Preparation of Microcapsules Composed of Waste-Expanded Polystyrene and Paper Fiber by Semichemical Recycle

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ABSTRACT: Microcapsules composed of waste paper fibers and plastics were prepared by semichemical recycle method. Newspaper and expanded polystyrene (EPS) for packing electric appliances were used as the raw materials of paper fiber (FB) and plastics, respectively. In this experiment, fibers were treated with a few surface treating agents prior to the encapsulation operation in order to improve the dispersability in the nonaqueous liquid phase and then in the shell of microcapsules. Microcapsules prepared thus were found to be of single-cored type. Furthermore, it was found that the mechanical strength of microcapsules was increased by addition of fibers and there were the optimum concentrations of the surface treating agents. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2662–2669, 2001

Key words: microcapsule; semichemical recycle; waste paper fiber; expanded polystyrene

INTRODUCTION

Disposals of all kinds of industrial and general wastes, which cause such various environmental problems as soil contamination and the lack of reclaimed land, are the important problems to be solved urgently. Especially, plastics among these wastes have been mostly dealt with burying or burning. For this reason, various techniques for recycling waste plastics effectively by chemical recycle, thermal recycle, and material recycle have been actively developed.[1] Material recycle among them is thought to be the most recommended one, when taking account of wasted energy and natural resources and environmental pollution. The composite materials made from various waste raw materials, belonging to the material recycle method, have the possibility of developing new materials. Taking this into consideration, we tried to prepare microcapsules composed of waste plastics and paper fiber. The composite materials made from plastics and paper fiber have the following advantages:

1. increasing the mechanical strength of composite material,
2. giving the biodegradable property to microcapsules, and
3. losing weight of microcapsules themselves

In the experiment, the conditions of treating paper fibers were varied, and how these affected the size and mechanical strength of microcapsules was investigated.

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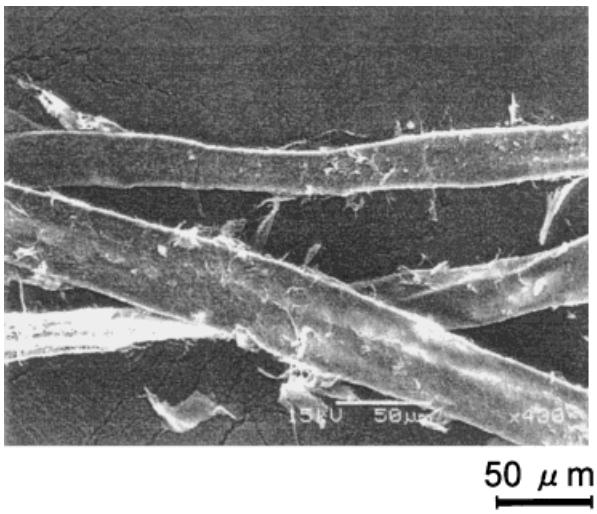

Figure 1 SEM of adjusted FB.

EXPERIMENTAL

Pretreatment of Fiber (FB)

FB was pretreated prior to the encapsulation operation as follows: Newspapers were cut into pieces 1 × 1 cm. This operation will be called the first adjustment for fiber hereafter. After these pieces were soaked in deionized water for a day, they were unbound into fibers by mixing for 15 min at the revolution velocity of 167 s^{-1} with a homogenizer (Nihonseiki Kaisha Ltd., AM-T). This operation will be called the second adjustment for fiber hereafter. Figure 1 shows the SEM micrograph of the adjusted FB. From this figure, it is found that the diameter of a fiber is from 20 to 40 μm. Furthermore, in order to adjust the affinity of FB to the solution dissolving EPS, FB was pretreated according to the following methods:

1. *Treatment by Heating and Drying*: Water absorbed by FB was removed by the filter paper, and then dried at 40°C for a day.
2. *Treatment by Acetone:* After Treatment 1, FB was soaked in acetone for 12 h.
3. *Treatment by Maleic Anhydride:* After Treatment 2, FB was filtered by the filter paper, and then soaked in acetone containing two kinds of maleic anhydrides (S1, S2) for 12 h. In this case, the concentration of maleic anhydride was changed stepwise.
4. *Treatment by Surfactant:* After Treatment 2, FB was filtered by the filter paper, and then soaked in acetone containing oil-soluble surfactant (Span80) for 12 h. In this case, the concentration of surfactant was changed stepwise.

Preparation of Microcapsule

EPS for packing electric appliances was used as the shell material of microcapsule. EPS was dissolved in dichloromethane to prepare the EPS solution of 15 wt %. The given amount of the pretreated FB was added in the fixed volume (3.0×10^{-2} dm^3) of the EPS solution and mixed for 30 min with magnetic stirrer. Then, the given volume (1.5×10^{-2} dm^3) of water as core material was poured into this mixed solution. After this, this solution was stirred for 5 min at the revolution speed of 169 s^{-1} with a biomixer (Nihonseiki Kaisha Ltd., BM-T) to form the (W/O) dispersion. Next, the (W/O) dispersion was added in the fixed volume (0.3 dm^3) of the polyvinyl alcohol (PVA) aqueous solution under stirring of the impeller speed of 3.33 s^{-1}. Thus, the second [(W/O)/W] dispersion was prepared. After keeping stirring for 30 min, microcapsules were prepared according to the drying-in-liquid method.

In this operation, dichloromethane as solvent was removed by the aspirator under vacuum. The structure of microcapsules prepared was observed by a scanning electron microscope (SEM) and optical microscope.

Figure 2 shows the schematic diagram of the experimental apparatus. The reactor used for preparing microcapsules was a separable flask (ID = 85 mm, V = 0.5 dm^3) with 4 baffles (l = 60 mm, w= 10 mm) made of aluminum. The impeller of the six-bladed disk turbine (d = 50 mm, L= 12 mm, b = 10 mm) was set at the position of one third the liquid height from the bottom.

Measurement of Physical Properties of Liquid Concerned

The physical properties of the EPS solution, where FB is dispersed, affect such characteristics as shape, size, and structure of the microcapsule. For this, a few of the physical properties of the EPS solution were measured as follows: The viscosity was measured with an oscillating viscometer (Yamaichi Electronics Co. Ltd, VM-1A-L) and the interfacial tension was measured with the Wilhelmy surface tensiometer (Kyowa Interface Science Co. Ltd, CBVP-A3), respectively.

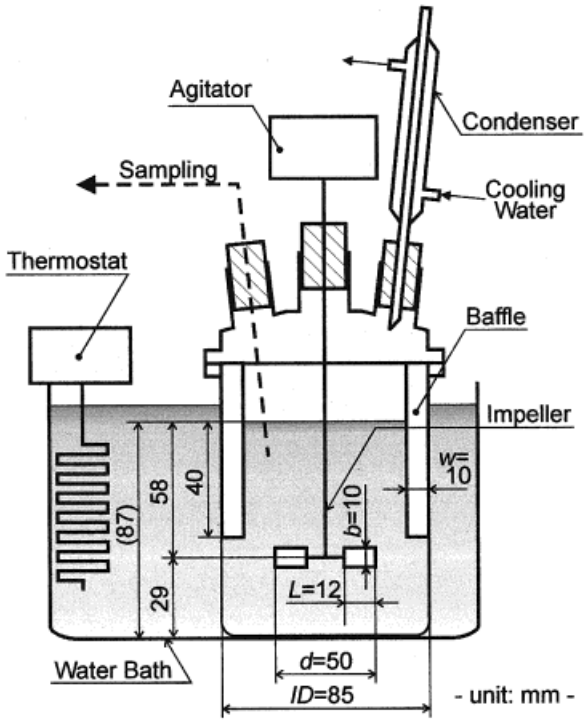

Figure 2 Schematic diagram of experimental apparatus.

Evaluation of Characteristics of Microcapsules

Particle Size Distribution and Mean Diameter

First, microcapsules were washed with water, filtered by filter paper, and then dried at room temperature. After these operations, the microcapsules were classified with Tyler meshes, and then each classified microcapsules was weighed to obtain the particle size distributions and the mean sizes. The Sauter mean diameter was adopted as the mean size (in mm), and it was calculated from the following equation:

$$dp_a = \sum(n \cdot dp^3) / \sum(n \cdot dp^2) \quad (1)$$

where n was the number of microcapsules in each mesh and dp was the mesh size (in mm), respectively.

Mechanical Strength

Mechanical strength of microcapsules was measured with the destruction tester (Aikoh Co. Ltd., MODEL-1307). Figure 3 shows the schematic diagram for this measurement. To explain specifically: the sample stage (b), on which a microcapsule (a) is put, is moved upward and downward automatically by controller. Then, the force loaded on the load sensor (c) was measured. In this measurement, microcapsules with the same size were selected and measured.

Observations of Microcapsule and Dispersing State of FB

By use of the microcapsules broken after the measurement of mechanical strength, the inner structure of the microcapsule was observed by SEM. The shapes of microcapsules were directly observed by optical microscopy. Furthermore, the dispersal state of FB in the shell of the microcapsule was observed as follows:

Microcapsules themselves and those cut in half to expose the cross section were soaked in methylene blue aqueous solution for 10 min. If there is FB on the surface of the wall and on the cross section of microcapsule, FB was dyed blue. Then, these microcapsules were dried at the room temperature and directly observed by the optical microscopy. Figure 4 shows the SEM micrographs of the cross section of microcapsule. It was found that microcapsules were of the single-cored type.

Experimental Conditions

The experimental conditions adopted in this study are as follows:

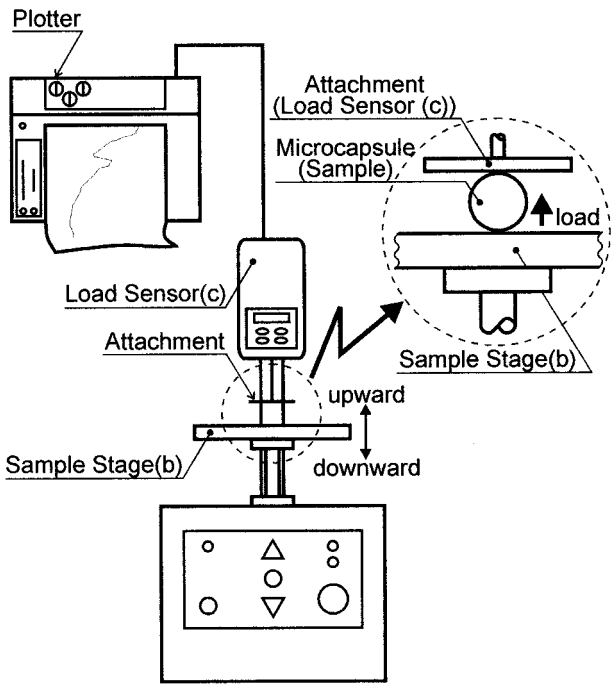

Figure 3 Schematic diagram of destruction tester.

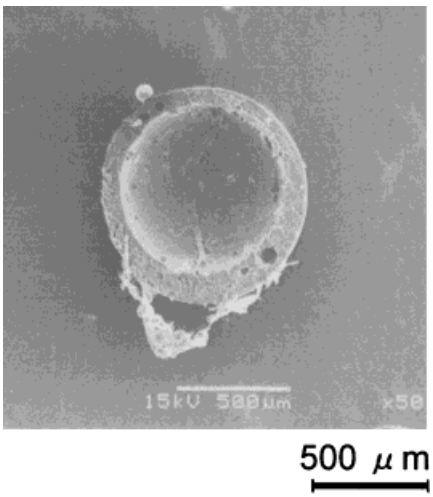

Figure 4 SEM of cross section of microcapsule.

Preparation of the (W/O) Dispersion

Continuous phase: Polystyrene/dichloromethane solution: 15 wt %, 1.5×10^{-2} dm^3

Dispersed Phase: Deionized water: 3.0×10^{-2} dm^3

Amount of FB: C_{FB} = 5 wt % EPS (C is the concentration)

Adjustment of Initial Water Droplet Size:

First stirring speed: $Nr_1 = 167\ s^{-1}$

Stirring time: t_1 = 5 min

Preparation of Microcapsule

Continuous Phase: Deionized water: 3.0×10^{-4} m^3

Dispersed Phase: Dichloromethane solution containing EPS, FB, and core material (water): 4.5×10^{-5} m^3

Second Stirring Speed: $Nr_2 = 3.33\ s^{-1}$

Stirring Time: t_2 = 2 h

Dispersing Agent: Polyvinyl alcohol (PVA, polymerization degree P_n = 500, 0.5 wt % continuous phase)

Drying Temperature: 40°C

Treating Agent of FB

The molecular structures of two kinds of styrene maleic acid and surfactant (Span80) are as follows:

S1: C_S = 10–50 wt %

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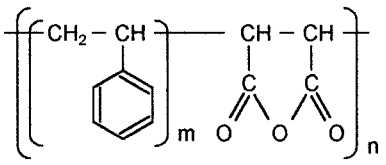

S2: C_S = 10–50 wt %

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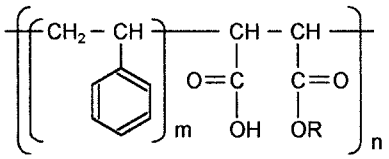

Span80: C_S = 10–50 wt %

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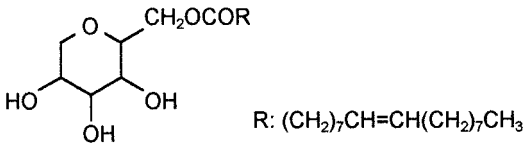

where C_S is the concentration of the treating agent.

RESULTS AND DISCUSSION

Physical Properties of Liquids Concerned

It may be thought that the viscosity of the EPS solution is affected by the dispersing state of FB

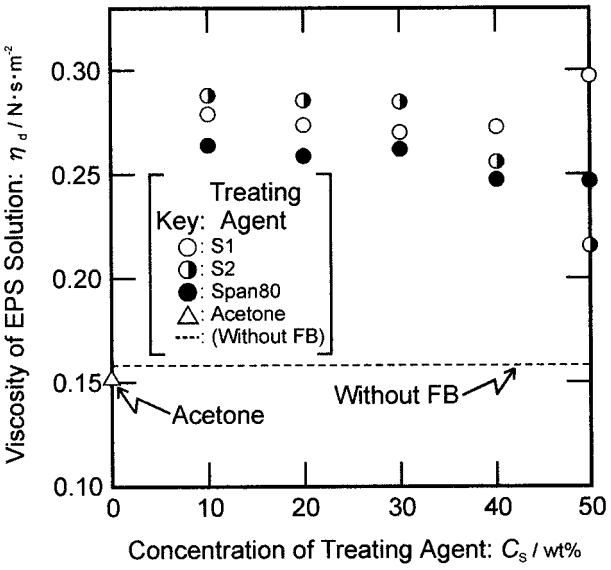

Figure 5 Effects of treating agent species and concentration (C_S) on viscosity of EPS solution (η_d) (in Pa s).

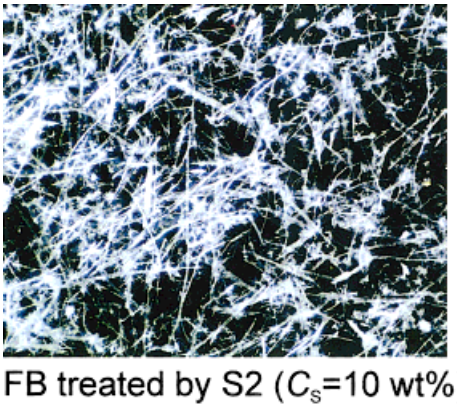

Figure 6 Dispersing state of FB treated by S2 in EPS solution.

and the dispersing state is dependent on the treatment of FB. Figure 5 shows how the viscosity of the EPS solution is affected by the treating agent species and their concentrations. In the case of treatment by acetone, the viscosity was found to be almost the same as that without FB (η_α = 0.15 N s/m^2). This is considered to be attributable to the aggregation of FB in the EPS solution. From this result, it may be thought that treatment by acetone does not make FB more lypophilic. In the case of treatment by the other treating agents, the viscosity of the EPS solution becomes the highest in the concentration region from 10 to 30 wt %. However, the viscosity slowly decreases with increasing the concentration except for the treating agent S1. For example, in the case of treatment by S2, the viscosity becomes the highest (η_α = 0.29 Ns/m^2) at the concentration of 10 wt %, decreases with increasing the concentration, and then falls to the value of 0.21 Ns/m^2 at the concentration of 50 wt %. This is considered to be attributable to the degree of lypophilicity of FB becoming too strong to disperse in the EPS solution. In this case, it is thought that FB trends to aggregate.

Figure 6 shows the dispersed state of FB treated by S2 at the concentration of C_S = 10 wt %. FB is found to disperse well in the EPS solution.

Figure 7 shows how the interfacial tension between the continuous water phase and the EPS solution is affected by the treating agent species and their concentrations. From this figure, it is found that the interfacial tension decreases with increasing the concentration of any treating agents. For example, when Span80 is added to the EPS solution, the interfacial tension decreases by $\gamma = 2 \times 10^{-3}$ N/m.

Particle Size Distribution and Mean Size

Figure 8 shows how the particle size distributions of microcapsules are affected by the treating agent species and their concentrations. The distributions do not necessarily show the distinct systematic dependency. However, from this figure it can be seen that the distributions tend to shift to smaller size with increasing concentration for all the treating agents. In general, it is known that the distributions are affected by the interfacial tension between the continuous phase and the EPS solution and the viscosity of the EPS solution. Here it is found that the interfacial tension decreases by addition of the treating agent and the viscosity increases by addition of FB, respectively. It can be seen in the case of Span80, which results in the lowest interfacial tension as shown in Figure 7, that the distributions are situated in the region of the smallest particle size. Furthermore, it is seen that the distributions shift to the region of the smaller size with the concentration. This is considered to be attributable to the viscous resistance to the breakup of a droplet made from the EPS solution. Namely, the viscosity of the EPS solution decreases with the concentration in the region of concentration beyond 10 or 20 wt %. For this, as the resistance to breakup decreases, the distribution shifts gradually to the region of the smaller size.

Figure 9 shows the dependencies of the mean diameters of microcapsules on the concentrations

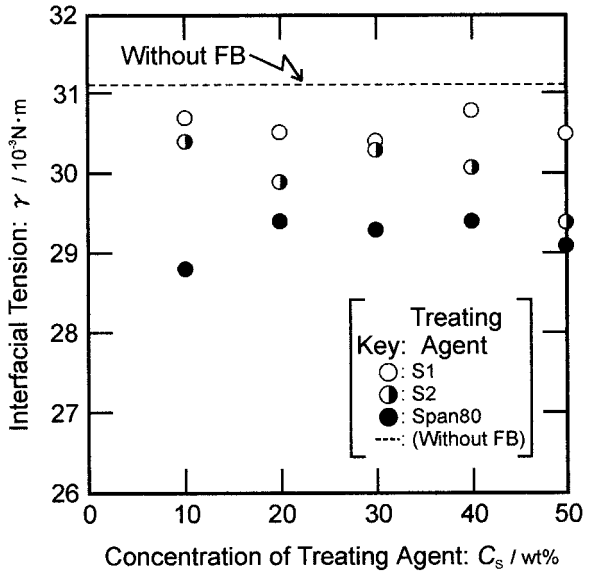

Figure 7 Effects of treating agent species and concentration (C_S) on interfacial tension between the continuous water phase and EPS solution (γ).

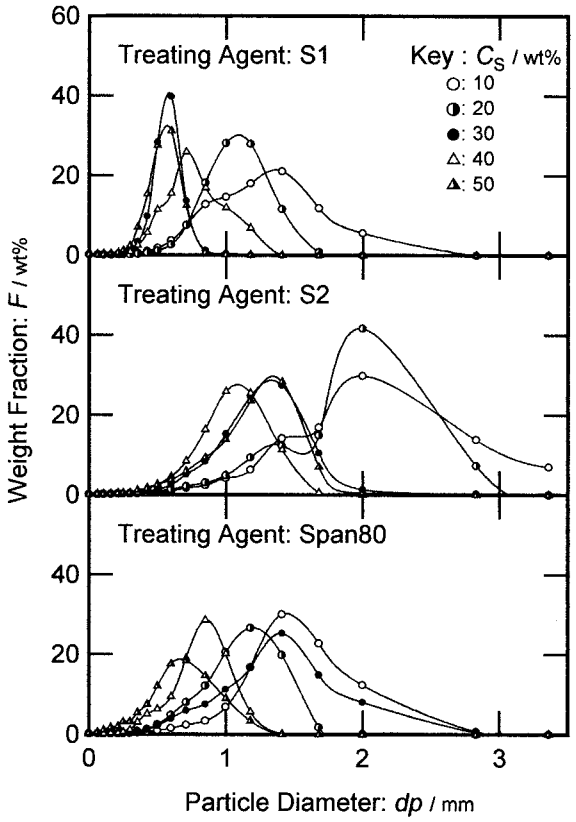

Figure 8 Effect of treating agent species and concentration (C_S) on particle size distribution.

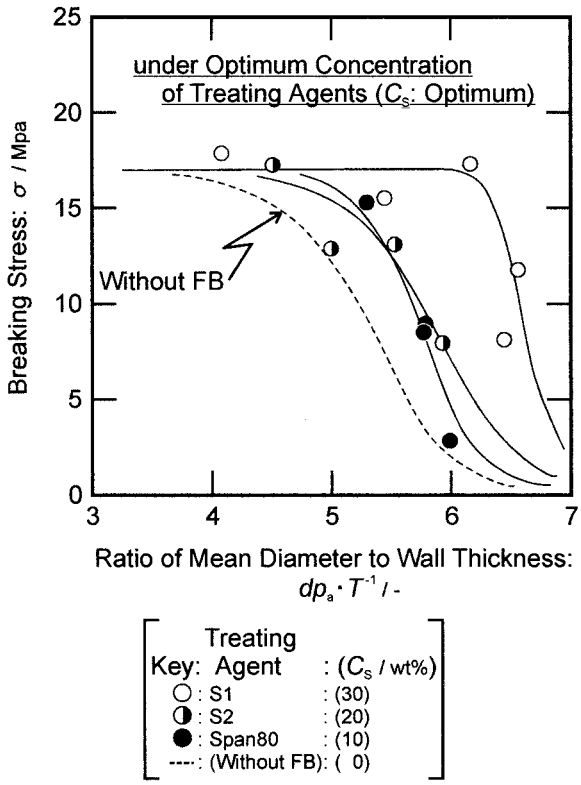

Figure 10 Relationship between ratio of mean diameter to wall thickness (dp_a/T) and breaking stress (σ).

of the treating agents. The mean diameters are larger than those without the treating agents, and increase with the viscosity of the EPS solution. These dependencies show the same tendency as that for the dependency of the viscosity on the concentration of the treating agents.

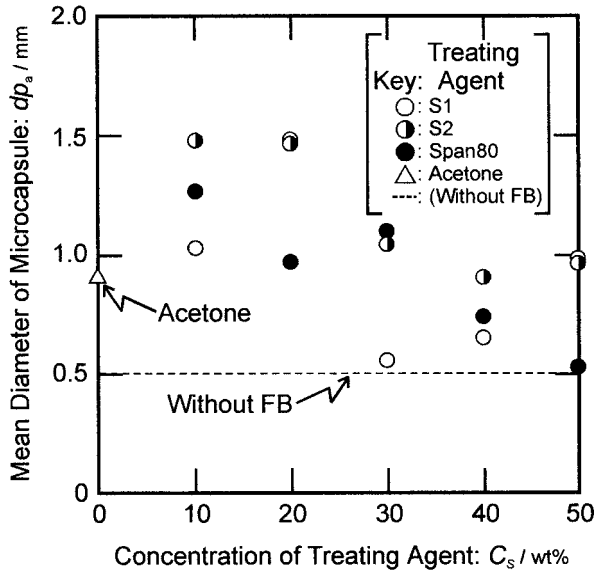

Figure 9 Dependencies of mean diameter of microcapsules (dp_a) on concentration of treating agents (C_S).

Physical Properties of Microcapsules

Figure 10 shows the relationship between the ratio ($\boldsymbol{dp_a/T}$) of the mean diameters ($\boldsymbol{dp_a}$) to the wall thickness (T) (in mm) and breaking stress ($\boldsymbol{\sigma}$) (in Pa). Here, the values of breaking stress are calculated according to the Oishi's theory using the following equation:

$$\boldsymbol{\sigma = P/[4(dp_a/T)]} \tag{2}$$

where P is the loaded pressure (in Pa) that can be calculated according to the following equation:

$$\boldsymbol{P = W/[(\pi dp_a/2)^2]} \tag{3}$$

where $\boldsymbol{W}$ is the load imposed on the microcapsule (in N).

In this evaluation, the experimental values obtained at the concentration of 10 wt %, at which the viscosity of the EPS solution shows the high-

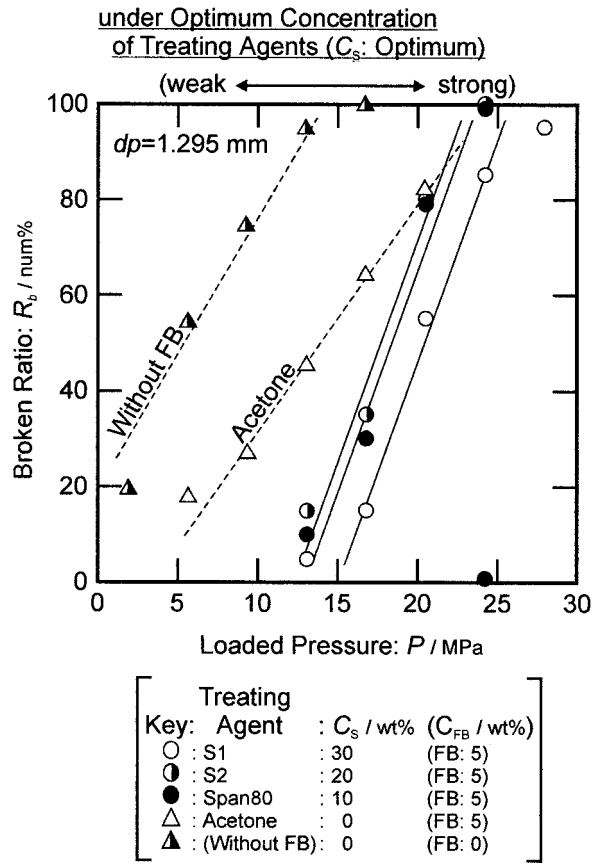

Figure 11 Dependencies of broken ratio (R_b) (in num %) on loaded pressure (P).

est value, are adopted. From this figure, for all the treating agent species, it is found that the microcapsule is broken at the larger dp_a/T than that without FB at the constant breaking stress and the breaking stress decreases with the value of dp_a/T. As the increase in the value of dp_a/T is attributable to both the increase in the diameter and decrease of wall thickness, microcapsules come to be broken easily. This result shows that the mechanical strength of the microcapsules can be increased by addition of FB. With respect to the effect of the treating agent species, it is found that the microcapsule is broken at the largest value of dp_a/T for S1. This is considered to be attributable to the fact that the mechanical strength of microcapsule is caused by the uniform dispersion of FB in the wall of microcapsule.

Figure 11 shows the dependency of the broken ratio on the loaded pressure. This measurement was performed for the microcapsules with the largest mechanical strength, which can be obtained at the optimum concentration of each treating agent. Here, the broken ratio is defined as the ratio of number of microcapsules broken at the given pressure to that of all microcapsules measured. From this figure, it is found that the broken ratio becomes the smallest when FB treated by the concentration of 30 wt % of S1 is added. In other words, the microcapsules become stronger in order by addition of FB treated by acetone, 20% of S2, 10 wt % of Span80, and 30 wt % of S1.

Figure 12 shows the photographs of microcapsules taken by optical microscopy. It is found that,

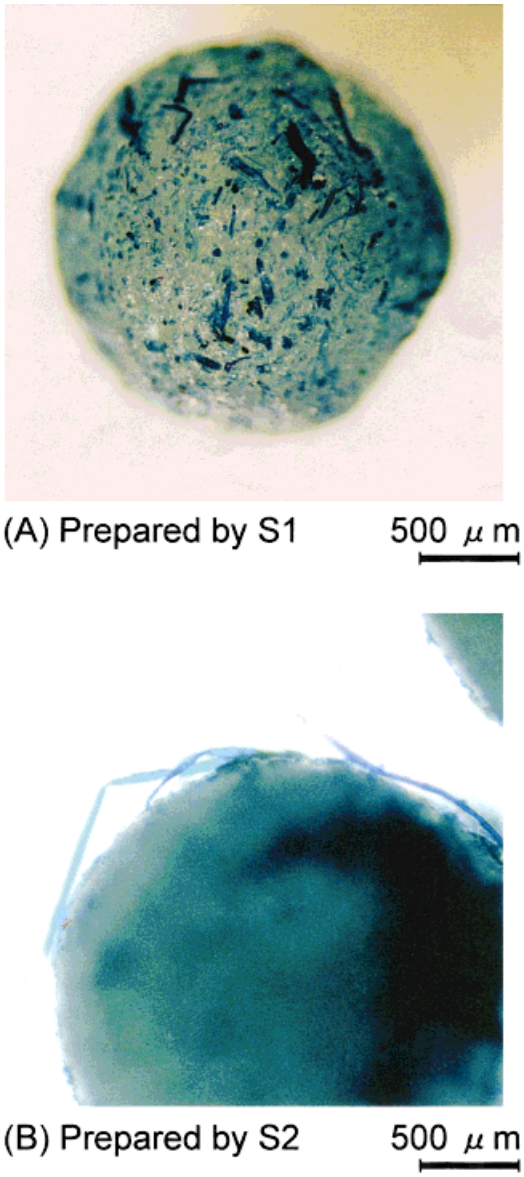

Figure 12 Photographs of microcapsules by optical microscopy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in the case of treatment by S1, FB is dispersing very well in the wall of microcapsule, and in the case of S2, a part of FB is exposed from the wall. These results are found to correspond well to those of mechanical strength.

CONCLUSION

In preparation of microcapsules composed of waste paper fibers and plastics by the semichemical recycle method, the following results are obtained:

1. Mechanical strength of the microcapsule can be increased by addition of FB.
2. Treating conditions of fibers affects the dispersing state of FB in the wall of microcapsule and then mechanical strength.
3. Particle size distributions and mean sizes of microcapsules depend on the dispersing state of FB in the wall of microcapsule.
4. There are optimum concentrations for each treating agent at which mechanical strength increases.

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