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Original Article

Investigation of a New Natural Adhesive Composed of Citric Acid and Sucrose for Particleboard

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ABSTRACT:

The development of a natural adhesive composed of materials derived from non-fossil resources is a very important issue. In this study, only citric acid and sucrose were used as adhesive materials for particleboard. A water solution in which citric acid and sucrose were dissolved was used as an adhesive, and the manufacture of particleboard with a target density of 0.8g/cm^3 was attempted under a press condition of 200˚C for 10 min. The optimum mixture ratio of citric acid and sucrose and the optimum resin content were 25 to 75 and 30wt%, respectively. The modulus of rupture (MOR) and the modulus of elasticity (MOE) in bending were 20.6MPa and 4.6GPa, respectively. The internal bond strength (IB) was 1.6MPa, indicating that the adhesive had excellent bond strength. The thickness swelling (TS) after water immersion for 24h at 20˚C was 11.9%. The board did not decompose even under more severe accelerated treatments. This meant that the adhesion had good water resistance. The MOR, IB and TS of the board were comparable to or higher than the requirement of the 18 type of JIS A 5908 (2003). Consequently, there is a possibility that a mixture of citric acid and sucrose can be used as a natural adhesive for particleboard.

KEYWORDS: Citric acid, Sucrose, Natural adhesive, Particleboard

1. Introduction

Most current wood adhesives such as formaldehyde-based resins, vinyl acetate resins and isocyanate-based resins are composed of various materials derived from fossil resources. The wood adhesives have been developed in the petrochemical industry and have excellent performance, good working properties and are economically satisfactory. However, it is believed that the use of the current wood adhesives will be unavoidably restricted in the future due to decreases in the reserves of fossil resources. Many studies on natural-based adhesives using bio-resources have been conducted to resolve the resources problem. [1]. Tannin-based, lignin-based, and protein-based natural adhesives are especially familiar. However, chemical substances derived from fossil resources are essential to obtain satisfactory bond performance [2-5]. This means that it will be difficult to eliminate the dependence on fossil resources. In addition, conventional natural adhesives often contain harmful chemical substances that cause environmental problems and health disorders. Considering the global effort to establish a sustainable society, it is very important to develop a novel natural adhesive without using both of fossil resources and harmful chemical substances.

We recently found that citric acid can be used as a natural adhesive for wood-based molding [6-8]. Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is an organic polycarboxylic acid containing three carboxyl groups. It is contained in citrus fruits such as lemons and limes and is commercially produced by fermenting glucose or glucose- and sucrose-containing materials [9,10]. It is widely used in food, beverages and pharmaceuticals. In addition, citric acid has been researched as a crosslinking agent for wood [11,12], plant fiber [13], paper [14], starch [15] and bio-based elastomers [16]. According to our previous researches [6-8], citric acid had good bond performance for wood-based molding, and its main bonding mechanism was ester linkages between the carboxyl groups of citric acid and hydroxyl groups of wood components. In this study, the manufacture of particleboard using citric acid as an adhesive was attempted. However, the adhesion area of the particles used for the particleboard is generally smaller than that of the wood flour used for wood-based molding. Therefore, sucrose was added in an attempt to enhance the bond performance. The effects of the ratios of citric acid to sucrose and the resin content on the physical properties were investigated.

2. Materials and methods

2.1 Materials

Recycled wood particles consisting mainly of softwood were obtained from a particleboard company in Japan. The wood particles were screened by a sieving machine, and the particles remaining between aperture sizes of 5.9 and 0.9 mm were used as materials. The particles were dried in an oven at 80ºC for 12 h. Citric acid (anhydrous) and sucrose were purchased from Nacalai Tesque, Inc. (Kyoto, Japan), and used without further purification.

2.2 Manufacture of particleboards

Citric acid and sucrose were dissolved in water under a certain ratio, and the concentration of the solution was adjusted to 59wt%. The mixture ratios of citric acid / sucrose were 100/0, 75/25, 50/50, 25/75 and 0/100. The viscosity and pH of the solutions are shown in Table 1. The solution was used as an adhesive and sprayed onto the particles in a blender at 5 ~ 40wt% resin content based on the weight of the oven-dried particles. In the case of a high resin content of more than 30wt%, the sprayed particles were dried at room temperature for 12 h to reduce moisture content. The moisture content of the mat was 12 ~ 20%. The particles were mat-formed using a forming box of 300×300 mm. The mat was hot-pressed at 200˚C for 10 min with a distance bar of 9 mm to control the board thickness. To prevent blisters, the press pressure was reduced temporarily at 3 min after the start of the press. The size of the manufactured board was 300×300×9 mm, and the target density was 0.8 g/cm^3. The detailed conditions are shown in Table 2.

2.3 Evaluation of board properties

After being conditioned for 1 week under 20˚C and RH about 60%, the boards were evaluated according to the Japanese Industrial Standard for particleboard (JIS A 5908, 2003)[17]. The static 3-point bending test in dry condition was conducted on a 200 mm×30 mm×9 mm specimen from each board. The effective span and loading speed were 150 mm and 10 mm/min, respectively. The modulus of rupture (MOR) and the modulus of elasticity (MOE) were calculated. The internal bond strength (IB) test was performed on a 50 mm×50 mm×9 mm specimen from each board, and thickness swelling (TS) after water immersion for 24h at 20˚C was measured in specimens of the same size from each board. Following the TS test, thickness changes under cyclic-accelerated aging treatment (drying at 105˚C for 10 h, warm water immersion at 70˚C for 24 h, drying at 105˚C for 10 h, boiling water immersion for 4h, and drying at 105˚C for 10 h) were measured. The weight changes of the specimen in the treatment were also measured. Each experiment was performed in quintuplicate, and the average value and standard deviation were calculated.

3. Results and discussion

3.1 Effects of mixture ratio of citric acid and sucrose

When the water solution in which citric acid and sucrose were dissolved was used as an adhesive, particleboard was obtained as shown in Figure 1. The color of the board was a dark brown, irrespective of the condition of manufacture. First, the effects of the ratio of citric acid and sucrose on the physical properties were investigated under a resin content of 20wt%. Figure 2 shows the bending properties of the particleboards bonded with different ratios of citric acid and sucrose. The MOR and MOE of the board banded with only citric acid (100/0) were 10.7 MPa and 3.3 GPa, respectively, indicating that citric acid developed a bond performance to some extent. The bending properties increased gradually as the sucrose ratio increased. In the case with a ratio of citric acid to sucrose of 25 / 75, the MOR and MOE values were 20.1 MPa and 4.4 GPa, respectively. Compared to the case using only citric acid, the improvements in MOR and MOE were 88 and 33%, respectively. According to the standard of the 18 type of JIS A 5908 [17], which is for construction use, an MOR of 18.0 MPa or more is required. Therefore, it was clarified that the bending strength of board bonded using a ratio of citric acid to sucrose of 25 / 75 was comparable to the standard. When only sucrose (0/100) was used as an adhesive, the MOR and MOE values were 11.6 MPa and 3.3 GPa, respectively. These values were similar to those of only citric acid, and sucrose offered a certain bond performance. Figure 3 shows the IB strength of the particleboard. The value increased with increasing sucrose ratio, and a value of 1.13 MPa was recorded in the ratio of citric acid to sucrose of 25 / 75. This was 3.5 times higher than that using only citric acid. The addition of sucrose brought marked improvement of the bond strength between particles. The strength of the board bonded using a ratio of citric acid to sucrose of 25 / 75 was much higher than the requirement (> 0.3MPa) providing for the 18type of JIS A 5908 [17]. The value of the board bonded with only sucrose was 0.19 MPa. Judging from the results in Figures 2 and 3, it was clarified that the mechanical properties of the boards bonded with citric acid and sucrose were greatly affected by the ratio, and the optimum ratio of citric acid to sucrose was 25 / 75. Figure 4 shows the results of TS (immersion at 20˚C for 24h) and the subsequent cyclic-accelerated aging treatment. The TS value of the board bonded with only citric acid was 33.8%, and the TS decreased with increasing sucrose ratio. In the case of a ratio of citric acid to sucrose of 25 / 75, the value of TS was 20.0%. The TS of the board bonded with only sucrose was over 100%, indicating that the dimensional stability of the board was extremely low. When sucrose is heated at about 200˚C, it converts to caramel, which contains many water-soluble substances [18]. Consequently, the board had low dimensional stability and was excluded from the subsequent measurement. The subsequent cyclic-accelerated aging treatment brought a stepwise increase of thickness irrespective of the kind of board. In particular, a marked change was recognized in the board bonded with only citric acid. The final thickness change after the treatment was 75.8%. The thickness change during the treatment was restricted by an increase of the sucrose ratio, and the final thickness change of the board bonded using a ratio of citric acid to sucrose of 25 / 75 was 50.7%. In other words, the increase of the sucrose ratio in the adhesion system contributed to the inhibition of the thickness change of the boards. Figure 5 shows the weight changes of the boards in the cyclic accelerated aging treatment. In the first treatment (immersion at 20˚C for 24h), the weight increase dropped as the sucrose ratio increased. The lowest weight increase value was 47.3% in the board in which the ratio of citric acid to sucrose was 25 / 75. The values in the boards bonded with only citric acid and only sucrose were 65.5 and 109.0%, respectively. In the drying after the treatment, weight decreases ranging from -3.5 to -8.0% were observed, indicating that some elusion including adhesive occurred. In the second treatment (immersion at 70˚C for 24h), the weight increase ranged from about 80 to 95% and dropped as the sucrose ratio increased. The opposite tendency, namely that the average value became high with increasing sucrose ratio, was recognized in the third treatment (boiling for 4h), but the overall weight change between the second and third treatments was almost the same. The final weight decrease with drying at 105˚C ranged from -10.0 to -14.4%, and a high sucrose ratio corresponded to a slight weight decrease. Based on the results shown in Figures 4 and 5, a high sucrose ratio brought good water resistance for the adhesion system. As a result, the board exhibited water resistance. In our previous reports [6,7], it was elucidated that citric acid reacts with wood components containing hydroxyl groups when molding is made at 200˚C and 4MPa for 10 min. The formation of ester linkages to bond wood together was recognized. In this study, citric acid would react with the sucrose and wood components. Research on the reaction of citric acid in particleboard will be reported in our next paper. In any case, the particleboard bonded using the citric acid and sucrose in the ratio of 25 / 75 brought excellent physical properties.

3.2 Effects of resin content

The effects of resin content on the physical properties of the particleboard were investigated under a ratio of citric acid to sucrose of 25 / 75. Figure 6 shows the bending properties of the particleboards bonded with different resin contents. Both the MOR and MOE increased with increasing resin content up to 20wt% and then kept an almost constant value. The maximum average values of MOR and MOE were 21.5 MPa (40wt%) and 4.6 GPa (30wt %), respectively. The boards bonded with 20wt% resin content or more were comparable to the requirement of the 18 type of JIS A 5908 [17]. A resin content more than double the general resin content (4 to 10w%) for particleboard [19] was needed to obtain satisfactory properties. Figure 7 shows the IB strengths of the particleboards bonded with different resin contents. The value increased linearly with increasing resin content up to 30wt% and then kept an almost constant value. The average value at 30wt% was 1.61MPa more than five times higher than that at 5wt%. Compared to the increase of the bending properties, a remarkable increase was recognized. The IB strength required in the 18 type of JIS A 5908 is more than 0.3MPa [17]. Therefore, the adhesion system composed of citric acid and sucrose developed excellent bond strength. Figure 8 shows the thickness changes of the particleboards with different resin contents in a cyclic accelerated aging treatment. In the water immersion treatment at 20˚C for 24h, TS exhibited a low value as the resin content increased. The average values for 30 and 40wt% was 11.9 and 9.3%, respectively, and those values were less than the standard value (12%) in the 18 type of JIS A 5908 [17]. Generally, the main factors to have an influence on TS are the compressibility of the board, the type of adhesive and the resin content. In this research, the density of the board is constant, irrespective of the resin content. This means that an increase in the resin content leads to a decrease in the amount of particles. The decrease of the reaction-force of compressed particles and the coating of particles with the adhesive resulted in the decrease of TS. In the subsequent more severe treatments, the changes in the thickness of all types of the boards increased. This increase would be caused by the degradation of adhesion between particles and the swelling of each particle. However, decomposition of the board was not observed, and it was indicated that the adhesion system of citric acid and sucrose has a basically good water resistance. The degree of thickness change became small with increasing resin content, indicating the high dimensional stability of the board. The values in 30 and 40wt% resin contents in boiling water for 4h were 40.7 and 29.8%, respectively. Figure 9 shows the weight changes of the particleboards in a cyclic accelerated aging treatment. In the first water immersion treatment, the weight increase exhibited a low value as the resin content increased. This indicated that water absorption was inhibited with increasing resin content. The weight decrease in the subsequent drying treatment was about -4 to -7%, irrespective of resin content. Slight elution containing the adhesive components would occur. The overall weight increase in the subsequent warm water immersion treatment was higher compared to that in the first treatment. This would be due to the lowering of the water resistance of the adhesive and the penetration of water into the wood. However, marked change in the weight increase in the subsequent boiling water treatment was hardly observed. When the slight weight decreases in the second and third drying treatments are taken into consideration, the mechanism of the weight increase in the boiling water treatment seemed to be similar to that in the warm water immersion treatment.

Conclusions

Particleboards bonded with citric acid and sucrose were manufactured to investigate the feasibility of a natural adhesive which does not depend on fossil resources. A water solution in which citric acid and sucrose were dissolved was used as an adhesive. Particleboard was obtained under the press condition of 200˚C for 10 min. The mechanical properties and water resistance increased as the sucrose ratio increased. In this study, the optimum mixture ratio of citric acid and sucrose and the optimum resin content were 25 to 75 and 30wt%, respectively. The MOR, IB and TS of the board manufactured under the optimum condition were comparable to or higher than the requirement of the 18 type of JIS A 5908. The IB strength was over 1.5MPa and the board exhibited good water resistance, indicating that the adhesive system had excellent bond performance. Therefore, there is a possibility that this adhesion system can be used as a natural adhesive for particleboard. Further investigation is necessary to determine the optimal detailed manufacture conditions and to clarify the bonding mechanism of the adhesion system.

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Figures

Fig.1. Particleboard bonded with citric acid and sucrose.

Fig.2. Effects of citric acid / sucrose ratio on bending properties. *Error bars* indicate standard deviations

Fig.3. Effect of citric / sucrose ratio on IB strength. *Error bars* indicate standard deviations

Fig.4. Thickness change in a cyclic accelerated aging treatment. *Error bars* indicate standard deviations

Fig.5. Weight change in a cyclic accelerated aging treatment. *Error bars* indicate standard deviations

Fig.6. Effects of resin content of citric acid / sucrose on bending properties. *Error bars* indicate standard deviations

Fig.7. Effects of resin content of citric acid / sucrose on IB strength. *Error bars* indicate standard deviations

Fig.8. Thickness change in a cyclic accelerated aging treatment. *Error bars* indicate standard deviations

Fig.9. Weight change in a cyclic accelerated aging treatment. *Error bars* indicate standard deviations

Table

Table 1. Viscosity and pH of mixture solutions of citric acid and sucrose.

Table 2. Manufacture condition of particleboards.

Fig.1. Particleboard bonded with citric acid and sucrose

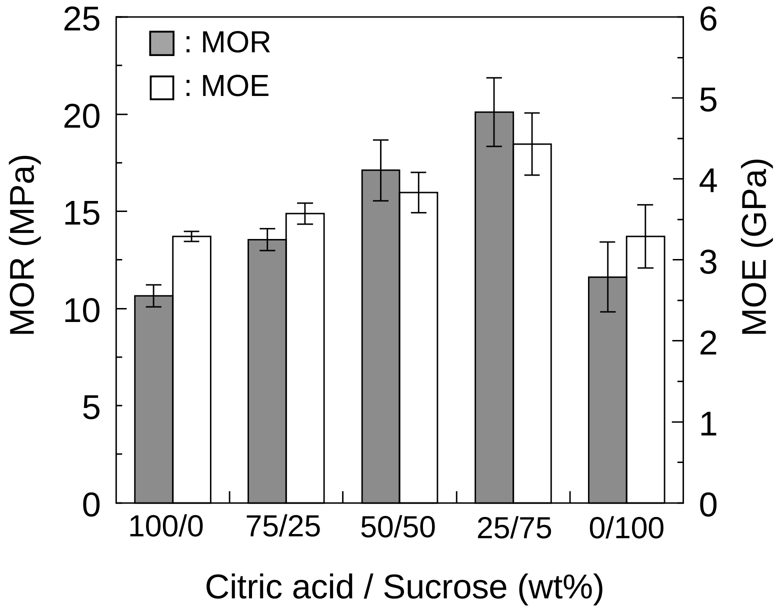

Fig.2. Effects of citric acid / sucrose ratio on bending properties. Error bars indicate standard deviations

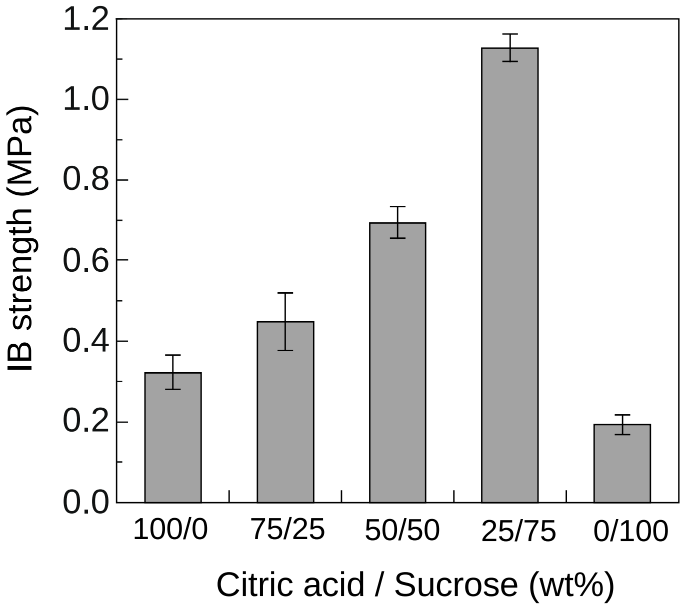

Fig.3. Effect of citric / sucrose ratio on IB strength. Error bars indicate standard deviations

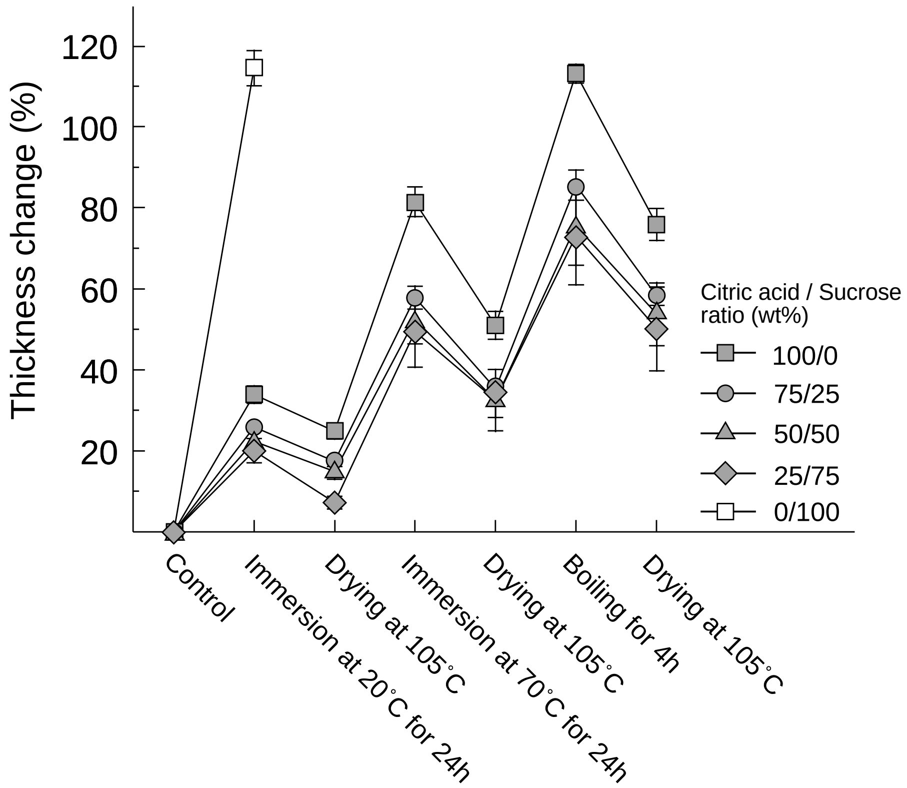

Fig.4. Thickness change in a cyclic accelerated aging treatment. Error bars indicate standard deviations

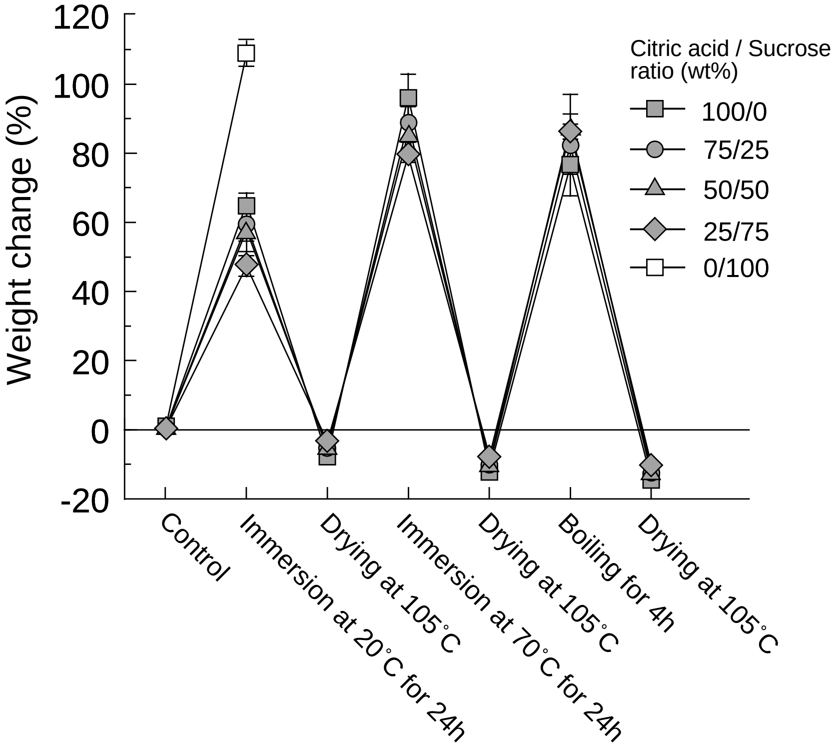

Fig.5. Weight change in a cyclic accelerated aging treatment. Error bars indicate standard deviations

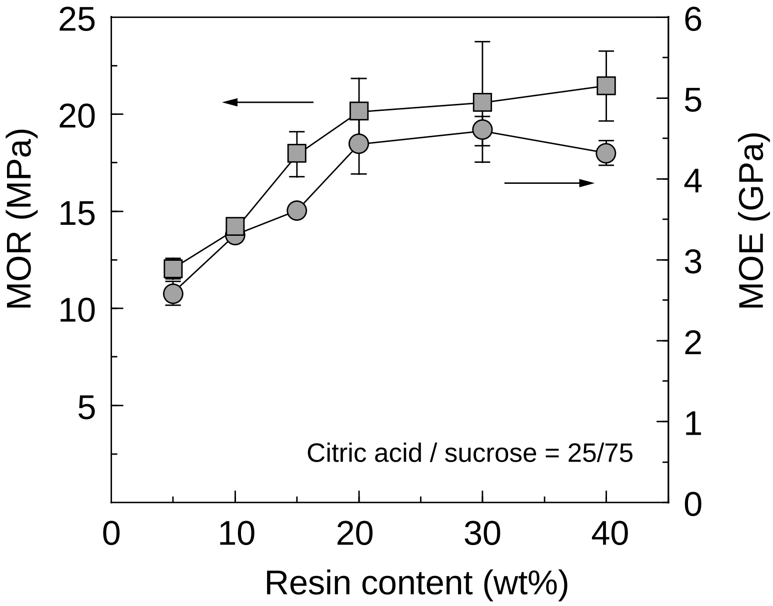

Fig.6. Effects of resin content of citric acid / sucrose on bending properties. Error bars indicate standard deviations

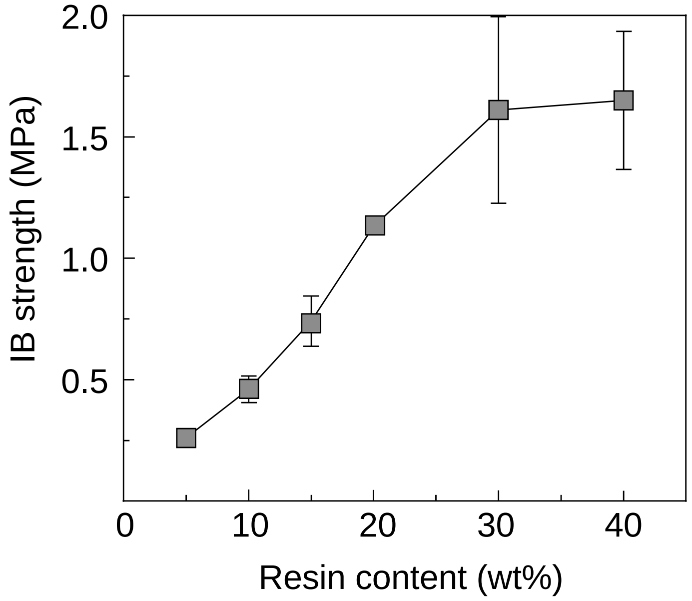

Fig.7. Effects of resin content of citric acid / sucrose on IB strength. Error bars indicate standard deviations

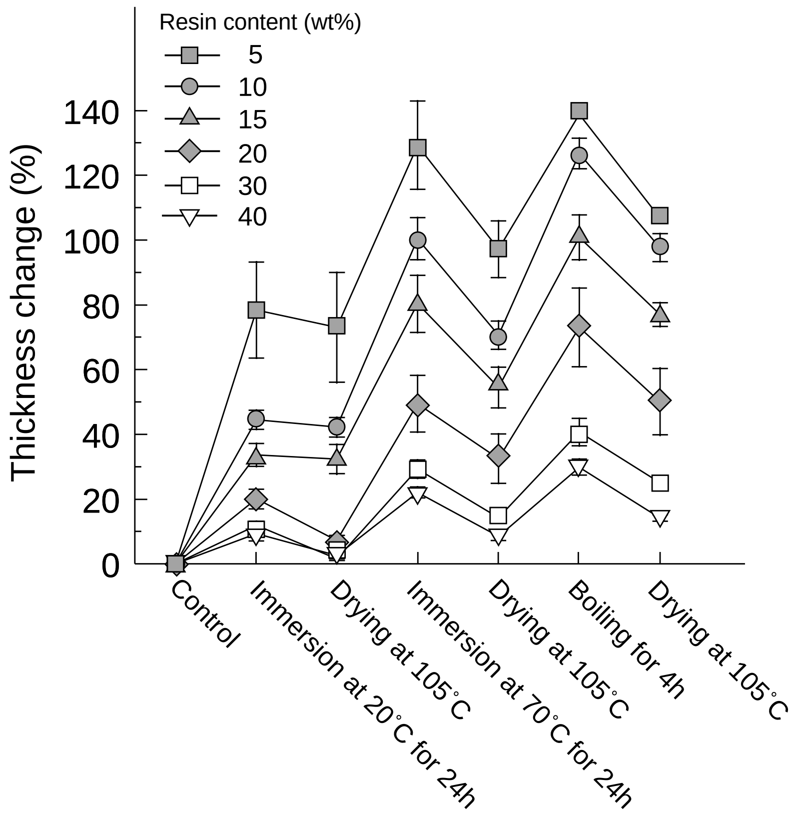

Fig.8. Thickness change in a cyclic accelerated aging treatment. Error bars indicate standard deviations

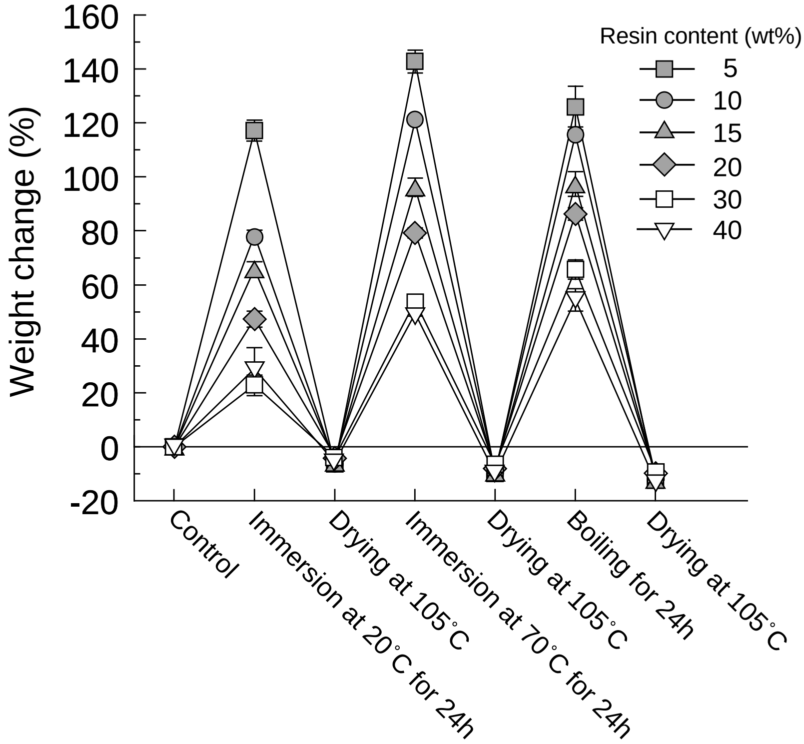

Fig.9. Weight change in a cyclic accelerated aging treatment. Error bars indicate standard deviations

Table 1. Viscosity and pH of mixture solution of citric acid and sucrose.

Mixture ratio of citric acid and sucrose (wt%)	Concentration (wt%)	Viscosity at 20˚C (mPa·S)	pH
100 : 0		59.3	0.36
75 : 25		70.4	0.54
50 : 50	59	81.9	0.80
25 : 75		93.1	1.03
0 : 100		109.2	4.30

Table 2. Manufacture condition of particleboards.

Mixture ratio of citric acid and sucrose (wt%)	Resin content (wt%)	Pressing temperature (˚C)	Pressing time (min)	Target density (g/cm^3)
100:0				
75:25				
50:50	20	200	10	0.8
25:75				
0:100				
	5			
	10			
	15			
25:75	20	200	10	0.8
	30			
	40			