Introduction

Although fertilizers and pesticides are widely used in agriculture, they sometimes cause hazards to both humans and the environment. Recently, controlled-release granules have been studied to save on labor and to reduce environmental load.1)

In the field of fertilizer, granular fertilizers coated with polymers or sulfur have been developed as controlled-release fertilizers.2,3) Two release types of coated granular fertilizers have been developed: sustained-release type and timed-release type.4) Timed-release technology was first developed by Fujita et al.5) The timed-release granule (TRG) was designed to release the active ingredient at a predetermined time (the lag time) after application. There has been a number of reports on water-soluble core granules used as fertilizers.6–8)

In the field of pesticides, Sato et al. attempted to develop granules containing water-soluble or volatile active ingredients coated with thermoplastic polymers,9) while Nagai et al. attempted to develop timed-release granules with a double layer membrane structure.10–13) However, it was difficult to apply those technologies to slightly water-soluble active ingredients.

Herbicides are used for pre- and early post-emergence, mainly in transplanted rice seedlings to control grass weeds. Herbicides have often been detected in surface waters during the rice-cropping season.14–17) Paddy fields occupy about 7% of the land area in Japan, and pesticides, including herbicides, easily flow out through drainage into rivers and lakes.18) The herbicide concentration of water is highest in May, when most herbicides are applied in the field. The effluent of herbicides is expected to decrease greatly by the effective timed-release application of herbicides, the same as release-controlled fertilizers.

We have succeeded in developing a TRG of slightly water-soluble herbicides using a single layer membrane. The objective of this study was to develop timed-release technology by coating the commonly used slightly water-soluble herbicide with a polymer composition.

The effect of the membrane composition, that is low-density polyethylene (LDPE), fillers and additives, was examined for the release profile of mefenacet from the TRG.

A novel timed-release system with a certain lag time (or release-suppression time) of pesticides has been developed using coated water-swelling granules including a slightly water-soluble herbicide. The lag time and release profile of the herbicide are controlled by the polymer composition of the membrane that contains low-density polyethylene (LDPE), talc and water-permeable materials such as surfactant, highly water-absorbent resin (HWAR) and paraffin. © Pesticide Science Society of Japan

Keywords: timed-release, herbicide, lag time, membrane, water-swelling material.

Materials and Methods

1. Chemicals

2-(2-Benzothiazolyloxy)-N-methylacetanilide (purity 85%; D<sub>50</sub> about 6 μm) was kindly supplied by Bayer CropScience K. K. (Tokyo, Japan). The compound has a melting point of 134.8°C and a solubility of 4.0 mg l<sup>−1</sup> in water at 20°C.19) Mefenacet herbicide<sup>20)</sup> is commonly used in paddy fields in Japan. Bentonite (HOTAKA<sup>TM</sup>, particle size <53 μm), a water-swelling material and binder, was supplied by HOJUN Co., Ltd. (Gunma, Japan), while clay (No. 5 Clay, particle size <45 μm) used as filler was supplied by Takehara Kagaku
Kogyo Co., Ltd. (Hyogo, Japan). These were used as the core granule materials.

A low-density polyethylene [MIRASON™, Melt Flow Rate (MFR)=23 g/10 min], used as a water-insoluble membrane material, was supplied by Mitsui Chemicals Inc. (Tokyo, Japan). Talc (Magnesium Silicate Hydroxide, average particle size 5 μm), used as a filler, was supplied by Fuji Talc Industry Co., Ltd. (Osaka, Japan). A surfactant (NONION™, Polyoxyethylene Monostearate, HLB=13.6), a highly water-absorbent resin (KI Gel™201K-F2, Isobutylene Polymer, water absorption ratio about 200 ml/g resin) and paraffin (melting point 68–70°C), used as water-permeable materials, were supplied by NOF Corp. (Tokyo, Japan), Kuraray Co., Ltd. (Okayama, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan), respectively.

2. Preparation of core granules

The composition of the core granules is shown in Table 1. After mefenacet was mixed with powder components, the mixed powder was kneaded with water (using a kneader PN-5, made by Irie Shokai Co., Ltd.), extruded through a 1.2 mm screen (using a Xtruder™ EXKS-1, made by Fuji Paudal Co., Ltd.), and then brought to a rotating disc spheroniser (Marumerizer™ QJ-230, made by Fuji Paudal Co., Ltd.) where the extrudates were broken down into short lengths and became substantially spherical granules. The granules were then dried in a fluid-bed dryer. After sieving at 1.4/1.7 mm, granules containing 3.4% by weight of mefenacet were obtained.

3. Preparation of coated granules

3.1. Apparatus for coating

A schematic diagram of the experimental set up is shown in Fig. 1. It consisted of a spouted bed coater, a slurry mixer (dissolution vessel), a spraying and heating system, and a cyclone fine particle collector which acts as a dust remover. The spouted bed coater has a tower of 250 mm diameter, 4000 mm high, bottom cone of 50-degree angle with an air exhaust inlet of 50 mm diameter and one fluid nozzle of 0.4 mm diameter for coating materials.

3.2. Coating of core granules

Three kilograms of coated granules were introduced into the coating apparatus via the hopper inlet wherein hot gas was flowing at a speed of 240 m³/hr⁻¹. A spouted bed was formed after the introduction of all granules into the tower. The membrane materials in tetrachloroethylene slurry (5% by weight) were fed at the rate of 300 g min⁻¹ to the spouted bed via the spray nozzle. The temperature of the granules was maintained at 70°C by controlling the hot gas temperature at 68 to 72°C. The compositions of the membrane materials are shown in Table 2.

4. Measurement of release (dissolution test in water)

The release of mefenacet from granules was measured by the following method. High performance liquid chromatography (HPLC) was used to detect mefenacet in water, which was released after the burst of coated granules.

One coated granule was placed in each of one hundred test tubes (diameter 12 mm, 72 mm high) filled with 1.5 ml of water. Each tube was capped and immersed in a water bath maintained at 20°C. Visual observations of the condition of the coated granules were performed to evaluate the release of the herbicide in the granules. Visual observations were carried out every day from the time the granules were soaked in water. In this work we stated a 0–10% release period of mefenacet as the lag time.

5. Observation of surface and cross-section of TRG by scanning electron microscopy (SEM)

Electron micrographs of the surface area and cross-section of TRG were obtained using SEM after coating with gold under vacuum pressure.

Results and Discussion

1. Design of TRG

TRG has a single-layered structure of a core granule and membrane as shown in Fig. 2. The core granules consist of the active ingredient, swelling material, and inorganic filler. Membrane materials are a water-insoluble polymer and an inorganic filler. Water-permeable materials such as surfactant, paraffin and highly water-absorbent resin were added to the membrane.

![Fig. 1. Schematic diagram of the spouted bed coating system.](image-url)
2. **Microscopic image of TRG**

Images of the surface and cross-section of TRG with talc in the membrane were observed by SEM (Fig. 3). The lamellar structure of talc was observed, which lined parallel to the surface of the membrane.

3. **Release mechanism of mefenacet from TRG**

The release profile of the coated granules in water was investigated. Release of mefenacet from the coated granule started with the cracking of the membrane and burst of the core granule (Fig. 4).

Figures 4 and 5 show morphological changes in the membrane during the release of mefenacet in water. After being soaked in water, the coated granules swelled and the membrane expanded, but no cracks were observed in the membrane during the release-suppression time (Fig. 4A). Cracks were observed several days (release-suppression time) after the start of the measurement (Fig. 5A). The cracks became larger in accelerated disintegration of the membrane and the core burst within about 10 min (Fig. 5A–C).

On the other hand, when a membrane without talc was used and the ratio of the membrane materials to coated granule (coating ratio) was 20% by weight, the coated granule slightly swelled but did not release mefenacet even after 1 month in water (Fig. 6). Complete dissolution of the uncoated core granules took place within less than 10 min. The higher talc content in the membrane provided water more rapidly to the core materials, resulting in the earlier release of mefenacet to the water. The released fraction of coated granules increased more slowly than uncoated granules since the membrane acts as a wall, inhibiting the diffusion of the mefenacet.

4. **Effect of the type of water-permeable materials on release profile of mefenacet**

The lag times of mefenacet release are listed in Table 3, when 1% by weight of surfactant, highly water-absorbent resin (HWAR) and paraffin were used as water-permeable additives in the membrane of TRG. The lag time of mefenacet release from TRG could be controlled in the range of 3 to 14 days by the addition of water-permeable materials to the water-insoluble polymer membrane of LDPE and talc. The order of the water-permeable materials addition effects was as follows:

surfactant > paraffin > HWAR

This may suggest the water permeation strength order.
5. Effect of amount of surfactant on release profile of mefenacet

The relationship between the rate of mefenacet release and the amount of surfactant (0.5–3% by weight) contained in the membrane, was investigated. The amount of LDPE was fixed at 20% (by weight). It was found that the lag time became shorter and the release rate of mefenacet increased along with the increase of surfactant (Fig. 7). Lag times and the amount of surfactant were fitted by linear regression 

\[ Y = -1.167X + 3.871, \quad Y: \text{lag time (days)}, \quad X: \text{the amount of surfactant (wt.%)} \]

coefficient of determination: 0.985. There was a good linear correlation between the amount of surfactant in the membrane and the total release time.
6. **Effect of LDPE to talc ratio with HWAR of 1 wt.% on release profile of mefenacet**

The relationship between the rate of mefenacet release and the LDPE to talc ratio used as coating materials was investigated at an LDPE to talc ratio of 10/89, 15/84 or 17/82 by weight in the membrane. Here, the amount of HWAR was fixed at 1% by weight. It was found that the lag time became longer and the release rate of mefenacet decreased with the increase of LDPE (Fig. 8). Lag time and an LDPE to talc ratio with HWAR of 1% (by weight) were fitted by a power approximate equation $[Y = -0.7383X + 4.486, Y$: total release time (days), $X$: the amount of surfactant (wt.%), coefficient of determination: 0.989]. From the above result, it appears that the lag time and total release time could be controlled by the amount of surfactant contained in the membrane.

It has been shown by Tashima et al.\textsuperscript{21} that lag time and release rate could be controlled by the amount of white carbon contained in the water-insoluble polymer membrane. In this study, the change in lag time may be related to water permeability into the TRG.

It has been shown by Nagai et al.\textsuperscript{10} that a coated granular pesticide could be prepared by a double-layered membrane composed of HWAR (inside layer) and water-insoluble polymer (outside layer). In this study, the membrane is a single layer structure. The change in lag time was considered to relate to the water permeability change and the strength change of the membrane, which were caused by the HWAR.

7. **Effect of amount of paraffin in the membrane on release profile of mefenacet**

The relationship between the mefenacet release profile and the amount of paraffin (1–5% by weight) used as a water-permeable additive in the membrane, was investigated. Here, the amount of talc was fixed at 80% (by weight). It was found that the lag time became shorter and the release of mefenacet became faster along with the increase of the paraffin amount.  

---

**Table 3. Effect of the type of water-permeable materials on the release profile of mefenacet**

<table>
<thead>
<tr>
<th>Water-Permeable Materials</th>
<th>Lag time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc (without additive)</td>
<td>19</td>
</tr>
<tr>
<td>Surfactant</td>
<td>3</td>
</tr>
<tr>
<td>HWAR\textsuperscript{b}</td>
<td>14</td>
</tr>
<tr>
<td>Paraffin</td>
<td>10</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Membrane materials were fixed at 20 wt.% LDPE and 1 wt.% water-permeable materials.  
\textsuperscript{b} Highly water absorbent resin.

---

**Fig. 7.** Release profiles of TRG with single-layered membrane containing a surfactant. LDPE was fixed at 20% by weight.

**Fig. 8.** Effect of LDPE/talc ratio at fixed 1% highly water absorbent resin (HWAR) in the membrane on the release profile of mefenacet.

**Fig. 9.** Release profiles of TRG with single-layered membrane containing paraffin. Talc was fixed at 80% by weight.
(Fig. 9). Lag times and the amount of the paraffin were fitted by linear regression \[ Y = -0.588X + 6.572, \] where \( Y \): lag time (days), \( X \): the amount of paraffin (wt.%), coefficient of determination: 0.880. From the above result, it appears that lag time could be controlled by the amount of paraffin contained in the membrane.

**Conclusion**

Coated granules utilizing LDPE and talc in the single layer membrane and bentonite in the core granule displayed a timed-release function, i.e. release-suppression time was observed in the release profile and the slightly water-soluble herbicide was released rapidly after the release-suppression time. Adding water-permeable materials to the membrane could control the lag time.

**References**