PROPERTIES OF NOVEL ORNAMENTAL MATERIAL BOARDS MADE FROM SILK FIBROIN SHEET

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Introduction

The material used for 'Bekko' art work is the shell of the hawksbill sea turtle, which has been imported from tropical countries for about 400 years.

However, recent enforcement of the Washington treaty has prohibited the importing of turtlesell material, because the hawksbill sea turtle has been recognized as a creature in danger of extinction. We have therefore tried to utilize effectually unused materials (waste) (Mori *et al.*, 1995) and develop new materials as substitutes for the shell of the sea turtle in order to protect both the turtle and the traditional art

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industry. We have previously reported that the properties of silk fibroin are similar to those of turtleshell (Hosokawa *et al.*, 1993), but a hot melt board made from fibroin powder was opaque, and showed weak strength which made it unsatisfactory as a substitute material for 'Bekko' (Hosokawa *et al.*, 1993).

In this study, we try to develop laminated boards obtained by the hot-pressing of about 30–100 layers of silk fibroin sheet, and we discuss the appearance and properties of new materials.

1. Experimental

1.1 Material

The hawksbill sea turtle, *Eretmochelys imbricata*, is usually caught in tropical seas including the Caribbean Sea (Hendrickson *et al.*, 1977). The physical properties of the shell depend on the region where the turtle comes from. In this study, we prepared a sample of the shell of turtle caught in the Caribbean Sea. The silk protein (fibroin) was prepared from silk thread produced by the silkworm, *Bombyx mori*. The silk thread was refined, and dissolved in a hot aqueous solution containing calcium chloride and ethanol. The solution was dialyzed sufficiently to remove the salt and ethanol and the concentration of the fibroin reached ca. 5%. The molecular weight of fibroin obtained was in the range of 50,000 to 100,000. To produce handiwork samples, fibroin solution for making laminated boards was obtained from Kanebo SILK ELEGANCE, LTD (Nagano Pref. Japan).

Preparation of the Turtle Shell Sample: The shell was cut into pieces of 10×20 mm, and reduced to 1 mm thickness with sandpaper. Hot water treatment, in which some pieces were immersed in hot water for 5 min and pressed at about 9.81 MPa for 10 min, was carried out in order to increase the clarity of the shell.

For the SEM observation, the surfaces of turtleshell and laminated boards were polished with a fine sand paper, and etched with a 10% NaOH aq. solution to get the original structure pattern.

Preparation of Laminated Boards: A fibroin sheet of ca. 0.1 mm thickness was formed from a fibroin solution containing 1% glycerol by cast-drying on a large glass dish at 40°C for one day. After drying, the sheet was cut into pieces of 800×900 mm, and washed with water to remove glycerol. The cut pieces (thirty to one hundred) were stacked after immersing in the fibroin solution, then the pile was hot-pressed at 19.6–29.4 MPa at 90°C for 5 min. The laminated boards obtained were dried in a convection oven at 90°C, and kept in the oven at 20°C in 65% relative humidity.

1.2 Measurement of mechanical properties

The hardness of surfaces of turtleshell and

1a; Turtleshell(belly)

1b; Laminated board

Fig. 1 SEM photographs of a cross section of turtle shell and laminated boards made from silk fibroin sheet
1a; Turtleshell (belly) 1b; Laminated board

laminated boards was measured by a micro Vickers hardness tester. Measurement of the three-point-bending strength of turtleshell and the laminated board was conducted on the test pieces (9 mm-clearance, 5 mm-width and 1 mm-thickness) using an AUTOGRAPH AG-100A (Shimadzu Co. Tokyo). Ring folding endurance was tested after soaking the test pieces (20 mm long and 1 mm thick) in hot water at 80°C for 30 min. The degree of water absorption by the air-dried turtleshell and laminated boards was

Table 1 Various properties of laminated fibroin board, hotmelt fibroin board, and turtleshell

	Fibroin		Turtleshell	
	Laminated board	Hotmelt board	Belly-shell	Back-shell
Vickers hardness (kPa)	24	31	27	23
Bending strength (kPa)	15.8	7.1	12.2	18.4
Ring folding endurance	No break	Break	No break	No break
Specific gravity	1.35	1.36	1.30	1.29
Water absorption (% of air dry sample)	33	22	7	5

Fig. 2 Handiwork samples made from laminated boards and turtleshell by "Bekko" art work method
Left; laminated boards; Right; turtleshell

calculated from the weight of water absorbed after soaking in water at 20°C for 24 hrs. The moisture content of the air-dried samples was ca. 10% before the soaking.

2. Results and Discussion

Figures 1a and 1b show SEM photographs of a cross section of turtleshell and laminated boards made from fibroin sheets, respectively. Figure 1a shows that the cross section of turtleshell consists of a multi-layer structure of fiber as described in the previous report (Hosokawa *et al.*, 1993). On the other hand, the hotmelt fibroin-powder boards have no such multi-layer structure, and this should be related to poor mechanical properties as shown in Table 1. However, the pattern of cross section for laminated boards seems to be very similar to that for turtleshell.

The various properties of laminated boards were compared with those of turtleshell (Table 1). The Vickers hardnesses of laminated boards, turtleshell, and hotmelt boards of fibroin powder were almost the same. The maximum bending strength of the laminated boards was also comparable to that of turtleshell. This suggests that the laminated structure of the boards should be important for enhancement of strength. The flexibility of laminated boards under hot and wet conditions also improved in the ring folding endurance test, and was different from the

break case of hotmelt boards. Furthermore, the specific gravity of laminated boards was almost the same as those of turtleshell and hotmelt boards. This result is necessary for an ornamental material to be used as a substitute for turtleshell.

However, the degree of water-absorption by laminated boards was much higher than that by turtleshell. This fact means that boards easily absorb water and become soft when they are soaked in water for a long time. Therefore, we should take care of water on the surface of laminated boards if these materials are used in wet conditions.

An attempt was made to use laminated materials in the 'Bekko' art work method as substitutes for turtleshell. These handiwork samples are shown in Fig. 2. According to trials by 'Bekko' art craftsmen, it was suggested that the laminated board materials might be slightly difficult to work, because these materials were more fragile than turtleshell. On this point, further improvement may be necessary in order to apply these materials widely in the 'Bekko' art industry.

Conclusion

We found for the first time that laminated boards obtained by hot-pressing about 30 – 100 layers of silk fibroin sheet have similar appearance and mechanical properties to the turtleshell used in 'Bekko' art work. However, it is necessary to decrease the degree of water absorption of laminated boards in order for the materials to be used as substitutes for turtleshell.

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