A study of the physical strength of fenitrothion microcapsules

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Fenitrothion, a widely used organophosphorous insecticide, was microencapsulated with polyurethane via an interfacial polymerization method, and the relationship between the formulation factors, such as mass median diameter (D) and wall thickness (T), and the physical strength of the microcapsules was studied. It was found that the larger the ratio D/T, the smaller the pressure per capsule required to break 50% of microcapsules (P_{50}). This result agreed with the theory of the destruction of an empty sphere with a thin wall. Moreover, the result obtained by the physical breaking test coincided with that obtained by the breaking test of microcapsules by cockroaches.

(Keywords: encapsulation; polyurethane; mechanical properties)

INTRODUCTION

Much work has been done on microencapsulated insecticides for agricultural and household use, because microencapsulation is suitable for improvement of residual efficacy, stabilization of insecticides against environmental degradation and reduction of mammalian toxicity, fish toxicity, phytotoxicity and irritation, etc.[1–4]. Such characteristics are said to be affected by formulation factors, such as kind of wall material, particle size and wall thickness, which are thought to regulate the physical and physicochemical properties of microcapsules[5,6].

We have studied the relationship between such factors and the residual efficacy of fenitrothion microcapsules with a polyurethane wall against German cockroaches, and have reported that the main action of the fenitrothion microcapsules was by a 'trampling effect' (cockroaches trample the microcapsules during crawling and contact the fenitrothion released), and that the residual efficacy was controlled by the parameter D/T, the ratio of the mass median diameter (D) to the wall thickness (T), which was considered to be related to the strength of the microcapsules by the biological breaking test[7,8]. For microcapsules whose mode of action against target insects is by breaking, a fundamental study of the physical strength of microcapsules is important. Although several studies have been reported on the breaking behaviour of microcapsules used for carbon-less paper[9], such work has not been done on pesticide microcapsules.

In this study, we prepared fenitrothion microcapsules with a polyurethane wall by an interfacial polymerization method, and investigated the relationship between the physical strength of the microcapsules and the formulation factors of the microcapsules, such as D, T, D/T and particle-size distribution.

EXPERIMENTAL

Microencapsulation procedure

Six kinds of fenitrothion microcapsules with a polyurethane wall, i.e. samples 1–6 in *Table 1*, were prepared by an interfacial polymerization method using Sumidur® L (ethyl acetate solution containing 75 wt% of aromatic polyisocyanate made by Sumitomo-Bayer Urethane Co. Ltd; content of isocyanate groups, 13.3 wt% in the solution) and ethylene glycol as reactants[10,11]. A premixture of technical-grade fenitrothion (Sumithion®, Sumitomo Chemical Co. Ltd) and Sumidur L was dispersed into 360 g of an aqueous solution containing 5 wt% of gum arabic as a dispersant and 2 wt% of ethylene glycol using a TK Auto Homomixer M-Type (Tokushukika Kogyo Ltd) for 5 min. After dispersion, the interfacial polymerization reaction was initiated by heating the dispersed solution. The reaction temperature was 60°C and the reaction period was 24 h. The mass median diameter (D) of the microcapsules was controlled by the rotation speed of the Homomixer in the dispersing process, and the wall thickness (T) was controlled by the ratio of the Sumidur L to fenitrothion. Feed amounts of fenitrothion and Sumidur L, and rotation speed of the Homomixer are summarized in *Table 1*.

Sample No. 7 was fractionated from sample No. 4 shown in *Table 1* by sieving with 280 mesh and 330 mesh sieves.

Measurement of particle size

Mass median diameter D and the coefficient of variation of the particle-size distribution of the microcapsules, $CV = (\text{standard deviation}/D) \times 100$, were measured by using a Coulter Counter model TA-II (Coulter Electronics Inc.).

Calculation of wall thickness

Wall thickness T was calculated from[12]:

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

where W_w = weight of wall material, W_c = weight of core material, ρ_w = density of wall material, ρ_c = density of core material and D = mass median diameter.

In this experiment, $\rho_c/\rho_w = 1$, and it was assumed that W_w was the sum of the weights of the aromatic

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polyisocyanate contained in Sumidur L and the ethylene glycol that reacts with the polyisocyanate, and that W_c was the sum of the weights of fenitrothion and the ethyl acetate in Sumidur L, because the wall material was prepared by the reaction of the aromatic polyisocyanate in Sumidur L with ethylene glycol. As the content of isocyanate groups was 13.3 wt% in Sumidur L, which was an ethyl acetate solution containing 75 wt% of the aromatic polyisocyanate as described above, W_w and W_c were calculated by:

$$W_w = (13.3/100)W_{sdl}(M_{eg}/2M_{iso}) + 0.75W_{sdl} \quad (2)$$

where W_{sdl} = feed amount of Sumidur L, M_{eg} = molecular weight of ethylene glycol and M_{iso} = molecular weight of isocyanate group, and:

$$W_c = W_{fnt} + 0.25W_{sdl} \quad (3)$$

where W_{fnt} = feed amount of fenitrothion.

Infra-red spectroscopy of wall material

A slurry of sample No. 2 shown in *Table 1* was centrifuged. The precipitated microcapsule particles were washed several times with deionized water by decantation. Fenitrothion core material was extracted with acetone from the particles and the residual wall polymer was dried.

The infra-red spectrum of the polymer obtained was measured by using a Hitachi infra-red spectrophotometer 270-30.

Scanning electron microscopy of microcapsules

A slurry of sample No. 2 shown in *Table 1* was dried. After gold coating, the surface of the sample was observed by using a Shimadzu scanning electron microscope ASM-SX.

Physical breaking test of microcapsules

A prescribed amount of fenitrothion microcapsules was applied onto a glass plate (2.6 cm × 7.6 cm) and dried. Another glass plate was softly attached onto the surface of the treated plate and a rubber sheet was put on the top and bottom sides. The physical breaking test was carried out using samples prepared by the method mentioned above (*Figure 1*). The prescribed weight was softly loaded on the sample for 1 min. After removing the weight, the total amount of fenitrothion (F_t) and the amount of fenitrothion outside the microcapsules (F_0) were analysed by g.l.c. and the broken ratio was calculated by using[7]:

$$\text{broken ratio } (\%) = (F_0/F_t) \times 100 \quad (4)$$

The amount of fenitrothion outside the microcapsule before the breaking test was confirmed to be negligible and did not affect the calculation.

RESULTS AND DISCUSSION

Characterization of fenitrothion microcapsules

The samples used in this study are characterized in *Table 1*. *Figure 2* shows the i.r. spectrum of the prepared polyurethane. The specific absorption of isocyanate groups at 2270 cm^{-1} disappears and the specific absorption of urethane groups around 1730 cm^{-1} appears.

Molecular weight of the polyurethane could not be measured because the polymer did not dissolve in any solvents such as acetone, methanol, chloroform, *N*,*N*-dimethylformamide and dimethylsulphoxide. The polymerization was supposed to proceed three-dimensionally, as the aromactic polyisocyanate in Sumidur L had at least three isocyanate groups in the molecule.

Figure 3 shows an example of the scanning electron microscopy of sample No. 2. The surfaces of all samples were smooth, and no cracks and pores were observed.

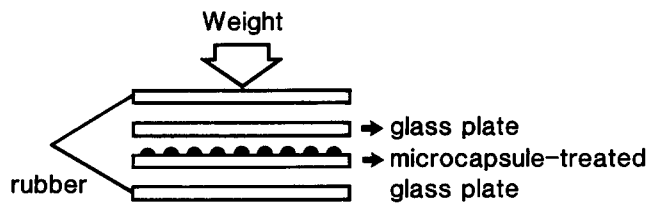

Figure 1 Method for the breaking test

Table 1 Formulation factors and breaking behaviour of fenitrothion microcapsules

	Sample No.						
	1	2	3	4	5	6	7[g]
Feed amount of fenitrothion[a] (g)	217.2	217.2	217.2	217.2	217.2	217.2	217.2
Feed amount of Sumidur L (g)	5.2	11.0	22.0	2.2	4.4	8.8	2.2
Rotation speed[b] during dispersion process (rpm)	5500	5500	5500	2950	2950	2950	2950
D[c] (μm)	18.7	20.2	20.5	47.5	46.0	47.0	48.1
T[d] (μm)	0.067	0.143	0.287	0.068	0.131	0.267	0.069
D/T[e]	279	141	71	699	351	176	697
CV[f] (%)	14.4	14.4	14.3	17.9	18.7	18.8	4.9
W_{50} (g)	2.5×10^3	6.3×10^3	1.2×10^4	2.7×10	1.2×10^3	1.7×10^3	2.5×10

[a] Fenitrothion, technical-grade (purity = 96.7 wt%)
[b] Rotation speed of TK Auto Homomixer M-Type
[c] Mass median diameter
[d] Wall thickness
[e] Mass median diameter/wall thickness
[f] Coefficient of particle-size variation
[g] Fractionated from sample No. 4

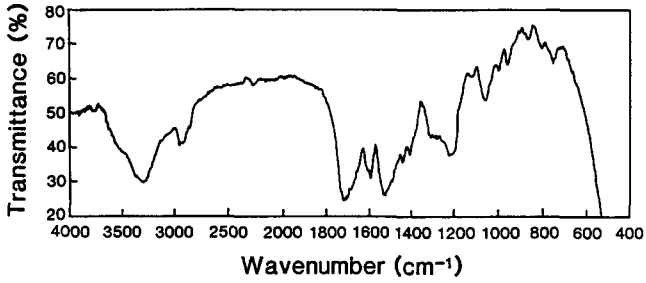

Figure 2 Infra-red spectrum of the wall material

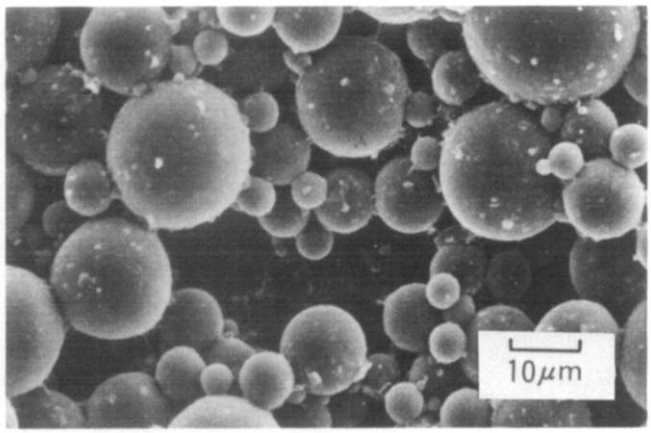

Figure 3 Scanning electron microscopy of sample No. 2

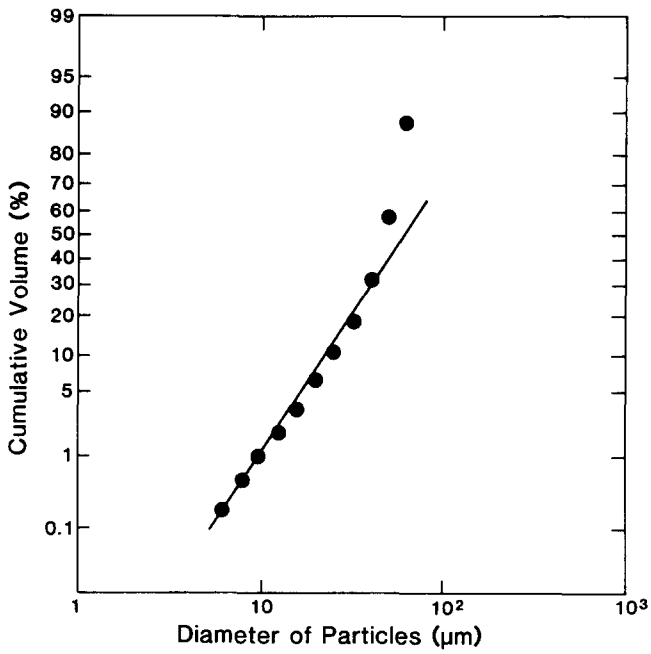

Figure 4 Particle-size distribution of sample No. 4

Figure 4 shows an example of the particle-size distribution of sample No. 4. Plots of the particle-size distributions of all samples on logarithmic probability graph paper gave straight lines.

Relationship between broken ratio and W

Watanabe[9] reported the breaking behaviour of a microcapsule used for carbon-less paper. In his report, the broken ratio was plotted against the loaded weight. In our case, the weight per milligram of fenitrothion (W) was used as the parameter of the weight loaded on to the sample instead of the weight per unit area, and W was calculated from the weight added onto the glass plate and the amount of fenitrothion applied on the plate.

Figure 5 shows the breaking behaviours of the samples with different mass median diameters and wall thicknesses but almost the same CV. All the lines are straight on logarithmic probability graph paper, and the broken ratio increases with increase in W.

If all microcapsules have the same size and wall thickness, all of them should be broken at the same value of W, that is, the broken ratio should be 0% when W is lower than the minimum critical value at which microcapsules are broken and 100% when W is higher than that value. However, samples had particle-size distributions like sample No. 4 in *Figure 4*. As a result, the weight is concentrated onto the largest particles at first, causing them to break, and the smaller ones should be broken subsequently.

Consequently, the breaking of microcapsules is thought to proceed from larger particles to smaller ones. Thus, the particle-size distribution is supposed to affect the breaking behaviour. It is considered that this is the reason why the plots of the broken ratio against W give straight lines on logarithmic probability graph paper.

Figure 6 shows the results of the breaking tests of two samples with the same D and T values but different CV.

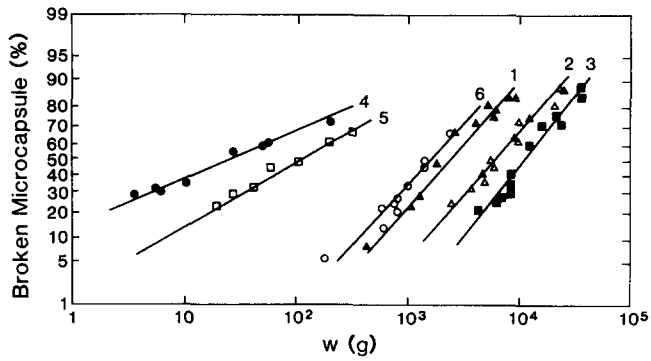

Figure 5 Relationship between broken ratio and W for samples No. 1–6

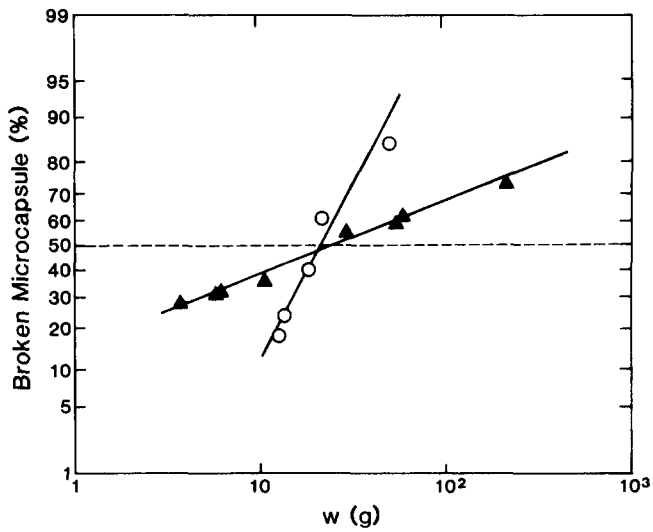

Figure 6 Relationship between broken ratio and W: (▲) sample No. 4; (○) sample No. 7

The straight lines have different slopes and cross at 50% broken ratio. The slope of sample No. 7 with small *CV* was steeper than that of sample No. 4 with large *CV*. It is confirmed that *CV*, which represents the particle size distribution, affects the breaking behaviour of microcapsules. In other words, the sharper the particle-size distribution, the narrower the range of *W* for the broken ratio to increase from 0% to 100%. This result supports the above discussions about the relationship between the particle-size distribution and the breaking behaviour. The two lines cross at *W* where 50% of particles are broken (W_{50}). This result may suggest that the parameter W_{50} is independent of *CV* when *D* and *T* of microcapsules are constant. Thus, W_{50} is considered to be a suitable parameter of *W* without incorporating *CV* and to simplify the formulation factors.

Comparing samples with nearly the same *D* values, i.e. samples No. 1, 2 and 3 or samples No. 4, 5, 6 and 7, the samples with thinner *T* are broken at lower W_{50}. Comparing samples with almost the same *T* values, i.e. samples No. 1, 4 and 7, samples No. 2 and 5 or samples No. 3 and 6, the samples with larger *D* are broken at lower W_{50} (*Table 1*). However, there is no clear relationship between the broken ratio, W_{50} and *D/T*, which has been proposed as a parameter of capsule strength in our previous biological examination with German cockroaches[8].

Application of the theory of an empty sphere with a thin wall

Komatsu[13] has already reported that breaking of a microcapsule may be explained according to the theory of the destruction of an empty sphere with a thin wall. However, a detailed study on this aspect has not been carried out.

According to the theory[14], the strength of an empty sphere is calculated by:

$$\sigma = (p/4)(d/t) \tag{5}$$

where σ = stress, p = pressure, d = diameter of sphere and t = wall thickness of sphere.

When the sphere is destroyed, the allowable stress (σ_{max}) can be used instead of σ in equation (5), to give:

$$\sigma_{max} = (p/4)(d/t) \tag{6}$$

Equation (6) shows that p is inversely proportional to d/t when σ_{max} is constant.

Introducing the above theory to the breaking of microcapsules, the pressure on a capsule (*P*) is defined as a parameter corresponding to p in equation (6) using equations (7) and (8):

$$W_s = W/\{(1/\rho_{mc})/[\tfrac{4}{3}\pi(D/2)^3]\} \tag{7}$$

where W_s = weight loaded onto a microcapsule, σ_{mc} = density of a microcapsule; and

$$P = W_s/[\pi(D/2)^2] \tag{8}$$

Figure 7 shows the relationship between the broken ratio and *P* on logarithmic probability graph paper when the *CV* of the samples are almost constant. The plots give straight lines like the plots of the broken ratio *versus W* shown in *Figure 5*. *Figure 8* shows the breaking of samples No. 4 and 7. The lines cross and the slope of sample No. 7 with small *CV* is steeper than that of sample No. 4 with larger *CV*. From these results, it is supposed that the plots of the broken ratio *versus P* in *Figures 7* and *8* are also affected by the particle-size distributions of the microcapsules.

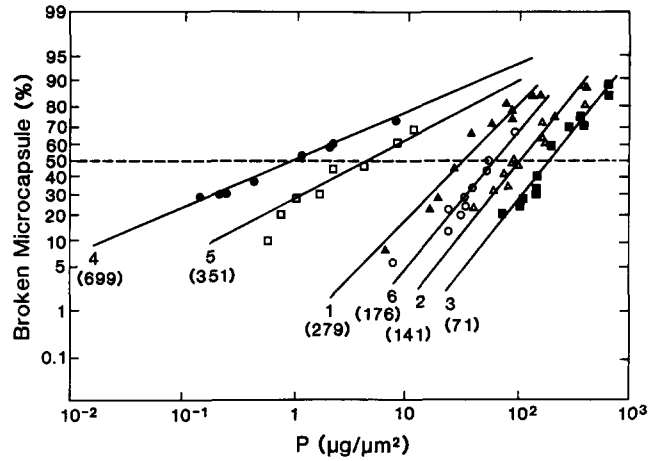

Figure 7 Relationship between broken ratio and *P* for samples No. 1–6: the ratio of mass median diameter to wall thickness (*D/T*) is given in parentheses near each sample number

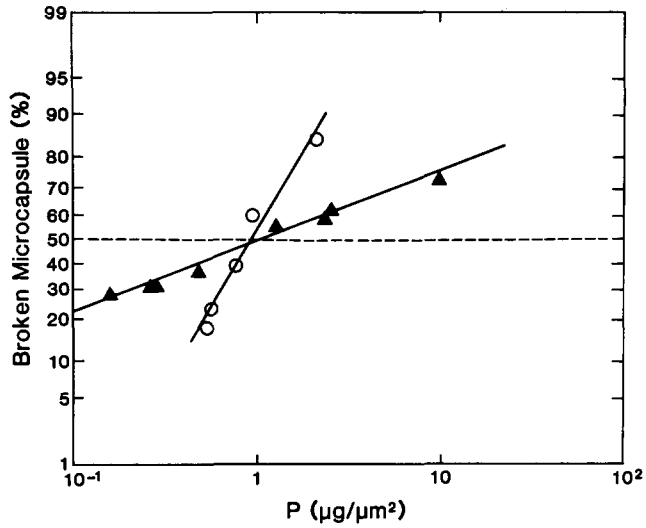

Figure 8 Relationship between broken ratio and *P*: (▲) sample No. 4; (○) sample No. 7

In *Figure 8*, the two lines crossed at a *P* value where 50% of particles are broken (P_{50}). This result may suggest that the parameter P_{50} is independent of *CV* when *D* and *T* of microcapsules are constant. Thus, P_{50} is considered to be a suitable parameter of *P* without incorporating *CV* and to simplify formulation factors.

As shown in *Table 2*, the higher the *D/T* (the larger the *D* and/or the thinner the *T*), the lower the P_{50}. *Figure 9* shows the relationship between *D/T* and σ_{max} (the product of $P_{50}/4$ and *D/T*). When *D/T* is lower than ~200, σ_{max} is constant. This result follows the theory perfectly, and the allowable stress (σ_{max}) of the wall was supposed to be ~3.4 mg μm^{-2}.

When *D/T* increases beyond 200, the product $P_{50}(D/T)$ decreases. This relation has not been clearly explained, but it might not be suitable to apply the theory to microcapsules with too high *D/T*, or the physical structure of the wall might change because the wall was too thin in the case that *D/T* was too high. It is considered that some optimum range of *D/T* exists to apply the theory to the breaking behaviour of microcapsules.

Table 2 Relationship between D/T and P_{50}

	D/T^a						
	697	699	351	279	176	141	71
P_{50} ($\mu g\ \mu m^{-2}$)	9.2×10^{-1}	1.0	4.8	3.5×10	6.8×10	1.2×10^2	2.1×10^2

[a]Mass median diameter/wall thickness

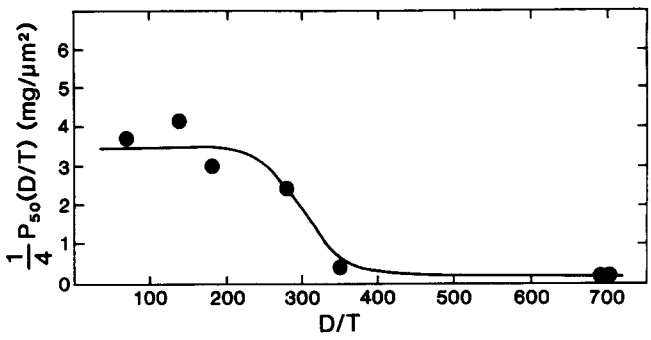

Figure 9 Relationship between D/T and allowable stress

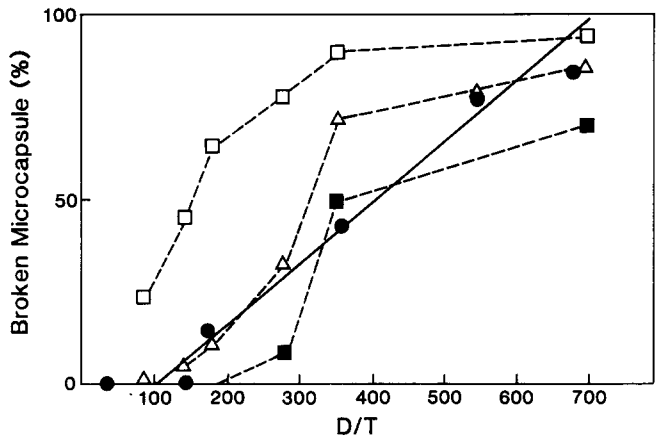

Figure 10 Breaking behaviour of microcapsules when P is constant: (□) $P = 100\ \mu g\ \mu m^{-2}$; (△) $P = 20\ \mu g\ \mu m^{-2}$; (■) $P = 5\ \mu g\ \mu m^{-2}$; (●) breaking by German cockroaches

As described above, the theory is not applicable in the case that D/T is higher than 200. However, P_{50} increases with decreasing D/T as shown in *Table 2*, that is, the larger the D/T, the weaker the microcapsule.

When target insects crawl on a microcapsule-treated surface, they may add a certain pressure on the surface. To estimate this, *Figure 7* was converted into a relationship between the broken ratio and D/T when P was constant. As shown in *Figure 10*, the larger the D/T, the higher the broken ratio. This result shows that a microcapsule with higher D/T breaks more easily when P is constant. When P is $20\ \mu g\ \mu m^{-2}$, the plots agree best with the breaking behaviour of fenitrothion microcapsules with a polyurethane wall by German cockroaches in our previous paper[8]. If cockroaches crawl with a constant pressure applied to the treated microcapsules, the pressure is supposed to be around $20\ \mu g\ \mu m^{-2}$.

CONCLUSIONS

Our conclusions are as follows:

(1) The particle-size distribution of microcapsules affects the breaking behaviour.

(2) The plot of breaking ratio *versus* P (pressure applied to a single microcapsule) is the most suitable for discussing the breaking behaviour of microcapsules.

(3) P_{50} (pressure when 50% of microcapsules are broken) is the most suitable parameter to represent P.

(4) D/T, that is, the parameter proposed for the strength of microcapsules on the basis of the biological experiment, is explained in terms of the theory of the destruction of an empty sphere with a thin wall.

(5) When P is $20\ \mu g\ \mu m^{-2}$, the physical breaking behaviour of the microcapsules agrees best with the biological breaking by German cockroaches.

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