Effectiveness of Granular Cold-Water-Soluble Starch as a Controlled-Release Matrix[1]

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ABSTRACT

Granular cold-water-soluble (GCWS) starches (waxy maize, normal maize, Hylon-5, and Hylon-7; amylose content <1, 28, 54, and 68%, respectively) prepared by alcoholic-alkaline treatment are potential encapsulation materials. The cold-water-soluble starch is desirable for encapsulation of volatile and toxic chemicals. Controlled release of atrazine encapsulated in the GCWS starch matrices was selected for the study. Results showed that atrazine was physically embedded in the starch matrices. GCWS Hylon-7 starch had the best encapsulation efficiency among all the starch types tested. The release rate of atrazine in aqueous ethanol solution (10%, v/v) was affected by starch cultivar, particle size, and release temperature. Changes of pH between 5 and 9 had no significant effect on the atrazine release rate. The release rate of GCWS starch-encapsulated atrazine decreased as amylose content and particle size increased; however, the release rate increased as the release temperature increased.

During the past decades, controlled-release technology has received increasing attention. A basic controlled-release formulation includes an active agent (drugs, fertilizers, etc.) and a carrier (commonly a polymer). The active agent within the carrier can be released at the target over a period of time at a controlled rate. Since release of the active agent at a controlled rate provides a continuous concentration during most of the release period, the amount of material needed to offer the same activity for the same time period is much smaller than that of traditional applications. The loss of the active agents by degradation, leaching, evaporation, or surface run-off is also minimized (Boydston 1992, Fleming et al 1992).

Different methods for the controlled release of bioactive agents encapsulated in starch-based matrices have been found effective. Some encapsulation methods are based on chemical cross-linking (Shasha et al 1976, 1981, 1984; Trimnell et al 1982; Wing et al 1987a). However, the use of a cross-linking agent in food or feed products sometimes confines their application. In addition, environmental pollution caused by cross-linking agents has been a matter of concern. For this reason, the use of steam injection or twin-screw extrusion for preparing starch-based encapsulations (without chemical modification) were developed (Wing et al 1987b, Carr et al 1991, Trimnell et al 1991). The encapsulation ability of both methods are controlled by retrogradation of the starch, and some disadvantages are associated with these methods. Both processes required heat for gelatinizing starch, especially for high-amylose maize starch. As a result, neither process is suitable for active agents that are volatile or heat-labile. Loss of agent by heating and vapor inhalation may be major concerns.

This study evaluated the effectiveness of atrazine encapsulation using granular cold-water-soluble (GCWS) starches prepared by alcoholic-alkaline treatments (Jane and Seib 1991; Chen and Jane 1994a,b) and to investigate the effects of environmental variables on the herbicide releasing rate.

MATERIALS AND METHODS

Materials

GCWS starches were prepared by the methods of Chen and Jane (1994a,b). GCWS normal maize, Hylon-5 (HA5), and Hylon-7 (HA7) starches were produced by treating native starches with aqueous alcohol (40%, w/w) and NaOH (3*M*) solution (starch, H_2O, absolute ethyl alcohol, and 3*M* NaOH [1.0:4.2:2.8:5.0, w/w]) at 35°C. GCWS waxy maize starch was produced with weight proportions of starch to reagents as starch, absolute ethyl alcohol, and 3*M* NaOH solution (1.0:7.0:3.2) at 25°C. Potato starch was purchased from Sigma Chemical Co. (St. Louis, MO). Powdered atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine, technical grade containing 97.5% active agent) was donated by Ciba-Geigy Corp. (Greensboro, NC). Other chemicals were all reagent grade and were used without further treatment.

Encapsulation of Atrazine

Three grams of atrazine (10% of starch base) was weighed and added into a 1,000-ml beaker containing about 70 g of distilled water. The suspension was stirred constantly to evenly disperse the atrazine. GCWS starch (30 g, dry weight) was mixed with atrazine suspension. The mixture was thoroughly mixed using an electric handmixer. After being mixed, the semisolid mass was dried overnight at 60°C in a forced-air oven. The dried solid was then ground and sieved through 9-20 and 20-35 mesh screens.

Recovery and Encapsulation Efficiency of Atrazine

The measurements of atrazine recovery and encapsulation were conducted by following the method of Carr et al (1991). Nitrogen content of sieved samples (0.5 g) was determined by the Kjeldahl method to quantify atrazine in the samples. Recovery of atrazine was then calculated as: Recovery (%) = mg of atrazine in 1 g of product/88.8 × 100%. The value of 88.8 (mg/g of product) was a theoretical value of atrazine in the product, which was calculated from encapsulation process (3 g × 97.5%/30 g + 3 g). Chloroform-washed 0.5-g samples were also analyzed by the same procedure. Atrazine on the surface of the samples was washed off with $CHCl_3$. The total nitrogen content of the washed samples was determined by the Kjeldahl method to quantify encapsulated atrazine. The encapsulation efficiency (EE) was calculated as: EE (%) = mg of atrazine in chloroform-washed product/mg of atrazine in the unwashed product × 100%.

Swellability

Swellability was determined by following the method of Carr et al (1991). Sieved samples (1 g) were placed in a 10-ml graduated cylinder and the dry volume was recorded. Ten milliliters of aqueous alcohol solution (10%, v/v) was added to each sample. The graduated cylinders were placed in a water bath set at 30 and 40°C. The percentage increase in volume of the swollen samples was calculated after 24 hr.

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Release of Encapsulated Products

Release of atrazine was conducted by monitoring the concentration of atrazine in the supernatant of the media following the method of Carr et al (1991). An aqueous ethanol solution (10%, v/v) was used as the media, which provided a rapid laboratory procedure to study atrazine release rates (Carr et al 1991). Chloroform-washed samples containing about 10.0 mg of atrazine were added into a 125-ml polyethylene bottle filled with 75 ml of aqueous ethanol solution (10%, v/v). The bottles, sealed with caps, were then agitated in a water bath (Versa-Bath S, model 236, Fisher Scientific) at 20, 30, or 40°C with shaking at 100 strokes/min for up to 72 hr. Samples of supernatant were taken at intervals of 1, 2, 4, 24, 48, and 72 hr, and the concentration of released atrazine was determined by measuring its spectrophotometric (model U-2000, Hitachi, Japan) absorbance at 230 nm. A calibration curve with standard solutions was prepared. Atrazine release was calculated as a percentage.

Statistical Analyses

Data were analyzed (SAS 1990) and Duncan's multiple range test was applied to compare means.

Scanning Electron Microscopy (SEM)

The sample was placed on a metallic tape (3M Corp., St. Paul, MN) mounted on brass disks and coated with platinum-palladium alloy (60:40). Scanning electron micrographs were taken with a scanning electron microscope (JSM-35 JEOL, Tokyo, Japan).

Complex Formation Between Atrazine and Amylose

The test was conducted by following Kuge and Takeo's (1968) method with modifications. Potato starch (10 g) was dispersed into boiling water (1,000 ml) in a 2,000-ml flask with vigorous stirring for 1 hr. The starch solution was then autoclaved for 3 hr. After being autoclaved, the starch solution was placed in a boiling water bath in a hood for 1 hr and stirred vigorously. Atrazine (1 g) was added into the solution. The mixture was refluxed and stirred for 30 min. The flask was then covered with aluminum foil and placed in a dewar flask half-full of boiling water. The dewar flask was sealed with a lid, and the hot potato starch and atrazine mixture inside was slowly cooled to room temperature over a period of 24–36 hr. The cooled mixture was centrifuged (8,700 × *g* for 30 min). The precipitant was twice rinsed with ethanol and dried in a vacuum oven at 60°C for at least 4 hr. Two control samples, one without any complexing agent and the other with *n*-butyl alcohol as a complexing agent, were prepared in the same way. The dried samples were kept in a sealed bottle for X-ray diffraction analysis.

X-ray Diffraction

X-ray diffraction patterns of the starch samples were recorded on a diffractometer (D500, Siemens, Madison, WI) with a nickel-filtered Cu X-ray tube operated at 40 kV and 25 mV. A step-scan was set at an angle of 0.05° per step with a counting time of 2 sec.

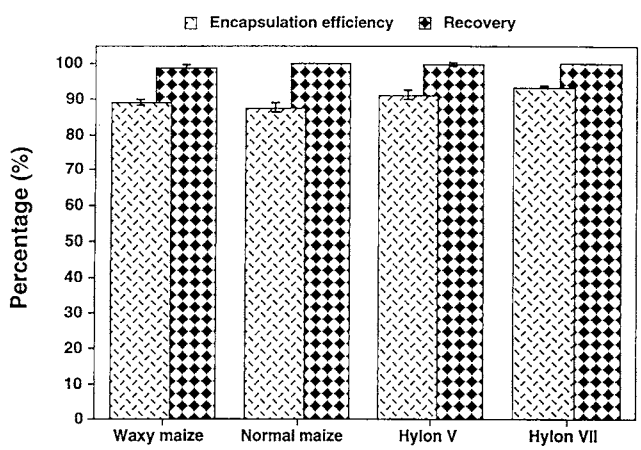

Fig. 1. Encapsulation efficiency and recovery of atrazine in granular cold-water-soluble starch-encapsulated atrazine products. Values were means of two replicates.

RESULTS AND DISCUSSION

GCWS starches prepared by alcoholic-alkaline treatments (Jane and Seib 1991; Chen and Jane 1994a,b) displayed effective controlled release of atrazine. When GCWS starch was added to atrazine-distilled water suspensions at room temperature, the mixture became a viscous paste. After vigorous mixing, all mixtures of atrazine and starch, except GCWS waxy maize, became cakelike semisolids. When the semisolid mixtures were cut with a spatula, the cut edges were very smooth, especially the mixtures containing GCWS high-amylose starches. The smooth edge could be attributed to starch retrogradation. A marked physical feature of retrograded starch gel was a progressive increase in gel firmness. This

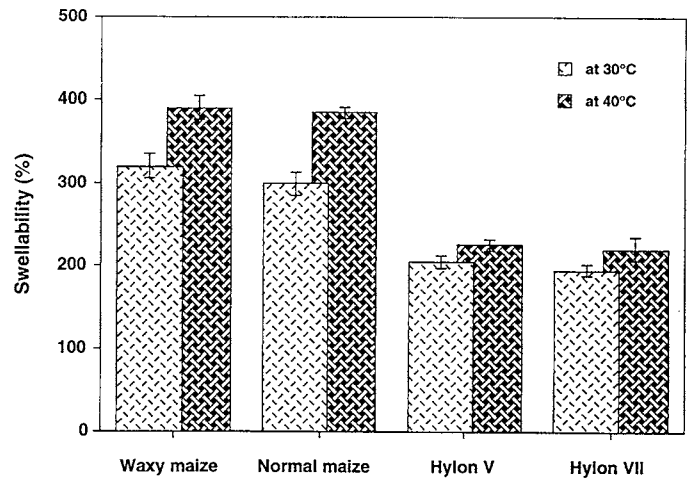

Fig. 2. Effect of temperature on swellability of granular cold-water-soluble starch-encapsulated atrazine products. Products of 9–20 mesh were soaked in aqueous alcohol solution (10%, v/v) for 24 hr. Values were means of two replicates.

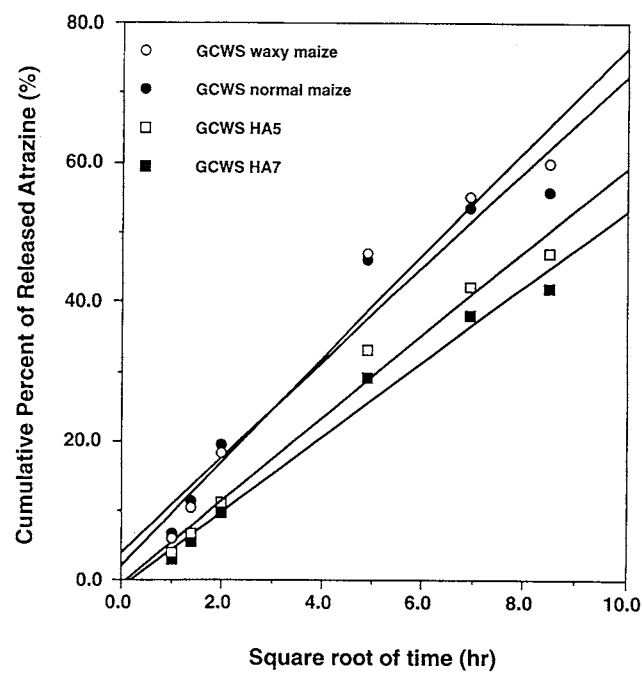

Fig. 3. Controlled release of granular cold-water-soluble (GCWS) starch-encapsulated atrazine products. Linear relationship from square root transformation. Samples of 9–20 mesh were used for the study at 30°C, pH 5. Data were means of two replicates. Statistical analyses of *k* constants are summarized in Table I.

TABLE I
k Constants of Controlled Release of Granular Cold-Water-Soluble (GCWS) Starch-Encapsulated Atrazine Product Under Different Conditions[a]

GCWS Starch Matrix	pH			9–20 Mesh			20–35 Mesh		
	5	7	9	20°C	30°C	40°C	20°C	30°C	40°C
GCWS waxy maize	7.4 a	7.2 ab	7.5 a	5.3 j	7.4 fg	10.1 c	5.6 ij	8.0 ef	16.6 a
GCWS normal maize	6.8 b	6.8 b	7.1 ab	5.1 j	6.8 h	9.3 d	5.6 ij	7.4 fg	16.9 a
GCWS HA5	6.0 c	6.0 c	6.1 c	4.0 k	6.0 i	8.6 e	5.4 ij	7.2 gh	11.0 b
GCWS HA7	5.4 d	5.4 d	6.0 c	3.7 k	5.4 ij	8.0 f	5.4 ij	6.8 h	11.0 b

[a]Means not sharing the same letter are significantly different within column of pH or size (Duncan's multiple range test, $\alpha = 0.05$).

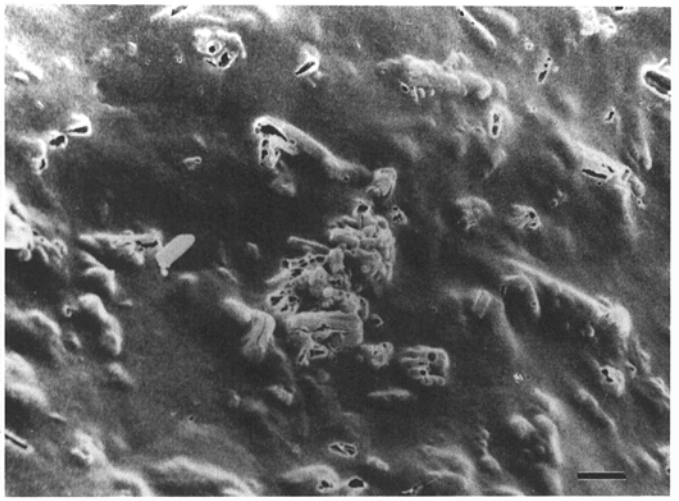

Fig. 4. Scanning electron micrograph of granular cold-water-soluble (GCWS) starch-encapsulated atrazine products. Size bar = 10 μm.

feature was advantageous for preparing the GCWS starch-encapsulated products.

All the GCWS maize starches (waxy, normal, HA5, and HA7; amylose content <1, 28, 54, and 68%, respectively) (Lineback 1984, Takeda et al 1989) demonstrated ~100% recovery of atrazine (Fig. 1). The results indicated that atrazine recovery was independent of amylose content, which differed from the results obtained by using jet-cooked starches with various amylose contents (Wing et al 1988). When jet-cooked starch was used for the study, Wing and co-workers observed that butylate recovery decreased from 100 to 51% when the amylose content increased from 0 to 70%. The encapsulation efficiency of the GCWS starches varied from 87 to 93%; normal starch (28% amylose) was the lowest and HA7 (70% amylose) was the highest (Fig. 1). The encapsulation efficiencies of the GCWS starches were also substantially higher than those obtained by jet-cooked starches (77% for normal maize and 41% for HA7) (Wing et al 1988). The encapsulation rates of GCWS starches, however, were comparable with those obtained by extrusion (Carr et al 1991).

The discrepancy between the GCWS starches and jet-cooked starches could be attributed to their starch matrix moisture contents and to their drying processes. The high-moisture contents in jet-cooked starches and the relatively slow drying process might enhance the amylose retrogradation (crystallization). As a consequence, butylate separated from the starch matrices and decreased the atrazine recovery rate and encapsulation efficiency.

When GCWS starch-encapsulated atrazine products were placed in aqueous alcohol solutions (10%, v/v) (Carr et al 1991), the starch-atrazine matrices swelled to different extents (Fig. 2). The data clearly showed two distinct groups. One group consisted of those products made with GCWS waxy maize and normal maize starches; the other contained those made with GCWS, HA5, and HA7 starches. The former group (lower amylose content) swelled more than the latter group (greater amylose content). These results were consistent with the data reported by Wing et al (1988) and were attributed to a semicrystalline amylose network, which restricted the starch matrices from rehydration and swelling. Increasing the temperature of the medium could increase the swellability of GCWS starch-encapsulated atrazine products (Fig. 2).

The data from release studies displayed a linear relationship between the cumulative percentage of released atrazine and the square root of time (Fig. 3). These results followed the equation for controlled-release matrix diffusion (Higuchi 1963): Cumulative percentage of released atrazine (%) = $k(t)^{1/2}$ where t was time (hour) and k was a constant. The k constants calculated by linear regression analyses were used as references for comparing release rate. The greater the k constant, the faster the release rate. Effects of variables, such as particle size, temperature, and pH on the release rate of GCWS starch-encapsulated atrazine products were investigated. Table I summarizes the k constant for each sample under different conditions. In general, the k constants of the products followed the swellability: the higher the swellability, the faster the release rate. The release rate increased with temperature and decreased with particle size (Table I). The result was consistent with the data previously reported (Trimnell and Shasha 1990, Trimnell et al 1991). The effect of particle size on the release rate was less significant at 20 and 30°C ($\alpha = 0.05$) than it was at 40°C. The pH range between 5 and 9 was chosen for the study because most crops grow within this range. The result showed that changes of pH between 5 and 9 had no significant effects on release rate ($\alpha = 0.05$) (Table I).

The speedy release rates of atrazine in 10% aqueous ethanol obtained in this study did not reflect the release rate of atrazine in the field. The results, however, provided information on relative release rates encapsulated by those different starches.

In SEM analysis of the GCWS starch-encapsulated atrazine product, it appeared that atrazine particles were embedded in starch matrices (Fig. 4). A test conducted for amylose-atrazine helical-complex formation (Kuge and Takeo 1968) demonstrated a negative result. An X-ray study of atrazine-treated potato starch exhibited a B-type diffraction, a characteristic of retrograded starch. The X-ray data showed no V-type diffraction resulting from a helical complex (data not shown). The conclusion was that atrazine was physically embedded in the starch matrices without complexing with amylose. The inability of atrazine to complex with amylose might be attributed to its low solubility (70 ppm) in water or to its bulky chemical structure with amine groups (Kuge and Takeo 1968). Kuge and Takeo (1968) reported, on the basis of their survey of more than 100 chemicals, that aliphatic and aromatic amines did not form complexes with amylose.

CONCLUSIONS

The release rate of starch-encapsulated atrazine followed the swellability of the encapsulated products. The release rate can be controlled by the amylose content of GCWS starches, by particle size, or by release temperature. As the amylose content increased, the release rate decreased because of the retrogradation of amylose. Small particle size and higher temperature promoted the swelling of the starch-encapsulated atrazine product and resulted in a faster release rate. The release rate was not affected by pH changes between 5 and 9. Scanning electron micrographs and the X-ray study of helical complex formation between the potato starch and atrazine matrices revealed that atrazine was embedded in starch matrices.

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