molecular chains can expand dramatically if the space between the chains is occupied by lots of water molecules, resulting in a strong ability to absorb water. When the urea was added into PVA, a large amount of hydrogen bonds formed between the hydroxyl of PVA chains and functional groups on the urea surface, which means part of the hydroxyl was locked by hydrogen bonds and lose the hydrophilic ability, furthermore, the hydrogen bonds limited the cross-linked networks expansion simultaneously, leading to the reduction of SR for PVA/U films.

3.6 Analysis of urea release from PVA/U film

The release ratio (RR) was measured to characterize the content of urea release from PVA/U film into liquid water, and is defined by Eq. (5). After PVA/U composite films absorb water, a large number of water molecules are present in the PVA coating. The urea dispersed in the PVA coating can be dissolved in this water and diffused from the coating into the surrounding environment, resulting in a weight loss of the films. Except for a small amount of dissolved PVA coating, the weight loss was mostly attributed to the release of urea from the coating into water. The RR of urea as a function of urea weight content and release time is shown in Fig. 6, showing that RR increased with increasing release time. After 5 h, 70.9 % of the urea in PVA/U4 film was released into the water, and the value increased up to 79.8 % after 25 h. The RR patterns of PVA/U2 and PVA/U3 have the same tendency as well as PVA/U4, however the absolute values are a little smaller than that of PVA/U4.

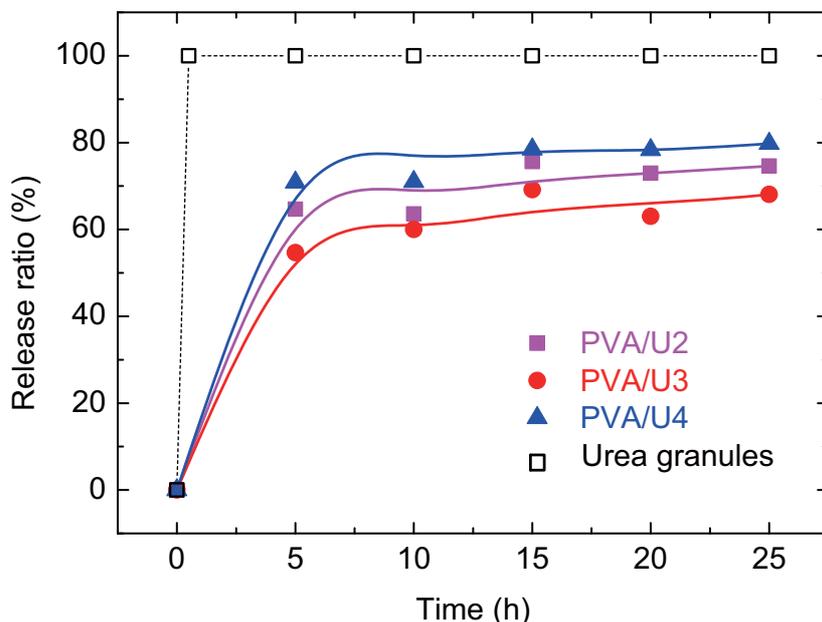


Fig. 6 The release ratio of urea from PVA/U composite films as a function of release time and urea weight content. Lines are drawn to guide the eyes.

Even though hydrogen bonds exist between PVA and urea, they can be broken under the action of water molecules [1, 10], so that most of the urea dissolved freely into the water and is released out from the PVA coating after 25 h. The results show that nearly 80 % of urea can be released from the PVA coating after absorbing water, and the RR is not sensitive to the urea loading in PVA/U films. It is clear that the urea granules can dissolve in water within several minutes and to verify the slow release efficiency of PVA/U films, the RR of urea granules in water was also drawn in Fig. 6 showing that the PVA coating slows down the release rate of urea, indicating that PVA has a slow release property. It can be confirmed that even if the swelling ratio drops to 43.52 % for PVA/U4 film, the amount of water in the film is sufficient to dissolve the urea particles and ensure their release.

As a slow-release carrier of urea, PVA has many advantages. Firstly, PVA molecular chains contain a large number of hydroxyl groups, PVA is also hydrophilic and easily absorbs a large amount of moisture, including liquid water and water vapor, which is the best solvent for urea and plays a key role for urea fertilizer entering into the soil. Secondly, the PVA/U films contain hydrogen bonds as the interfacial interaction between PVA and urea, which are weak and can be easily destroyed under the action of water molecules after swelling. Hydrogen bonds not only give the urea have a more uniform dispersion, but also ensure the urea is easily released from PVA coatings under certain conditions. The third and the last advantage is the sharp increase of free volume holes. Although the incorporation of urea makes the water absorption of PVA/U films lower, the dramatically increased mean size and fraction of free volume holes supplies abundant diffusion channels for water and urea molecules and ions, ensuring a stable release of urea from PVA coating.

4. Conclusion

In this work, PVA coated urea composite films were prepared by simple tape casting. The interfacial interaction between PVA and urea was identified as hydrogen bonds by FTIR. XRD was employed to determine the crystal structure and crystallinity of the films, and results showed that no characteristic peak of urea appeared in the patterns, implying that urea was well dispersed in PVA coating. The

crystallinity of composite films decreased as a function of urea loading, ascribed to the limitation in the packing of PVA chains by hydrogen bonds. The mean size of free volume holes in the amorphous region of the films was measured by PALS, and increased with increasing urea weight content, supplying much bigger and more diffusion channels for molecules and ions. The swelling ratio increased with time but decreased from 150.2 % to 43.5 % as a function of urea loading. This may be caused by the increasing crosslinking degree of the PVA coating, inhibiting the expansion of PVA networks. The release ratio of urea also increased with time, and about 79.8 % of urea was released from the composite film after 25 h. Even when the amount of water absorbed in the PVA coating is reduced as a function of urea loading, the increased mean size and fraction of free volume holes ensure a high water diffusion efficiency, thus ensuring the stability of the urea release.

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