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Development of new natural polymer-based wood adhesives I: dry bond strength and water resistance of konjac glucomannan, chitosan, and their composites

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Abstract Bonding properties of konjac glucomannan (KGM), chitosan, and their composites were investigated. After preparing three-ply plywood glued with these materials, the dry bond strength and the bond strength after water immersion treatment were measured. The bond strength of urea-formaldehyde resin adhesive, casein, and soybean glues was also studied for comparison. KGM developed relatively good dry bond strength in extremely small solid amounts, irrespective of alkaline treatment. However, the water resistance was extremely low for all of the conditions. Chitosan also developed good dry bond strength in small solid amounts and was better than conventional adhesives. Chitosan also exhibited excellent water resistance compared to casein and soybean glues. When KGM and chitosan were combined, the adhesiveness under the dry condition was enhanced, and the bonding properties were superior to those of casein and soybean glues. Therefore, it is expected that chitosan and chitosan–KGM composite can be used as environmentally friendly wood adhesives.

Key words Konjac glucomannan · Chitosan · Bond strength · Wood adhesives

Introduction

Natural polymers such as casein and soybean protein were used as wood adhesives until they were replaced by synthetic resin adhesives. However, the use of natural polymer-based adhesives is currently limited because of low durability, especially low water resistance. Synthetic resin adhesives have many advantages, such as high bond strength and high water resistance, but most of them contain formaldehyde and a chemical agent that cause environmental problems. The increasing concern over environmental pollution has forced the wood industry to develop environmentally friendly wood adhesives. Studies on new natural polymer-based adhesives are necessary for the development of wood adhesives and the wood industry in general.

Konjac glucomannan (KGM), a polysaccharide, is extracted from the tuber of *Amorphophallus Konjac*, K Koch. The chemical structure of KGM consists of D-glucose and D-mannose linked by β -1,4 linkage. It has mannose and glucose units in a molar ratio of 1.6:1.0, with some branching at C-3 of the mannose unit.¹ An acetyl group is attached to 1 per 19 sugar residues.² Generally, KGM forms a gel in the presence of an alkaline coagulant, and the KGM gel is stable in boiling water. The reason for this stability is that the deacetylation reaction occurs, and crosslinks are formed by hydrogen bonding between KGM molecules deficient in acetyl groups.³ KGM has long been used in Japanese traditional dishes. Research on KGM has been done in such fields as food and chemical engineering.^{4–6} In addition, KGM was sometimes used as a paste for paper during World War II,⁷ but no studies have tried to investigate its use as a wood adhesive.

Chitosan is a deacetylated product of chitin, which is a naturally occurring polysaccharide that is available in large amounts from the epidermis of crustaceans such as crabs and shrimps. The chemical structure of chitosan consists of β -1,4-linked D-glucosamine residues with a variable number of randomly located N-acetyl-glucosamine groups.⁸ Recently, chitosan has received much attention as a potential

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polysaccharide resource owing to its specific structure and properties, and it has been studied extensively for industrial applications.^{8–10} However, only a few studies have been conducted on the application of chitosan to wood, and the study of its adhesiveness has been superficial.¹¹ In this study, the adhesiveness of KGM, chitosan, and their composites were clarified with the object of developing new natural polymer-based adhesives.

Materials and methods

Materials

The KGM powder was obtained from Shimizu Chemical Co. (Hiroshima, Japan) and was used without further purification. This powder is distributed under the commercial name Propol RS. The color and size of the powder were almost white and 80 mesh pass, respectively. The molecular weight and the degree of polymerization were about 1200000 and 6200, respectively. The pH and viscosity of 1 wt% aqueous solution were 5–7 and >20 Pa·S (25°C), respectively. Sodium hydroxide was used as an alkaline coagulant.

Chitosan powder was purchased from Junsei Chemical Co. (Tokyo, Japan) and was used without further purification. The molecular weight and degree of deacetylation were about 35000 and 80%–90%, respectively. The viscosity of 1 wt% dissolved in 1 wt% acetic acid solution was 15 mPa·S (20°C). When chitosan was used as an adhesive, it was dissolved in a 1 wt% acetic acid solution.

The representative wood adhesive used here was urea-formaldehyde (UF) resin. The F/U molar ratio, solid content, and viscosity were 1.15, 53.2%, and 150 mPa·S (25°C), respectively. A 20% ammonium chloride aqueous solution was added to the UF resin at 1% (based on solid resin weight) prior to making plywood. In addition, commercial powdered casein and soybean glues were obtained from Honen Co. (Tokyo, Japan). These glues are distributed under the commercial names CW-603 and LY-703, respectively. When the casein and soybean glues were used, they

were mixed at ratios of two and three parts by weight of water, respectively.

Spread method for plywood preparation

Three-ply plywoods (30 × 30 cm) were prepared using rotary-peeled lauan (*Shorea* spp.) veneers of 1.6 mm thickness. The average moisture content of the veneers was 9.2%. Usually, wood adhesive is applied to the veneer in a liquid state. However, when KGM powder is dissolved in water, the solution exhibits high viscosity even at low concentration, so it is difficult to apply the required amount of KGM in a liquid state. Consequently, a certain amount of water was first sprayed on the core veneer, and the KGM powder was then sprinkled on it using a 100-mesh sieve. When sodium hydroxide was used, it was dissolved in water at 1% concentration (based on KGM weight) prior to spraying. The detailed formulations are shown in Table 1. In the case of chitosan, a suitable amount of the chitosan solution was applied to the core veneer using a rubber roller. The detailed formulations are shown in Table 2. When KGM and chitosan were used as a composite, the chitosan solution was first applied to the veneers by double spread, and then, KGM powder was sprinkled on the core veneer. The detailed formulations are shown in Table 3.

The UF resin adhesive, casein, and soybean glues were applied to the core veneer at a spread rate of 140 g/m² or more using a rubber roller. This means that the solid-based spread rates were 50 g/m² or more. The detailed formulations of the conventional adhesives are shown in Table 4.

Table 2. Formulation of chitosan solutions

Specimen	Chitosan (g/m ²)	Acetic acid 1 wt.% (g/m ²)	Spread rate (g/m ²)
b-1	6	154	160
b-2	8	152	160
b-3	12	148	160
b-4	16	152	168
b-5	20	148	168
b-6	32	118	250
b-7	64	186	250

Table 1. Formulation of KGM solutions

Specimen	KGM content (%)	KGM (g/m ²)	Water (g/m ²)	Addition of NaOH	Spread rate (g/m ²)
a-1	5	10	190	Yes	200
a-2	5	8	152	Yes	160
a-2'	5	8	152	No	160
a-3	5	6	114	Yes	120
a-4	5	4	76	Yes	80
a-5	10	20	180	Yes	200
a-5'	10	20	180	No	200
a-6	10	16	144	Yes	160
a-7	10	8	72	Yes	80
a-8	10	6	54	Yes	60
a-9	20	32	128	Yes	160
a-9'	20	32	128	No	160
a-10	20	16	64	Yes	80
a-11	20	8	32	Yes	40
a-12	20	6	24	Yes	30

KGM, konjac glucomannan

Table 3. Formulation of KGM–chitosan composites

Specimen	KGM (g/m ²)	Chitosan (g/m ²)	Acetic acid 1 wt.% (g/m ²)	Spread rate (g/m ²)
c-1	6	2	152	160
c-2	4	4	152	160
c-3	2	6	152	160
c-4	8	2	152	162
c-5	8	4	152	164
c-6	8	6	152	166
c-7	8	8	152	168
c-8	8	10	152	170
c-9	2	16	152	170
c-10	4	16	152	172
c-11	8	16	152	176
c-12	16	16	152	184

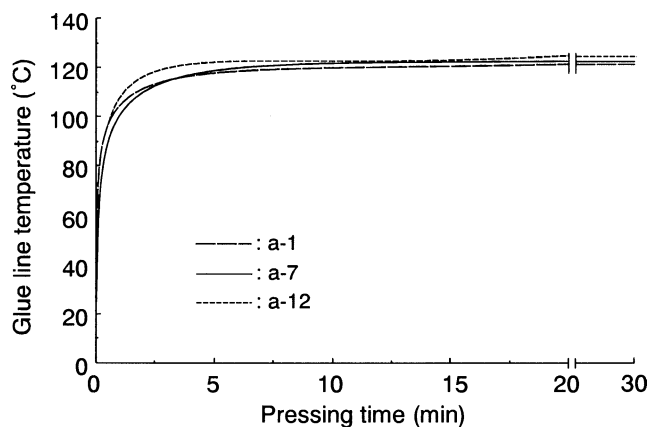
Table 4. Formulation of urea-formaldehyde (UF) resin adhesive, casein, and soybean glues

Substance	Spread rate (g/m ²)	Solid-based spread rate (g/m ²)
UF resin adhesive	140	74
Casein glue	200	67
Soybean glue	200	50

Pressing conditions

In the case of KGM, chitosan, and KGM–chitosan composite, the assembled three-ply veneers were cold-pressed under a pressure of 0.98 MPa and then were hot-pressed at 130°C under the same pressure. The cold-pressing time was determined in consideration of the gel formation of KGM. Generally, the gel formation by alkaline treatment occurs after a certain induction period. The deacetylation reaction is thought to proceed during the induction period.¹² The relation between the induction period and the concentration of alkali can be expressed by the equation $v = k[\text{OH}^-]^n$, where v (min⁻¹) is the induction reaction rate defined by the inverse of the induction period; $[\text{OH}^-]$ (M) is the concentration of hydroxide ion in the solution; and k and n are constants.¹³ In the case of sodium hydroxide, the k and n values are 1.12 and 0.32, respectively.¹³ The equation indicated that it would take a few minutes for gel formation to occur in this study, so we settled on a cold-pressing time of 10 min. To determine the hot-pressing time, a preliminary experiment was performed in which the temperature in the glue line of three-ply plywood during hot-pressing was measured by inserting thermocouples into the center of the core veneer.

In the case of UF resin adhesive, the assembled three-ply veneers were cold-pressed under a pressure of 0.98 MPa for 5 min and then were hot-pressed at 120°C under the same pressure for 10 min. To prevent blistering, degassing was done after a hot-pressing time of 5 min. When casein and soybean glues were applied, the assembled three-ply veneers were cold-pressed under a pressure of 0.98 MPa for 10 min and then were hot-pressed at 120°C under the same pressure for 15 min. Degassing was also done after a hot-pressing time of 5 min.

**Fig. 1.** Temperature behaviors of the glue line of three-ply plywood with different spread rates at 130°C

Bond strength measurement

The prepared plywoods were cut into standard tensile shear test specimens according to Japanese Industrial Standard (JIS) K6851. The tensile shear strength of the adhesive bonds after conditioning at room temperature was measured under a loading rate of 2 mm/min. The water immersion test (water immersion at 30°C for 3 h, cooling in water, and testing in the wet condition) was also performed under the same loading rate. Altogether, 14 or 16 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

Preliminary experiment

The bond strength development of water-based adhesives can be markedly affected by the evaporation or migration of water away from the bond line. In this study, a large amount of water was sometimes applied to the veneer, so extra hot-pressing time was required. To determine the pressing time, temperature behaviors of the glue line of three-ply plywoods with different spread rates were observed. The results are shown in Fig. 1. Despite the amount of water, the glue-line temperature increased rapidly for a few minutes and then leveled off. The hot-pressing time was set at 15 min in consideration of the results obtained. In addition, degassing was done after a hot-pressing time of 5 min to prevent blistering.

Bonding properties of conventional adhesives

To clarify the bonding properties of conventional adhesives, the dry bond strength and the bond strength after water immersion treatment were measured. The results are shown in Fig. 2. In the dry condition the average bond strength of UF resin adhesive was similar to that of casein glue, with an

average value of 1.82 MPa. The value for soybean glue (1.45 MPa) was somewhat lower than those for the other adhesives. The wood failure of the samples glued with these adhesives exhibited low values. With water immersion treatment, the average bond strength of the UF resin adhesive increased slightly compared to the average dry bond strength. This was likely due to after-curing of the resin. The UF resin adhesive maintained a good bonding property after water immersion treatment. The average values for casein and soybean glues were 0.90 and 0.61 MPa, respectively. The bond strengths decreased by about 50% compared to dry bond strengths. Generally, among the conventional natural polymer-based adhesives, casein glue has relatively good water resistance.¹⁴ However, the bonding property after water immersion treatment was significantly inferior to that of the UF resin adhesive.

Bonding properties of KGM

Figure 3 shows the dry bond strength of three-ply plywood glued at various KGM/water (alkaline solution) ratios. For

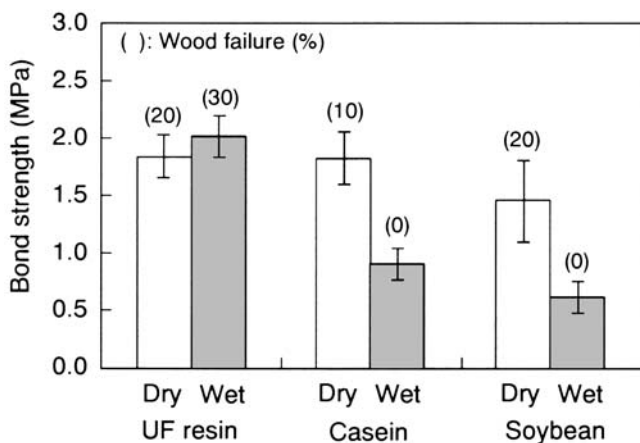


Fig. 2. Bond strength of three-ply plywood glued with urea-formaldehyde (UF) resin adhesive, casein, and soybean glues

a KGM content of 5%, the maximum average bond strength was 1.41 MPa for specimen a-2. The bond strength was somewhat weaker than those of conventional adhesives, as shown in Fig. 2. The wood failure of the sample exhibited extremely low values. In this case, however, the solid-based spread rate of KGM was 8 g/m². The solid-based spread rate of KGM was about one-tenth that of the UF resin adhesive. Therefore, KGM developed a relatively good dry bond strength when used in extremely small solid amounts. The maximum average bond strengths obtained under the conditions of 10% and 20% KGM content were 1.27 MPa for specimen a-5 and 0.93 MPa for specimen a-9, respectively. These values were inferior to that for specimen a-2. This means that the bond strength was not necessarily improved by increasing the amount of KGM. In addition, the amount of water influenced the bond strength even if the amount of KGM was the same. Therefore, the KGM/water ratio is important when developing the bond strength. Generally, when the concentration of the KGM solution is higher than 8%, the solution forms a highly stable structure.¹⁵ In the case of 10% and 20% KGM content, a highly stable structure would be formed. Consequently, the wettability of KGM to the veneer was believed to be lower. Under the conditions for specimens a-11 and a-12, it was impossible to bond with KGM. The reason seemed to be that the spread rate was low. When the water immersion test was performed, delamination occurred in all of the samples during water immersion, indicating that the water resistance of KGM was extremely low.

The bond strength using KGM without adding sodium hydroxide was also investigated. The average values for specimens a-2', a-5', and a-9' were 1.21, 1.55, and 1.15 MPa, respectively. The differences in bond strength were observed under each condition and compared to that of NaOH-containing KGM. Overall, there was no clear effect of NaOH on the dry bond strength. The cause of the differences would be an incomplete glue line due to the small amount of KGM. When the water immersion test was performed, delamination also occurred in all of the samples. It

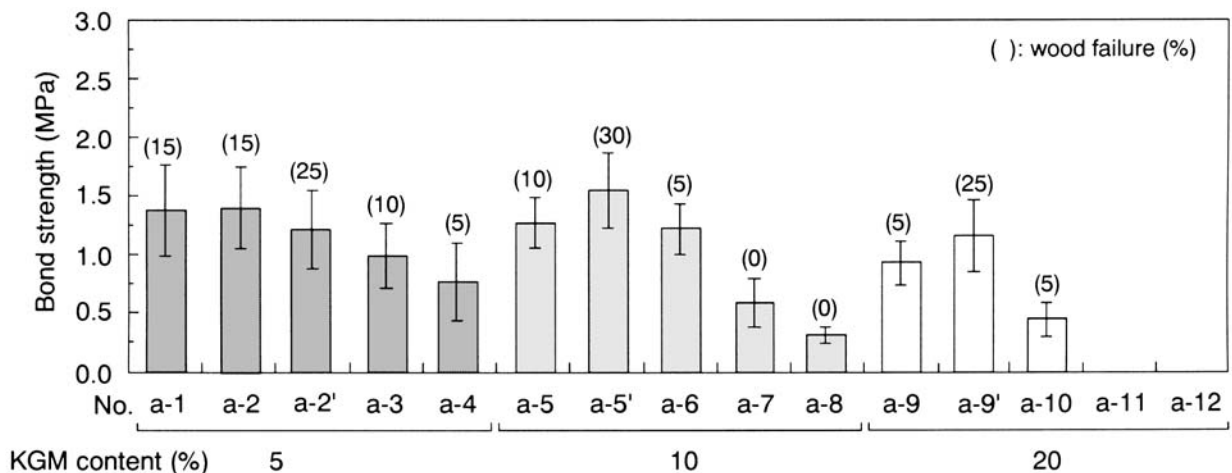


Fig. 3. Dry bond strength of three-ply plywood glued with various konjac glucomannan (KGM)/water ratios

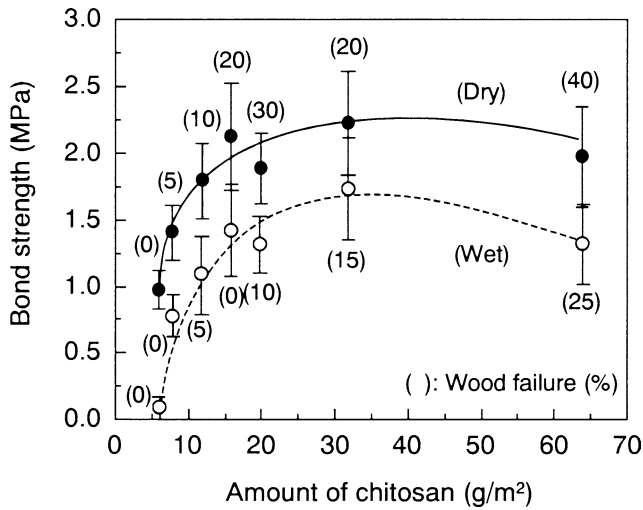


Fig. 4. Bond strength of three-ply plywood glued with chitosan before and after water immersion treatment

was clarified that the water resistance of KGM was extremely low, irrespective of alkaline treatment.

Bonding properties of chitosan

Figure 4 shows the bond strength of three-ply plywood glued with various amounts of chitosan before and after water immersion treatment. The dry bond strength increased with increasing chitosan to 16 g/m^2 and then decreased slightly. In the case of 16 g/m^2 , the average bond strength was 2.13 MPa . Compared to the conventional adhesives shown in Fig. 2, chitosan developed good dry bond strength when used in small solid amounts. As with the conventional adhesives, wood failure of the chitosan sample was low. After water immersion treatment, the bond strength increased as the amount of chitosan increased, but it then decreased. The maximum average value of the bond strength was 1.74 MPa in the condition of 32 g/m^2 . The bond strength after water immersion treatment was inferior to that of UF resin adhesive, as shown in Fig. 2. Compared to the casein and soybean glues, however, chitosan exhibited excellent bond strength. Ohmori et al. reported that chitosan treatment of the wood surface helped improve the dry bond strength and water resistance of UF resin and polyvinyl acetate resin adhesives.¹⁶ When chitosan only was used as a wood adhesive, the bonding properties were poor. Ohmori et al. concluded that chitosan could be a good wood adhesive if it were improved somehow.¹⁶ However, their research was done only for extremely small amounts of chitosan. Judging from the results obtained in our experiment, chitosan could develop good bonding properties if used in larger amounts. Therefore, it is expected that chitosan can be used as a natural polymer-based wood adhesive without further improvement.

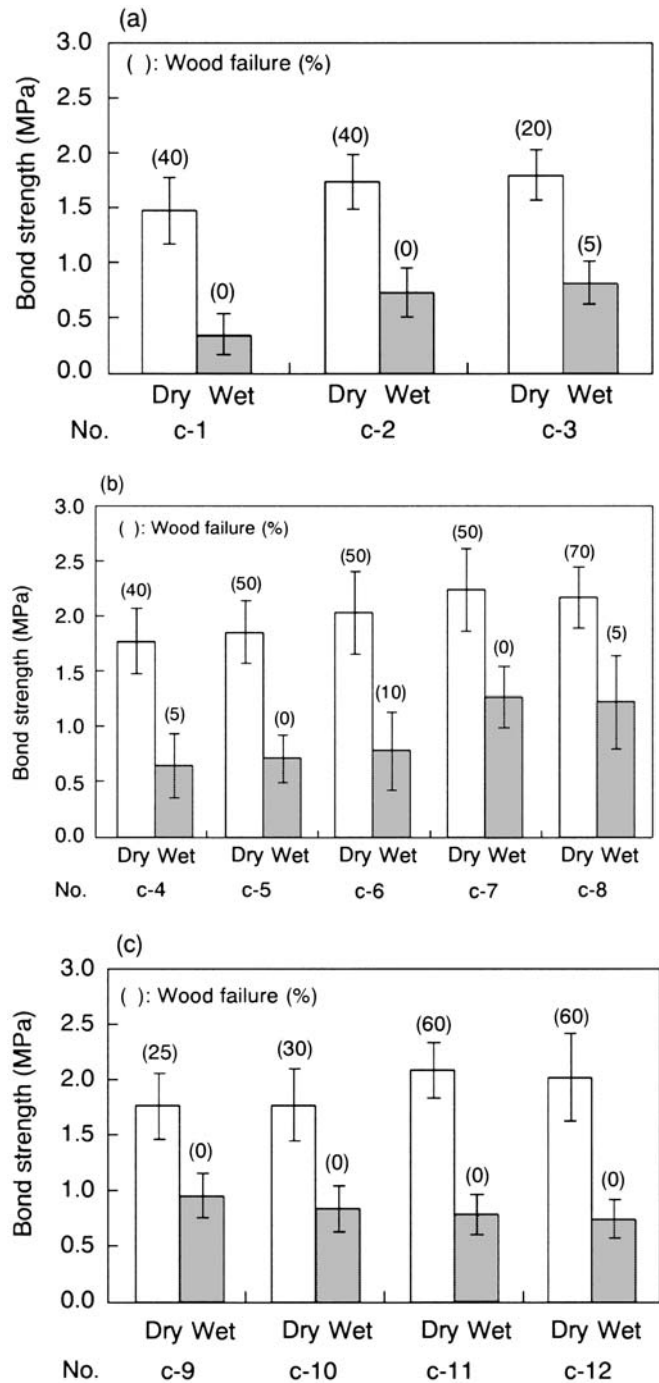


Fig. 5a-c. Bond strength of three-ply plywood glued with various amounts of KGM-chitosan

Bonding properties of KGM-chitosan composites

A composite of the natural polymers KGM and chitosan seems to have good bonding properties when used as a solid in small amounts. The bond strengths of various KGM-chitosan composites were investigated under a solid-based spread rate of 8 g/m^2 . The results are shown in Fig. 5a. The dry bond strength increased slightly by increasing the proportion of chitosan. The maximum average value was 1.80 MPa for specimen c-3. Compared to KGM or chitosan

alone, the strength was about 20% higher under the same solid-based spread rate. In addition, the strength was similar to that of UF resin adhesive and casein glue. The bond strength after water immersion treatment also increased with an increased proportion of chitosan. The average bond strength of specimen c-3 was 0.81 MPa, similar to that of chitosan alone under the same solid-based spread rate shown in Fig. 4. Accordingly, the KGM–chitosan composites developed good dry bond strength and had water resistance under a solid-based spread rate of 8 g/m².

The effects of the chitosan amount in KGM–chitosan composites were investigated. KGM was kept at 8 g/m², and chitosan was varied from 2 to 10 g/m². The results are shown in Fig. 5b. The dry bond strength increased gradually with increasing chitosan amount. When chitosan at 8 g/m² or more was added, the average bond strength exceeded 2.1 MPa. The wood failure recorded was 50% or more. The bond strengths obtained under these conditions exceeded the values for UF resin adhesive and casein glue. This indicated that excellent adhesiveness developed under a dry condition. After water immersion treatment, the bond strength also increased as the amount of chitosan increased. Compared to the KGM alone, the water resistance was improved by adding chitosan. When chitosan at 8 g/m² or more was added, the average bond strength exceeded 1.2 MPa.

The effects of the KGM amount in the KGM–chitosan composites were also investigated. The chitosan was kept at 16 g/m², and KGM was varied from 2 to 16 g/m². The results are shown in Fig. 5c. The dry bond strength increased when KGM was increased. When KGM at 8 g/m² or more was added, the average bond strength exceeded 2.0 MPa. The wood failure recorded was 60%. The bond strengths obtained under these conditions also exceeded those of UF resin adhesive and casein glue. Therefore, markedly improved adhesiveness was observed when using the KGM–chitosan composites. After water immersion treatment, the bond strength decreased gradually with increasing KGM amount. However, no marked decrease in bond strength was observed, likely due to the high water resistance of chitosan.

Conclusions

The bonding properties of KGM, chitosan, and their composites were investigated. When KGM was used as an adhesive, good dry bond strength was obtained with extremely small solid amounts. However, the KGM/water ratio had a

significant effect on bond strength. The water resistance of KGM was low for all of the conditions, and alkaline treatment had little effect on the bonding properties. When chitosan was used, good dry bond strength and good water resistance developed as the solid-based spread rate increased. Compared to casein and soybean glues, chitosan developed excellent bonding properties with small solid amounts. Simultaneous use of KGM and chitosan enhanced adhesiveness under dry conditions, especially as it pertained to wood failure. Consequently, it is expected that chitosan and chitosan–KGM composites can be used as natural polymer-based wood adhesives.

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