Original Article

Formulation Factors Affecting the Efficacy, Phytotoxicity and Rainfastness of Fenitrothion Microcapsules for Agricultural Use

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Fenitrothion 20 wt% microcapsules equal in mass median diameter (*ca.* 20 μm) but different in wall thickness (*T*) were prepared and tested for efficacy against tobacco cutworms (*Spodoptera litura*), phytotoxicity to cabbage and rainfastness compared with a fenitrothion 50 wt% emulsifiable concentrate. LC_{50} values of the microcapsules increased with increasing in *T* and there was an optimum range in *T* to maintain the efficacy for a long period. A way of action of the microcapsules against tobacco cutworms was supposed to be breaking by the insects. The microcapsules was less phytotoxic than the emulsifiable concentrate. The thicker the wall of the microcapsules, the lower the phytotoxicity. Microcapsules with a thin wall excelled the emulsifiable concentrate in rainfastness both immediately after spray and after drying.

INTRODUCTION

Generally, pesticide microcapsules have advantages such as long residual efficacy, low mammalian toxicity, phytotoxicity and fish toxicity compared with conventional formulations.¹⁻³⁾ In order to achieve such characteristics, particle design is a key. When microcapsules are produced by the interfacial polymerization method, wall material, wall thickness, wall structure, capsule diameter and core material are the factors that affect the properties, *e.g.*, release mechanism, release rate and capsule strength. We have reported that such formulation factors as wall thickness and mass median diameter affected the efficacy, fish toxicity, mammalian toxicity, rainfastness and phytotoxicity of fenvalerate and fenprothrin microcapsules.^{4,5)}

In the present investigation, fenitrothion microcapsules different in wall thickness were prepared by the interfacial polymerization method and the effect of wall thickness on the

efficacy, phytotoxicity and rainfastness was examined.

MATERIALS AND METHODS

1. Microencapsulation Procedure

Fenitrothion 20 wt% microcapsules were prepared with polyisocyanate and H_2O by the interfacial polymerization method.⁶⁾ The wall material was polyurea and the core material was fenitrothion. The mass median diameter of the microcapsules was adjusted to *ca.* 20 μm . Actual mass median diameter was measured with a Coulter Counter TA-II (Coulter Electronics Inc.).

The wall thickness was controlled by changing the amount of polyisocyanate and the actual figures were calculated by the following equation proposed by Madan *et al.*⁷⁾

$$T = (W_w/W_c)(\rho_c/\rho_w)(D/6) \quad (1)$$

where W_w , weight of the wall material; W_c , weight of the core material; ρ_w , density of the wall material; ρ_c , density of the core material

and D , mass median diameter.

2. Contact Toxicity Test of Fenitrothion Microcapsules against Tobacco Cutworms

The fenitrothion microcapsules were diluted with aqueous solution containing 200 ppm Tokusei Rino® (Nihon Nohyaku Co., Ltd.) wetting agent, and a fenitrothion 50 wt% emulsifiable concentrate (Yamamoto Nohyaku Co., Ltd.) with water to prescribed concentrations. The dilution was sprayed on potted cotton plants at a rate of 40 ml per pot. Ten 3rd-instar larvae of tobacco cutworm *Spodoptera litura* were confined to come into contact with a leaf cut from the treated plant in a plastic cup (12 cm i.d.). The LC_{95} value (the concentration at which 95% of larvae were killed) was determined after two days. At the same time, a leaf treated with microcapsules having a wall thickness of $0.097\ \mu\text{m}$ was observed under a Shimadzu ASX-SX scanning electron microscope.

3. Determination of Residual Efficacy of Fenitrothion Microcapsules against Tobacco Cutworms in a Greenhouse

Fenitrothion in the microcapsules and in the 50 wt% emulsifiable concentrate was diluted with water to 400 ppm. In the case of microcapsule, aqueous solution containing 200 ppm Tokusei Rino® wetting agent was used instead of water. The treated cotton plants were kept in a greenhouse and a leaf of each plant was cut off to examine the contact toxicity against tobacco cutworms on a predetermined date. Ten 3rd-instar larvae of tobacco cutworms were confined to come into contact with the leaf for two days and mortality was calculated.

4. Outdoor Trial of Residual Efficacy of Fenitrothion Microcapsules against Tobacco Cutworms

Fenitrothion in the microcapsules and the 50 wt% emulsifiable concentrate was diluted to 500 ppm with aqueous solution containing 200 ppm Tokusei Rino® and with water, respectively. The dilution was sprayed on potted cabbage. The treated cabbage was kept outdoor and a treated leaf of each head was cut off on a predetermined date to examine

the contact toxicity against tobacco cutworm by the same method as described above. Ten 3rd-instar larvae of tobacco cutworm were confined to come into contact with the leaf for two days and the mortality was calculated.

5. Determination of Phytotoxicity of Fenitrothion Microcapsules to Chinese Cabbage

Fenitrothion in the microcapsules and the 50 wt% emulsifiable concentrate was diluted to 200 or 800 ppm with aqueous solution containing 200 ppm Tokusei Rino® and water, respectively. The dilution was sprayed on Chinese cabbage (Musu). The treated cabbage was kept in a greenhouse and the phytotoxicity was observed after two days. The degree of phytotoxicity was calculated by the following Eq. (2) under the criterion shown in Table 1.

$$\begin{aligned} & \text{Index of the degree of phytotoxicity} \\ & \frac{\sum(\text{index of damaged area} \times \text{number of classified leaves})}{\times 100} \\ & = \frac{\text{(total number of observed leaves)} \times 5}{\text{}} \quad (2) \end{aligned}$$

where index of damaged area=index in Table 1 and number of classified leaves=number of leaves classified into the corresponding index in Table 1.

6. Determination of Rainfastness of Fenitrothion Microcapsules on Cabbage

Fenitrothion in the microcapsules and the 50 wt% emulsifiable concentrate was diluted to 500 ppm with aqueous solution containing 200 ppm Tokusei Rino® and water, respectively. The dilution was sprayed on cabbage. The cabbage was artificially rainwashed (40 mm rainfall in one hour) immediately and an hour after drying with an artificial rainwashing equipment DIK-6000 (Daikirikakogyo Ltd.).

Table 1 Criterion of phytotoxicity.

Index	Damaged area on a leaf
0	0
1	Less than 5%
2	5%–30%
3	30%–60%
4	60%–80%
5	More than 80%

Persistency of fenitrothion on the cabbage was examined by checking the contact toxicity against tobacco cutworms by the same method as described above.

RESULTS AND DISCUSSION

1. Contact Toxicity of Fenitrothion 20 wt% Microcapsules

Our previous papers^{4,8)} reported the efficacy of fenitrothion microcapsules against cockroaches and that of fenvalerate microcapsules against tobacco cutworms. The way of action of the two microcapsules was breaking by the insects, and D/T , the ratio of mass median diameter (D) to wall thickness (T), affected the strength: the larger the D/T , the higher the efficacy.

In the present investigation, D was fixed at *ca.* 20 μm . If the way of action of fenitrothion microcapsules against tobacco cutworms is breaking, the efficacy increases with decreasing in wall thickness. On the other hand, release of fenitrothion from microcapsules is proposed to be an alternative mechanism. In the latter, the efficacy is thought to increase as $D \cdot T$, the product of D and T , increases, because the parameter regulates the release rate of the active ingredient from microcapsules by diffusion.⁴⁾

As shown in Table 2, the LC_{95} values of the microcapsules increased with increasing in wall thickness. Thus, it is proposed that the way of action of the fenitrothion microcapsules against tobacco cutworms is breaking by the insects.

The efficacy of the microcapsule with a wall thickness of less than 0.047 μm was higher than that of the fenitrothion 50 wt% emulsifiable concentrate. Scanning electron micrograph shows that microcapsule particles remain on leaves uniformly making clusters after spraying (Fig. 1), while sprayed emulsion particles are considered to attach on leaves uniformly. When the insects contact with clusters made of the microcapsules, microcapsules with a weak wall, that is, with small T in the case of constant D is supposed to show high broken ratio.^{8,9)} As soon as the wall is broken, the insects come into contact with a large amount of fenitrothion at once and are killed. This is one of the reasons why the

Table 2 Contact toxicity of fenitrothion 20 wt% microcapsules against tobacco cutworms.

$D^{\text{a)}$ (μm)	$T^{\text{b)}$ (μm)	LC_{95} (ppm)
19.4	0.097	>400
21.4	0.047	216
21.2	0.037	187
19.3	0.024	172
21.2	0.016	177
$\text{EC}^{\text{c)}$		295

a) Mass median diameter.

b) Wall thickness.

c) Fenitrothion 50 wt% emulsifiable concentrate.

Fig. 1 Scanning electron micrograph of fenitrothion microcapsules having a wall thickness of 0.097 μm on a cotton plant after spraying.

efficacy of microcapsules with a thin T is higher than that of the emulsifiable concentrate.

2. Prolongation of Residual Efficacy

Since the vapor pressure of fenitrothion is high (1.5×10^{-6} mbar at 20°C),¹⁰⁾ fenitrothion evaporates faster when applied on leaves in a form of emulsifiable concentrate than in a form of microcapsule whose wall works as a barrier. Thus, the efficacy of microcapsule is expected to last longer. Actually, the efficacy of all the fenitrothion microcapsules we used against tobacco cutworms was maintained for a relatively long period while the efficacy of the emulsifiable concentrate was lost within seven days as shown in Fig. 2.

Among the microcapsules, ones with a very thin wall (0.016 μm) had short residual efficacy,

Fig. 2 Residual efficacy of fenitrothion 20 wt% microcapsules against tobacco cutworms on a cotton plant (greenhouse trial).

Fenitrothion 50 wt% emulsifiable concentrate: ▲; wall thickness of fenitrothion microcapsule: ○, 0.097 μm ; ●, 0.047 μm ; □, 0.037 μm ; ■, 0.024 μm ; △, 0.016 μm .

Fig. 3 Residual efficacy of fenitrothion 20 wt% microcapsules against tobacco cutworm on cabbage (outdoor trial).

Symbols are the same as Fig. 2.

while ones with a very thick wall (0.097 μm) had low initial efficacy (on day 0). This result indicates that there is an optimum range of T to maintain the efficacy of microcapsules not only initially but also for a long period.

Figure 3 shows the result of the outdoor trial. The efficacy of the emulsifiable concentrate was lost after eight days and the mortality with microcapsules having a relatively thin or thick wall decreased in a short time. Microcapsules having a proper wall thickness, i.e., 0.024 μm and 0.037 μm , however, had

long-lasting efficacy.

If the way of action of fenitrothion microcapsules is breaking as described above, it is easy to understand that T affects the residual efficacy. When microcapsules have a very thin wall, the broken ratio of microcapsules per one contact with insects is extremely high. Once the microcapsules are broken, fenitrothion released from them disappears quickly due to its high vapor pressure and the efficacy does not last long. When microcapsules have a very thick wall, it is difficult for insects to break them enough to be killed.

3. Reduction of Phytotoxicity

Fenitrothion is known to be phytotoxic to some kinds of *Brassica* spp. in some cases. However, as shown in Fig. 4, the fenitrothion microcapsules were less phytotoxic than the fenitrothion 50 wt% emulsifiable concentrate on Chinese cabbage. Reduction of the phytotoxicity of the microcapsules was closely related with T : the thicker the wall, the lower the phytotoxicity.

In our previous investigation,⁴⁾ phytotoxicity by fenvalerate microcapsules was mainly controlled by wall thickness, and mass median diameter was not a dominant factor, and we proposed that the mechanism of phytotoxicity of fenvalerate microcapsules was breaking and/or release of the active ingredient from the microcapsules by diffusion. The present result agrees with the previous result with fenvalerate microcapsules: phytotoxicity of microcapsules may be due to the same mechanism regardless of the sort of active ingredients.

4. Improvement of Rainfastness

Figure 5 shows rainfastness of the fenitrothion microcapsules compared with the fenitrothion 50 wt% emulsifiable concentrate. Rainfastness of fenitrothion improved as the wall of microcapsules became thinner. This result is consistent with the rainfastness of fenvalerate microcapsules tested in our previous investigation.⁴⁾ It is noteworthy that the fresh deposit of microcapsules having a relatively thin wall excelled the emulsifiable concentrate in rainfastness.

Rainfastness of the emulsifiable concentrate improved after drying and the mortality with

Fig. 4 Phytotoxicity of fenitrothion 20 wt% microcapsules on Chinese cabbage. Applied concentration of fenitrothion 20 wt% microcapsules: ●, 800 ppm; ▲, 200 ppm; applied concentrations of fenitrothion 50 wt% emulsifiable concentrate: ○, 800 ppm; △, 200 ppm.

Fig. 5 Effect of rainwashing on the persistency of fenitrothion 20 wt% microcapsules on cabbage.

Fenitrothion 20 wt% microcapsules: ●, no rainwashing; ▲, rainwashing after drying; ■, rainwashing immediately after spray; fenitrothion 50 wt% emulsifiable concentrate: ○, no rainwashing; △, rainwashing after drying; □, rainwashing immediately after spray.

it was higher than that with fenitrothion microcapsules having a relatively thick wall ($T=0.097$, 0.047 and $0.037 \mu\text{m}$). It is supposed that fenitrothion in the emulsifiable concentrate penetrated into the leaf surface while the microcapsules with a relatively thick wall were easily washed away by rain.

When the wall was relatively thin, on the contrary, mortality after rainwashing was higher with microcapsules ($T=0.024$ and $0.016 \mu\text{m}$) than with emulsifiable concentrate. The reason was not clear, but some kinds of deformation may have occurred to prevent the microcapsules from being washed off.

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要 約

農業用フェニトロチオンマイクロカプセルの殺虫効力、薬害および耐雨性を制御する製剤要因

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粒径が一定(約 20 μm)で膜厚の異なるフェニトロチオンマイクロカプセルを製造し、ハスモンヨトウ幼虫に対する効力、キャベツ葉に対する薬害および耐雨性について、フェニトロチオン乳剤と比較検討した。マイクロカプセルの LC_{05} 値はその膜が薄くなるにつれ減少した。また長期間効力を維持するためには、膜厚に関して最適な領域が存在することを確認した。マイクロカプセルのハスモンヨトウに対する作用機構は、虫体によるカプセル破壊と推定された。またマイクロカプセルの薬害は、乳剤よりも軽減された。マイクロカプセル間では膜が厚いほど薬害の程度が低下した。最後に、膜の薄いマイクロカプセルは、乳剤と比較して、散布直後の降雨および風乾後降雨のいずれの条件においても、優れた耐雨性を示した。