Bionic Design of the Scallop Shell
Development of New Products that Apply Its Functions

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Abstract

Scallops are harvested in Tohoku and Hokkaido area of Japan, and about two hundred and ten thousand tons of scallops are scrapped each year. Year by year, the amount of scrapped shells increases, and there is a waste problem. We prepared scallop shell ceramics (SSC) by heating at 1050 ℃ and found their several functions such as antibacterial action, deodorant action, and reduction of harmful chemical material, for example, formaldehyde in the atmosphere.

Based on the results, this paper reports the structure and the functions of the scallop shell. Moreover, the problems that the scallop shell ceramics may solve, and the benefits to health and the environment are discussed.

1. Introduction

In Aomori Prefecture, the shells of about fifty thousand tons of scallops a year are scrapped by being piled in fields along with the scallop aquaculture deposits in Mutsu Bay. It is estimated that about seventy thousand tons or more are piled in fields in Aomori Prefecture alone. The amount of scrapping is estimated to increase further because the scallop culture industry feeds plankton, the cost of the aquaculture is low, and aquaculture is now prospering. Research was conducted to effectively apply, from an engineering viewpoint, the structure and the functions of the scallop shells attained through the process of the evolution.

The research aimed to use the scallop shell as a structural material, and aspects of shell structure and deformation were studied as a first step in bionic design of the shell. The structure of the surface and a cross-section of the shell were examined in detail using a scanning electron microscope(SEM), and the relationship between strength and structure was explained [1,2]. For practical applications, Chafflose Corporation, Co., Ltd., Yokohama, Japan, manufactured wall materials and paint mainly consisting of scallop shells that were heated to 1050 C (scallop shell ceramics) in 1995.

Hachinohe Institute of Technology in Hachinohe (HIT), Japan, and Chafflose Corporation, Co., Ltd. started collaboration between academia and industry in 1999 by discussing functions of the scallop shell. The collaboration aimed to investigate and develop the application of scallop shell ceramics, and to manufacture products using scallop shell ceramics by applying bionic design techniques.

The resulting products containing scallop shell ceramics were put to practical use, such as

for wall materials for interiors, insulation, *tatami*-matting, wallpaper, sliding screen paper, detergent, and so on. These products are potential countermeasures against sick building syndrome.

2. The concept of the bionic design

Researchers examine the mechanism of the birth, the growth, the formation, the structure, the composition and the extinction of organisms and apply the idea which they could obtain from the results of research to the artificial design technology. This is the general idea of the bionic design. Although, from the viewpoint of a study of the material, the materials of the organism is made of under the limited conditions such as temperature, pressure, the material element, etc., these biological materials are very marvelous and frequently commonsense materials and the organization. Therefore, the structure, organization, and ecology of organism in nature should be used to develop new artificial materials, machines, structures, systems, and functional materials. This concept corresponds to the fundamental concept of zero-emissions.

When a scallop shell is examined from the viewpoint of bionic design, it is composite material that has very high strength and is composed of 99% calcite and about 1% organic matter. Two water jets are jetted from the part called as the ear by violently opening and closing two sheets of shell, and the scallop swims to protect itself against the starfish and so on which is a natural enemy. For this reason, the shell is lightweight and its strength is high. The gummy material called ligament is an excellent composite material through which the particles of calcite crystals are dispersed. The shell opens using the ligament and closes using the adductor muscle. The scallop feeds on plankton and it develops faster than other shellfish, growing to a shell height of 12 cm in 2 or 3 years; at this point, it can be shipped.

3. The structure of the scallop shell

Generally, the structure of each part of the living creature is rational, and acquires biological systems through evolution to protect the body against environmental factors. The shell is the exoskeleton of the mollusk, and it is mainly composed of calcium carbonate crystals and a small quantity of consecutive organic compounds. The calcium carbonate crystals of the scallop shell are hexagonal calcite. The organic substances which make protein comprise about 0.001 to 0.8 % in the crossed lamellar structure which is the middle layer of the scallop shell, although it varies in each layer[3].

A cross-section of the scallop shell reveals a 3-layered structure. Fig. 1 shows the tensile fracture surface of the scallop shell observed using SEM. The inner layer consists of the crystals of a pillar-shaped part of the calcite, which is vertical to the inner surface (Figs. 2 and 3). A cross-section of shell reveals that the crystals of the pillar-shaped part calcite are rectangular and size of rectangular is less than 5 μm. The middle layer is a crossed lamellar structure in which the crystal bundle of the pillar-shaped part of the calcite crosses, like

plywood board, at an angle of 90 ° (Fig. 4). Mainly, this layer is subjected to the load that loaded to the shell. A part of the tip of this pillar-shaped crystal is settled in the whole on the inner surface of the shell, and an unevenness of several micrometers is formed. This structure is called the leaf-shaped structure (Fig. 5). The upper half in this photograph shows the inside surface of the shell and the bottom half shows a cross-section.

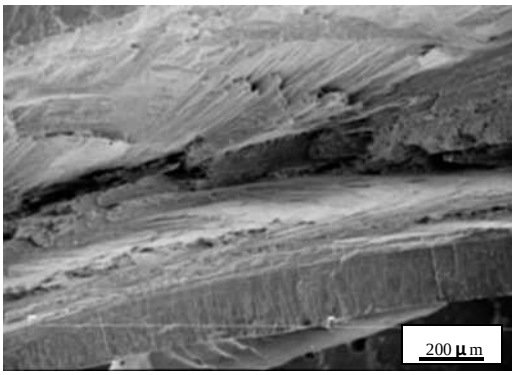


Fig.1. Tensile fracture surface of scallop shell.
Inner layer: Leaf-shaped structure,
Middle layer: Crossed lamellar structure.

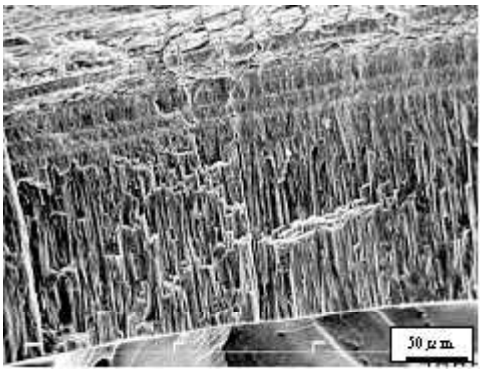


Fig.2. A leaf-shaped structure of inner layer.

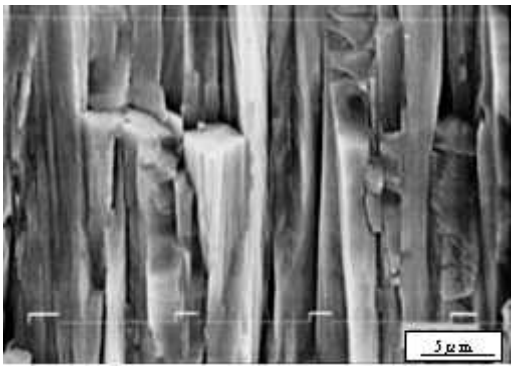


Fig. 3. Leaf-shaped structure.
Square size of cross-section
2 ～ 5 μ m.

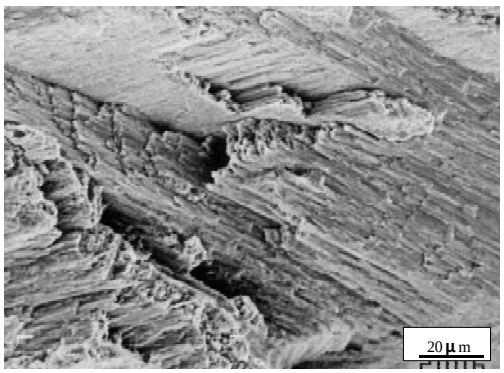


Fig. 4. Crossed lamellar structure.
Some bundles of calcite crystallites crossed each other vertically like plywood.

The test specimen (30 mm x 10 mm) was cut out from a scallop shell of a height of about 120 mm, tensile tests were carried out and stress-strain curves of the scallop shell were obtained (Fig. 6). The curve between A and B in Fig. 6 is discontinuous, showing that each layer fractured one after the other within it. Moreover, the scallop shell has a similar strength to acrylic polymer material. A little strain of the shell suggests that the material is brittle.

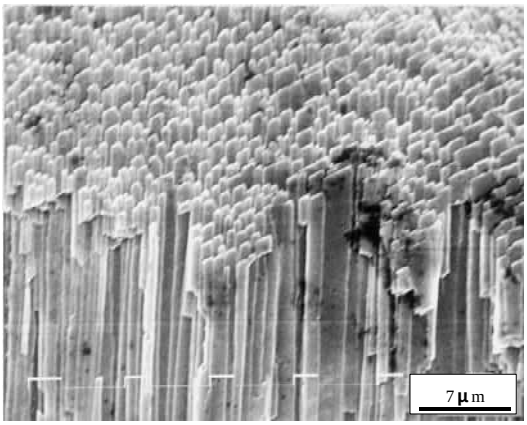


Fig.5. Inner surface and cross-section at the tip of shell.

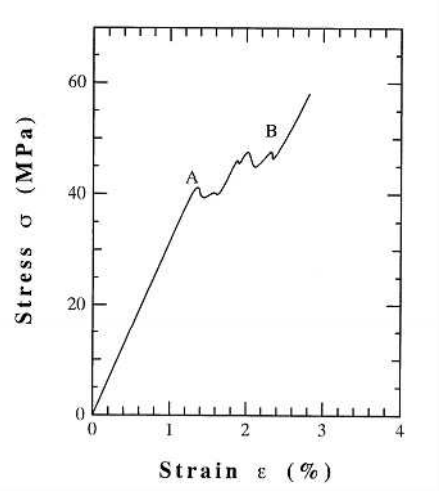


Fig.6. Stress - strain curve of. scallop shell

As for comparison, the inside surface of an abalone shell (*Haliotis*) was examined by electron microscope is shown (Fig. 7). The growing zone of the shell is about 5 mm in width at the tip of the shell, which does not have the luster of a pearl. The conformation of abalone shell crystals is different in its bivalve, accumulating lamellate crystals and showing a pyramidal structure. Abalone shells are strengthened by engaging adjacent board-shaped crystals with each other (Fig. 8).

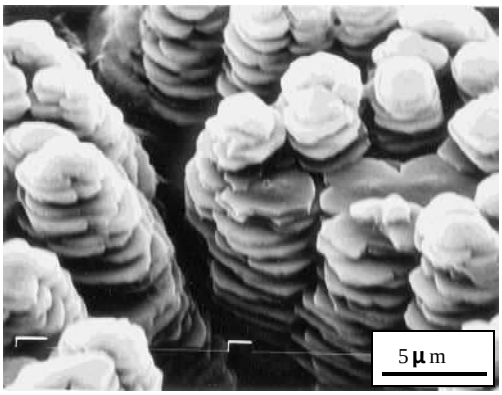


Fig.7. Inner surface of abalone shell at the tip of shell (pyramid structure).

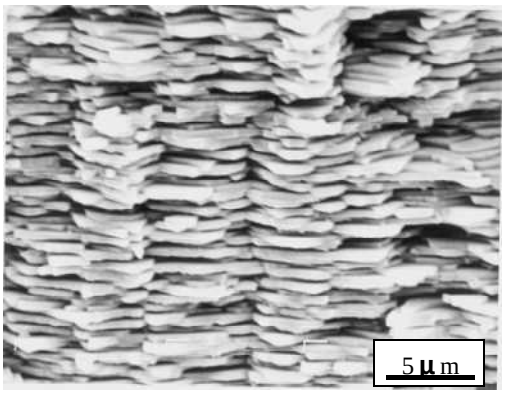


Fig.8. Cross-section of abalone shell.

The shell grows by excreting colloidal mother liquor from the shell to form the mother's body of the shellfish. The mother liquid is a glycoprotein complex, and calcium carbonate is deposited from both Ca^{++} taken from seawater and carbonate from the carbon dioxide yielded by respiration. Fig. 7 is a photograph of the inside surface of an abalone shell. The structure of the abalone shell differs from that of the bivalve, and has pyramidal, superposed, lamellate crystals. The tip of the pyramidal crystal is small, showing that the shell is in the process of growing.

4. The functions of the scallop shell ceramics

4.1 Antimicrobial function

Although scallop shells depurate the polluted effluent of waterways and are effective insect repellents, shell material crushed to about 200 μm and heated for 3h at 1050 ℃ under special conditions has the various functions described below.

The size of the particles of this material observed under an electron microscope is less than 10 μm (Fig. 9). X-ray analysis reveals these particles to be a mixture of calcium carbonate, calcium oxide and calcium hydroxide, which dissolve in water into about 0.1 wt%. The pH value of this solution was about 12.5.

Table 1 Chemical components of scallop shell ceramics (wt%)

Sample	C	O	Na	Al	Si	P	S	Cl	K	Ca	Mn	Fe	Zn	Sr	Mg
SSC	23.0	39.0	<0.1	0.3	0.9	0.1	0.1	1.0	<0.1	36.0	<0.1	<0.1	<0.1	0.1	0.1

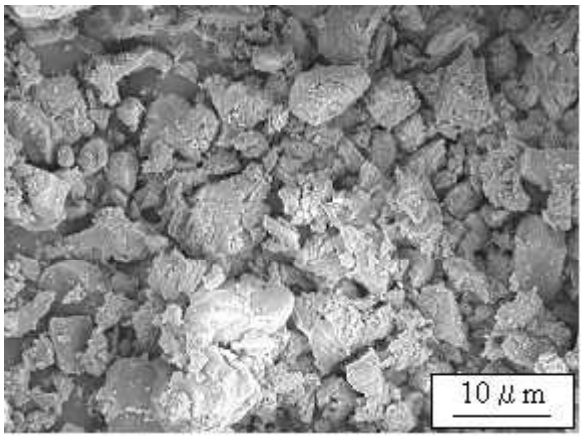


Fig.9. Photograph of scallop shell ceramics.

4.1.1 Antibacterial examination against *Escherichia coli* and *Staphylococcus aureus*

Coli bacillus (*Escherichia coli*) and *Staphylococcus aureus* were cultured at 30 ℃ in an LB broth composed of 1.0% polypepton (Wako Pure Chemicals Ind. Ltd., Osaka, Japan), 0.5% yeast extract, 0.5% NaCl and 0.1% glucose (pH 7.0 to 7.2). One part of the overnight culture of *E. coli* or *S. aureus* culture was added to 9 parts of the SSC solution or a physiological saline as a control, and incubated at 37 ℃ to determine the antibacterial activity of SSC. The pH value of the SSC solution was 12.7. After incubation, the mixtures were diluted into a physiological saline, spread onto an LB agar plate, and cultivated for 1 day at 37 ℃. The viability was estimated by counting the number of colonies formed after incubation.

Although in the presence of SSC the viability of *E. coli* decreases to less than 10^{-4} % after incubation for 1 h, the antibacterial activity of SSC was extremely potent, and the viability of *E. coli* and *S. aureus* by mixing cells with SSC immediately decreased to 35 and

52% of the control, and to 0.4 and 0.5% after 1 min, respectively (Table 2 and Fig. 10). Even though the SSC solution was strongly alkaline (pH 12.4), the viability of *E. coli* treated for 36 h with the SSC solution neutralized with hydrochloric acid was 5% [4].

Table 2 The viability of *Escherichia coli* and *Staphylococcus aureus* cells

Strains	0 min	1 min	5 min	10 min
Escherichia coli	36	0.4	$<10^{-3}$	$<10^{-4}$
Staphylococcus aureus	62	0.6	$<10^{-4}$	$<10^{-4}$

Viability (%) against a control

(a) Colony formation in the absence of SSC. (b) Colony formation in the presence of SSC.

Fig .10. Effect of scallop shell ceramics on the viability of *E. coli* cells after incubation for 5 min.

4.1.2 Antibacterial examination against *Salmonella choleraesuis*

The antibacterial activity of SSC against *S. choleraesuis* was also examined as for *E. coli* (Table 3 and Fig. 11)[5]. The SSC solution showed a strong antibacterial effect, as well as the results obtained from *E. coli*.

Table 3 The viability of *Salmonella choleraesuis* cells

Additive	0min	1min	5min	10min
Physiological saline	100	-	-	-
SSC Solution	22	$<10^{-2}$	$<10^{-4}$	$<10^{-4}$

Viability (%) against a control, - : Not determined.

(a) Colony formation in the absence of SSC.

(b) Colony formation in the presence of SSC.

Fig. 11. Effect of scallop shell ceramics on the viability of *Salmonella choleraesuis* cells after incubation for 5 min.

4.1.3 Antibacterial examination against cariogenic streptpcoccus, *Streptococcus mutans*

S. mutans, one of pathogens of a dental caries, was cultured in a medium composed of 0.5% polypepton, 0.5% yeast extract, 0.5% glucose, and 0.1% $MgSO_4 \cdot 7H_2O$ (pH 6.6-6.8) at 37 ℃ under semi-anaerobic conditions. After 2 to 3 days of cultivation, 1 part of the culture was mixed with 9 parts of the SSC solution, and the mixture was incubated at 37 ℃. After 1 h, a portion of aliquot was added to the same medium, and incubated at 37 ℃ for 1 day. Essentially, no growth of the culture was observed by monitoring an optical density at 660 nm.

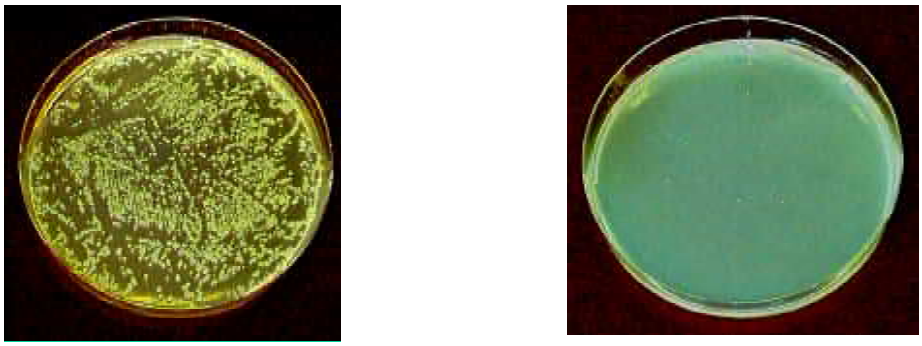
4.1.4 Antibacterial examination against MRSA

MRSA (Methicillin Resistant *Staphylococcus aureus*) is a serious clinical problem. We also examined the antibacterial activity of SSC against MRSA. Two strains of MRSA, No. 60905 and No. 951121, which were kindly provided by Prof. Masatoshi Noda, Department of Molecular Infectiology, Graduate School of Medicine, Chiba University, Japan, were used as test organisms of MRSA. MRSA cultures and a methicillin-sensitive strain of *S. aureus*s were treated with the SSC solution, as for *E. coli*, and antibacterial activity was examined (Fig. 12 and Table 4). The viabilities of MRSA treated with SSC were 4.3, 0.02 and 0.0004% at incubation times of 5, 15 and 30 min, respectively. A sodium hydroxide solution adjusted to the same pH value of 12.7 as the SSC solution decreased the viability to 0.006% at 30 min of incubation, suggesting the antibacterial activity of SSC.

Table 4 The viability of MRSA (No.60905) cells

Additive	0 min	5 min	15 min	30 min
Physiological saline	100	–	–	0.882
SSC Solution(pH12.7)	100	4.3	0.02	0.0004
NaOH Solution(pH12.7)	100	–	*	0.006

*: Uncountable number of colonies were detected, - : Not determined.
Viability (%) against a control



(a) Colony formation in the absence of SSC.

(b) Colony formation in the presence of SSC.

Fig. 12. Effect of scallop shell ceramics on the viability of MRSA(No.60905) cells after incubation for 15 min.

4.1.5 The antifungal examination of SSC against dermatophytes

The antifungal activity of SSC against 2 species of pathogenic dermatophytes of athlete's foot, *Arthroderma vanbreuseghemii* and *Arthroderma benhamiae,* and the yeast *Saccharomyces cerevisiae* was examined. These fungi were cultivated for 1 to 2 days in a malt-extract medium (pH 7.0) composed of 15% malt extract , 0.5% yeast extract and 0.5% NaCl at 30 ℃. These cells were streaked onto the malt extract media with or without SSC and incubated for 2 days (Fig. 13 (a), (b)). Colonies of 2 strains of *Arthroderma* could not be detected in the presence of SSC. On the other hand, yeast colonies were detected even in the presence of SSC. These results suggest that SSC has a potent antifungal effect against dermatophytes, but not against yeast.

(a) SSC absence.

(b) SSC presence.

Fig.13. Effect of scallop shell ceramics on the viability of *Arthroderma vanbreuseghemii* ①, *Arthroderma benhamiae* ② and *Saccharomyces cerevisiae* ③.

SSC is an active antibacterial agent, and it was expected that SSC could be used for detergents for vegetables, eggs, kitchenware, exhaust fans, house furnishings, etc. A

detergent, Chaffclean™ was developed and put to practical use in 2001. Chaffclean™ is a 100% natural material, with scallop shell ceramic as its main ingredient. Because no heavy metals are detected in scallop shell (Table 1) and certain food manufactures in Japan use it as a calcium additive, Chaffclean™ is a safe washing detergent even if ingested. Furthermore, SSC is a deodorant, and prevents damage by chemical materials such as formaldehyde.

4.2 Function for the reduction and decomposition of chemical materials

4.2.1 Effect of SSC on formaldehyde reduction in the atmosphere

We developed Chaffwall™ in 1996 as a wall material. It is composed of 83% scallop shell powder, 3% SSC, and 14% cellulose acetate as a binder. The effect of this wall material on the decrease in formaldehyde in the atmosphere was examined in a grove box (capacity: 140*l*). The concentrations of formaldehyde were monitored using Formtector™ (New Cosmos Electric Co., LTD., Tokyo, Japan) and a gas detector pipe (Gastec Co., Ltd., Tokyo, Japan). The powder of unbaked shells, SSC or Chaffwall™ was applied to both sides of 5 sheets of glass plate (420 mm x 300 mm), which was wrapped in a vinyl bag and settled in the grove box. With the unbaked powder, 14% cellulose acetate was used as an agglutinant. The initial concentration of formaldehyde in the grove box was adjusted to 1 ppm, and the glass plates were exposed to formaldehyde vapor. The formaldehyde concentration in the grove box was measured every 1 min for 10 to 30 min. As is shown in Fig. 14 and Fig. 15, both SSC and Chaffwall™ effectively reduced formaldehyde within 10 min[6]. The plates to which Chaffwall™ was applied were also effective even when the plates were repeatedly exposed 3 times to a high concentration (40 ppm) of formaldehyde (Fig. 16) suggesting the possibility of resolving formaldehyde with Chaffwall™. The durability of this wall material to reduce formaldehyde is now under investigation.

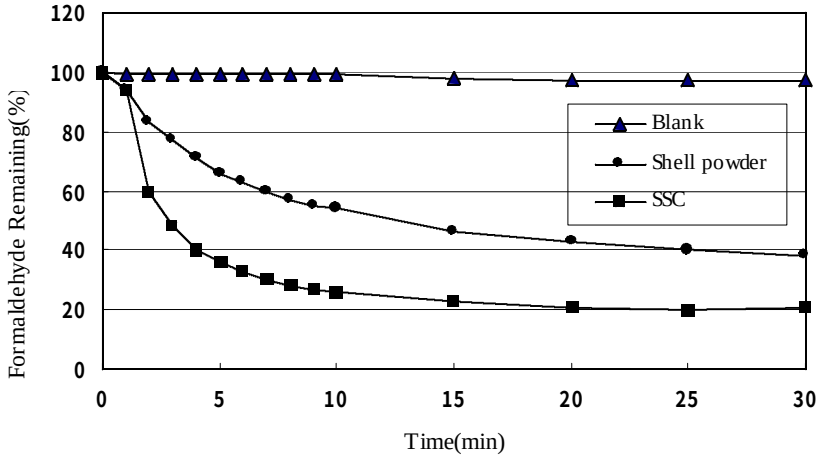


Fig. 14. Reducing effect of the shell ceramics and the shell powder on the concentration of formaldehyde in the atmosphere.

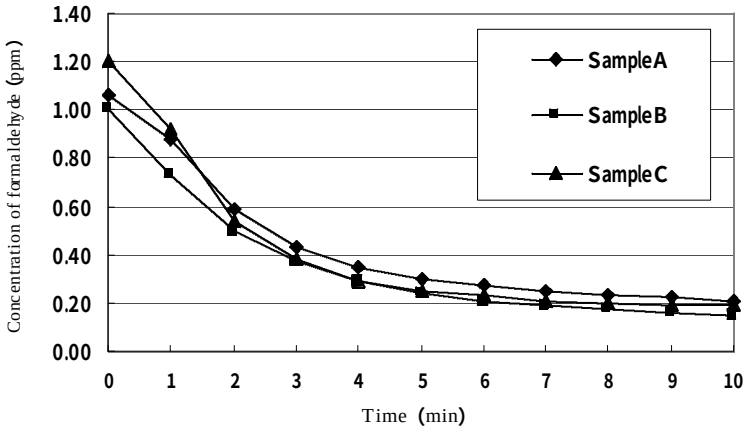


Fig. 15. Reducing effect of Chaffwall™ on the concentration of formaldehyde in the atmosphere.

It was confirmed that Chaffwall™ is effective in reducing formaldehyde, and a novel technique was developed, which produced Japanese paper containing about 10% SSC. In addition, it was expected that these paper products counter sick building syndrome. Therefore, we developed the practical new products such as paper products, *tatami*-matting, *shoji*-paper (sliding screen paper), *fusuma*-paper, wallpaper, etc. These products effectively reduce formaldehyde in the atmosphere, and the results of an experiment using *shoji*-paper are shown in Fig. 17. The figure shows the initial concentrations of 1 ppm and 2 ppm . The effect of shoji-paper on formaldehyde reduction is smaller than that of wall material because of the smaller amount of SSC.

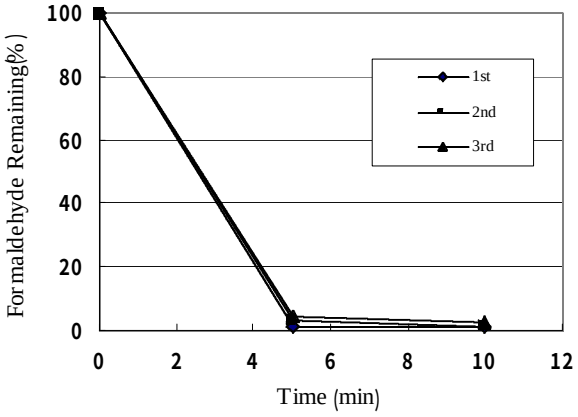


Fig. 16. Cyclic reducing effect of Chaffwall™ on the concentration of formaldehyde in the atmosphere.

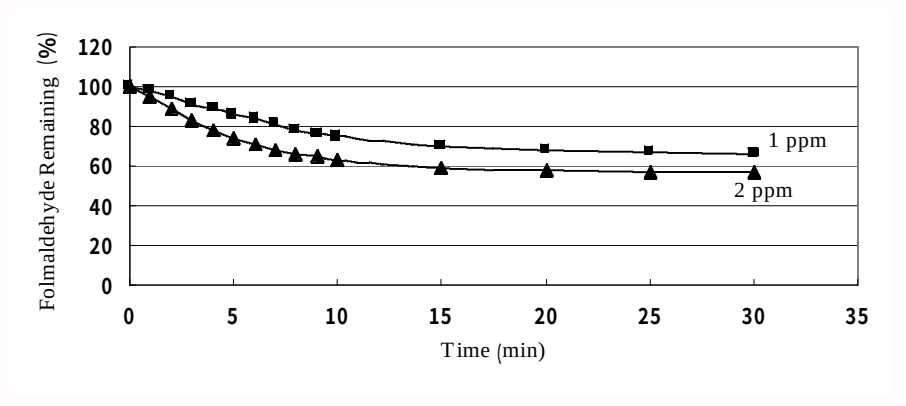


Fig. 17. Reducing effect of sliding screen paper on the concentration of formaldehyde in the atmosphere.

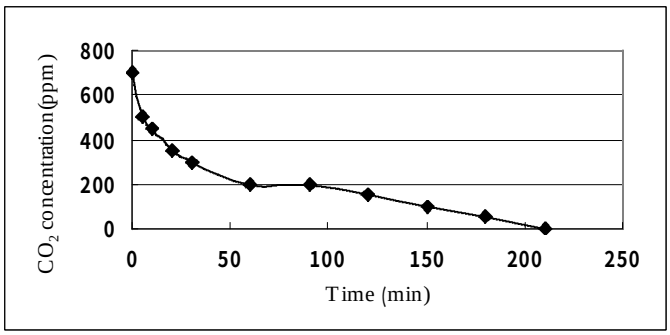


Fig. 18. Reducing effect of Chaffwall™ on the concentration of carbon dioxide in the atmosphere.

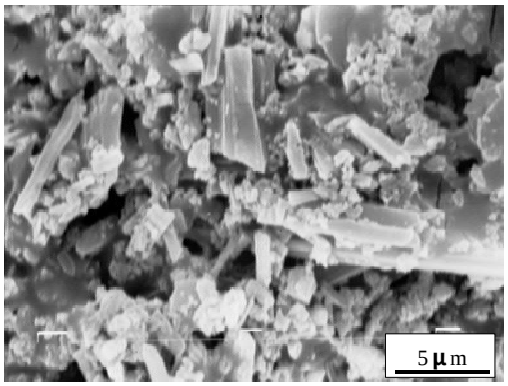


Fig. 19. Photograph of surface of Chaffwall™ (spray finishing).

It was revealed that SSC also reduces carbon dioxide in the atmosphere. Five sheets of test settlement to which SSC was attached were placed in the grove box, and reduction in carbon dioxide concentration was monitored as a function of time (Fig. 18). Carbon dioxide concentration in the grove box decreased from 700 ppm to practically zero after 210 min. This indicates that SSC reduces carbon dioxide in the environment, and experiments on this activity are now in progress.

It is assumed that calcium carbonate, which is the main ingredient of SSC, calcium oxide and / or calcium hydroxide have a catalytic effect on the decrease in formaldehyde in reforming it into carbon dioxide and hydrogen gas. Formaldehyde is an intermediate in certain chemical reactions in the field of catalytic chemistry, and is easily decomposed through the Langmuir-Hinshelwood mechanism. In fact, we detected carbon dioxide and hydrogen as reaction products (data not shown). Therefore, the effect of formaldehyde reduction using Chaffwall™ (Fig. 19) may be reproducible. In addition, a reduction in VOC (volatile organic compounds) was also observed.

4.2.2 Dissolving polyurethane sponge in the SSC solution

Polyurethane sponges (70 mm x 40 mm x 10 mm) available on the market were put into the SSC solution, and incubated at 25 ℃. After about 20h of incubation, the nylon part and the urethane part exfoliated, and a section of the urethane part began to solubilize and then precipitated (Fig. 20(a)). Furthermore, the urethane sponge continued to dissolve after 20 days of incubation (Fig. 20(c)); after 27 days, the sponge almost completely dissolved, resulting in the precipitation of only the red pigment part (Fig. 20(d)).

Although the study on dissolving polyurethane sponge in SSC solution is now in progress, the plastic waste may be treatable by SSC.

(a) 20 h (b) 63 h (c) 20 days (d) 27 days

Fig. 20. Dissolving polyurethane sponge in the SSC solution.

4.3 Products that apply the functions of SSC were applied to.

Collaborative research between academia and industry on useful application of the scallop shell has resulted in the development of a number of products that apply the functions of the shell as follows.

The wall material, Chaffwall™, with scallop shell as its main component, has antibacterial and deodorant characteristics, besides a reducing action on several chemical substances. This wall material is a mixture of 83% unbaked shell, 3% baked shell (shell ceramics) and 14% cellulose acetate. Chaffwall™ is made of 100% natural material, and does not release any chemical toxic substances. This wall material can be used by dissolving it in water, and is applied with a roller brush or a spray gun. Fig. 14 shows the surface structure of the wall material that was applied with a spray gun. Because this wall material

can also directly applied to a vinyl cloth, it is suitable for house renovation. Moreover, vinyl cloth distributed with Chaffwall™ does not generate dioxin when vinyl cloth is incinerated, because more than 90% of the dechlorination is suppressed (data not shown). Moreover, this wall material is antibacterial and a deodorant, and is effective in freshening rooms. It is also useful in preventing sick building syndrome, anaphylaxis due to chemical substances, and allergies to house dust, such as fungi, ticks, bacteria, etc. Therefore, this material should attract attention as a novel wall and paint material instead of new synthetic building materials. In this study, SSC was an active antibacterial agent, and it is expected that SSC can be used in detergents for vegetables, eggs, kitchenware, exhaust fans, house furnishings, etc. Chaffclean™ is a 100% natural material made from scallop shell ceramic as its main ingredient. As no heavy metals have been detected (Table 1) in the scallop shell, and it is used as a calcium additive in certain foods in Japan, Chaffclean™ is a safe washing detergent even if ingested. Furthermore, SSC is a deodorant, and prevents damage by chemical materials such as formaldehyde.

Therefore, it is anticipated that products made from shell ceramics will have many functions and SSC can be used in many industrial fields.

5. Summary

Several years ago, we realized that a large amount of scallop shells accumulated as waste, and considered methods of practically using these shells as a resource. We then realized that there were many social problems to be instantly resolved such as waste disposal, sick building syndrome, hospital infection and food poisoning. These social problems indicate that people require many fundamental conveniences and comforts, which are spoiled by various deleterious materials. It is essential to consider the environment, and human health and living creature's safety, as well as issues of economy and service when manufacturing new materials. Based on these concepts, we investigated making natural materials and developing novel products.

SSC has an insect repellent effect as well as its many other functions. It is rare for one material alone to have many functions. We assume that this is a special characteristic of biomaterial. Current research on biomaterial functions is insufficient, and it is necessary to elucidate the available functions. Our investigations concern the development of more reliable and more functional wall materials and paint, unknown functions, and their mechanisms. Moreover, studies on technical development for practical application for medicines and cleaning agents based on our research, and the quantification of several functions, are in progress. At present, one of specific products for a practical application is the remedy against an athlete's foot. Clinical experiments of this remedy are already started and it will be commercially manufactured after about 1 year.

Research and development that apply the functions of the scallop shell contribute to people's health and safety, and it may be possible to prevent MRSA infection, from which

one cannot be protected, in hospitals. Furthermore, the waste management problem of about two hundred and ten thousand tons a year in Tohoku and Hokkaido also requires a solution, and the advanced development of use-circulation technology is possible using the waste of unused resources through development of a product.

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