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Controlled release of urea encapsulated by starch-g-poly(L-lactide)

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Abstract

This paper presented a new approach for preparing a new type of slow-release membrane-encapsulated urea fertilizer with starch-g-PLLA as biodegradable carrier materials. By solution-casting and washing rapidly with water the urea was individually encapsulated within the starch matrix modified by L-lactide through *in situ* graft-copolymerization. The release behavior of urea encapsulated in the films was studied, and following conclusions were achieved: (1) the introduction of hydrophobic PLLA reduced the swellability of starch matrix and decreased the release rate of urea; (2) the urea release rate could be controlled from several hours to 1 day by adjusting the graft efficiency; (3) scanning electron microscopy revealed that the urea encapsulated within the starch matrix was uniformly dispersed in the form of tiny cell and the urea encapsulated in the modified starch film released through a diffusion mechanism. Therefore, the modified starch products for controlled release could be expected to have widely potential application in agriculture industry as fertilizer carrier.

Keywords: Starch; Graft-copolymerization; Poly(L-lactide); Urea; Controlled release

1. Introduction

Starch is a natural polymer available in large amounts from several renewable plant sources, and it is produced in abundance beyond available markets. It is the cheapest biopolymer and it is entirely biodegradable. Therefore, more and more efforts are made to explore nonfood usage of starch-based products for applications in which synthetic polymers have traditionally been used. It can be effectively used as an encapsulating matrix in the controlled release for agrochemicals after derivatization and crosslinking (Bramwell, Eyles, & Oya Alpar, 2005; Dave, Mehta, Aminabhavi, Kulkarni, & Soppimath, 1999; Kulkarni, Rajagopalan, Kale, & Khilar, 1992; Kulkarni, Soppimath, Aminabhavi, Dave, & Mehta, 1999; Shasha, Doane, & Russell, 1976; Shukla, Rajagopalan, Bhaskar, & Sivaram, 1991; Tarvainen et al., 2004; Tuovinen, Peltonen, & Jarvinen, 2003; Yýlmaz et al., 2002). In recent years, the development of modified natural polymers as controlled release devices in agroindustries has emerged as a new technology with better commercial viability than the use of conventional synthetic polymers since these are known to create some environmental concern (Hong & Park, 2000; Kulkarni, Soppimath, & Aminabhavi, 1999; Kulkarni, Soppimath, & Aminabhavi, 2000; Kumbar, Kulkarni, Dave, & Aminabha, 2001). Therefore, the research orientation has been ongoing to find a suitable alternative and film-forming membrane material that can be safely used in agroindustries. Hong and Park (2000) reported the possibility of using polyurea microcapsules to encapsulate both liquid and solid bioactive compounds, but these systems are not cost-effective in agroindustries. A process for the encapsulation of pesticides using urea formaldehyde (UF) crosslinked starch and guar gum matrices was reported by Kumbar et al. (2001), and the release kinetics and encapsulation efficiency for the controlled release of solid (chlorpyrifos) and liquid (neem seed oil) pesticides was studied clearly.

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Fertilizers are the main factors that limit the development of agricultural production, so it is very important to improve the utilization of fertilizer nutrients. Nitrogen is the most vital nutrient for crops. Among the nitrogen fertilizers, the most widely used one is urea because of its high nitrogen content (46%) and comparatively low cost of production. However, due to surface runoff, leaching, and vaporization, the utilization efficiency or plant uptake of urea is generally below 50%. About 40–70% of nitrogen of the applied normal fertilizers escapes to the environment and cannot be absorbed by crops, which causes not only large economic and resource losses but also very serious environmental pollution (Dave, Mehta, Aminabhavi, Kulkarni, & Soppimath, 1999; Guo, Liu, Zhan, & Wu, 2005; Liu, Liang, Zhan, Liu, & Niu, 2007). Research has shown that slow- or controlled-release technology could effectively resolve these problems, and avoid or decrease the loss of normal fertilizers and environmental pollution. Although the natural starch is also an effective material for agrochemical encapsulation, natural starch is a polysaccharide polymer with many hydroxyl groups that make the starch matrix hydrophilic and capable of absorbing water and swelling dramatically in aqueous solution. Consequently, the matrix provides an effective control over the fertilizer encapsulated in the starch only for a relatively short period of time after rainfall or irrigation, which reduce the survival life in field uses, especially in heavy-water environments.

In order to improve starch properties, starch is graft-copolymerized with various monomers. Through the variation of grafting monomers, different changes in properties can be achieved (Arvanitoyannis, Nakayama, Kawasaki, & Yamamoto, 1995, 1999; Zhu & Zhuo, 2001). A hydrophobic behavior can be obtained if the graft-copolymerized monomers are hydrophobic such as L-lactide. Our group has prepared the starch-g-poly (L-lacide) (starch-g-PLLA) (Chen, Qiu, Chen, & Jing, 2005; Chen, Qiu, Xie, Hong, 2006), which has a core-shell structure with the core of hydrophilic starch and the shell of hydrophobic PLLA grafts. Therefore, by the direct encapsulation of urea fertilizer within the hydrophobic starch matrix, the hydrophobic behavior of the modified starch would make the matrix swell less.

On the basis of the above background and our previous studies on starch-g-PLLA, this paper presents a new approach for preparing a new type of slow-release membrane-encapsulated urea fertilizer with starch-g-PLLA. This starch-g-PLLA membrane can also be used for the encapsulation of herbicides and other fertilizers.

2. Experimental

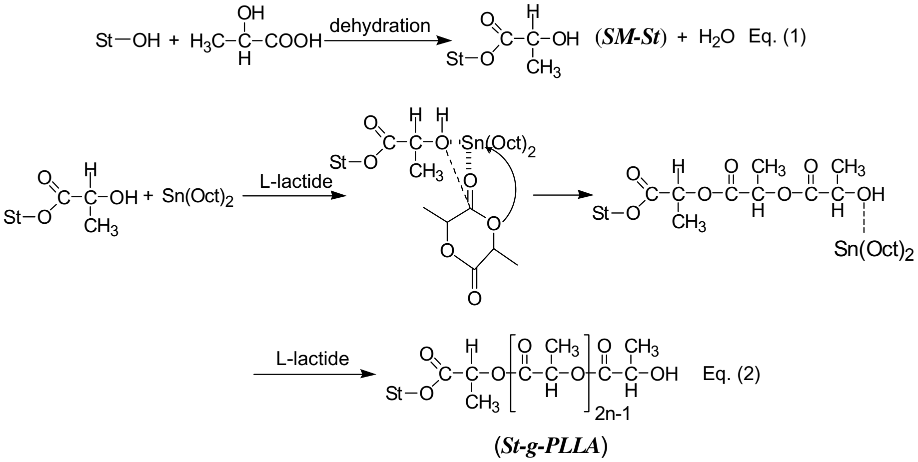
2.1. Materials

The corn starch was from Changchun Dacheng Corn Development Co. Ltd. in Jilin province, China. The amylose content was 27% and the water content in the starch was about 12% in weight measured by water loss at 60 °C in a vacuum oven.

The urea (diameter 1–2 mm) was industrial grade from Shenyang Chemical Plant (Shenyang China). *p*-Dimethylamino benzaldehyde (PDAB), dimethylsulfoxide, sulfuric acid and other solvents were all of analytical grade and used as received.

2.2. Preparation of starch-g-poly(L-lactide)

The encapsulating matrix, starch-*g*-poly(L-lactide) (St-g-PLLA), was synthesized and characterized as described in our previous study (Chen et al., 2005): the starch surfaces were firstly modified by reacting the hydroxyl groups on the starch with L-lactic acid, and then the St-g-PLLA was synthesized *in situ* by the ring-opening graft-polymerization of L-lactide (LLA) monomers onto the modified surfaces of the starch granules in the presence of $Sn(Oct)_2$ as a catalyst depicted in Scheme 1. After the polymerization reaction, the unreacted LLA monomer and PLLA homopolymer were washed off with ethanol and toluene, respec-



Scheme 1. The surface modification of starch with L-lactic acid Eq. (1) and the *in situ* graft-polymerization of L-LA on the modified starch initiated by $Sn(Oct)_2$ Eq. (2).

tively. The graft efficiencies of the final product, St-g-PLLA, were summarized in Table 1.

2.3. Preparation of composite films

The starch-g-PLLA/urea composite films were prepared by a solution-casting method. The graft copolymer starch-g-PLLA (2.0 g) and urea (0.2 g) were dissolved in DMSO (30 mL). The solution was stirred for 0.5 h at room temperature and then cast in a Teflon-coated Petri dish. The solvent was allowed to evaporate slowly at 60 °C over 2 days through a vented lid on the dish. Small films were cut from this film using a circular whole cutter. In order to compare with the natural starch matrix, the starch/urea composite film was made by the following method: two grams (dry base) of the starch and 20 mL of distilled water were placed in a glass beaker and stirred mechanically for 20–30 min to form dispersion. The beaker was maintained in a thermostat oil bath at about 90 °C for 20–30 min under stirring to gelatinize the starch. Then, the urea particles were thoroughly mixed with the gelatinized starch paste with a glass rod. Finally the mixture was poured into a Teflon-coated Petri dish. The water was evaporated slowly at 80 °C over 2 days. Before the release experiment, the composite films were all washed rapidly with water in order to remove the urea exposed on the surface of the films. The thickness of these films was approximately 0.5 mm.

2.4. Characterization of composite films

The IR spectra of the composite films were recorded on Bruker Vertex 70 Fourier transformation infrared (FTIR) with attenuated total internal reflectance (ATR) to measure the structure of the film materials.

The surface elemental analysis of the composite films was performed on an ESCALAB 250 X-ray photoelectron spectroscopy. The X-ray source was an AlKα radiation ($hv = 1486.6$ eV), and the measurement was carried out in a vacuum of 8.0×10^{-10} bar.

The composite film SEM images were obtained with a Model XL 30 ESEM FEG from Micro FEI Philips after the sputter coating of gold on the specimen surface. The solid–liquid contact angle of the free films, which were stored in a desiccator at least 3 days before testing, was measured with a Kruss DSA10 MK2 (Germany) apparatus. A water droplet was dropped on the surface of a horizontal small sample cut from the film. The evolution of the droplet shape was recorded by a CCD video camera and was analyzed to determine the contact angle evolution. The test was carried out at room temperature.

Table 1
The St-g-PLLA characterization

St-g-PLLA No	LA[a] (g/100 g of SM-St)	LA monomer conversion (%)	Graft efficiency[b] (%)
1	10	94.1	12
2	20	95.0	25
3	34	96.0	43
4	50	96.4	65

[a] Bulk reaction process; the polymerization temperature was at 130 °C. The lactic acid content in SM-St is 6.0%.

[b] Determined according to the definition of graft efficiency.

2.5. Water absorbency of composite films

A weighed quantity (m_1) of the composite films of starch-g-PLLA or starch was immersed in distilled water at room temperature to reach swelling equilibrium. After 12 h, the swollen film was taken out and the liquid on the film surface was absorbed by a filter paper. The film was maintained in the air at room temperature for 10 min to get rid of the surface water and then weighed (m_2) accurately. The water absorbency (Q_{H_2O}, expressed as grams of water absorbed by per gram of sample) of the composite films was calculated using following equation:

$$Q_{H_2O} = (m_2 - m_1)/m_1$$

2.6. Encapsulation efficiency

Encapsulation efficiency is the weight percentage of the actually encapsulated amount of urea over that in feeding. The film sample with dry weigh W_0 (e.g., 500 mg) was washed with 20 mL of water to remove the surface urea. The urea content (ΔW) in the water was detected by UV–Vis spectrophotometer (UV-2401PC, Shimadzu). The encapsulation efficiency was calculated according to following equation:

$$\begin{aligned}\text{Encapsulation efficiency (\%)} &= (W_0 \times C - \Delta W)/(W_0 \times C) \\ &\quad \times 100\% \\ &= [1 - \Delta W/(W_0 \times C)] \\ &\quad \times 100\%\end{aligned}$$

where C is the urea content of the film sample calculated from the feed composition.

2.7. Release behavior of urea from the composite films in water

To study the release behavior of urea from the composite films in water, the following experiment was carried out: the dry film (encapsulated by starch or starch-g-PLLA) sample (500 mg) was immersed in 100 mL distilled water in a glass beaker properly covered at 25 °C. A quantity of 5.0 mL of solution was taken out to estimate for the contents of nitrogen after a certain interval, and then the same volume of fresh water was replenished. According Ehrlich reaction, the amount of released urea from the starch-g-PLLA or starch matrix was measured at 440 nm by UV–Vis spectrophotometer (UV-2401PC, Shimadzu). All the release experiments were done in duplicate, and their results were averaged.

3. Results and discussion

3.1. Synthesis and characterization of the graft copolymer starch-g-PLLA

According to our previous study (Chen et al., 2005, 2006), the surface modification reaction and the polymerization procedure are depicted in Scheme 1. First, after azeotropic dehydration of the starch with toluene, the hydroxyl groups on the surface of the starch granules react with L-lactic acid to form starch L-lactate that has active hydroxyl end groups (St-OOCCH(CH_3)*OH*), Eq. (1)). Then, in the presence of $Sn(Oct)_2$ as catalyst, the active hydroxyl end groups of starch L-lactate initiate the polymerization of L-lactide to give the graft copolymer St-g-PLLA. At the same time, some homo-poly(L-lactide) (PLLA) may be generated because of the initiation by free OH groups or the transesterification of the growing molecular chains. The graft copolymer and PLLA could be easily separated based on their different solubilities in toluene. The homo PLLA can be attracted by toluene.

The graft efficiency data of St-g-PLLA are summarized in Table 1. It is defined as the weight content of the grafted PLLA with respect to the starch used. Four graft copolymers were used to prepare composite films as shown in Table 1. Their graft efficiency was from 12% to 65%.

3.2. Characterization of the composite films

The IR spectra of St-g-PLLA film and St-g-PLLA/urea composite films are shown in Fig. 1. Comparison of the IR spectrum of St-g-PLLA (a) with those of the composite films (b and c) shows that new absorptions appear at 1660, 3359–3100 and 1625 cm^{-1}. They can be assigned to ν_{CO}), ν_{NH} and δ_{NH} of urea, respectively, indicating that the urea had been encapsulated in the St-g-PLLA matrix.

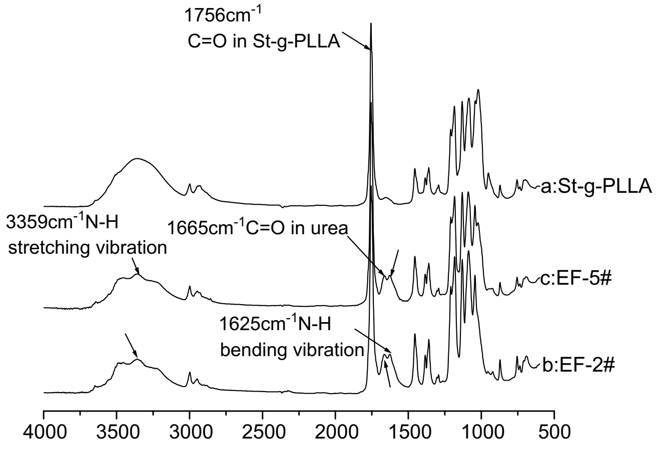


Fig. 1. IR spectra of St-g-PLLA (a), composite films CF-2# (b) and CF-5# (c) in Table 2.

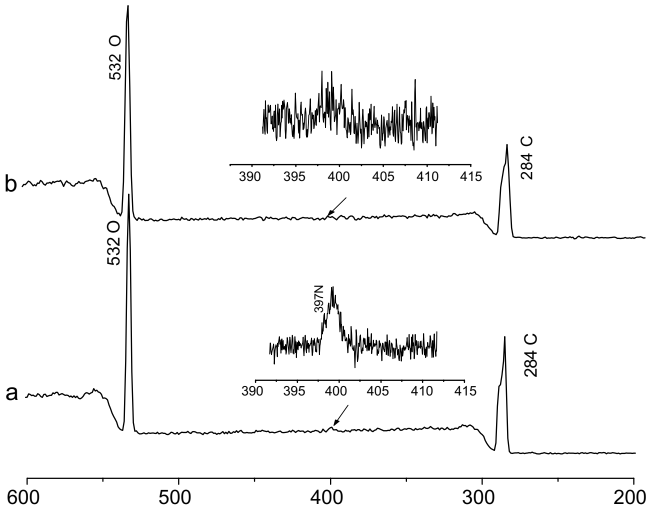


Fig. 2. XPS of CF-2# before (a) and after (b) water washing.

The elemental composition on the surface of the composite films was determined by XPS in Fig. 2. Before water washing, the surface of the composite films showed an XPS peak at 399 eV (Fig. 2a) attributed to N_{1s}, and then after washing, this peak disappeared completely (Fig. 2b). This testified that the urea exposed on the surface of films could be removed by washing with water. Combined with the results of IR analysis, it could be concluded that the urea could be encapsulated successfully inside the St-g-PLLA matrix by solution-casting and subsequent water washing.

The SEM images of the composite films are presented in Fig. 3. The figures revealed that the urea particles were regularly dispersed in the continuous St-g-PLLA matrix phase. After removing the urea exposed on the surface of the films by washing rapidly with water the outermost St-g-PLLA formed a barrier. This meant that the composite film was a reservoir-type system. The urea was surrounded by a St-g-PLLA wall and released through diffusion. In the previous paper (Chen et al., 2005) it had been proved that the amphiphilic St-g-PLLA had a core-shell structure with a hydrophilic starch core and a hydrophobic grafted PLLA shell. With the slow evaporation of DMSO solvent, the hydrophobic PLLA shell formed a wall-like barrier outside, while the hydrophilic starch part and the urea particles were encapsulated inside the matrix as shown in Scheme 2. At the same time, the images also showed that the starch and the urea particles encapsulated in the PLLA could be seen clearly when the graft efficiency of the PLLA was low (12% Fig. 3a). With the increase of the graft efficiency, the starch and urea particles inside became blurrier (65% Fig. 3b) because the PLLA shell of the St-g-PLLA films became thicker and encapsulated the starch and urea particles.

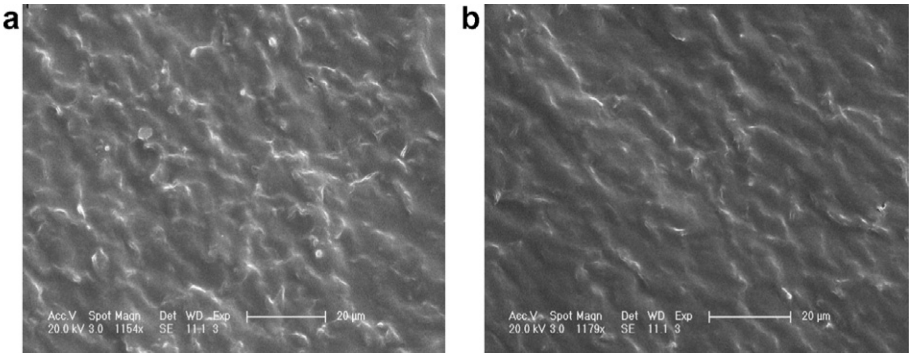
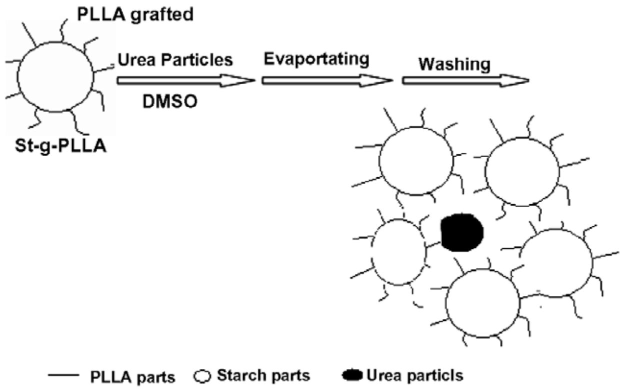


Fig. 3. SEM images of St-g-PLLA/urea film surface. (a) CF-2# and (b) CF-5#.



Scheme 2. The mechanism of the urea encapsulation film formed by the PLLA modified starch.

3.3. Water absorbency of composite films

It is well known that most fertilizers are water-soluble and prone to evaporate at room temperature. Due to surface runoff, leaching, and vaporization, the utilization efficiency or plant uptake of urea is generally low and most of the urea escapes to the environment, resulting in not only huge economic and resource losses but also very serious environmental pollution. It has been proved in our previous paper (Chen et al., 2005, 2006) that the St-g-PLLA has stronger water-resistance compared to pure starch. When the St-g-PLLA is used as matrix to encapsulate the urea particles, the St-g-PLLA/urea composite films still have strong water-resistance. This is testified by contact angle and water absorbency measurements. The contact angle, formed between a water droplet and the surface of a material, and the kinetics of spreading are related to the hydrophilic character of the material. The initial angle (in degree) and the kinetic of water sorption on the surface are given by this method. The composite films were quantitatively analyzed by the initial contact angle just after deposition of a water droplet and by the evolution rate of the contact angle with time. The results are presented in Table 3. For the pure starch/urea composite film, the contact angle is 38° due to its hydrophilic nature. With increasing graft efficiency of PLLA, the contact angle of the composite films increases to 91°, indicating that the outmost surface of the composite films was the hydrophobic PLLA. The stability of the composite films in water increases with increasing graft efficiency of PLLA. Compared to the pure starch/urea composite film, the St-g-PLLA/urea composite films showed improved resistance

Table 3
Surface properties of the St-g-PLLA/urea composite films

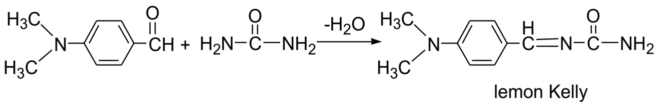
Film code	Initial value (°)[a]	Slope at the origin[a] (°/s)	Weight change in water after 12 h (wt %)
CF-1#	38	+0.15	Swollen and broken
CF-2#	74	−0.2	+1.7
CF-3#	78	−0.1	+1.2
CF-4#	87	−0.1	+0.9
CF-5#	91	−0.05	+0.8

[a] The data were from contact angle measurements and collected by mean of five independent experiments.

Table 2
Influence of the PLLA graft efficiency on the encapsulation efficiency of urea

Composite film code	Matrix materials	Graft efficiency (%)	Urea content in the film (%)		Encapsulation efficiency (%)
			Calculated[b]	Measured[c]	
CF-1#	Starch	–	9.1	4.8	53
CF-2#	St-g-PLLA 1[a]	12	9.1	6.4	70
CF-3#	St-g-PLLA 2	25	9.1	6.8	75
CF-4#	St-g-PLLA 3	43	9.1	7.0	77
CF-5#	St-g-PLLA 4	65	9.1	7.4	81

[a] From Table 1.
[b] The theoretical value according the feed rate in solvent-casting process.
[c] After water washing, the urea extracted from the film surface to the water was measured by UV–Vis spectrophotometer.



Scheme 3. The Ehrlich reaction.

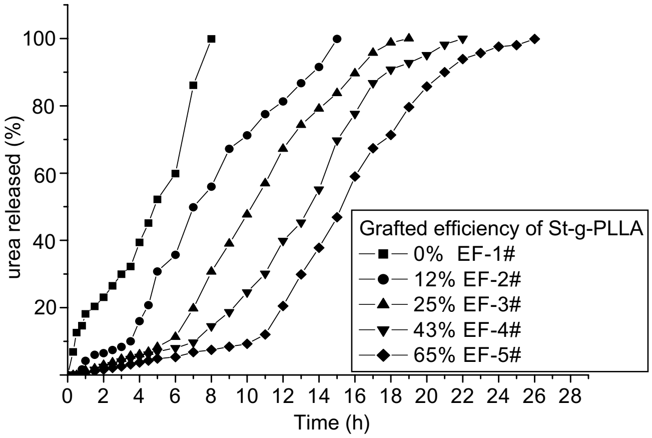


Fig. 4. The release curves of urea from starch/urea and the St-g-PLLA/urea composite films.

to water. When the pure starch/urea composite film was immersed in distilled water, it was firstly swollen, and quickly broken because both starch and urea are sensitive to water and can absorb a quantity of water. In all cases, the presence of PLLA in St-g-PLLA copolymer leaded to significant improvement of the film hydrophobicity. The water tolerance of the matrix could improve the capability of controlling urea release.

3.4. Encapsulation efficiency

Urea content in the films and encapsulation efficiency of the composite films are listed in Table 2. After water washing, the urea exposed on the surface of the films could be removed completely. By measuring urea content in the water, the released urea from the films could be determined. According to Ehrlich reaction, *p*-dimethylamino benzaldehyde could react with urea to give lemon Kelly which would absorb visible light at 440 nm (Scheme 3) (Werner & Odin, 1952). Therefore the content of encapsulated urea in the film could be determined. Compared to the pure starch/urea composite film that had an encapsulation efficiency of 53%, the St-g-PLLA/urea composite films exhibited higher urea encapsulation efficiency ranging from 70% to 81%, depending on the graft efficiency of PLLA.

3.5. Release behavior of urea from the composite films

The influence of graft efficiency on the rate of urea release from the composites is shown in Fig. 4. It is worthy of noting that pure urea dissolves in water entirely in five seconds. As shown in Fig. 4, the rate of urea release has been evidently slowed down by both pure starch and the St-g-PLLA matrices. In addition, the release rate of urea decreases with increasing graft efficiency of PLLA on starch, especially, the composite film prepared from St-g-PLLA with a graft efficiency of 65% resulted in complete release of urea in 26 h. These phenomena could be explained by different swellability of starch and the St-g-PLLA matrices. It is well known that starch can be easily swollen by water. The urea in the swollen starch can diffuse rapidly and can be released quickly. After the starch is hydrophobilized by grafting L-lactide on it, both the swellability and the water absorbability of the matrix films decreases so that the release rate of urea is reduced with increasing graft efficiency of PLLA on starch. Further more, all of the St-g-PLLA/urea samples exhibit a similar release kinetics that includes two stages as shown in Fig. 4, where urea releases slowly in the first stage and faster in the second stage, and only about 10% of urea was released during first stage. In the second stage, all samples show a comparable release rate (slope of the curves). These indicated that the most of urea could not be released until the St-g-PLLA films became swollen enough and in the swollen state, the urea has a comparable diffuse and release rate. As shown in Fig. 4, release curves of the St-g-PLLA/urea system with higher graft efficiencies consist of the third stage. It lasts up to 6 h for the sample with graft efficiency of 65%.

4. Conclusion

Both native starch/urea and PLLA-grafted starch/urea composite films were prepare and the release behaviors of urea from them were examined and compared to each other. It was confirmed that St-g-PLLA is an effective material for encapsulating water-soluble fertilizers such as urea for controlled release. The encapsulated urea is dispersed in the form of tiny particles and is released through diffusion from the matrix. The St-g-PLLA exhibits relatively low swellability, large encapsulating capacity, and slow-release rate. It can be applied especially to fertilizers or other agrochemicals with higher water solubility. Further more, the water-resistance of the matrix could be improved by increasing PLLA graft efficiency on the starch granules.

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