

Controlled Release of Carboxylic-Containing Herbicides by Starch-*g*-poly(butyl acrylate)

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ABSTRACT: The use of starch-*g*-poly(butyl acrylate) as a new material for encapsulating carboxylic-containing herbicides such as 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid for controlled release was studied. The herbicides were individually encapsulated within the modified starch substrate, which was graft-copolymerized with a small amount of butyl acrylate. The modification of starch induced a hydrophobic behavior in the matrix, made it swell less, and caused the release rate to slow, especially for herbicides with higher water solubility. Therefore, the survival life of the starch products for controlled release could be expected to extend to some extent compared with that of natural starch. In addition, the effects of the molecular weight, herbicide content, and particle size on the swellability and release behavior were also investigated. Scanning electron microscopy revealed that the herbicides encapsulated within the starch matrix were dispersed in the form of tiny cell. Consequently, the herbicides encapsulated were released through diffusion. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1535–1543, 2001

Key words: starch; controlled release; encapsulation; starch graft copolymer; carboxylic-containing herbicide

INTRODUCTION

Starch-encapsulated agrochemicals for controlled release can be created by the dispersal of the agrochemicals into an aqueous paste of gelatinized starch and the performance of a procedure of retrogradation or crosslinking. The technique has many advantages. In addition to a controllable release rate, the characteristics of improved efficacy, extended activity, economical encapsulation, biodegradable behavior of the matrix, less pollution to environments, reduced times and

amounts of application, increased safety in handling and to plants, effective control over the actives on targets, and reduced losses (through evaporation, degradation, leaching, etc.) of actives make the technique broadly accepted. Therefore, starch encapsulation as a method for controlling agrochemical release shows potential for solving some problems associated with the widespread use of agrochemicals.¹

For the reasons mentioned, starch encapsulation has received more and more attention recently. A large amount of research has been done on methods for encapsulating various agrochemicals within natural or modified starch matrices. Early reports showed that the starch xanthate was an effective substrate for encapsulating agrochemicals.^{2–5} Further studies indicated that the

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actives could be encapsulated within starch–calcium adducts^{6,7} or starch–borate complexes.^{1,8} Recent studies revealed that natural starch was also an effective material for agrochemical encapsulation.^{9–15} Moreover, laboratory, greenhouse, and field trials have been conducted year by year to evaluate the behaviors and effects of these starch products.^{16–20}

It should be noted that the water solubility of carboxylic-containing herbicides is alkali-sensitive. Although starch matrices such as starch xanthate, starch–calcium adducts, and starch–borate complexes can encapsulate a large number of herbicides in practice, the alkali conditions (pH \geq 12) required for starch gelatinization, modification, or crosslinking make the carboxylic-containing herbicides soluble in water. The survival time for controlling these herbicides' release would be greatly reduced by increased water solubility. For this reason, it is not feasible for carboxylic-containing herbicides to be encapsulated within these starch matrices. Moreover, 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 water. Consequently, the matrix provides an effective control over the herbicides encapsulated only for a relatively short period of time after rainfall or irrigation. The defects of the alkali sensitivity of the herbicides and the low water tolerance of natural starch matrices reduce the survival life in field uses, especially in heavy-water environments.

Graft copolymerization of starch with various vinyl and/or acrylic monomers constitutes a powerful means for improving starch properties. Through the variation of grafting monomers, different changes in properties can be achieved. A hydrophobic behavior can be obtained if starch is graft-copolymerized with a certain amount of hydrophobic monomers.^{21,22} Therefore, by the direct encapsulation of carboxylic-containing herbicides within the hydrophobic starch matrix, the hydrophobic behavior of the modified starch would make the matrix swell less. Moreover, this method favors the encapsulation and control of carboxylic-containing herbicides because it avoids crosslinking under alkali conditions. For this reason, the release rates of carboxylic-containing herbicides from the hydrophobic starch matrix in wet environments would be expected to be reduced.

The goal of this study was to determine if the hydrophobic chains-grafted starch matrix could provide more effective control over carboxylic-containing herbicides. We chose starch-g-poly(butyl acrylate) (starch-g-PBA) as the matrix material for controlling the release of carboxylic-containing herbicides.

EXPERIMENTAL

Materials

Commercial granular cornstarch from Qinyang Starch Factory (Qingyang, China) had a viscosity of 130 mPas (6%, 95°C). Prior to use, the starch was defatted²³ and refined as follows: 350 g of starch was dispersed and stirred in 500 mL of a methanol-distilled water medium (85/15 v/v) at 40°C for 1 h and then filtered and washed with 100 mL of the same medium three times. Finally, the starch was washed in 600 mL of distilled water two times and then dried and pulverized.

Butyl acrylate, chemically pure grade from Beijing Xinguang Reagent Plant (Beijing, China), was distilled under vacuum and stored in a refrigerator until use. Ceric ammonium nitrate, analytical reagent grade, was obtained from Xinhua Reagent Factory (Beijing, China). Methanol, ethanol, acetone, HNO₃, Na₂HPO₄ · 12H₂O, and KH₂PO₄ were all analytical reagent grade.

2,4-Dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) were chemically pure grade and supplied by Shanghai No. 4 Reagent Factory (Shanghai, China) and Beijing Chemical Plant (Beijing, China), respectively.

Synthesis of Starch-g-PBA

The graft copolymerization of starch with butyl acrylate was carried out in an aqueous dispersion in a four-necked vessel. The vessel was equipped with a stirrer, a thermometer, and two dropping funnels and maintained in a thermostatically controlled water bath at 30°C. The refined natural cornstarch (100 g, dry base) was dispersed in 300 mL of distilled water and transferred to the vessel. The gas in the vessel was changed with argon gas three times with a water aspirator. Certain amounts of butyl acrylate and ceric ammonium nitrate solution (dissolved in 1.0*N* nitric acid to give a molar concentration of 0.20) were added

Table I Characterization of Starch-*g*-PBA Prepared with Different Grafting Ratio

Starch- <i>g</i> -PBA Number	BA ^a (g/100 g of Starch)	Conversion of Monomer (%)	Grafting Ratio (%)	Grafting Efficiency (%)	Molecular Weight × 10 ⁻⁵	
					Grafted PBA	Homopolymer
1-1#	6	98.6	3.86	65.3	1.64	1.71
1-2#	9	98.6	5.74	64.7	1.85	1.62
1-3#	12	99.3	8.21	68.9	1.94	1.22
1-4#	15	99.0	9.92	66.8	1.08	1.02

The ceric ammonium nitrate/BA (molar ratio) was 26/1000.

^a Butyl acrylate.

through the dropping funnels continuously at such a speed that the addition was completed uniformly in 20–25 and 30–40 min, respectively, for butyl acrylate and the initiator solution. The reaction was carried out under stirring and under the protection of Ar₂ for 3 h. Finally, the product was neutralized, filtered, washed with distilled water, dried at 60°C, and pulverized.

Characterization of Starch-*g*-PBA

The grafting parameters for characterizing starch-*g*-PBA are defined and explained as follows. The conversion of the monomer (%) expresses a weight percentage of the synthetic polymer formed to the monomer charged.²⁴ The grafting efficiency demonstrates the weight percentage of the synthetic polymer in grafts to the total synthetics formed.²⁵ The grafting ratio indicates the weight percentage of the synthetic polymer in grafts to starch substrate.²⁶

Conversion of the Monomer

Because of the small amount of monomer used compared with the amount of starch, the weight percentage of the synthetics in the starch graft copolymers was very low. Therefore, the weight method for measuring the weight of synthetics in the starch graft copolymers after acid hydrolysis or enzymolysis would not be very accurate. For this reason, a bromination method was employed to determine the amount of residual monomer when graft copolymerization was just completed.²²

Extraction of Homopolymer

Nearly 10 g (dry base, exactly weighed) of vacuum-dried starch-*g*-PBA was extracted with 150

mL of acetone for 24 h to remove the homopolymer. The extracted samples were thoroughly dried to a constant weight under vacuum to measure the weights of the homopolymer. Moreover, after extraction the extracting solutions were filtered and evaporated to dryness to determine the molecular weights of the homopolymers.

Recovery of the Grafting Chains from Starch-*g*-PBA

After extraction, 6 g of the extracted sample was suspended in 150 mL of 1N HCl²³ and hydrolyzed by refluxing for 3 h. The insoluble residue was collected, washed, and dried under vacuum. Then, the sample was dissolved in 30 mL of acetone, and the solution was filtered. Finally, the grafting branches were recovered by the evaporation of the solution to dryness and were dried to a constant weight under vacuum.

Determination of Molecular Weights

The molecular weights of poly(butyl acrylate) (PBA), whether in grafts or homopolymers, were determined by the measurement of the intrinsic viscosity in acetone at 25°C and were calculated from the following equation:

$$[\eta] = 6.85 \times 10^{-3} \bar{M}_n^{0.75}$$

Evidence of Grafting

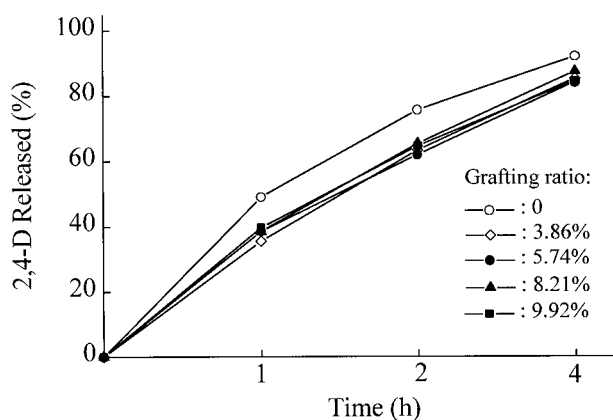
The infrared spectrum of the starch graft copolymers extracted with acetone showed carbonyl absorption at 1737 cm⁻¹ caused by the grafting branches of PBA, whereas this absorption was not present in an infrared spectrum of natural cornstarch.

Table II Effect of the Graft Modification and Grafting Ratio on the Behavior of Starch-*g*-PBA Matrices

Herbicide	Encapsulating Material	Grafting Ratio (%)	Herbicide Content (%)		Swellability in Water (%)	Encapsulation Efficiency (%)
			Calculated	Measured		
2,4-D	Unmodified starch	—	12.39	10.85	320	61.5
2,4-D	1-1#	3.86	12.33	10.18	230	71.1
2,4-D	1-2#	5.74	12.33	11.87	210	71.3
2,4-D	1-3#	8.21	12.21	11.37	210	73.4
2,4-D	1-4#	9.92	12.30	11.52	210	70.8
2,4,5-T	Unmodified starch	—	12.22	10.16	300	83.0
2,4,5-T	1-1#	3.86	12.30	10.44	200	84.4
2,4,5-T	1-2#	5.74	12.41	10.54	180	77.7
2,4,5-T	1-3#	8.21	12.41	11.74	170	78.9
2,4,5-T	1-4#	9.92	12.33	10.97	170	80.0

Encapsulation

Twelve grams (dry base) of the starch-*g*-PBA and 120 mL of distilled water were placed in a glass beaker and stirred mechanically for 20–30 min to form a dispersion. The beaker was maintained in a thermostatically controlled oil bath. The dispersion was heated to gelatinize the starch and kept at about 90°C for 20–30 min under stirring. Then, the herbicides were thoroughly mixed with the gelatinized starch paste with a glass rod. The mixture was kept at room temperature for 24 h to obtain a solid gel. Then, the gel was passed through a 10-mesh screen under pressure and dried at about 90°C. Finally, the samples were crushed into pieces and sieved for the collection of the 10–40-mesh fraction for analysis.

**Figure 1** Effect of the graft modification and grafting ratio on the rates of 2,4-D released at $18 \pm 3^\circ\text{C}$.

Product Analysis

Swellability

Swellability was determined and calculated in accordance with Wing's method.⁹ One-half of a gram of the granular sample was placed in a 10-mL graduated cylinder with 8 mL of distilled water at room temperature. The cylinders were gently shaken several times during the first few hours to prevent clumping. After 24 h, the height of the swelled samples in the cylinder was taken and used to calculate the percentage increase in volume.

Herbicide Content

The herbicide content is the weight percentage of the herbicides contained both on the surface and

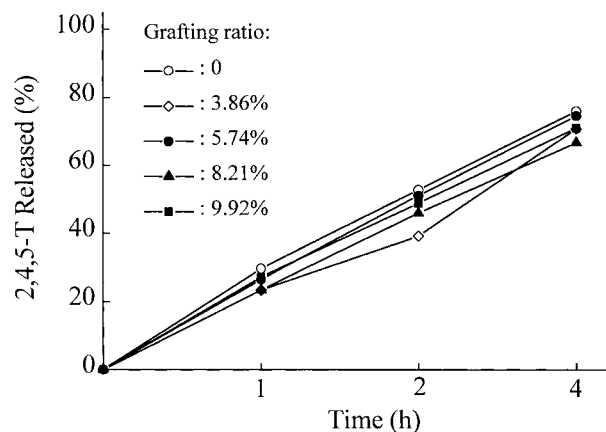
**Figure 2** Effect of the graft modification and grafting ratio on the rates of 2,4,5-T released at $18 \pm 3^\circ\text{C}$.

Table III Characterization of Starch-*g*-PBA Prepared with Different PBA Molecular Weights

Starch- <i>g</i> -PBA Number	Ceric Salt (g)	Molecular Weight $\times 10^{-5}$		Grafting Ratio (%)	Conversion of Monomer (%)	Graft Efficiency (%)
		Grafted PBA	Homo-PBA			
2-1#	2.05	1.29	1.24	5.72	99.6	63.8
1-2#	1.03	1.85	1.62	5.74	98.6	64.7
2-2#	0.62	3.87	2.46	5.53	97.7	62.9

Weight percentage of butyl acrylate used to starch was 9%.

within the matrix to the granular products. The samples (0.3 g) were thoroughly ground in a mortar, fully dried under vacuum, and exactly weighed. The ground samples were soaked in 30 mL of ethanol and shaken occasionally for 24 h. The soaking procedure was repeated with another 30 mL of ethanol for the same period. The samples in ethanol were filtered and washed with two portions of 5 mL of ethanol. Then, they were soaked again in 100 mL of buffered solution (distilled water buffered with 0.033 M/L KH_2PO_4 and Na_2HPO_4 , pH = 6.8) for at least 24 h before filtration. Finally, the amounts of herbicides both in ethanol and buffered solutions were determined with a UV-240 spectrophotometer at 284 and 289 nm for 2,4-D and 2,4,5-T, respectively.²⁷

Encapsulation Efficiency

Encapsulation efficiency is the weight percentage of the actives encapsulated to that contained within the matrix. The granular sample (3.0 g, dry weight, exactly weighed) was washed with 20 mL of ethanol to remove the herbicides exposed. The herbicide content in ethanol was also determined via spectrophotometric analysis as mentioned previously. The encapsulation efficiency was calculated with the following equation:

$$\text{Encapsulation efficiency (\%)} = \frac{W_1}{W_0 \cdot C} \times 100\%$$

where W_1 and W_0 denote the weight of the herbicide washed away in the ethanol solution and the weight of the granular sample, respectively, and C is the herbicide content of the sample.

Herbicide Release

The exactly weighed samples (1–2 g, dry weight) were impregnated with a buffered solution (dis-

tilled water buffered with 0.033 M/L KH_2PO_4 and Na_2HPO_4 , pH = 6.8). The volume of the buffered solution was chosen according to the water solubility of the herbicides to dissolve all the herbicides encapsulated. The herbicide concentrations in the water phase were also determined spectrophotometrically. All the release experiments were duplicated, and the data of the herbicides released were the mean values of the duplicate releases.

RESULTS AND DISCUSSION

Effect of the Graft Modification and Grafting Ratio

According to our experiments, starch-*g*-PBA cannot be completely gelatinized in boiling water if the weight percentage of butyl acrylate used to starch exceeds 20–30%. For this reason, the weight percentage of butyl acrylate used was varied from 6 to 15%, and correspondingly, the range of the grafting ratio measured was 3.86–9.92%. The parameters for characterizing the starch-*g*-PBA are summarized in Table I.

Table II shows the influence of the graft modification and grafting ratio on the matrix behaviors. The swellability of the starch-*g*-PBA matrices was obviously less than that of unmodified one. It decreased with the increase of the grafting ratio until 5.74%. However, only a small difference was noted when the grafting ratio exceeded 5.74%. It seems that a maximal effect on reducing the swellability was reached at nearly 6%.

The influences of the graft modification and grafting ratio on the rates of 2,4-D or 2,4,5-T released from the matrices are shown in Figures 1 and 2. The rates of 2,4-D released from starch-*g*-PBA matrices into water were generally reduced compared with those from the natural starch matrix. The decrease in release rates was directly

Table IV Influence of the Molecular Weights on the Behaviors of Starch-*g*-PBA Matrices Encapsulating 2,4-D

Encapsulating Material	Molecular Weight $\times 10^{-5}$		Herbicide Content (%)		Swellability in Water (%)	Encapsulation Efficiency (%)
	Grafted PBA	Homo-PBA	Calculated	Measured		
2-1#	1.29	1.24	12.32	10.66	200	74.2
1-2# ^a	1.85	1.62	12.33	10.31	210	67.3
2-2#	3.87	2.46	12.37	10.19	200	71.2

^a Test results for the sample of encapsulating 2,4-D again within 1-2# starch-*g*-PBA.

correlated with the reduction of the matrix swellability to some extent. As is well known, when a starch matrix is placed in contact with water, it converts into a swollen substance by the absorption of water. Diffusion of the herbicides encapsulated is accelerated thereafter. The increase in diffusion in the swollen matrix will facilitate the herbicides to diffuse out of the starch matrix. Consequently, the greater the swellability is, the faster the herbicide release is. It is the hydrophobilized modification of starch by which the matrix swellability is decreased and the rates of the herbicide release are reduced. Nevertheless, the grafting ratio did not exhibit an evident effect on the rate of 2,4-D released from the modified starch matrix.

Figure 2 indicates that the graft modification and grafting ratio had some influences on the rates of 2,4,5-T released from the matrices. The graft modification of starch did not show a notable difference on the release rate under all grafting ratios, in contrast with native starch matrix. Unexpectedly, under a high level of the grafting ra-

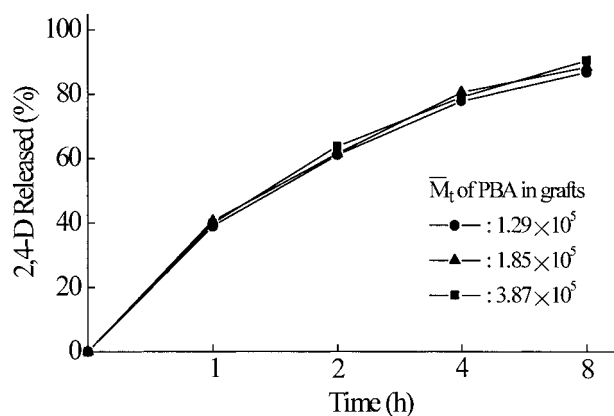


Figure 3 Effect of the molecular weights of PBA on the rates of 2,4-D released at $18 \pm 3^\circ\text{C}$.

tio, the release rates of 2,4,5-T were similar to the rate of a natural starch matrix. Generally, the rates reached a minimum at nearly 4% for 2,4,5-T.

The results of these release experiments demonstrated that the herbicides also played an important role on the release rate even under similar grafting ratios. 2,4,5-T and 2,4-D showed different effects of the grafting ratio on the release rate. The main reason was likely the water solubility of the herbicides. The solubility of 2,4,5-T (238 ppm, 30°C) is much less than that of 2,4-D (620 ppm, 25°C). Therefore, the release rate is slower, and the time for complete release is longer. It seems that the grafting ratio would come into function only when the herbicides encapsulated have relatively lower water solubility. However, the PBA molecular chains (both in grafts and homopolymers) in starch exhibit an unfavorable interference to starch gelatinization and retrogradation. They are two essential characteristics required for starch to encapsulate various chemicals. It was observed in our experiments that the greater the grafting ratio was, the more serious the interference for starch retrogradation and gelatinization was. Accordingly, with

Table V Effect of Herbicide Content on the Behaviors of the Starch-*g*-PBA^a Matrix Encapsulating 2,4-D

Herbicide Content (%)		Swellability in Water (%)	Encapsulation Efficiency (%)
Calculated	Measured		
8.31	7.53	220	75.2
14.16	12.49	200	70.8
20.18	21.52	190	66.3

^a Grafting ratio = 5.72%; \bar{M}_t of the grafts = 1.29×10^5 .

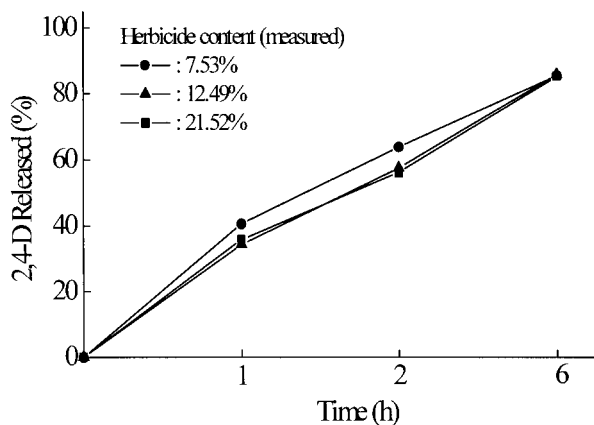


Figure 4 Effect of the herbicide content on the rates of 2,4-D released at $25 \pm 3^\circ\text{C}$.

the increase of the grafting ratio, the unfavorable interference gradually counteracted the favorable influence of the reduced swellability. Fortunately, the interference never became a problem seriously affecting the encapsulation and the release rate until the value was increased to about 6%.

Figures 1 and 2 also demonstrate that the matrix was favorable for reducing the release rate of the herbicide with higher water solubility. This is especially important because the herbicides are often released from starch matrices at higher speed. The demand for reducing the release rates of the herbicides with higher water solubility is more urgent than those with lower ones. Therefore, the modified starch does exhibit potential as a matrix for controlled release of carboxylic-containing herbicides.

Effect of the Molecular Weights of PBA

Starch-*g*-PBA with different molecular weights of PBA (both in grafts and homopolymers) was prepared by the alteration of the amounts of

ceric ammonium nitrate; this is characterized in Table III.

Table IV and Figure 3 show the influences of the molecular weights of PBA on the swellability and rates of 2,4-D released. The molecular weights only exhibited a small effect on swellability and encapsulation efficiency. Furthermore, no significant difference in the rates of 2,4-D release was observed with changes in the molecular weights of PBA both in grafts and homopolymers when the grafting ratio was similar. Therefore, the molecular weights did not show much effect on the release of the herbicide in wet environments.

Effect of Herbicide Content

The influences of herbicide content on the matrix behaviors and release rates are shown in Table V and Figure 4. With the increase in herbicide content, the swellability and encapsulation efficiency were all reduced obviously, whereas a small effect on the rates of 2,4-D release was observed. The swellability of these starch matrices did not correlate well with how fast the herbicide would be released. It is not doubted that the release rate would be decreased with the decrease of the swellability under the same circumstances. However, there are three changes for starch-*g*-PBA matrix to increase 2,4-D content: (1) a decreased swellability, (2) a reduced encapsulation efficiency, and (3) a lessened thickness of the capsule wall or membrane surrounding the herbicide particles. More exposed herbicide and short diffusing length all facilitate the herbicide release. Apparently, these two adverse effects on the release rate offset each other, and similar rates were observed. The phenomenon also reveals that the starch-*g*-PBA matrix has a large encapsulating capacity for the herbicide.

Table VI Effect of Particle Size on the Behaviors of the Starch-*g*-PBA^a Matrix Encapsulating 2,4-D

Particle Size	Herbicide Content (%)		Swellability in Water (%)	Encapsulation Efficiency (%)
	Calculated	Measured		
20–40 mesh	14.16	13.01	200	58.3
10–20 mesh	14.16	14.20	180	74.1

^a Grafting ratio = 5.72%; \bar{M}_t of the grafts = 1.29×10^5 .

Effect of Particle Size

Granular samples encapsulating 2,4-D were sieved to collect two mesh ranges (10–20, and 20–40 mesh). The effects of particle size on the matrix behaviors and rates of 2,4-D release are shown in Table VI and Figure 5. The swellability of large particles was lower than that of small ones, whereas the increase of particle size raised the encapsulation efficiency. Particle size did play an important role in 2,4-D release. The bigger the particle size was, the slower the release rate was. The herbicides encapsulated in large particles had a longer diffusing path than those encapsulated in small ones. The time for complete release with 10–20 mesh particles was about twice as long as the time for 20–40 mesh particles.

Particle Structure

A scanning electron micrograph in Figure 6 shows the structure of the starch-*g*-PBA matrix. Similar to the matrix structure of starch xanthide² and the starch–borate complex,⁸ the picture reveals that the herbicide particles (1–10 μm in diameter) were dispersed in the continuous starch phase. This means that the matrix belonged to a reservoir system. The herbicide was surrounded by a starch-*g*-PBA wall and released through diffusion.

CONCLUSIONS

Starch-*g*-PBA is an effective material for encapsulating carboxylic-containing herbicides such as 2,4-D and 2,4,5-T for controlled release. The

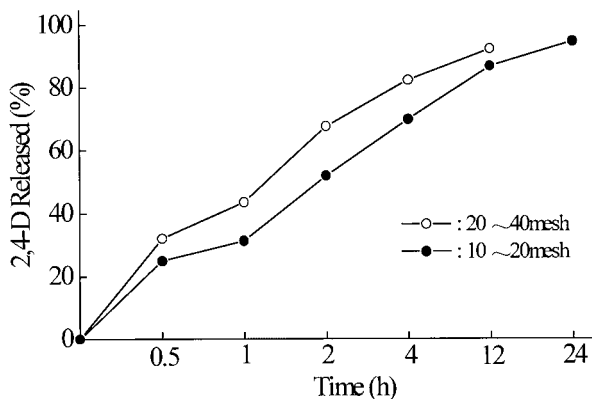


Figure 5 Effect of the particle sizes on the rates of 2,4-D released at 20 ± 3°C.

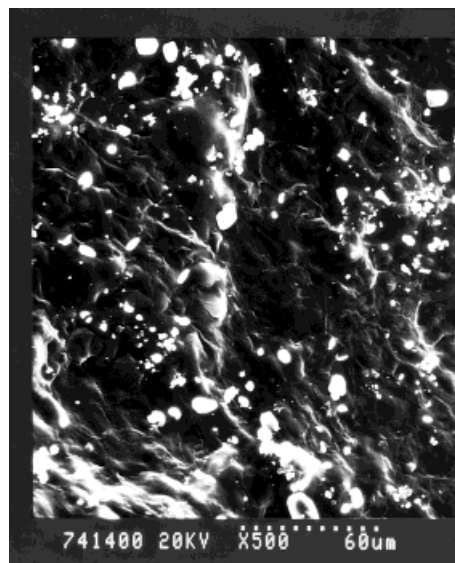


Figure 6 Scanning electron micrograph of a starch-*g*-PBA matrix encapsulating 2,4-D (herbicide content: 10%).

herbicides encapsulated are dispersed in the form of tiny cells and are released through diffusion in the matrix. The modified starch matrix exhibits low swellability, large encapsulating capacity, and a slow release rate, especially for herbicides with higher water solubility in wet environments. Consequently, water tolerance of the matrix for controlling those herbicides release will be improved. Moreover, the matrix exhibits a large encapsulating capacity for the herbicides. A favorable value of the grafting ratio for obtaining a slow release was found to be about 4–6%. Further increasing the grafting ratio will undermine starch gelatinization and retrogradation. The technique is especially suitable for encapsulating alkali-sensitive chemicals, such as carboxylic-containing herbicides, because the method avoids the crosslinking procedure under alkali conditions in encapsulation processes. The experimental results may imply that the hydrophobized modification of starch would exhibit a potential application in starch encapsulation for the controlled release of agrochemicals.

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