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APPLICATION OF HOLLOW CALCIUM CARBONATE PARTICLES TO PAPERMAKING

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ABSTRACT

Spherical particles made of calcium carbonate were reported to be available by the interfacial reaction method. When a potassium carbonate solution / benzene (W/O) emulsion is poured in a calcium chloride solution, spherical and sometimes hollow particles of calcium carbonate form, maintaining the shape of emulsified droplets. The surfactant concentration and emulsifying properties resulting from dispersion and homogenization determined particle shape, size and distribution. Prepared spherical particles were tried to be applied to paper making as a filler. They increased brightness of handsheets more than commercial coagulated particles. However, aggregates of calcium carbonate present in the paper hindered improvement of opacity.

INTRODUCTION

One of the disadvantages of recycled paper when compared to paper from virgin pulp is difficulty to gain high brightness. To improve brightness, papermakers make efforts to develop recycling processes such as introducing a strong surfactant in floatation and intensive bleaching. But, these processes demand more water and energy, causing adversity to environment. Another possible idea proposed here is to hide gray appearance with an efficient coating or internal loading for high opacity. Hollow spheres made of calcium carbonate could be suitable for this purpose because hollow structure scatters more light resulting in higher brightness and opacity.

This work was aimed at approaching this goal, but at the present time spherical (not always hollow) particles of calcium carbonate was tried to be prepared and was compared to another type of calcium carbonate in fundamental characterization and in application to loading to paper.

Nakahara[1)] reported that spherical and hollow particles of calcium carbonate were available by the interfacial reaction method. **Figure 1** represents the mechanism predicted by the author. At the surface of emulsified droplets, potassium carbonate and calcium chloride react to form a sphere sometimes with a hollow structure. Hollow structure can also be beneficial to light weight.

EXPERIMENTAL

Preparation of calcium carbonate

Calcium carbonate was prepared by the interfacial reaction method. First, a surfactant polyoxyethylene sorbitan monoolate (Tween-80) was dissolved in benzene at 0.5 wt. %. Second, a potassium carbonate solution of 1 mol/L was added to the benzene solution in a W/O volume ratio of

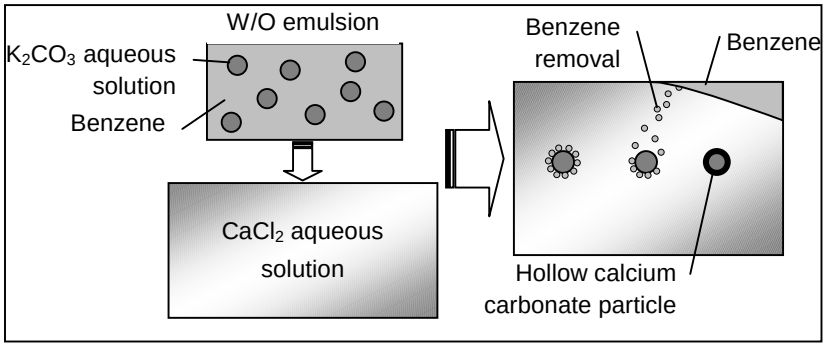

Fig.1 Predicted mechanism to produce hollow calcium carbonate particles by the interfacial reaction method.

3:7. Then, this mixture was emulsified by ultrasonic irradiation (Ultrasonic generator U0300FB, 26 kHz / 300 W, Kokusai Electric, Japan) for 10 min and then by homogenization with a homogenizer (Physcotron NS-20, Nihon Seimitsu, Japan) for 10 min at 15,000 min^{-1}. Last, this emulsion was poured into a stirred calcium chloride solution of 0.2 mol/L which contained twice as many calcium ions as carbonate ions. The amount of prepared calcium carbonate in one batch was 0.62 g on a regular basis, but for loading to paper it was 3.74 g. The mean yield was ca 80 %.

Paper making

Handsheets of paper were prepared according to ISO 5269-1. The prepared spherical particles of calcium carbonate was added to pulp stock of bleached kraft hardwood at 30 wt. % on dry pulp. Commercially available filler of calcium carbonate, PCX-850, Shiraishi Kogyo co. ltd., was also added to another stock for comparison. As well, unloaded handsheets were prepared. In advance, cationic polymer, polyamideamine-epichlorohydrin resin (WS-570, Japan PMC Co., Japan) was added at 0.1 wt. % on dry pulp to increase the retention of calcium carbonate.

Sheet properties

Apparent sheet density was calculated from basis weight and thickness for 5 handsheets each. Optical properties, namely, brightness and specific light scattering coefficient were determined from two reflectance values; one for single sheet with a backing of black cavity and the other for the same place of the same sheet with a backing of a white standard (the brightness is 93.0). **Equations (1)** and **(2)** transformed from the Kubelka-Munk equation by Hamada[2)] was used.

$$SW = \frac{1}{1/R_\infty - R_\infty} \ln \frac{(RR_g R_\infty - R{R_\infty}^2 - R_g + R_\infty)}{(RR_g R_\infty - R - R_g {R_\infty}^2 + R_\infty)} \qquad \text{Eq.(1)}$$

$$R_\infty = \frac{c - \sqrt{c^2 - 4}}{2}, \quad where\ c = \frac{(R_{g1} + R_2)(R_1 R_{g2} - 1) - (R_1 + R_{g2})(R_2 R_{g1} - 1)}{R_1 R_{g2} - R_2 R_{g1}} \quad and \quad R_1 < R_2 \qquad \text{Eq.(2)}$$

In the equations, the symbols used represent those in below:

R_∞ : brightness of a handsheet = reflectance of the paper so thick that further increase in thickness does not change the reflectance = reflectivity

S : specific light scattering coefficient

R_i : Reflectance of the handsheet which has behind it a surface (background) with a reflectance of R_{gi}, where black cavity for i = 1 and the white standard for i = 2 were used.

R_{gi} : Reflectance of the surface of the i-th background W : basis weight

RESULTS AND DISCUSSION

Characterization of spherical particles of calcium carbonate

Figure 2-a is a scanning electron micrograph of the spherical particles of calcium carbonate. The mean particle diameter was a little less than 2 μm in appearance including many small particles around 0.5 μm. **Figure 2-b** shows a close-up of a particle surface. The surface appears to be closely packed with primary scalenohedral (spin-shaped) and rhombohedral (cubic) particles both 50 to 100 nm in diameter as well as bent-string-shaped particles ca 50 nm in diameter and ca 300 nm long (not in this picture).

To obtain spherical particles at high yields, the concentration of surfactant (Tween-80) seemed to be one of the most important factors because it is related to the stability of a potassium carbonate / benzene emulsion. At 1.5 wt. %, an excess of the surfactant seemed to lose the stability of the

emulsion as there were large drops of separate phases of benzene and the potassium carbonate solution. In this condition, fine primary particles were not observed. Instead, much larger squared platelets as primary particles comprised sphere-like aggregates 3 to 5 μm in diameter. The surfactant added at 1.0 % and less than 0.8 % gave ca 30 % and ca 95 % of spherical particles, respectively.

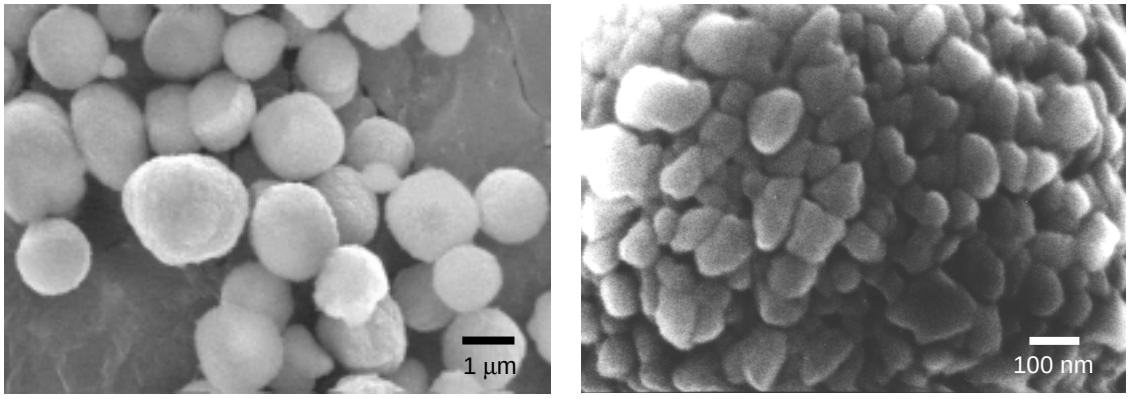

Fig.2 Scanning electron micrographs of spherical particles of calcium carbonate prepared by the interfacial reaction method (a) and a close-up of a particle surface (b).

Agitating intensity in emulsifying had important effects on the particle size distribution of spherical particles. Homogenization at 15,000 min^{-1} increased the ratio of the spherical particles less than 1 μm in diameter up to ca 20 %. Ultrasonic irradiation cannot render the particle diameter any more, but relatively large particles to 3 μm or less.

There are three crystal forms for calcium carbonate; calcite, aragonite and vaterite. Vaterite is not usually synthesized in reactions of aqueous solutions at room temperatures and at atmospheric pressures. The interfacial reaction method, however, provided appreciably high percentage of vaterite, the rest of which was calcite as shown in **Figure 3**. In this X-ray diffraction pattern, some peaks are in accordance with those of pure calcite, but the others are all attributed to those of vaterite. According to Nakahara[3], the vaterite ratio can amount to ca 50 %, but it depends on the concentrations of calcium chloride and potassium carbonate. Also those concentrations were reported to affect the synthesis ratio of spherical particles.

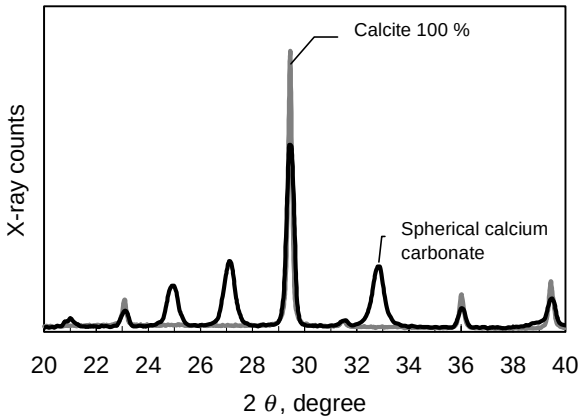

Fig. 3 X-ray diffraction patterns of spherical particles of calcium carbonate and pure

Properties of handsheets loaded with spherical calcium carbonate particles

Table 1 summarizes the physical and optical properties of the three kinds of handsheets loaded with calcium carbonate; one loaded with spherical particles; another loaded with coagulated particles; and the other unloaded. The density of the paper loaded with the spherical particles was lower than that of the unloaded one, as is often the case with loading because of acting as an obstruction to interfiber bondings, but was higher than that for coagulated particles. **Figure 4**, a scanning electron micrograph of a surface of a sheet loaded with the spherical particles, explains that there were more large aggregates for this type. The agglomerates seems to have become larger around the cubic particles as a core to ca 30 μm in diameter. Such a large aggregate was not observed for coagulated

ones.

Table 1 Physical and optical properties of the handsheets

Filler type	Basis weight, g/m^2	Density, kg/m^3	Brightness, %	Specific scattering coefficient, m^2/kg
Spherical particles	65.9	0.675	87.0	35.1
Coagulated particles	65.6	0.659	82.5	43.9
Unloaded	62.0	0.684	79.0	32.6

Brightness for the spherical calcium carbonate was the highest of the three types of handsheets, but specific light scattering coefficient for it was lower than that for the coagulated one and was a little higher than that for the unloaded. The brightness could be extraordinarily high maybe because the residual fluorescence due to the surfactant *per se* or an impurity in it. The structure of the coagulated particles is also expected to act as an excellent light scatterer. Conventional rhombohedral particles would show a lower value of specific light scattering coefficient.

For further researches, to hollow out spherical particles of calcium carbonate is necessary for additional functions. If attained, this type of calcium carbonate should be potential to function in many other ways in paper making industry. Possible value-added uses are, for example, microcapusules of odor extinguisher or colorant, and adsorbent.

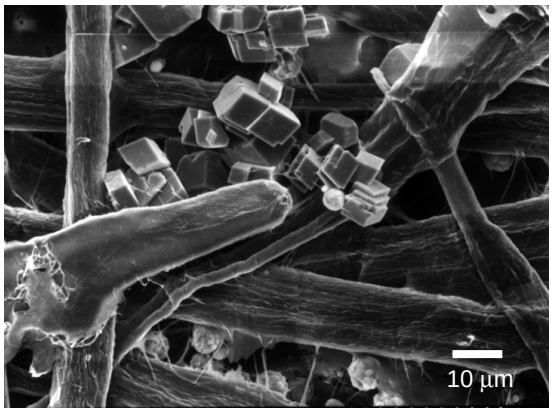

Fig.4 Spherical particles and aggregates of rhombohedral particles on a paper surface.

CONCLUSION

Spherical particles of calcium carbonate was successfully obtained by the interfacial reaction method. As a filler for internal loading to paper, they increased brightness of paper more than commercial coagulated particles. However, aggregates hindered improvement of opacity.

ACKNOWLEGEMENT

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