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Modification of Plant Materials by Water Soluble Protein

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For the purpose of chemical modification of wood, hinoki wood was treated with water soluble protein. Dimensional stability and bending properties caused by the treatment were improved. As a result of surface analysis and dyeing behavior, treated wood surfaces were activated.

1. INTRODUCTION

Nowadays, with the increasing concern with the environment, everyone has been paying attention to plant related materials that can be a resource of continuous recycling, especially to high storage capacity wood as well as wood based materials. In order to improve the weak point that wood has a biomaterial, a large number of compounds that use synthetic polymers have been developed. However, while the research to reduce the environmental impact is a very important subject, it has been looking for technologies that proportionate both the reduction of environmental impact and the improvement of wood properties. Therefore, based on examinations that have been done about the efficiency of using water soluble protein (silk fibroin) as a biopolymer and biodegradable polymer, it was made a wood composite with silk fibroin as a chemical quality improving agent of wood. The mechanical properties of the composite were discussed through a test of dimensional stability and bending properties. Besides, the characteristics of the composite surface were investigated by ESCA analysis and dyestuffs adsorption.

2. EXPERIMENT

2.1 Materials

The wood specimens used were sapwood of hinoki (*Chamaecyparis obtusa* Endl., air-dried density : 0.47) which were collected from Tokyo metropolitan. Regarding to the silk fibroin, it was used in the form of powder, commonly employed as an additive of cosmetics and food. The molecular weight was obtained through enzymatic hydrolysis. The powder of nominal molecular weight 3000 (SF3000 for short), and 10000 (SF10000) (both made by Aieskousan Co.,Ltd.) were dissolved in water to get a solution with fixed percentage weight concentration.

2.2 Wood and silk fibroin composite making

The pressure was lowered to get an atmosphere with water saturation, and the samples were submerged in water solutions of silk fibroin with different concentrations. Meanwhile, the pressure was decreased and increased cyclically (around 0.1Pa during 1 hour, and around 0.5MPa during 1 hour) several times. After the samples were impregnated with silk fibroin, they were placed in a room with a controlled temperature of 20℃,

and were kept there during 5 days. Afterwards, they were kiln-dried for 6 hours at 105±5℃.

2.3 Test of dimensional stability

The dimensions of the sample were 20mm (radial direction)×20mm (tangential direction) × 5mm (longitudinal direction). 8 samples were used in each condition of the test. Following the established procedures[1], samples of untreated wood and those of composite were evaluated. Measured was the weight percentual gain (WPG (%)) and the bulking effect (BE(%)). After that, by measuring the dimensional variation from the condition of complete dry up to that of water saturation, it was possible to evaluate the antiswelling efficiency(ASE).

2.4 Bending test

The dimensions of the samples in this test were 100 (longitudinal) × 10 (radial) × 5 (tangential) mm. Five samples were used in each condition of the test. The modulus of elasticity (MOE) was measured through the bending of the samples of untreated wood and those of composite in a Shimazu autograph AG-10T, at crosshead speed of 2.5mm/min and span of 70mm.

2.5 ESCA measurement

The spectrum of C(1s) was measured using a X-ray photoelectron spectroscopy (Shimazu ESCA850) with X-ray source of Mg (output of 6kV-30mA), under vacuum condition of 10^{-6}-10^{-5}Pa. The samples of wood and the composite were prepared as describe before (see item 2.2). Their dimensions were 0.5mm (thickness)× 10mm (diameter), and they had microtome cut finishing.

2.6Measurement of dyestuff adsorption

The samples were prepared as described at item 2.2, using wood meal of hinoki with mesh of 40-60. The samples used in the measurement of acid dyestuff adsorption were put through a buffer dye bath of pH 3.0, in order to remove non cured parts of silk fibroin and acid soluble portion that were included in the wood meal used to prepare the composite. Regarding the samples used in the measurement of direct dyestuffs adsorption, the samples were washed by pure water to remove the non cured portions.

2.6.1 Measurement of acid dyestuff adsorption

It was used Acid Orange 7 (C.I.No.15510, Wako Chemicals Ltd.) as the acid dyestuff. 1.0g of untreated wood and composite meal were added to 50ml of Clark-lub's buffer solution with pH3.0 (dye concentration of 5.0×10^{-4} mol/l) and churned in a water tank for 20 hours at a controlled temperature of 25 ± 1 ℃. After this, the mixture was centrifugated. Finally, the remaining solution was analyzed through spectral diffraction to verify the dye concentration variation and determine the dyestuff adsorption.

2.6.2 Measurement of direct dyestuff adsorpt ion

Congo Red (C.I.No.22120, Wako Chemicals Ltd.) was used as the direct dyestuff. 1.0g of untreated wood and composite meal were added to 45ml of a neutral dyestuff solution of concentration 5.0×10^{-4} mol/l and churned in a water tank for 20 hours at a controlled temperature of 25 ± 1 ℃. After this, the mixture was centrifugated. Then, a determined amount of Clark-lub's buffer solution was added to the centrifugated solution in order to get a solution of pH 10.0.

Finally, the solution was analyzed through spectral difracton to verify the concentration variation of dyestuff and determine the dyestuff adsorption.

3. RESULTS AND DISCUSSION

3.1 Dimensional stability of the composite

The wood changes its dimensions in order to correspond to environmental variations of temperature and moisture. Thus, in case of water adsorption, the control effect of dimensional variation to each kind of treatment is showed by ASE. The table 1 shows the WPG, ASE and BE of the composite. Regarding to the SF3000 composite, as the concentration increases, WPG and ASE increases too. On the other hand, in case of the SF10000, WPG increases similarly, whereas ASE increases just a little. A possible explanation for this is that SF3000 has a molecular weight distribution which allows small particles to permeate into the swelling wood cell walls and to cure inside them. Regarding to the SF10000, the permeation into the wood cell walls is impossible, and so, the deposition and cure occurs on the cell lumen. In terms of BE, depending on the composite, there is permeation and cure of matrix into cell walls.

Table 1. The effect of silk fibroin treatment on WPG, BE, and ASE.

Treatments	WPG (%)	BE (%)	ASE (%)
SF10000 10%	10.5	-0.28	1.0
SF3000 10%	11.0	0.47	13.3
SF3000 15%	17.5	0.68	17.4
SF3000 20%	23.3	0.93	19.1

It causes an increasing of the wood dimensions. To SF10000 the variation of BE is negative, whereas the SF3000 shows a positive increasing. This results support the above- mentioned discussion.

3.2 Bendi ng properties of the composite

The figure 1 shows the variation of MOE to treatment concentration of silk fibroin. As soon as concentration increases, MOE improves. In case of SF3000, to a concentration of 20 wt%, the MOE increases 24%. These results also support the explanation given at the item 3.1 to the different behavior of the SF3000 and SF10000 in terms of dimensional change.

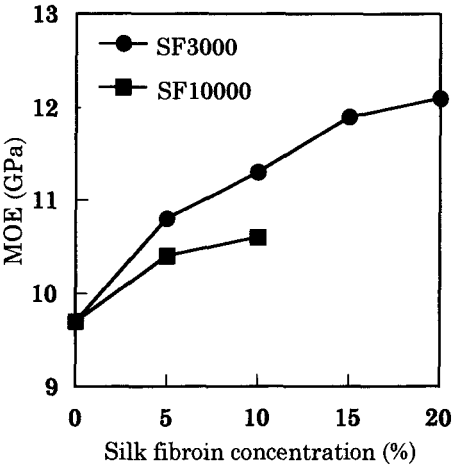

Fig.1. Modulus of elasticity (MOE) resulting from increasing concentrations of silk fibroin.

3.3 Analysis of ESCA

The figure 2 shows respectively the ESCA spectrum of C(1s) of untreated wood and silk fibroin. Generally, when alcohol-benzen extraction treatment is done, the surface of cellulose and hemicellulose is exposed. According to figure 3, around 285eV there are few chemical bonds of C-C and C-H. At 287eV the amount of C-O increases at the maximum[2]. In the figure 2 (silk fibroin composite 20%), at

values around 289eV there are traces of carbonyl and carboxyl groups whose peak is higher than the untreated wood. It is thought that this result is due to peptide bonds included in the silk fibroin.

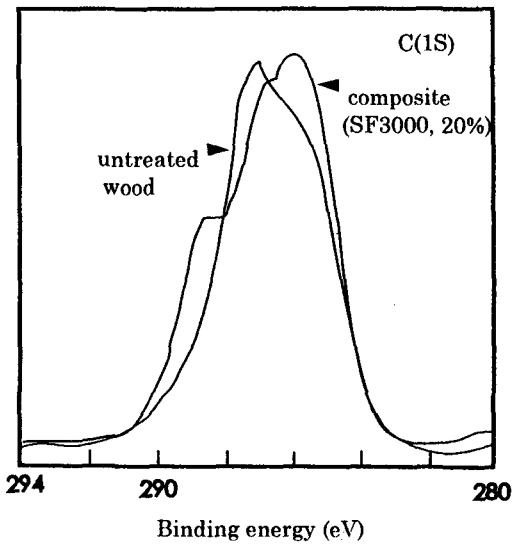

Fig.2. ESCA C(1s) spectrum of untreated wood and composite surface.

3.4 Amount of dyestuff adsorption

The figure 3 shows the relationship between the amount of dyestuff adsorption and the composite made from hinoki wood meal. Both the acid dyeing and direct dyeing increases suddenly to low concentration treatment of silk fibroin. It is thought that it happens because acid and direct dyeing have affinity with silk protein. Still, based on the results got with ESCA measurement at item 3.3, depending on the treatment there is a formation of carbonyl and carboxyl active functional groups on the surface of the composite that increases the dyestuff adsorption.

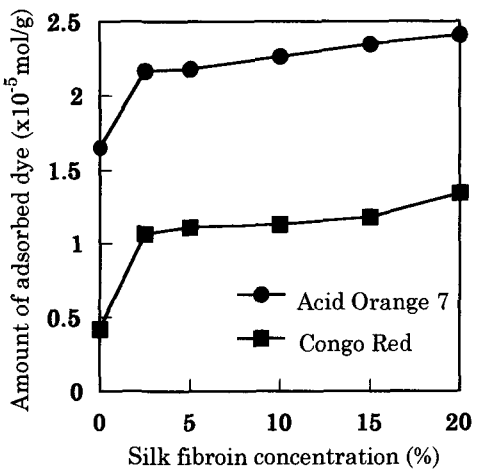

Fig.3. Influence of silk fibroin concentrations on dyeing behavior.

4. CONCLUSION

Through this experiment it was possible to develop a new composite of wood and silk fibroin that has a environmental low impact. The mechanical properties and surface characteristics of this new composite are as follows:

1)The anti-swelling efficiency and bulking effect depend on the molecular weight of silk fibroin. In case of low molecular weight silk fibroins, there is permeation of small particles into the wood cell walls.

2)There is a improvement in MOE to this composite.

3)Through ESCA analysis it was verified that because of the silk fibroin there is an increase of active function groups on the surface of the composite. It originates a surface activation that leads to an increase of dyestuff adsorption.

REFERENCES

1. Norimoto, M.: Mokuzai Gakkaishi, 37, 227 -233 (1991).

2. Kiguchi, M.: ibid.,36, 651-658 (1990).