

## Original

# Preparation and Characterization of Calcium Silicate/Vermiculite Composite

Masaru Akao<sup>1)</sup>, Yoshiaki Fukuda<sup>2)</sup>, Atsushi Yamazaki<sup>2)</sup>, Masahisa Inoue<sup>3)</sup>, Kojun Setsu<sup>3)</sup>,  
Tohru Takagi<sup>4)</sup>, Kan Rui<sup>4)</sup>, Miho Okauchi<sup>4)</sup> and Ryo Tamamura<sup>4)</sup>

<sup>1)</sup> Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, Tokyo 101-0062, Japan

<sup>2)</sup> Department of Mineral Resources Engineering, School of Science and Engineering, Waseda University, Tokyo, Japan

<sup>3)</sup> Laboratory for Structure and Function Research, Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Tokushima 770-8515 Japan

<sup>4)</sup> Department of Oral Pathology and Medicine, Graduate School of Medicine, Dentistry and Pharmaceutical Science, Okayama University, Okayama, Japan

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**Abstract:** A new calcium silicate/vermiculite composite for building material has been prepared from unfired vermiculite, calcium hydroxide, silica and pulp by autoclaving at 187°C at a pressure of 1.08 MPa. The product exhibited the vermiculite crystals dispersed uniformly in a definite direction among the matrix of calcium silicate. The composite showed marked plastic deformation caused by interlayer sliding of vermiculite. The building material was fixed by nails and screws and also possible to cut and saw like artificial wood. The board had superior humidity control originated from chemical adsorption of water molecules at the interlayer of vermiculite, and relative humidity in an experimental house was maintained to be 50%. Formaldehyde was chemically adsorbed to the composite, and there was no release of formaldehyde at elevated temperature.

**Keywords:** Calcium silicate, Vermiculite, Mechanical properties, Humidity control, Formaldehyde adsorption.

### Introduction

Vermiculite is a member of clay minerals, produced by the decompositions of micas and occurs as quite large crystals of mica-like appearance. It has a layer structure, and the interlayer contains water molecules and exchangeable cations, mainly Mg<sup>2+</sup> ions <sup>1)</sup>. Fired, exfoliated vermiculite is a low density material and utilized as a constituent of lightweight concretes and plasters, a filler for plastics, paints and fertilizers, and a soil enhancer, whereas little useful application in its natural state. We reported the development of a new calcium silicate/vermiculite composite for building material, made from unfired vermiculite, calcium hydroxide, silica and pulp by autoclaving at 187°C <sup>2)</sup>. It was made by a process of usual calcium silicate boards with minor alterations. Vermiculite was more chemically stable in the process, compared to diatom earth, allophane and zeolite which were added into various building materials to improve living environment. The material exhibited the vermiculite crystals dispersed uniformly in a definite

chemical properties of vermiculite in the calcium silicate matrix.<sup>4)</sup>

### Materials and methods

Vermiculite used in the present study was from Palabora, Transvaal, South Africa with an average grain size of 0.25 mm. Powder X-ray diffraction (XRD) pattern was taken with graphite-monochromatized Cu K $\alpha$  radiation at 40 kV and 20 mA. XRD pattern of the sample indicated a 1:1 mixture of vermiculite and hydrobiotite <sup>3)</sup>. A mixture of 30% vermiculite, 34% calcium hydroxide, 31% silica sand and 5% pulp was blended with distilled water to produce dense slurry. The resultant slurry was formed into a green sheet by suction filtration. The sheet was heated at 187°C at a pressure of 1.08 MPa for 6 h in an autoclave and dried at 60°C for 24 h. The product had a density of 0.87-0.91 g cm<sup>-3</sup>.

Fig. 1 shows phase contrast microscopy of a vertical section of calcium silicate/vermiculite composite. Several vermiculite crystals with highest phase contrast were embedded in calcium silicate matrix with lowest phase contrast, and the basal planes were parallel to the sheet plane. Quartz crystals dissolving after the hydrothermal reaction were also seen as medium contrast fine particles. As a result of XRD, crystalline phases detected in the

Correspondence to Masaru Akao, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10 Surugadai, Kanda, Chiyoda-ku, Tokyo 101-0062, Japan. Tel: +81-3-5280-8018; Fax: +81-3-5280-8005. E-mail: akao-bcr@tmd.ac.jp

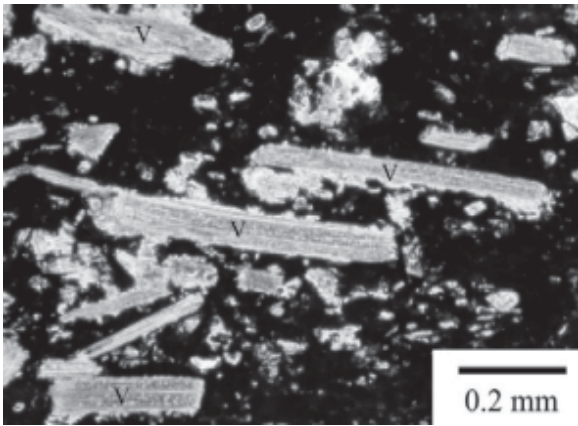


Fig. 1 Phase contrast micrograph of a vertical section of calcium silicate/vermiculite composite. Vermiculite crystals (V) are embedded in calcium silicate matrix.

composite were vermiculite, hydrobiotite, tobermorite-1.1 nm<sup>4)</sup> and quartz (Fig. 2). Vermiculite and hydrobiotite remained unchanged, although the  $d_{002}$  spacing of vermiculite changed from 1.43 to 1.48 nm owing to partial substitution of  $Ca^{2+}$  for  $Mg^{2+}$  ions located at the interlayer. The tobermorite had higher crystallinity compared to commercial calcium silicate boards, and calcite ( $CaCO_3$ ) was detected.

**Results**

**Mechanical properties of composite**

Test samples of 5.5 × 40 × 200 mm were cut from the calcium silicate/vermiculite composite which had 1.6% water content. Three-point bending tests were made on a 150 mm span at a crosshead speed of 0.008 mm s<sup>-1</sup>. The composite had an average bending strength of 12.2 MPa and modulus of elasticity of 6.6 GPa, which were similar to 12.5 MPa and 7.6 GPa of a commercial calcium silicate board. The test samples were placed in a thermohygrostat chamber at 90% relative humidity (RH) at 25°C, and the water contents was adjusted to be 15%. The sample had an averaged bending strength of 9.6 MPa and modulus of elasticity of 5.7 GPa. Stress-strain curves of the composites plotted from

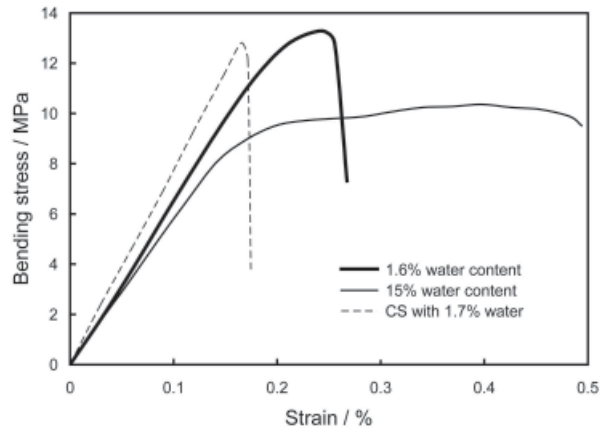


Fig. 3 Stress-strain curves of three-point bending tests for calcium silicate/vermiculite composite and calcium silicate board (CS), showing marked plastic deformation.

the results of the 3-point bending tests (Fig. 3) show marked plastic deformation caused by slip of vermiculite crystals. As the water content was increased, the plastic deformation increased and the fracture strength and elastic modulus decreased.

**Moisture adsorption and desorption**

Moisture adsorption and desorption of the composite was tested. Plate 100 × 100 × 9.5 mm was placed in the chamber at 25°C. The relative humidity was kept 90% for 6 h and then kept 30% for 6 h. This cycle was iterated 10 times. Weight variations in the plate were measured at each half cycle. The amount of moisture adsorption at the 9th cycle was 42.5 g m<sup>-2</sup> and greater than that of a calcium silicate board (31.2 g m<sup>-2</sup>) and a gypsum wall board (4.96 g cm<sup>-2</sup>)<sup>5)</sup>.

Isothermal moisture adsorption and desorption was measured at 25°C at 0-90% RH (IGAsorp, Hiden Analytical). Sample was loaded and dried at 25°C at 0% RH for 2 h before testing. Fig. 4 shows equilibrium water contents of the raw vermiculite and the composite.

Humidity control of the composite was evaluated in an experimental house with thermally insulated air-tight construction. A 39.7 m<sup>3</sup> room had a 16.5 m<sup>2</sup> wood floor, and interior walls and

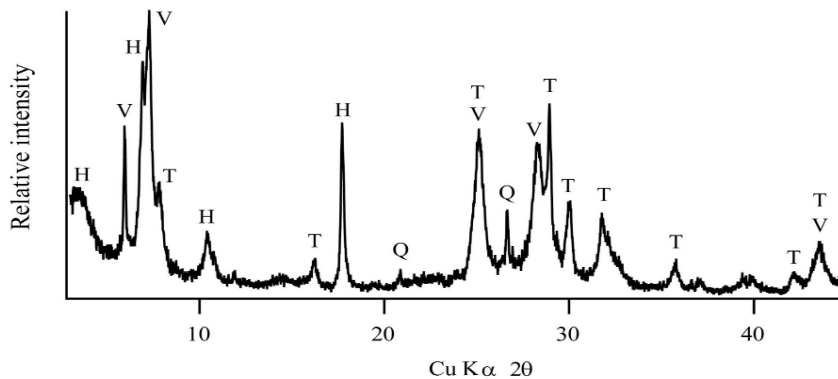


Fig. 2 XRD pattern of calcium silicate/vermiculite composite (V: vermiculite; H: hydrobiotite; T: tobermorite-1.1 nm; Q: quartz).

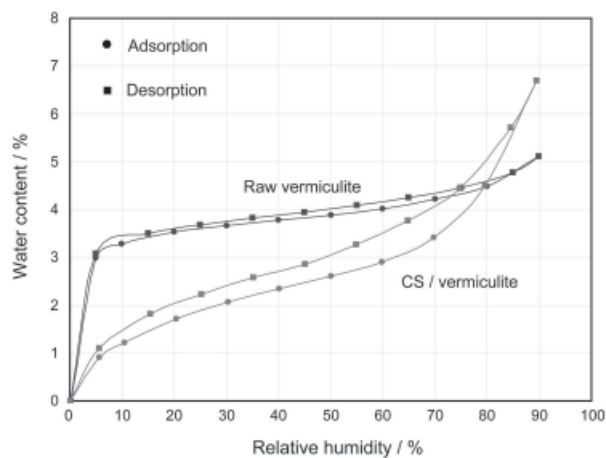


Fig. 4 Equilibrium water contents of raw vermiculite and calcium silicate/vermiculite composite measured at 25°C.

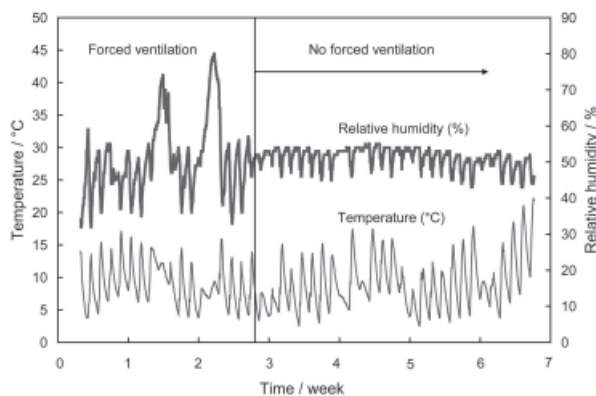


Fig. 5 Room temperature and relative humidity in an experimental house, showing humidity control by calcium silicate/vermiculite composite.

ceiling were made of the boards with a total area of 44.2 m<sup>2</sup>. Room temperature and relative humidity were recorded for 7 weeks (Fig. 5). The relative humidity in the room was maintained to be approximately 50% at no forced ventilation condition, although the room temperature varied extensively.

#### Formaldehyde adsorption

Formaldehyde adsorption onto the composite was investigated. Plates 100 × 100 × 9.5 mm of the composite and a commercial gypsum board were kept in the chamber at 30% RH at 25°C for 5 days to be in equilibrium. Each plate was placed in a polyvinyl fluoride bag 250 × 300 × 0.05 mm. An empty bag served as a control. The end of each bag was thermally sealed and a 3,000 cm<sup>3</sup> dry air was injected. A saturated formaldehyde vapor of commercial formalin (~40 cm<sup>3</sup>) was injected with a syringe into each bag so that formaldehyde concentration was 30 mg m<sup>-3</sup>. The concentrations were measured with formaldehyde detector tubes and gas samplers (Komyo Rikagaku Kogyo Co.). The bags were placed in a chamber at 25°C for 6 h and then kept in another chamber at 40°C for 6 h, and their formaldehyde concentrations were measured.

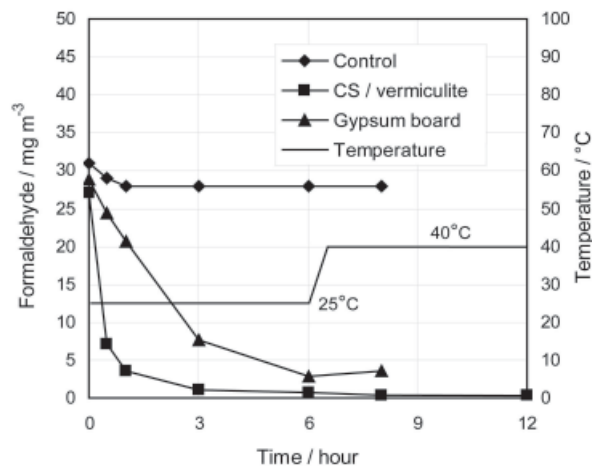


Fig. 6 Formaldehyde adsorption to composite and comparison to gypsum wall board.

Fig. 6 shows variations in formaldehyde concentrations in the presence of the composite and comparison to the gypsum board. The composite demonstrated higher formaldehyde adsorption compared to the gypsum board. As the temperature was increased from 25 to 40°C, the composite showed further reduction of formaldehyde concentration. In contrast, the gypsum board showed release of formaldehyde at the elevated temperature.

## Discussion

### Phase composition of composite

The composite was composed of vermiculite, hydrobiotite, tobermorite-1.1 nm and quartz. Vermiculite and hydrobiotite remained unchanged after the hydrothermal reaction, although the  $d_{002}$  of vermiculite changed from 1.43 to 1.48 nm owing to partial substitution of Ca<sup>2+</sup> for Mg<sup>2+</sup> ions at the interlayer. The tobermorite had higher crystallinity compared to calcium silicate boards. Thus, the crystallinity of tobermorite was increased by the addition of vermiculite to the calcium silicate matrix, and suggests an epitaxial growth of tobermorite on the surfaces of vermiculite. There was no calcite (CaCO<sub>3</sub>) in the present XRD pattern. It is suggested that release of Mg<sup>2+</sup> ions from the interlayer of vermiculite inhibits formation of calcite and stabilizes tobermorite in the calcium silicate matrix.

### Plastic deformation in bending

The stress-strain curves of the composites in three-point bending (Fig. 3) showed marked plastic deformation caused by slip of vermiculite crystals. Applying stress to the composite, the slip takes place at the interlayer of vermiculite parallel to the (001) plane and the plastic deformation appears macroscopically. The slipped interlayer binds again after the release of stress. The vermiculite used contained hydrobiotite which is a mixed layer mineral consisted of vermiculite and biotite (a member of micas). The vermiculite layer easily slips at low stress, but the biotite layer does not and requires higher stress to cleavage. When

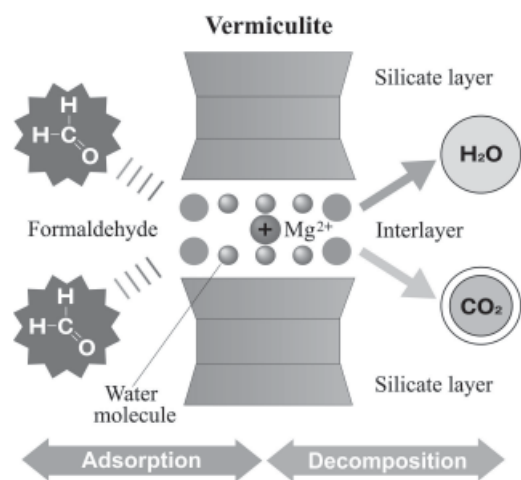


Fig. 7 Schematic representation of formaldehyde adsorption and decomposition at the interlayer of vermiculite.

mineralogically pure vermiculite is used, its mechanical properties become lower. The existence of hydrobiotite maintains mechanical properties of the composite.

Building material made of the composite is fixed by nails and screws, also possible to cut and saw and has good mechanical properties like artificial wood. Consequently, the board enables an adhesive-free interior finish work and prevented emission of volatile organic compounds (VOC) <sup>5-7</sup>.

#### Humidity control

The equilibrium water content of the raw vermiculite (Fig. 4) was kept constant at 10-80% RH and indicates chemical adsorption of water molecules at the interlayer of vermiculite. Equilibrium water content of the composite shows a combination of chemical adsorption to vermiculite and physical adsorption to calcium silicate matrix. The physical adsorption is predominant at high RH regions greater than 70%.

The relative humidity in the experimental house made of the boards was maintained to be approximately 50% at no forced ventilation condition, although the room temperature varied extensively. The humidity regulation is caused by releasing water molecules from the interlayer of vermiculite at low humidity conditions and adsorbing them into the interlayer at high humidity conditions.

#### Formaldehyde adsorption

The composite demonstrated higher formaldehyde adsorption compared to the gypsum board, and there was no release of formaldehyde at the elevated temperature. The results indicate

chemical adsorption of formaldehyde to the composite. Ryu <sup>6</sup> measured formaldehyde and total VOC concentrations in an experimental house and indicated that interior walls made of the boards significantly reduced both concentrations at various ventilation conditions.

The surface and interlayer of vermiculite adsorb various organic compounds such as glycerol and toluene. The basal plane is hydrophobic and acts as a solid acid. The substitution of  $\text{Ca}^{2+}$  for  $\text{Mg}^{2+}$  ions at the interlayer enhances a catalytic activity in vermiculite (Fig. 7). Zeolitic  $\text{Ca}^{2+}$  ions and water molecules are present in the structure of tobermorite <sup>4</sup>), and thus suggested a catalytic activity in tobermorite. It is assumed that vermiculite-tobermorite complex in the composite decomposes formaldehyde and VOCs with a cooperative catalytic reaction.

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