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Development of new natural polymer-based wood adhesives III: effects of glucose addition on properties of chitosan

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Abstract The effects of a Maillard reaction between glucose and chitosan on the resultant chitosan films and the bonding properties of chitosans with different molecular weights were investigated. In film preparation, chitosan and glucose were dissolved in 1% acetic acid and dried in a Petri dish at 50°C. The bonding properties of the Maillard-reacted chitosan in three-ply plywood were evaluated by a tensile shear test. The weight, color, free amino groups, insoluble fraction, and thermal properties of the film changed significantly as the amount of added glucose increased. However, few differences in these properties due to the use of chitosan of different molecular weights were observed. The effect of glucose addition on the tensile strength of the film differed for chitosans of different molecular weights. Improvement of the strength by 10 wt% glucose addition was observed in low-molecular-weight chitosans. The dry- and wet-bond strengths were significantly enhanced with increasing glucose addition for low-molecular-weight chitosans. In addition, good bond strength was maintained even in 1% acetic acid solution. It was thus clarified that the bonding properties of low-molecular-weight chitosan were improved markedly by the environmentally safe method of glucose addition.

Key words Chitosan · Glucose · Bond strength · Natural adhesive · Maillard reaction

Introduction

Large amounts of synthetic resin adhesives derived from fossil resources are widely used in today's wood products industry. Synthetic resin adhesives have excellent bonding

properties such as high dry-bond strength and good water resistance, but most of them contain chemical agents that cause health disorders and environmental problems. In addition, the utilization of these resins will be inhibited in the future with the increasing exhaustion of fossil resources. Natural adhesives derived from nonfossil resources have been considered as alternatives to synthetic resin adhesives to ease the above problems. However, the use of conventional natural adhesives is currently limited due to issues of performance and economy. Poor bonding properties in particular are thought to be one of the most serious disadvantages. Thus, the development of natural, renewable-source adhesives having good bonding properties is an important focus of research.

Chitosan is a deacetylated product of chitin, which is extracted from crab and shrimp shells. Recently, chitosan has been considered a promising biomass resource, and it has been studied extensively with regard to its industrial applications.^{1,2} In previous articles,^{3,4} we investigated the utilization of chitosan as a natural wood adhesive. When used as an adhesive, chitosan dissolved or swelled in 1% acetic acid solution. It was clarified that chitosan had good dry-bond strength and good water resistance. However, the bond strength in 1% acetic acid was lost due to the dissolution of chitosan. Generally, it is well known that chitosan is insoluble in water but soluble in dilute acid. This property results in poor adhesiveness. Therefore, it would be ideal to adapt chitosan to be insoluble in dilute acid after the gluing process. Chemical modification methods that use chemical agents derived from fossil resources such as acid anhydride and benzene compounds are usually adopted to change the properties of polymers. Much research has been done on the chemical modification of chitosan using such chemical agents.^{5,6} However, it is desirable to change the properties without using such chemical agents in the future.

The Maillard reaction brings about the browning of compounds (by the formation of melanoidins) due to interactions between carbonyl compounds such as reducing sugars and amino compounds such as amines, amino acids, peptides, or proteins (Fig. 1). This reaction occurs during the heating, storage, and processing of foods and influences the

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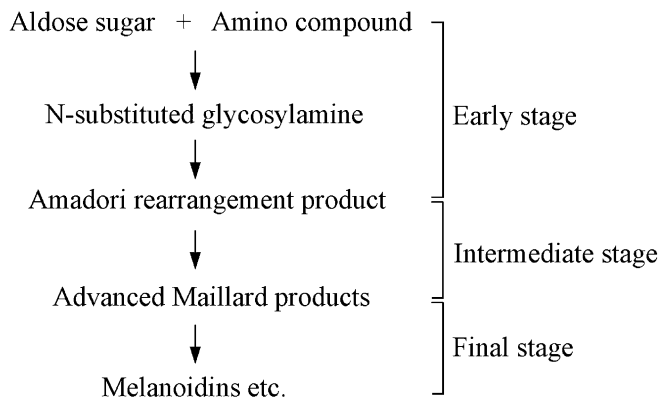


Fig. 1. General process of the Maillard reaction

food quality by affecting factors such as color, flavor, taste, and nutrition.^{7,8} Recently, Maillard reactions between chitosan and various reducing sugars were investigated.^{9,10} It was clarified that the reaction proceeded easily and the reaction product was insoluble in dilute acid. Accordingly, it may be possible to apply the Maillard reaction to improve the bonding properties of chitosan. In this study, effects of the Maillard reaction on the physical and chemical properties of chitosan film were evaluated using chitosan of various molecular weights, and the bonding properties of the resulting chitosan adhesives were clarified.

Experimental

Materials

Four types of refined chitosan powders with different molecular weights (Kimica, Tokyo, Japan) were used without further purification. The chitosans were derived from crab shells (*Chionoecetes japonicus*). The molecular weight and the degrees of deacetylation ranged from 35 000 to 350 000 (viscosity method) and from 75% to 90% (colloid titration method), respectively. The properties of each chitosan are shown in Table 1. D-Glucose was obtained from Sigma-Aldrich Japan (Tokyo, Japan). All materials were vacuum dried at 60°C for 24 h. Acetic acid, N/400 potassium polyvinyl sulfate, and 0.1% toluidine blue indicator solution were purchased from Wako Pure Chemical Industries (Osaka, Japan).

Film preparation

Each chitosan sample (0.50 g) was dissolved in 36 g of 1 wt% acetic acid solution, and glucose was added to the chitosan solution. The weight ratios of chitosan and glucose were adjusted to 10:0, 9:1, 8:2, 5:5, and 3:7. The solutions were stirred for 30 min at room temperature. After removal of air bubbles in vacuo, the solutions were poured into a Petri dish and dried in an oven at 50°C for 48 h. The films obtained were immersed in an ethanol and 4% sodium hydroxide mixture (7:3, w/w) for 1 h to remove residual acetic acid, and washed thoroughly with an ethanol and

Table 1. Properties of chitosans

Type	Molecular weight	Degree of deacetylation (%)
A	35 000	80–90
B	50 000	75–85
C	100 000–200 000	75–85
D	350 000	75–85

distilled water mixture (7:3, w/w) to remove alkali and residual sugar. After the washings showed a neutral pH, the films were dried at ambient temperature for 30 min. Furthermore, the films were put between glass plates, and the glass plates containing the films were vacuum dried at 50°C for 15 h. The dried films thus obtained were stored in a desiccator with silica gel.

Weight increase

The weight increase due to the Maillard reaction was determined according to the following equation:

$$\text{Weight increase (\%)} = (W_{c+g} - W_c) \times 100 / W_c$$

where W_{c+g} is the weight of the chitosan film with added glucose and W_c is the weight of the pure chitosan film. Experiments were performed in triplicate and average values with standard deviations were calculated.

Color measurement

The dried film was placed on white filter papers. The film color was measured using a spectrophotometer (CM-2600d, Konica Minolta, Tokyo, Japan) according to the CIELab color system. The sensor head was 8 mm in diameter and the measurement was performed under a D65 light source and an angle of 10°. Three positions on each film were tested and the average value was used to evaluate the film color. The film thickness of the measurement position was about 0.11 mm. CIELab color parameters (L^* , a^* , b^*) were used to calculate the color change. The color difference (ΔE^*) was calculated using the following formula:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where ΔL^* is the lightness difference and Δa^* and Δb^* are the chroma differences in comparison to pure chitosan film.

Free amino groups and insoluble fraction

The amount of free amino groups in the film was determined by the colloidal titration method. Each film sample (0.20 g) was dissolved in 99.80 g of 5 wt% acetic acid solution for 3 h at 20°C, and the insoluble matter was filtrated by a glass filter. A total of 1.00 g of the filtrate was mixed with 30 ml distilled water. After adding 2 or 3 drops of 0.1% toluidine blue indicator, the filtrate was titrated against N/400 potassium polyvinyl sulfate. The weight of the free amino groups in the solution was obtained, and the relative amount of free amino groups in the film was calculated

Table 2. Formulation of adhesives

Chitosan type	Chitosan (g/m ²)	Glucose (g/m ²)	Glucose content (wt%)	1% acetic acid (g/m ²)	Spread rate (g/m ²)	Viscosity (Pa·s)
A	32.0	0.0	0	218.0	250.0	3.2
	32.0	3.6	10	218.0	253.6	3.1
	32.0	8.0	20	218.0	258.0	3.1
	32.0	32.0	50	218.0	282.0	2.6
	32.0	74.7	70	218.0	324.7	2.4
B	32.0	0.0	0	268.0	300.0	680.1
	32.0	3.6	10	268.0	303.6	631.0
	32.0	8.0	20	268.0	308.0	615.2
	32.0	32.0	50	268.0	332.0	563.0
	32.0	74.7	70	268.0	374.7	516.3
C	32.0	0.0	0	368.0	400.0	855.6
	32.0	3.6	10	368.0	403.6	3803.4
	32.0	8.0	20	368.0	408.0	7115.6
	32.0	32.0	50	368.0	432.0	15235.7
	32.0	74.7	70	368.0	474.7	14674.6
D	32.0	0.0	0	368.0	400.0	1085.4
	32.0	3.6	10	368.0	403.6	2078.8
	32.0	8.0	20	368.0	408.0	3927.3
	32.0	32.0	50	368.0	432.0	5923.5
	32.0	74.7	70	368.0	474.7	10065.5

based on the value of pure chitosan film. Meanwhile, the insoluble fraction was washed with distilled water and vacuum dried at 50°C for 24 h. Experiments were performed in triplicate and average values with standard deviations were calculated.

Water resistance

Each film sample (0.20 g) was stirred for 3 h at 20°C in 99.80 g of distilled water. The insoluble fraction was filtrated by a glass filter and vacuum dried at 50°C for 24 h. Experiments were performed in triplicate, and the weight of insoluble matter was measured.

Thermogravimetric analysis

The films obtained were ground to a powder (<100 mesh) and vacuum dried at 50°C for 24 h. Thermogravimetric analysis (TGA) was carried out using a TGA 2050 (TA Instruments Japan). The weight changes of the samples were scanned from room temperature to 500°C at an increase rate of 10°C/min under nitrogen purging of 70 ml/min.

Tensile test

First, dried films were conditioned at 20°C, RH 60% for more than 1 week. No. 8 dumb-bell test pieces based on JIS K 6251 were punched out by a sample cutter (SDL-100, Dumbbell). A tensile test was performed using a universal testing machine (Instron 4411) at a cross-head speed of 2 mm/min. In total, 10–16 specimens were tested for each condition. Specimens that fractured near the grip were

excluded, and the average of at least 10 specimens was calculated.

Plywood preparation

Sheets of three-ply plywood (size 30 × 30 cm) were prepared using 1.6-mm-thick rotary peeled lauan (*Shorea* sp.) veneers. The average moisture content of the veneers was about 7.7%. Glucose was dissolved in a 1 wt% acetic acid solution and then chitosan was added to the solution. The detailed formulations are shown in Table 2. Based on the results obtained in previous studies,^{3,4} the solid-based spread rate of chitosan per one glue line was adjusted to 32 g/m². The solution was applied to the veneer using a rubber roller. The assembled three-ply veneers were hot-pressed at 130°C under a press pressure of 1 MPa for 15 min. To prevent blistering, degassing was conducted after a hot-pressing time of 5 min. All fabricated plywood sheets were conditioned at 20°C and 60% relative humidity for 1 week.

Bond strength measurement

The conditioned plywood was cut into standard tensile shear test specimens following Japanese Industrial Standard (JIS) K6851. The dry-bond strengths of the specimens were measured as a normal test. The warm water immersion test (water immersion at 60°C for 3 h, cooling in water, and testing in the wet condition) was performed. Resistance to dilute acetic acid was also measured. Specimens were immersed in 1 wt% acetic acid solution at 20°C for 24 h and then tested while wet. The tensile shear test was carried out at a crosshead speed of 2 mm/min. Fourteen or sixteen test specimens were used for each condition. The average value and standard deviation of the bond strength and the average wood failure were calculated for each condition.

Results and discussion

Degree of the Maillard reaction

Figure 2 shows the weight increase of each chitosan film to which glucose was added. Regardless of the type of chitosan, the weight increased similarly up to 50 wt% addition. In the case of 70 wt% addition, the average weight increase ranged from 150% to 200%. It was observed that glucose was remarkably well incorporated into the chitosan as the amount of added glucose increased. Assuming that glucose is incorporated into chitosan completely for the 10, 20, 50, and 70 wt% additions, the weight increases are 11.2%, 25.0%, 100.0%, and 233.2%, respectively. It is known that the reactivity of amino groups with monosaccharide is greatly affected by the reaction conditions. According to fundamental research on the Maillard reaction, more than 2 mol of monosaccharide is incorporated per mole of amino group.^{11–13} In addition, Tanaka et al. reported on the reactivity of chitosan with glucose in solution.¹⁴ They confirmed that the greater part of glucose was consumed with a chitosan/glucose weight ratio of 1/1. In this study, marked incorporation of glucose into chitosan was observed, even with 70 wt% addition of glucose.

Figure 3 shows the color difference ΔE^* of each chitosan film with added glucose. The value increased drastically up to 20 wt% addition and then maintained an almost constant value, irrespective of the type of chitosan used. Generally, it is well known that the Maillard reaction consists of three stages (Fig. 1). The early stage of the reaction involves condensation between carbonyl groups and amino groups. The glucose brings about a Schiff base and Amadori rearrangement, followed by production of the Amadori product. The products obtained in this stage are colorless.¹⁵ The intermediate stage occurs with the degradation of the Amadori product following complex pathways to give diverse compounds containing furfural derivatives. In the final stage,

dark brown polymeric compounds referred to as melanoidins are formed. The increase in coloring implies that the reaction is proceeding. In fact, the chitosan films with added glucose showed a consistent dark brown color at the higher amounts of glucose addition. This meant that the reaction occurred more extensively at glucose amounts of 20 wt% and more in this study.

Because amino groups were consumed during the Maillard reaction, the relative amount of free amino groups was observed in each film. The results are shown in Fig. 4. In type A chitosan, the free amino groups decreased rapidly with increasing glucose addition. When more than 20 wt% glucose was added, the value was less than 15%. This indicated that almost all amino groups in the film were consumed by the reaction. The rapid decrease in the number of free amino groups with glucose addition was also observed in films of other types of chitosan. As a whole, the behavior of the decrease correlated with the behavior of ΔE^* in

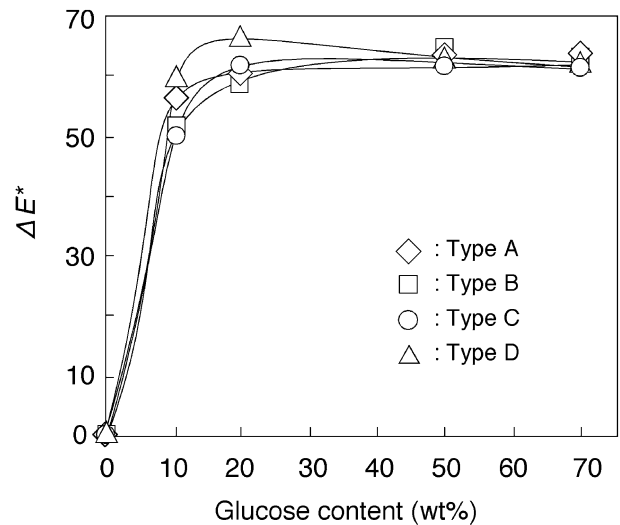


Fig. 3. Color difference (ΔE^*) of the chitosan films with added glucose

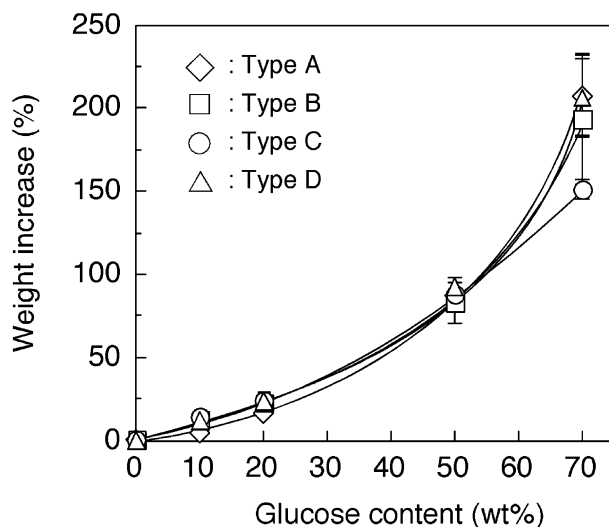


Fig. 2. Weight increase of the chitosan films with added glucose

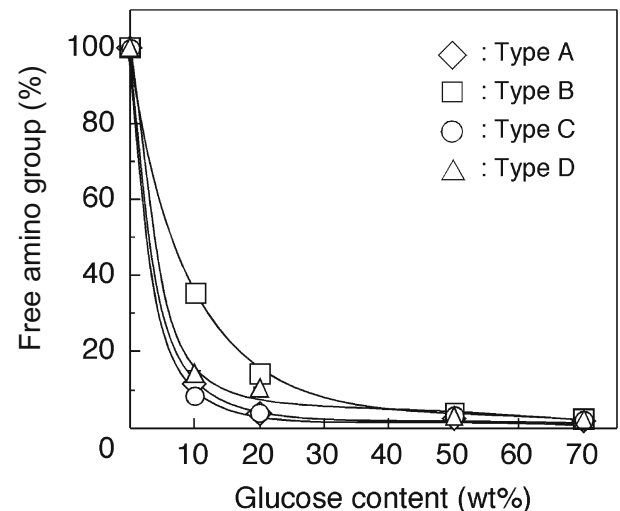


Fig. 4. Free amino groups of chitosan films with added glucose

Fig. 3. Kim and Lee observed the reaction between amino acids with different peptide chain lengths and glucose.¹⁶ They clarified that the consumption degree of glucose in glucose-diglycine and glucose-triglycine model systems was the same, indicating that the degree of glucose consumption did not necessarily correlate to the peptide chain lengths. They attributed this to the complicated nature of the reaction. In our study, hardly any effect of the molecular weight of chitosan on the degree of the Maillard reaction was observed.

Film characterization

Figure 5 shows the insoluble fraction of each chitosan film in 5 wt% acetic acid solution. The films without added glucose (0 wt%) were almost soluble in the solution, irrespective of the type of chitosan used. This is due to the formation of a salt. As a whole, the insoluble fraction increased rapidly and then decreased as the amount of added glucose increased. The maximum average values obtained for chitosan types A–D were 96.8%, 89.2%, 92.6%, and 96.5%, respectively. It was demonstrated that chitosan markedly changed to insoluble matter by 10 or 20 wt% addition of glucose, regardless of the type of chitosan. The insoluble fraction decreased with further addition of glucose. In the case of 70 wt% addition, the values of chitosan types A–D were 76.6%, 69.9%, 81.9%, and 88.1%, respectively. It was observed that the degree of decrease was lower in the higher-molecular-weight chitosans C and D. This seemed to be due to differences in the final reaction products depending on the molecular weight of chitosan. In addition to the solubility in acetic acid solution, the solubility in water was investigated. The results are shown in Fig. 6. The insoluble fraction for pure chitosan films (0 wt%) was about 90%. This is due to the insolubility of pure chitosan in water. The percentage of insoluble matter remained at about 90% up to 20 wt% addition of glucose, but decreased stepwise for

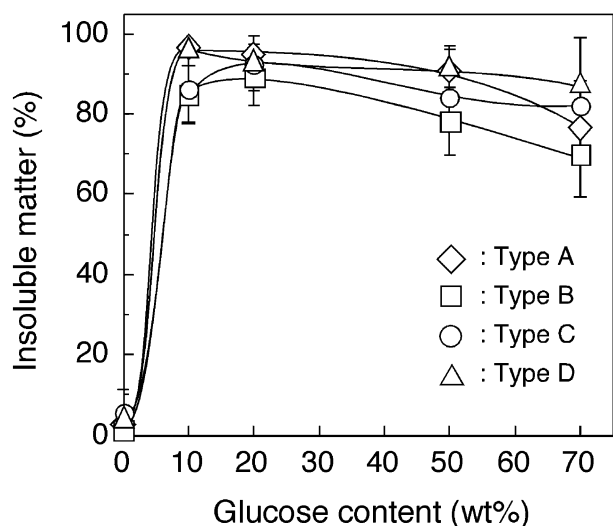


Fig. 5. Fraction of insoluble matter of the chitosan films with added glucose in 5% acetic acid

50 and 70 wt% additions. Similar behaviors were observed for all types of chitosan, irrespective of the molecular weight. In the case of 70 wt% glucose addition, the insoluble fractions for chitosans A–D were 72.3%, 70.7%, 73.6%, and 73.6%, respectively. This indicated that water-soluble substances were formed by relatively large additions of glucose. In this study, the Maillard reaction proceeded under acidic conditions due to the use of 1% acetic acid. Various water-soluble compounds such as osone, furfurals, carbonyl compounds, and pyrrolidine are formed as the reaction progresses.^{15,17} Therefore, the insoluble fraction would decrease as the amount of added glucose increases. Considering the results of Figs. 5 and 6, it was clarified that glucose addition of 10–20 wt% was effective in enhancing both the dilute acid and water resistances of chitosan.

Figure 7 shows TG and derivative TG (DTG) curves of types A and D chitosan with added glucose. In type A, pure chitosan degraded in two stages according to the DTG curve. The first stage was observed at less than 100°C, and the second stage was at around 250°C. The first stage is attributed to the evaporation of water loosely bound to the polymer, and the second stage is attributed to further dehydration, decomposition, and depolymerization of chitosan.^{18,19} When glucose was added to chitosan, the weight reduction observed at around 150°C was greater for the higher glucose levels. In contrast, the weight reduction at around 250°C gradually moderated. This indicated that the thermal stability was lowered by addition of glucose. Generally, the thermal stability of chitosan-based polymers is influenced by chemical modification of free amino groups such as the formation of Schiff bases.^{20,21} In addition, the progress of the Maillard reaction is accompanied by the degradation of substances and the formation of various compounds with low and high molecular weights.²² For type D chitosan, the weight decrease behavior of pure chitosan was similar to that of type A. This may be because the molecular weight distribution was not sharp enough to cause any significant difference. The behavior of chitosan with added glucose was also similar to that shown for type

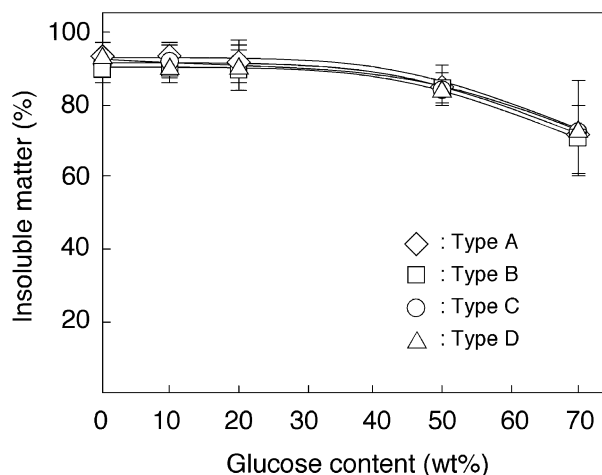


Fig. 6. Fraction of insoluble matter of the chitosan films with added glucose in water

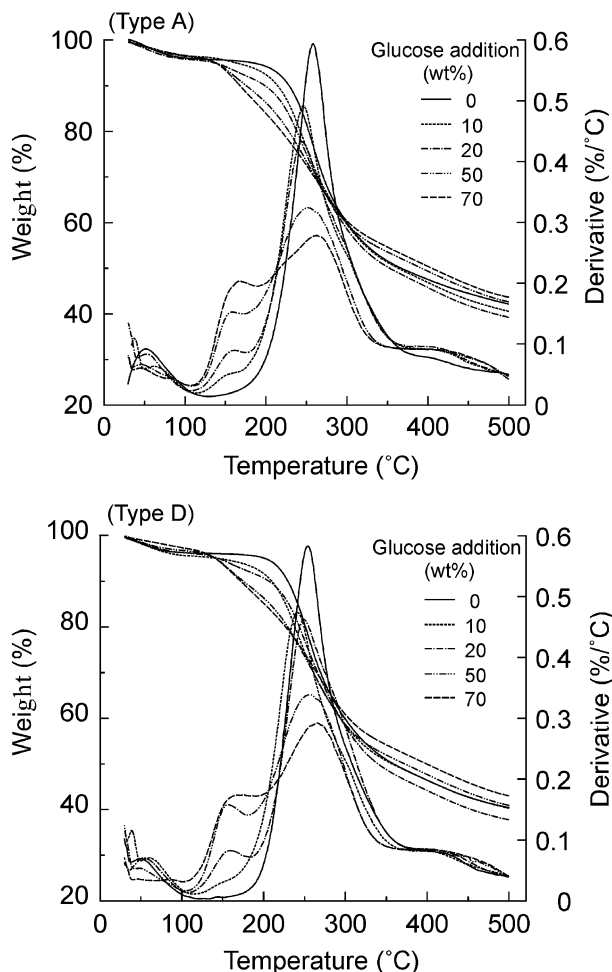


Fig. 7. Thermogravimetric analysis curves of chitosan films with added glucose for two types of chitosan

A. We confirmed that the TGA curves of types B and C showed similar behavior, i.e., hardly any effect of the type of chitosan on thermal stability was recognized. However, it was clarified that the thermal stability of chitosan was lowered by the addition of glucose.

Figure 8 shows the tensile strength of each chitosan film. The strength of pure chitosan film had a tendency to increase with increasing molecular weight. Other researchers have already explained this trend by describing the entanglement of molecules and the hydrogen bonding between hydroxyl groups and amino groups.^{23,24} In type A chitosan, the strength improved on glucose addition of 10 wt% but was lowered by further addition. The improvement achieved by adding a small amount was similar to that using chitosan of the same type in a previous article.⁹ A similar trend was also observed in type B. However, hardly any improvement of strength by 10 wt% addition was observed in type C. The strength of type D decreased continuously with increasing amounts of added glucose. This difference could be due to changes in the molecular weight, chemical structure, entanglement, and hydrogen bonding by the Maillard reaction.

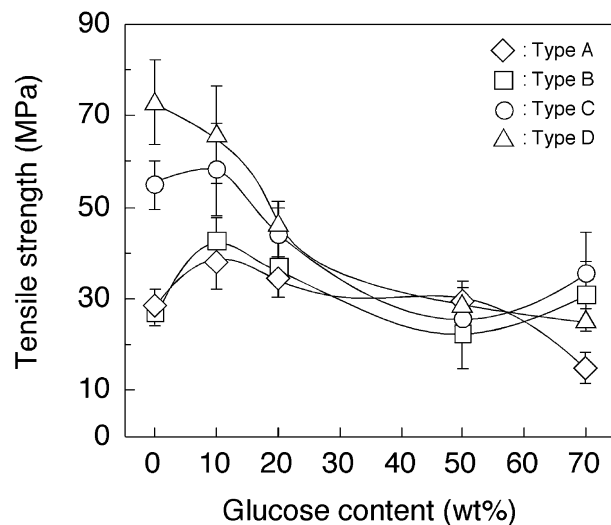


Fig. 8. Tensile strength of chitosan films with added glucose

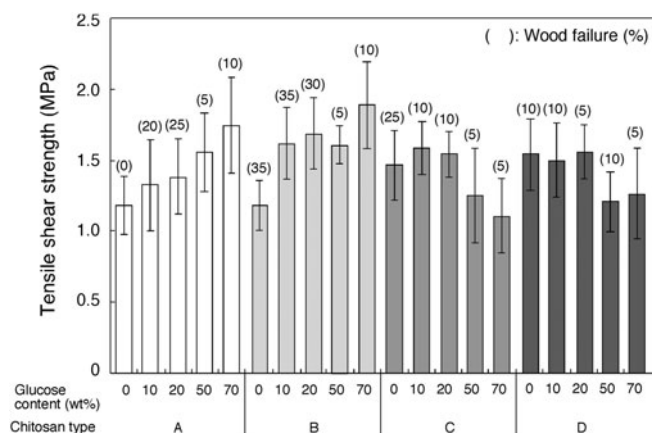


Fig. 9. Dry bond strength of three-ply plywood glued with glucose-enhanced chitosans

Bonding properties

The effects of glucose addition on the bonding properties of chitosan were investigated. Figure 9 shows the dry-bond strengths of three-ply plywood glued with different chitosans with added glucose. The pure chitosans (0 wt% glucose) having high molecular weight such as types C and D exhibited relatively high bond strengths compared to the low-molecular-weight chitosans type A and B. The bond strength increased gradually with increasing glucose addition in types A and B from 1.19 (0 wt%) to 1.75 MPa (70 wt%) in type A and from 1.18 (0 wt%) to 1.89 MPa (70 wt%) in type B. In contrast, the bond strength tended to decrease at greater amounts of added glucose for types C and D. As a whole, wood failure exhibited a relatively low value, irrespective of the conditions. Judging from the bond strength, it was indicated that glucose addition was effective in low-molecular-weight chitosan such as types A and B.

Figure 10 shows the results for warm water immersion tests. The effect of glucose addition was confirmed in chito-

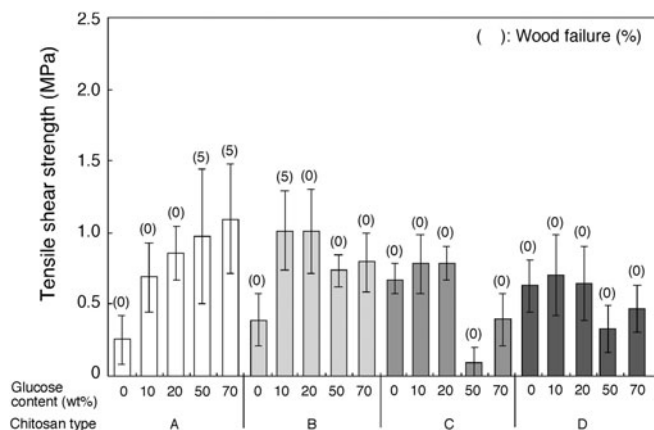


Fig. 10. Bond strength of three-ply plywood glued with glucose-enhanced chitosans after warm water immersion

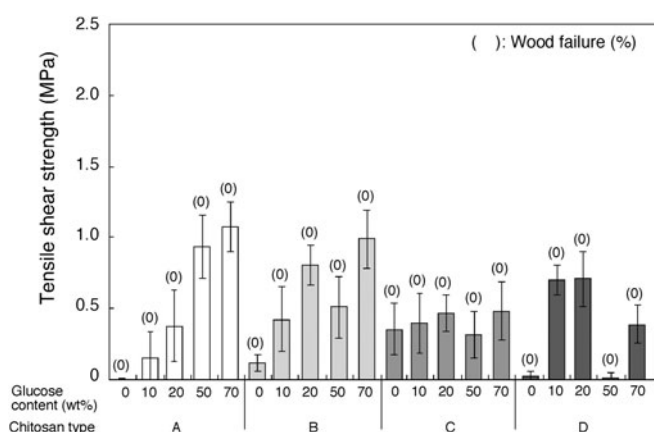


Fig. 11. Bond strength of three-ply plywood glued with glucose-enhanced chitosans after 1% acetic acid immersion

san types A and B. The maximum enhancement rate based on each pure chitosan for types A and B was 322% and 157%, respectively. For types C and D, the bond strength definitely decreased for greater amounts of added glucose. Comparing all conditions, the maximum average bond strength was 1.1 MPa for 70 wt% addition of glucose to type A chitosan. Therefore, it is clear that glucose addition to low-molecular-weight chitosan enhanced water resistance significantly. In addition, the water resistance of low-molecular-weight chitosan with added glucose was superior to that of pure high-molecular-weight chitosan.

Chitosan films became insoluble in dilute acetic acid on the addition of glucose, as shown in Fig. 5. Accordingly, the bond strength after 1% acetic acid immersion treatment was investigated. The results are shown in Fig. 11. For type A chitosan, hardly any bond strength of the pure chitosan was evident. This is due to the dissolution of the chitosan in the glue line.⁴ When glucose was added to chitosan, the bond strength increased significantly with increasing glucose addition. The maximum average bond strength was 1.07 MPa with the 70 wt% glucose addition. This value was equivalent to the maximum value in the warm water immersion treat-

ment. For type B chitosan, the bond strength also improved on addition of glucose. The maximum average bond strength was 0.99 MPa for the 70 wt% addition. For types C and D chitosan, the effect of glucose addition was confirmed; however, increasing amounts of added glucose did not necessarily contribute to marked improvement of the bonding strength. The maximum average bond strengths of these chitosans were inferior to those of types A and B. This means that glucose addition in low-molecular-weight chitosan effectively enhanced the bonding strength in dilute acid.

Based on the results in Figs. 9–11, the utilization of a Maillard reaction of chitosan with glucose enabled improvement of the bonding properties of chitosan. Low-molecular-weight chitosan, especially, tended to display beneficial effects of glucose addition. Further, the bonding properties were enhanced with increasing amounts of added glucose. These tendencies were different from the tendencies of film properties. The reason seemed to be that the bonding properties are greatly affected by the viscosity, wettability, and solid-based spread rate of chitosan with added glucose. For example, the viscosities of type A and D chitosan with 70 wt% added glucose were about 2 and 10065 Pa·s, respectively, as shown in Table 2. The difference would significantly affect the wettability for a veneer. The solid-based spread rate increased with increasing glucose addition, and as a consequence a good glue line would be formed. In any event, we succeeded in improving the bonding properties of chitosan by a method that employs safe chemicals and processes.

Conclusions

The film properties and the bonding properties of Maillard-reacted chitosan with the addition of glucose were investigated. The physical and chemical properties such as the weight, color, free amino groups, insoluble fraction, and thermal properties changed significantly as the amount of added glucose increased. However, hardly any difference in these properties was evident for chitosan of different molecular weights. This indicated that the Maillard reaction proceeded easily on glucose addition regardless of the type of chitosan. A small addition of glucose was effective for enhancement of the tensile strength of chitosan of low-molecular-weight, whereas glucose addition had an adverse effect on high-molecular-weight chitosan. For low-molecular-weight chitosan, the bonding properties were enhanced with increasing amounts of added glucose. In particular, the addition of glucose drastically improved the bond strength in 1% acetic acid solution. The addition of glucose did not necessarily contribute to improvement of the bonding strength in high-molecular-weight chitosan. Consequently, the addition of glucose to low-molecular-weight chitosan and the subsequent Maillard reaction are useful for the development of good bonding properties.

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