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An exploratory research of PVC-*Chlorella* composite material (PCCM) as effective utilization of *Chlorella* biologically fixing CO_2

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A new PVC-*Chlorella* composite material (PCCM) was investigated aiming at the effective utilization of biological CO_2 fixing *Chlorella*. The microalga *Chlorella*, after fixing CO_2, was molded with PVC. Molding conditions of PCCM, and physical properties of *Chlorella* were studied using tensile strength as an index for estimating the properties of PCCM. The optimum parameters for molding of PCCM were as follows: temperature = 180°C, pressure = 4.4 MPa and time = 5 min. The following physical parameters of *Chlorella* best enhance high tensile strength: water content of 2%, average particle size of 30–80 μm and a relatively homogeneous distribution of particle size. *Chlorella*, maintaining its original shape, exists in PCCM as an empty ball inlaid in the matrix of PVC. The PCCM shows a lower elongation and is more brittle than PVC, possibly as a result of gas and residual PVC primary particles around *Chlorella* grains. A comparison between theoretical and experimental results show that there is an effective combination between the PVC matrix and the *Chlorella* surface in PCCM. PCCM has a tensile strength higher than 30 MPa which meets the requirements for rigid PVC products, if *Chlorella* content is less than 20%. *Chlorella* can thus be effectively utilized as a practical filler. © *2000 Kluwer Academic Publishers*

1. Introduction

A reduction in the discharge of carbon dioxide (CO_2) into the atmosphere is a very serious problem faced by mankind, since the increase of CO_2 in the atmosphere causes global warming. Not only scientists but also governments of many countries are devoting a lot of attention and funds to the search for a practical solution. The New Energy and Industrial Technology Development Organization (NEDO) in Japan launched a research and development program for innovative technology for the earth in fiscal 1990. As a part of this program, a research project investigating biological CO_2 fixation and utilization has been conducted by the Research Institute of Innovative Technology for the Earth (RITE), in order to develop technologies by which CO_2 is fixed by utilizing microorganisms such as the green microalga *Chlorella* [1, 2].

Chlorella has a much higher utilization rate (10–20%) of light energy than common plants (0.1–0.5%) in photosynthesis [3]. Biological fixation of CO_2 means that CO_2 is fixed by controlled photosynthesis using microorganisms such as *Chlorella*, in which the photosynthetic functions are maximized in a photo-bioreactor. The process produces a large amount of *Chlorella* instead of discharging CO_2 into the atmosphere.

However the *Chlorella* must be further utilized as a material since it will gradually putrefy and decompose, resulting in the release of CO_2 into natural environment again after a certain time. As part of the utilization research, composite materials incorporating *Chlorella* in synthetic resins such as PVC have been studied aimed at making ecofriendly building materials. As long as *Chlorella* composites are used in materials such as floor tiles or plastic laminated boards, CO_2 fixation is likely to be semipermant and CO_2 will not be released into the air again. Moreover, as a great amount of PVC is now used as a building material, the use of *Chlorella* to replace partially PVC also has the potential to reduce the costs of these building materials [4].

Khanolkar and Shivkumar [5] have reported that *Cladophora glomerata*, an alga from fresh water rivers, can be used as a filler/reinforcement in polymers such

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as polystyrene, destructurized starch and polycaprolactones. Until now, however, little research has been carried out on composite materials of microalgae and polymers. In this paper, we report on a PVC-*Chlorella* composite material (PCCM) which effectively utilizes biological CO_2 fixing *Chlorella*. The molding conditions and physical properties of *Chlorella* were investigated, using tensile strength as an index for estimating material properties. Microstructure observation of the materials revealed the composite behavior of PVC and *Chlorella*. We demonstrated that *Chlorella* is a suitable filler for PVC.

2. Experimental

2.1. Materials

Chlorella was obtained from Yaeyama Shokusan Co., Ltd. in Japan. It is a product which is spray-dried after being strained by centrifugal filtration. *Chlorella* was vacuum-dried at 60°C for 6 days before it was molded with PVC. The average particle size of *Chlorella* was about 62.66 μm. The PVC used was a polymer with a degree of polymerization of 1100, and grain size from 50 μm to 150 μm. Two commercially available PVC stabilizers, PSE-227 and KM-55, were used. PSE-227 is a complicated fat acid salt of barium and zinc, and KM-55 consists mainly of complicated compounds of organic tin. The other chemicals used in this study were all of reagent grade.

2.2. Molding and heat-pressurizing

The PVC-*Chlorella* composite material (PCCM) was prepared by a heat-pressurizing method. A mold was made of aluminum. It had a rectangular shape with an inner size of 120 × 20 × 7 mm (length × width × height). Eight grams of the mixture having a composition of 80% PVC and 20% *Chlorella* (expressed as 0.8 P-0.2C) was thoroughly mixed, put into the mold, and then heat-pressurized under selected molding conditions. After molding, the mold was cooled to room temperature and PCCM was peeled from the mold. Molding was conducted at least 2 times under identical conditions. Test samples for tensile strength measurement were made according to the size listed in the literature [6].

2.3. Analyses

Test sheet samples were conditioned at 20°C and 65% relative humidity (RH) in an environmental chamber for 24 h before measuring tensile strength (TS) and elongation (E). A tensile tester (AG-100A, Shimadzu Co.) was used to measure TS and E in accordance with the testing method for tensile properties of plastics (at a crosshead speed of 5 mm/min) [6]. The microstructure of PCCM was observed with a S-2460N Scanning Electron Microscope (SEM) (Hitachi Co.). The TG-DTA analyses of *Chlorella* were carried out from room temperature to 200°C using a MAC Science 2000 Thermal Analyzer (MAC Science Co.). The particle size distribution of *Chlorella* was measured by a LMS-24 Laser Micron Sizer (Seishin Co.) using ethanol as a medium, after it was scattered by an ultrasonator.

3. Results and discussion

3.1. Optimum molding conditions of PCCM

3.1.1. Temperature

When PVC is molded by heat-pressurizing, PVC grains go through three changes; the original PVC grains (50–150 μm) are broken up into primary particles (~1 μm) as the temperature rises from 100 to 150°C, the primary particles then melt and bond to each other as the temperature continues to rise from 150 to 190°C, and finally the PVC matrix consisting of domain (~0.1 μm) or microdomain (~0.01 μm) is formed [7]. Fig. 1 shows the relation between the TS of resultant 0.8P-0.2C PCCM and molding temperature. The TS of PCCM increases with temperature rising up to 200°C, but decreases if the temperature exceeds 200°C. PCCM molded at 200°C has the highest TS. This demonstrates that a higher temperature is advantageous in melting PVC, but that deterioration of PVC decreases the TS of PCCM if the temperature exceeds 200°C.

The color of *Chlorella* begins to change when the molding temperature rises to 190°C, the deep green of *Chlorella* changing into brown. Fig. 2 shows the TG-DTA result of *Chlorella*. The weight loss is greater above 180°C than between 110°C and 180°C. This may be due to the volatilization and decomposition of volatile substances such as chlorophyll, considering the color change (from deep green to brown) of *Chlorella* if the molding temperature is greater than 190°C. Thus the molding temperature should be restricted below 190°C so that *Chlorella* does not deteriorate during heat-pressurizing.

3.1.2. Pressure

Fig. 3 shows the effects of molding pressure on the tensile strength of resultant 0.8P-0.2C PCCM when

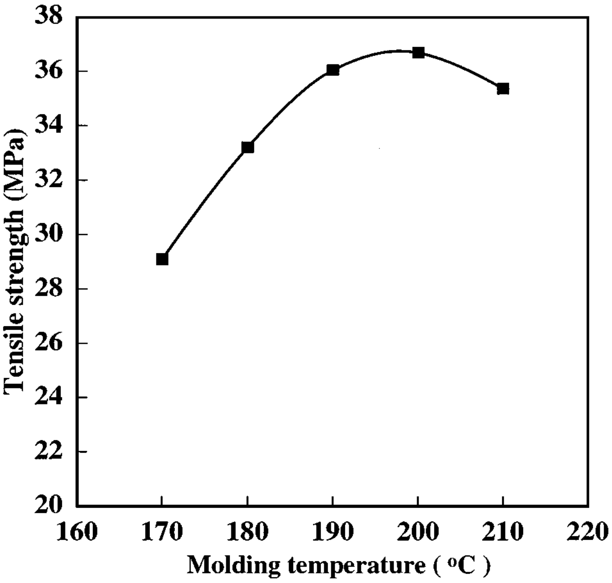

Figure 1 Tensile strength of 0.8P-0.2C PCCM as a function of molding temperature at a pressure of 2.2 MPa for 5 min.

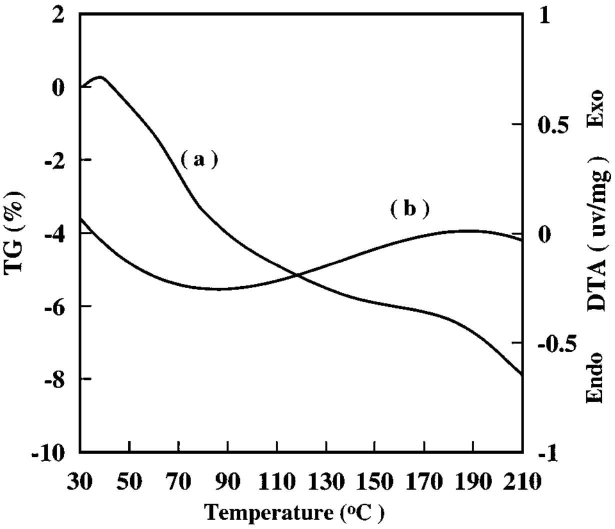

Figure 2 Thermogravimetric analysis (TG) (a) and differential thermal analysis (DTA) curve (b) of *Chlorella* at a heating rate of 5°C/min in air.

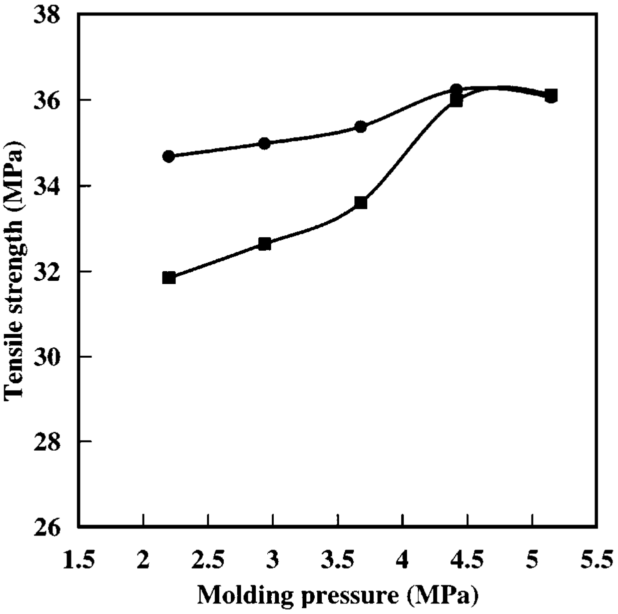

Figure 3 Tensile strengths of 0.8P-0.2C PCCM as a function of molding pressure at temperatures 180°C (■) and 190°C (●) for 5 min.

molding temperatures are fixed at 180°C and 190°C. The tensile strength increases with pressure increase from 2.2 MPa to 4.4 MPa, especially when the temperature is at 180°C. This indicates that high pressure facilitates heat conduction between particles, resulting in a better melting of PVC particles. Higher pressure is also considered to improve the adherence between PVC and *Chlorella*. Accordingly, if pressure is greater than 4.4 MPa, TS depends on very little pressure at temperatures of either 180°C or 190°C.

3.1.3. Time

The dependence of the tensile strength of 0.8P-0.2C PCCM on molding time is shown in Fig. 4. The effect of molding time on TS varies with molding temperature. At 180°C, the tensile strength barely changes if the molding time is over 5 min, but a concomitant color change of *Chlorella* occurs, which is a signal of *Chlorella* deterioration. On the other hand, at 190°C, a shorter molding time of up to 3 min is long enough to maximize tensile strength, but color change of *Chlorella* occurs when the time exceeds 2 min.

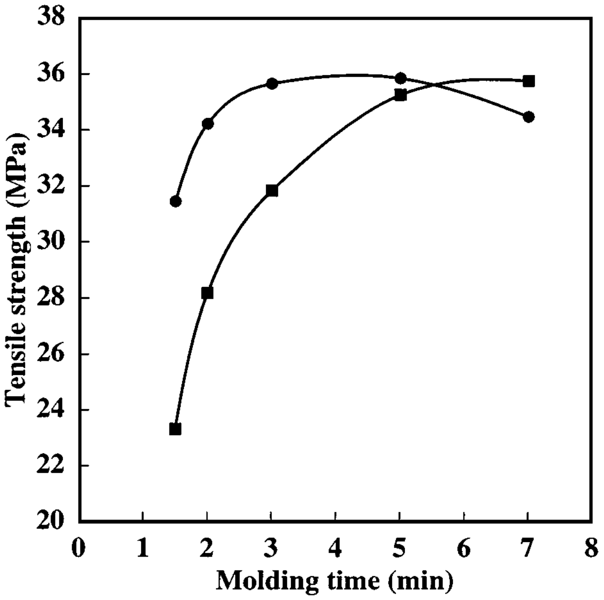

Figure 4 Tensile strengths of 0.8P-0.2C PCCM as a function of molding time at temperatures 180°C (■) and (●) 190°C, and pressure 4.4 MPa.

Based on the experimental results described above, the optimum molding conditions for preparing PCCM are as follows: temperature of 180°C, pressure of 4.4 MPa, and time of 5 min. PCCM with high TS and no color change of *Chlorella* can be made under these conditions.

3.2. Influence of physical properties of *Chlorella*

Chlorella is a kind of microalga, belonging to chlorophyceae. *Chlorella* cells have a size of about 5 μm and when dried, they aggregate to form larger particles (Fig. 5). The cell is mainly composed of protein, fat and carbohydrate. The cell shell containing about 30% cellulose exists on the surface of the *Chlorella* particle.

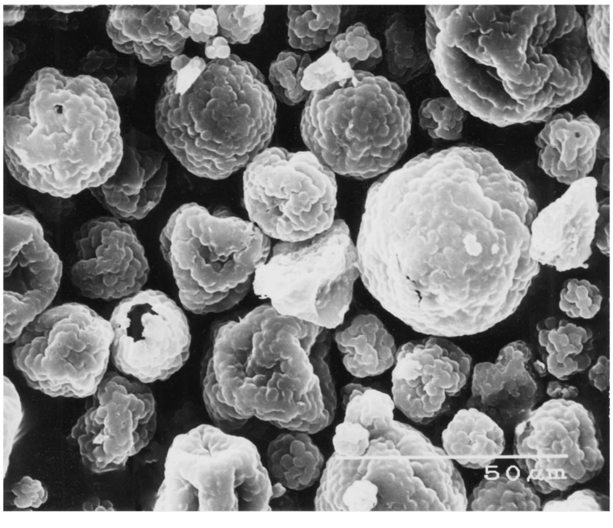

Figure 5 A SEM micrograph of *Chlorella* grains.

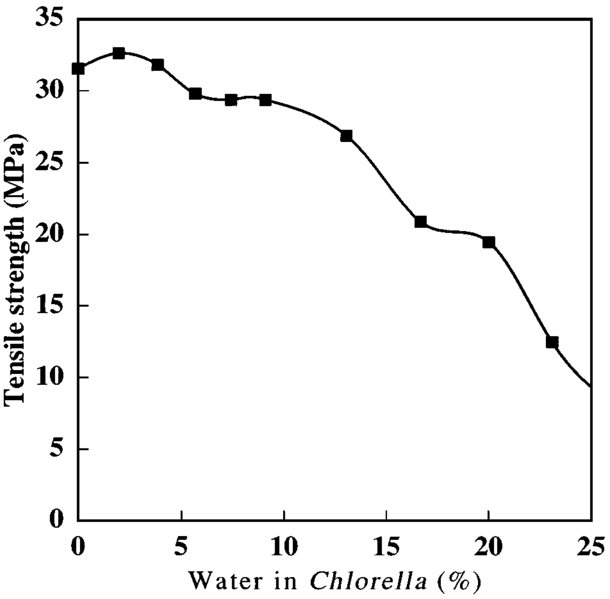

Figure 6 Influence of water content in *Chlorella* on tensile strength of 0.8P-0.2C PCCM at molding temperature 180°C, pressure 6.6 MPa, and time 5 min.

Because the composition of *Chlorella* is very complicated, it is very difficult to understand clearly the interactions between PVC and *Chlorella*. We investigated the influence of some physical properties of *Chlorella*.

3.2.1. Water content in Chlorella

Chlorella vacuum-dried at 60°C for 6 days is considered to contain no water. *Chlorella* samples containing different amounts of water were prepared by adding specific amounts of water to the dried *Chlorella*. After grinding to improve mixing, they were immediately molded with PVC. Experimental results demonstrate that the existence of a little water (2%) in *Chlorella* seems to enhance the tensile strength of PCCM (Fig. 6). This is possibly due to a little water restraining the evaporation of volatile substances in *Chlorella*. The TS decreases sharply when the water content is above 13%. It is obvious that evaporation of a lot of water will weaken the adherence of PVC and *Chlorella* in PCCM. Fig. 7 shows a large crack in PCCM containing 16.67% water (b), but no crack in PCCM containing 5.66% water (a).

3.2.2. Average particle size and distribution of particle size

Chlorella samples with different average particle sizes were obtained by sieving of original *Chlorella*. Fig. 8 demonstrates that both very large and very small average particle sizes inhibits the achievement of high tensile strength and that the optimum range of average particle size is from 30 μm to 80 μm. Furthermore, the distribution of particle size also has a great influence on the tensile strength of the material. Sieved *Chlorella* with an average size of 59.8 μm has a much higher tensile strength than the original *Chlorella* with an average size of 62.66 μm (marked ★ in Fig. 8) which is not sieved; the former (59.8 μm) has a particle size

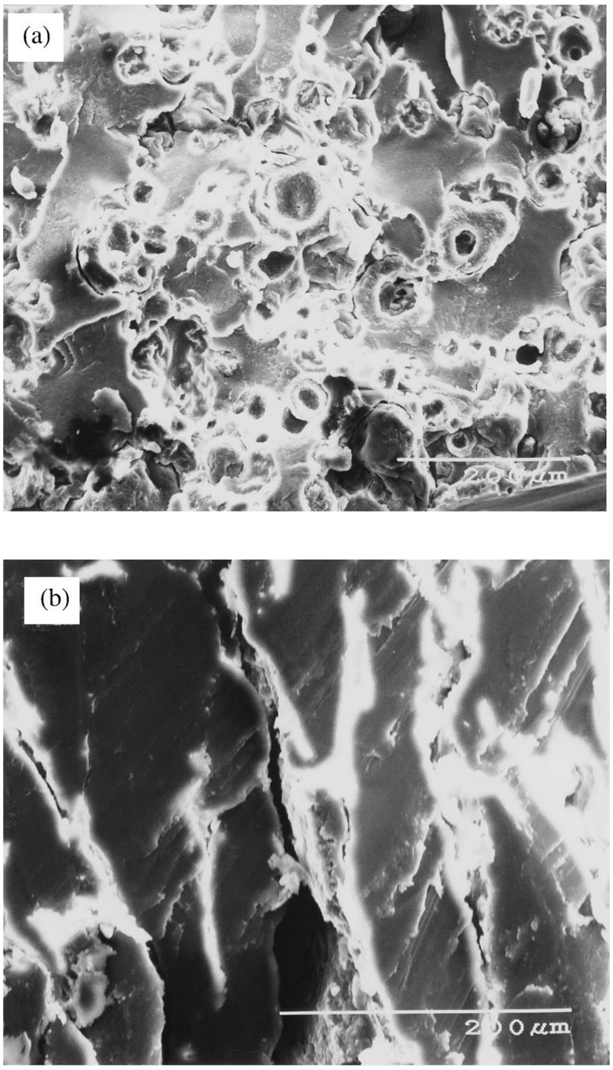

Figure 7 Cross-sections of 0.8P-0.2C PCCM obtained from *Chlorella* containing 5.66% (a) and 16.67% water (b).

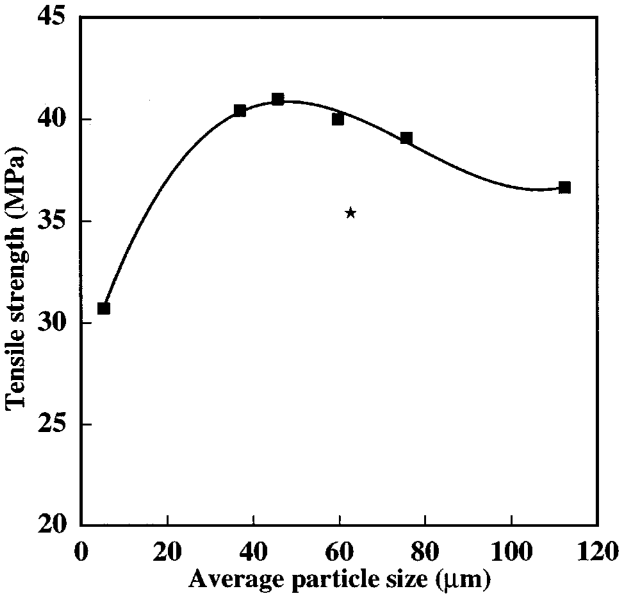

Figure 8 Tensile strength of 0.8P-0.2C PCCM as a function of the average particle size of *Chlorella* at molding temperature 190°C, pressure 2.2 MPa, and time 5 min; *Chlorella* sieved (■) and Original *Chlorella* before sieving with average particle size of 62.66 μm (★).

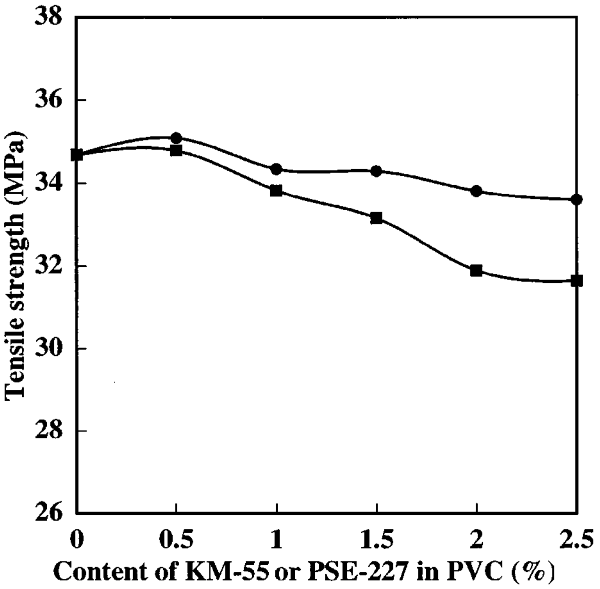

Figure 9 Effects of KM-55 (■) and PSE-227 (●) on tensile strength of 0.8P-0.2C PCCM at molding temperature 190°C, pressure 2.2 MPa and time 5 min.

distribution from 52 μm to 75 μm, versus 3 μm to 150 μm for the latter.

3.3. Effect of stabilizers

PVC is a rather unstable polymer and will deteriorate when it is heated above 100°C or exposed to strong light. Generally, because there are active points such as unsaturated double bonds, branched chains, and catalyzer remaining in PVC, free radicals first form at these active points when PVC is irradiated with heat or light energy, after which a decomposing reaction and twofold conjugated combination occur, resulting in the release of HCl and coloration [8, 9]. Accordingly, when PVC is processed, stabilizers are generally used to suppress such deterioration.

Fig. 9 displays the effects of stabilizers PSE-227 and KM-55 on TS of 0.8P-0.2C PCCM. Both stabilizers show hardly any effect on the TS of PCCM. The tensile strength increases only slightly when the stabilizer content is 0.5%; however it decreases if the content is above 1%, especially in the case of KM-55. This implies that *Chlorella* itself possibly has some effect as a stabilizer of PVC.

3.4. Microstructure and combination of *Chlorella* with PVC

Fig. 10 shows the microstructure of the surface and cross-section of PCCM as observed by SEM. *Chlorella* particles as empty balls are inlaid in the matrix of PVC. *Chlorella* grains retain their original shape and are not crushed or melted during the molding. Gas gaps appear around the *Chlorella* grains. Unmelted primary particles of PVC (white parts in the photo) can be seen around the *Chlorella*.

TABLE I Comparison of PVC and PCCM

	PVC	PCCM
Composition (g)	PVC 8, KM-55 0.032	PVC 6.4, *Chlorella* 1.6
Tensile strength (MPa)	50.2	34.6
Elongation (%)	180	1.86
Volume (cm^3)	5.8	7.08

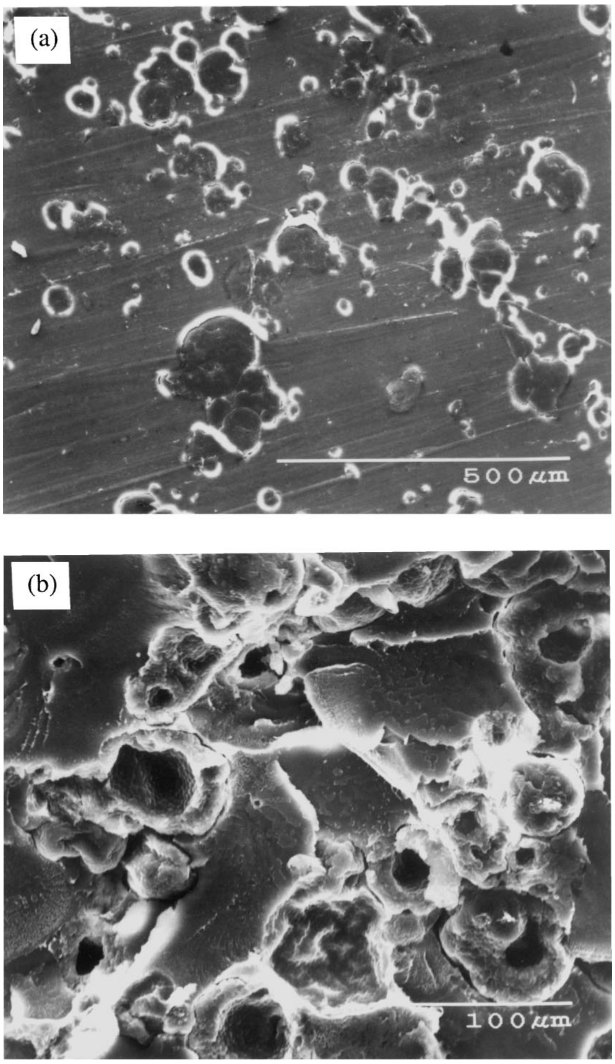

Figure 10 SEM micrographs of 0.8P-0.2C PCCM: surface (a) and fracture (b).

Table I lists some properties of PVC and PCCM. PCCM exhibits poor plastic elongation. Its elongation is only 1.86% in contrast to PVC with about 180%. This is probably owing to the unmelted primary particles remaining around the *Chlorella* grains in PCCM. That the volume of 0.8P-0.2C PCCM containing 20% *Chlorella* is 22% greater than that of PVC indicates that *Chlorella* is a good filler for increasing the material volume.

Based on the SEM observation and experimental result, different combinations of PVC with *Chlorella* may be described by the following models (Fig. 11). *Chlorella* combines well with PVC (a), partially combines with PVC (b), and shows no combination with PVC, where *Chlorella* is completely separated from PVC matrix by a gas gap (c).

The gas gap existing around *Chlorella* grains is possibly due to air remaining in the material and/or gas from evaporation of water or volatile substances in *Chlorella* while molding. Gas gaps may become enclosed in

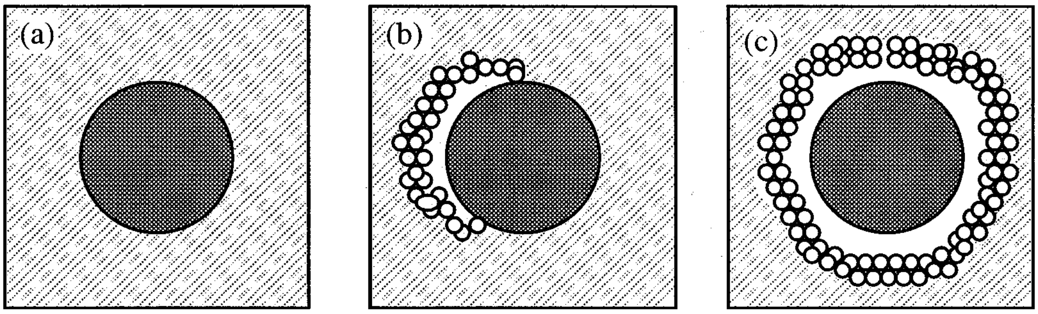

Figure 11 Combination modes of *Chlorella* with PVC. ▨ PVC matrix, ○ primary particle of PVC, ● *Chlorella* grain

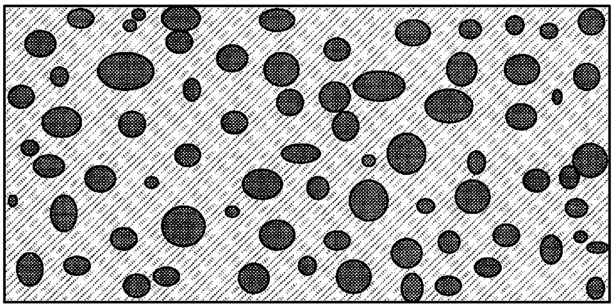

Figure 12 Sketch diagram of cross-section of PCCM. ▨ PVC matrix, ● *Chlorella*

PCCM since the outer surface of the PVC melts first due to the conduction of heat from the surface toward the center.

It is feasible that the primary particles of PVC appear mainly around *Chlorella* grains in PCCM because of the poor heat conductivity of the gas gap around *Chlorella*. The distribution of molding stress is not homogeneous around *Chlorella* since the shape of *Chlorella* is irregular. Accordingly, it may be difficult to melt further the PVC primary particles located in the portion with the lower molding stress to form the domain or microdomain matrix because of both the looser contact between PVC particles and the tendency for gas to gather there.

3.5. Effect of *Chlorella* content on tensile strength

The cross-section of PVC-*Chlorella* material can be illustrated as in Fig. 12. We assume that the total section area (A) is equal to the summation of the section areas of PVC matrix (A_p) and *Chlorella* part (A_c). The strength of the material can be given by Equation 1.

$$\sigma = F/A \tag{1}$$

where F is the tension load added on the PCCM. Provided that the tensile strength of PCCM is contributed only by the PVC matrix, the tension load can be calculated by Equation 2.

$$F = \sigma_p A_p \tag{2}$$

where σ_p is the tensile strength of the PVC material. Introducing Equation 2 into Equation 1 yields Equation 3.

$$\sigma = \sigma_p A_p/A \tag{3}$$

If there are no gas holes in the PCCM, the volume of PCCM (V) consists of the volumes of PVC matrix (V_p) and *Chlorella* (V_c). V_p and V_c can be defined as

$$V_p = W_p/D_p \tag{4}$$

$$V_c = W_c/D_c \tag{5}$$

where W_p and D_p are the weight and density of PVC, and W_c and D_c are the weight and density of *Chlorella*, respectively. Assuming that all the cross-sections of PCCM have the same values of A_p and A_c,

$$A_p/A = V_p/V \tag{6}$$

By using $V = V_p + V_c$ and Equations 4 and 5, Equation 6 can be rewritten as

$$A_p/A = 1/(1 + D_p W_c/W_p D_c) \tag{7}$$

We used the experimental D_c and D_p values of 0.7 and 1.4, respectively. Using the weight content of *Chlorella* in PCCM (expressed as C%), then $W_c/W_p = C\%/(1 - C\%)$. Thus, by introducing Equation 7 into Equation 3, Equation 8 is obtained.

$$\sigma = \sigma_p\{1/[1 + 2C\%/(1 - C\%)]\} \tag{8}$$

Equation 8 indicates the relation between *Chlorella* content and tensile strength of PCCM. The theoretical TS values of PCCM can be calculated by Equation 8.

Fig. 13 shows the theoretical curve according to Equation 8 and the experimental results. The experimental values match well the theoretical curve when the content of *Chlorella* is lower than 20%. But the experimental values are larger than the theoretical values when the *Chlorella* content exceeds 20%, and the difference gradually increases with an increase in *Chlorella* content. It can be inferred that there is a generally effective combination of *Chlorella* with PVC although there are three different combination models, as mentioned above. When the *Chlorella* content is lower ($<$20%), the contribution to the strength of PCCM is mainly from the PVC matrix; however, if the *Chlorella* content is higher ($>$20%), the contribution of *Chlorella* to the strength of PCCM gradually increases, indicating that the interface combination of *Chlorella* with PVC gradually plays an increasing role in the strength of PCCM. Practical fractures occur in the portion where the PVC

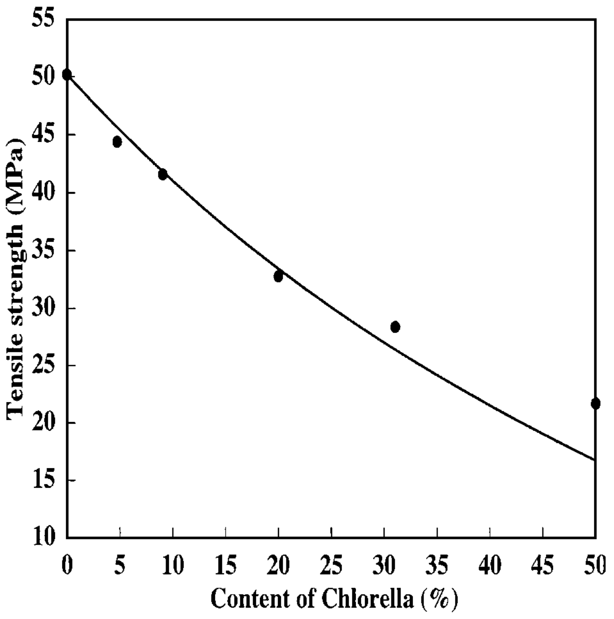

Figure 13 Relation between tensile strength and *Chlorella* content in PCCM (●) at molding temperature 180°C, pressure 4.4 MPa and time 5 min, using KM-55 with a 0.5% content. The solid curve represents the theoretical result according to Equation 8.

matrix has the smallest area and therefore *Chlorella* has the biggest area. Furthermore, there are gas gaps or holes in the practical PCCM. Considering these practical features of PCCM, we can reconfirm the effective combination of *Chlorella* with PVC by comparing the theoretical and experimental TS in Fig. 13. Thus, PCCM has a tensile strength higher than 30 MPa, which can meet the need of rigid PVC products [10] if the *Chlorella* content is kept below 20%, and has a tensile strength higher than 15 MPa, which can meet the need for products of plasticized PVC [11] if the *Chlorella* content is kept below 50%.

4. Conclusions

1. PVC-*Chlorella* composite material (PCCM) can be made by heat-pressurizing. In order to obtain a material with high tensile strength but without the deterioration of *Chlorella*, the optimum molding conditions are as follows: temperature = 180°C, pressure = 4.4 MPa, and time = 5 min.

2. The physical properties of *Chlorella* itself have effects on the tensile strength of PCCM. A water content of 2%, average particle size from 30 μm to 80 μm and an homogeneous distribution of particle size enhance tensile strength.

3. The stabilizers commercially available for PVC, PSE-227 and KM-55, do not obviously enhance the tensile strength of PCCM. *Chlorella* possibly has some effect in stabilizing PVC.

4. *Chlorella* exists in the composite material as an empty particle ball inlaid in the matrix of PVC. There are gas gaps and residual primary particles of PVC around *Chlorella* grains, restricting the plastic elongation of PCCM.

5. *Chlorella* is a suitable filler for PVC. It not only plays a role in increasing the volume of PCCM and decreasing the density, but also contributes to the tensile strength of PCCM because of combination of the *Chlorella* with PVC. PCCM has a tensile strength higher than 30 MPa when *Chlorella* content is below 20%, which meets the requirements for rigid PVC products, and a tensile strength higher than 15 MPa when the content is below 50%, which meets the requirements for plasticized PVC products.

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