Development of Wood-Based Materials Bonded with Citric Acid*

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Abstract

The development of biobased adhesives without harmful chemical agents is very important for the future. In this study, citric acid was used as a wood adhesive. Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is a very safe substance, and it is commercially produced by the fermentation of glucose or glucose- and sucrose-containing materials.

This article shows the bonding properties of citric acid in wood-based moldings and particleboards. In wood-based molding, wood and bark powders were used as elements. Citric acid powder was mixed with wood or bark powders, and the mixture was hot pressed at 200°C for 10 minutes. The wood-based moldings had good mechanical properties and excellent water resistance. When wood powder was used as an element, the specific modulus of rupture and modulus of elasticity values were 38.1 kN·m/kg and 4.9 MN·m/kg, respectively. In the case of particleboard, sucrose was used in addition to citric acid; both were dissolved in a water solution and used as an adhesive. Particleboard was manufactured at 200°C for 10 minutes. The board had good mechanical properties and water resistance. When bonded with a 25/75 ratio of citric acid and sucrose, the mechanical properties of the board were comparable to the 18 type JIS A 5908 standard. We conclude that citric acid could be used as a bioadhesive for wood.

Generally, wood-based materials, which are renewable and environmentally friendly, consist of a wood element and an adhesive. This means that adhesives are indispensable in the manufacture of wood-based materials. Large quantities of synthetic resin adhesives derived from fossil resources are currently used in the wood industry. In addition, such adhesives usually contain harmful chemical substances such as aldehyde compounds and some organic solvents that pollute the environment and cause health problems such as allergies (Shebe 2013). As part of the global sustainability effort, it is therefore desirable to reduce the use of synthetic resin adhesives. One approach to resolving this problem has been to use natural adhesives from nonfossil resources, such as biomass. Research has been conducted on conventional natural adhesives using protein, tannin, lignin, and polysaccharide as the main materials (Pizzi 2006). However, harmful chemical substances derived from fossil resources have generally still been needed to obtain a satisfactory bond performance.

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 fermentation of glucose or glucose- and sucrose-containing materials (Abou-Zeid and Ashy 1984, Tsao et al. 1999). It is a widely used substance in food, beverages, and pharmaceuticals. Citric acid has also been investigated as a cross-linking agent for wood (Vukusic et al. 2006), plant fiber (Ghosh et al. 1995), paper (Yang et al. 1996), starch (Reddy and Yang 2010), and biobased elastomers (Tran et al. 2009). Recently, it was found that citric acid has adhesiveness for wood (Umemura 2009; Umemura et al. 2012a, 2012b, 2012c, 2013). In this article, the results of research performed in

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our laboratory on the bonding properties of citric acid in wood-based moldings and particleboards are reviewed.

Materials and Methods

Materials

Bark and wood powders from the Japanese cedar (*Cryptomeria japonica*) were used. Each size of bark and wood powders was less than 150 and 250 μm, respectively. Citric acid was also powdered to less than 250 μm. The materials were vacuum dried at 60°C for 15 hours. 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 80°C for 12 hours. Citric acid and sucrose were purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and used without further purification.

Preparation and evaluation of wood-based molding

The citric acid powder was put into a beaker with the bark or wood powders. Citric acid content (percent by weight) was adjusted to 20 percent (wt/wt), giving a weight ratio of bark or wood powders/citric acid powder of 4:1. The top of the cup was covered with aluminum foil, and the cup was shaken by hand for a few seconds. A dumbbell-shaped mold of the Japanese Industrial Standard (JIS) K 7139-1966 A type was used in the molding process (JIS 2007). The powder mixture was poured into the mold and hot pressed at 200°C and 4 MPa for 10 minutes. Figure 1 shows the wood-based molding bonded with citric acid. Both edges of the dumbbell-shaped molding were cut, and rectangular specimens measuring 80 by 10 by 4 to 6 mm were prepared. The static three-point bending test was carried out under 50 mm of span and 5 mm/min of loading speed. The test was performed in triplicate, and the average value with standard deviation of the specific modulus of rupture (specific MOR) and of the specific modulus of elasticity (specific MOE) were calculated. The Charpy impact test was carried out according to JIS K 7111-1 (JIS 2006). A rectangular 80 by 10 by 4 to 6-mm specimen was prepared, and the impact strength in the flatwise direction was measured with five unnotched sample replicates. The average value and standard deviation were calculated. The weight changes caused by a repeated boiling treatment were observed using the edge (about 20 by 20 mm) of the dumbbell-shaped molding. The treatment condition was boiling water immersion for 4 hours, drying at 60°C for 20 hours in an oven, boiling water immersion for 4 hours, and finally vacuum drying at 60°C for 15 hours. The experiment was performed in triplicate, and the average value and standard deviation were calculated. The infrared spectra were obtained with a Fourier transform infrared (FT-IR) spectrophotometer, using the KBr disk method, and recorded by means of an average of 16 scans at a resolution of 4 cm^{-1}.

Preparation and evaluation of particleboard

To prepare the particleboard, sucrose was used in addition to citric acid to enhance the bond performance. Citric acid and sucrose were dissolved in water under a certain ratio, and the concentration of the solution was adjusted to 59 percent (wt/wt). The mixture ratios of citric acid/sucrose were 100/0, 75/25, 50/50, 25/75, and 0/100. The solution was used as an adhesive and sprayed onto the particles in a blender at 20 percent (wt/wt) resin content, based on the weight of the ovendried particles. The particles were mat formed (300 by 300 mm), and the mat was hot pressed at 200°C for 10 minutes. The size of the board was 300 by 300 by 9 mm, and the target density was 0.8 g/cm^3. Figure 2 shows the particleboard bonded with citric acid and sucrose. After conditioning for 1 week at 20°C and relative humidity of about 60 percent, the boards were evaluated according to the Japanese Industrial Standard for particleboard (JIS 2003). The static three-point bending test in dry conditions was conducted on a 200 by 30 by 9-mm specimen from each board. The effective span and loading speed were 150 mm and 10 mm/min, respectively. The MOR and MOE were calculated. The internal bond (IB) strength test was performed on a 50 by 50 by 9-mm specimen from each board, and thickness swelling (TS) after water immersion for 24 hours at 20°C was measured in specimens of the same size from each board. Each experiment was performed in quintuplicate, and the average value and standard deviation were calculated.

Results and Discussion

Mechanical properties of wood-based moldings

First, bond performance of citric acid was investigated in wood-based molding. Figure 3 and Table 1 show the bending properties of wood-based moldings using bark and wood powders. The specific MOR and MOE values of bark

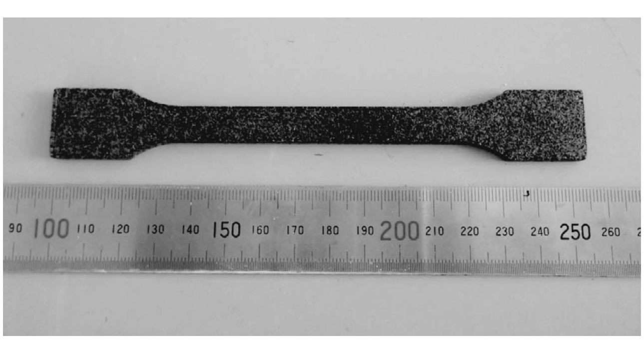

Figure 1.—Wood-based molding bonded with citric acid.

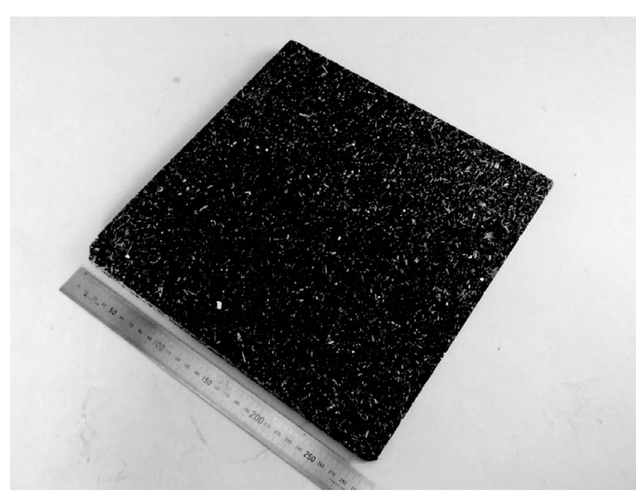

Figure 2.—Particleboard bonded with citric acid and sucrose.

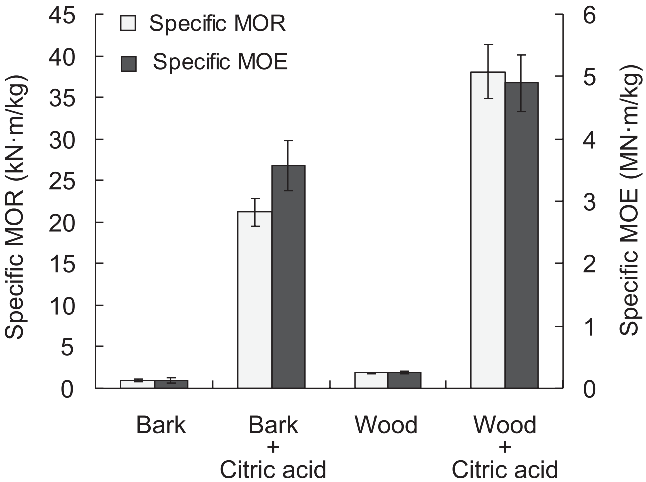

Figure 3.—Bending properties of the wood-based moldings. MOR = modulus of rupture; MOE = modulus of elasticity.

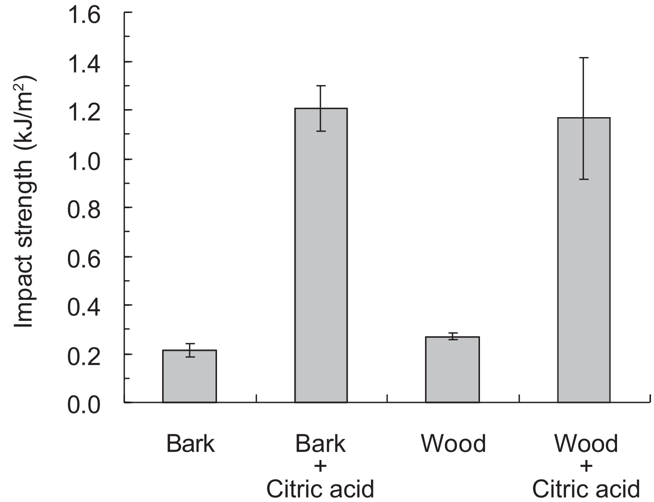

Figure 4.—Impact strength of the wood-based moldings.

powder–only molding were 0.9 kN·m/kg and 0.1 MN·m/kg, respectively. In wood powder–only molding, those values were also very low. The results indicated that the bark and wood powders developed almost no bonding strength under this molding condition. Bending properties were drastically increased, however, when citric acid was added. The specific MOR and MOE values of bark powder molding with citric acid were 21.2 kN·m/kg and 3.6 MN·m/kg, respectively, 20 times higher than those of bark powder–only molding. In wood powder molding with citric acid, the specific MOR and MOE values were 38.1 kN·m/kg and 4.9 MN·m/kg, respectively. Thus, the bending properties of wood powder molding with citric acid were superior to those of bark powder molding with citric acid. Generally, bark contains relatively more extractive and lignin content compared with wood. The different chemical components seem to cause the different bending properties.

Figure 4 and Table 1 show the impact strength of the wood-based moldings. The values of bark powder–only molding and wood powder–only molding were 0.2 and 0.3 kJ/m^2, respectively. When citric acid was added, the values were about 1.2 kJ/m^2, irrespective of the raw materials. The strength of wood-based moldings with citric acid was more than four times higher than that of the molding without citric acid. The results made it clear that the addition of citric acid substantially improves bonding properties.

Water resistance of wood-based moldings

Figure 5 shows the water resistance of wood-based moldings with citric acid in a repeated boiling treatment. The moldings prepared without citric acid decomposed completely during the first boiling treatment, while the form of the moldings with citric acid was maintained, irrespective of the raw materials. The weight increase of the wood powder molding was higher than that of the bark powder molding in both the first and second boiling treatments. This seems to be an effect of the morphology of the raw materials. Weight decrease was observed in the first and second drying treatments, indicating that some elution from the moldings occurred during boiling treatments. However, the moldings with citric acid had good water resistance, irrespective of the raw materials.

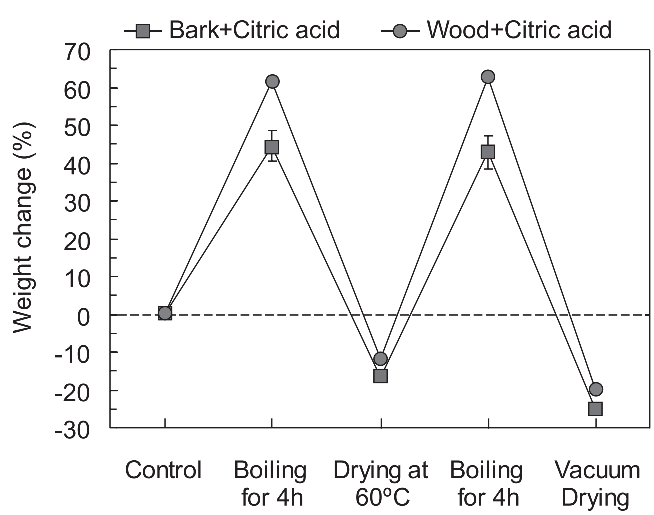

Figure 5.—Weight changes of the wood-based moldings in a repeated boiling treatment.

Table 1.—Physical properties of the wood-based moldings with citric acid.[a]

Molding	Specific MOR (kN·m/kg)	Specific MOE (MN·m/kg)	Impact strength (kJ/m^2)
Bark	0.90 (0.14)	0.13 (0.04)	0.21 (0.03)
Bark + citric acid	21.16 (1.68)	3.57 (0.41)	1.21 (0.09)
Wood	1.85 (0.10)	0.26 (0.02)	0.27 (0.02)
Wood + citric acid	38.07 (3.21)	4.89 (0.45)	1.17 (0.25)

[a] Values in parentheses are standard deviations. MOR = modulus of rupture; MOE = modulus of elasticity.

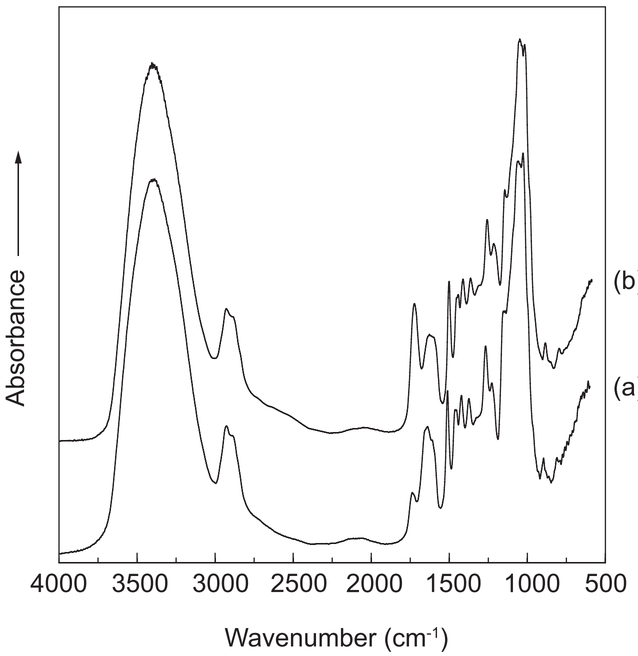

Figure 6.—Infrared spectra of wood powder (a) and wood powder molding with citric acid after repeated boiling treatment (b).

Chemical structure of wood-based molding

The chemical structure of the wood powder molding with citric acid was investigated by FT-IR. Figure 6 shows the infrared spectra of wood powder (a) and wood powder molding with citric acid after a repeated boiling treatment (b). The peaks at around 3,400 and 2,900 cm^{-1} were attributed to OH group and CH stretching and/or CH_2 valence vibration, respectively. The peak at around 1,640 cm^{-1} was ascribed to C=O stretching (Schwanninger et al. 2004). The peak of around 1,736 cm^{-1} in (b) was obviously higher than that in (a). This peak suggests ester linkages (Yang and Wang 1996, Yang et al. 1996) resulting from the reaction between the citric acid's carboxyl group and the wood's hydroxyl group. Consequently, the ester linkages brought adhesiveness, resulting in good physical properties.

Mechanical properties of particleboard

Based on the results of the moldings, manufacture of particleboard was attempted (Umemura et al. 2013). In the case of particleboard, the adhesion area of the particles used is generally smaller than that of the powder used for wood-based molding. Therefore, sucrose was added in an attempt to enhance the bond performance. Figure 7 and Table 2 show the effects of the citric acid/sucrose ratio on the bending properties. The MOR and MOE of the board bonded with citric acid only (100/0) were 10.7 MPa and 3.3 GPa, respectively. This indicated that citric acid developed a bond to some extent. The bending properties increased gradually with increased amounts of sucrose. MOR and MOE values were highest when the ratio of citric acid to sucrose was 25/75. The bending properties of the board bonded using this 25/75 ratio were comparable to type 18 of JIS A 5908 (JIS 2003). When sucrose alone (0/100) was used as an adhesive, the values were similar to those of citric acid alone. Figure 8 and Table 2 show the IB strength of the particleboards. The value increased with increasing sucrose ratio, and 1.1 MPa was recorded at a citric acid/sucrose ratio of 25/75. The addition of sucrose brought marked improvement in the bond strength between particles. The value of the board bonded with only sucrose, meanwhile, was very low. Judging from the results in Figures 5 and 6, the mechanical properties of the boards bonded with citric acid and sucrose are greatly affected by the ratio, and the optimum ratio of citric acid to sucrose was 25/75.

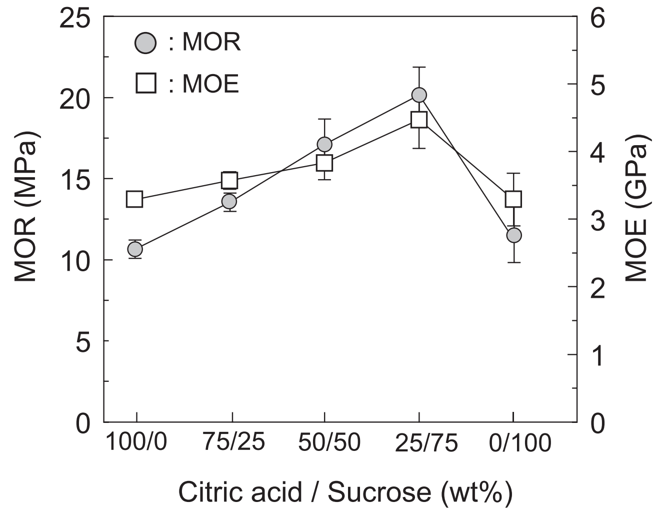

Figure 7.—Effects of citric acid/sucrose ratio on bending properties. MOR = modulus of rupture; MOE = modulus of elasticity.

Dimensional stability of particleboard

Figure 9 and Table 2 show the TS of the particleboards (Umemura et al. 2013). The TS value of the board bonded with only citric acid was 33.8 percent, and TS decreased as the sucrose ratio increased. In the case of the optimum bonding ratio of 25/75 of citric acid/sucrose, the TS value was lowest at 20.0 percent. The TS of the board bonded with only sucrose was over 100 percent, indicating that the

Table 2.—Physical properties of the particleboards bonded with citric acid and sucrose.[a]

Citric acid/sucrose	MOR (MPa)	MOE (GPa)	IB (MPa)	TS (%)
100/0	10.65 (0.52)	3.29 (0.05)	0.32 (0.04)	33.8 (2.1)
75/25	13.55 (0.51)	3.57 (0.12)	0.45 (0.07)	25.9 (0.7)
50/50	17.11 (1.52)	3.83 (0.24)	0.69 (0.04)	22.4 (2.5)
25/75	20.11 (1.72)	4.43 (0.37)	1.13 (0.03)	20.0 (3.0)
0/100	11.62 (1.75)	3.29 (0.38)	0.19 (0.02)	114.6 (4.2)

[a] Values in parentheses are standard deviations. MOR = modulus of rupture; MOE = modulus of elasticity; IB = internal bond; TS = thickness swelling.

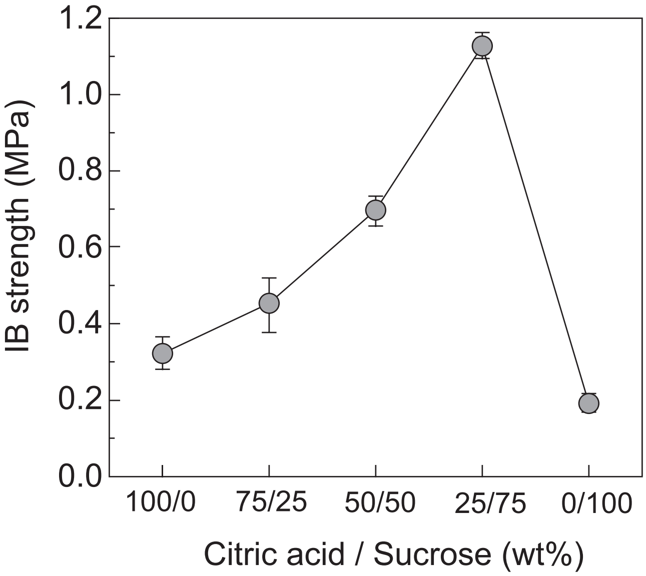

Figure 8.—Effect of citric acid/sucrose ratio on internal bond (IB) strength.

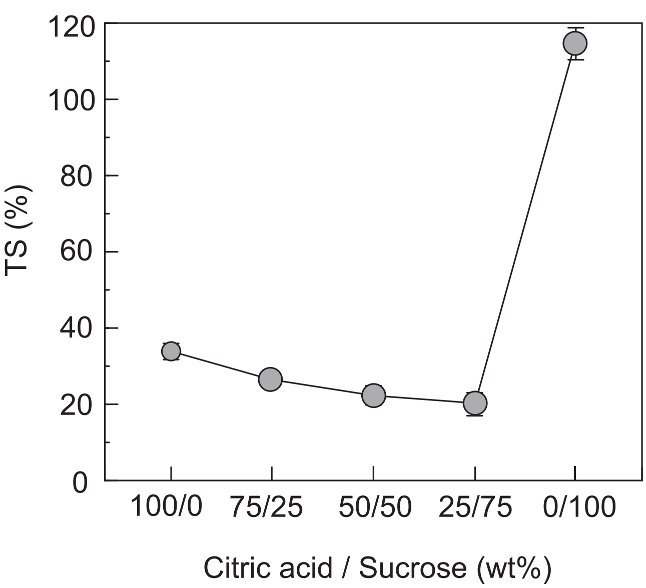

Figure 9.—Effect of citric acid/sucrose ratio on thickness swelling (TS).

dimensional stability was extremely low. Considering the results of wood-based moldings, citric acid seems to react with the sucrose and wood components. Consequently, a suitable addition of sucrose in the adhesion system would contribute to the enhancement of bond performance in particleboard. Further investigation is required to clarify the detailed reaction mechanism of citric acid and sucrose.

Conclusions

Wood-based molding and particleboard were manufactured using citric acid as an adhesive. The wood-based moldings had good mechanical properties and high water resistance. Wood powder contributed to better physical properties compared with bark powder. In particleboard, the addition of sucrose was effective in enhancing board properties. The optimum ratio of citric acid to sucrose was 25 to 75. The bending properties and IB of the board bonded at this optimum ratio of citric acid to sucrose was comparable to the standard of the 18 type JIS A 5908. There is a possibility that citric acid can be used as a natural adhesive for wood-based materials.

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Literature Cited

Abou-Zeid, A.-Z. A. and M. A. Ashy. 1984. Production of citric acid: A review. *Agric. Wastes* 9:51–76.

Ghosh, P., D. Das, and A. K. Samanta. 1995. Modification of jute with citric acid. *J. Polym. Mater*. 12:297–305.

Japanese Industrial Standards (JIS). 2003. Particleboard. JIS A 5908. Japanese Standards Association, Tokyo.

Japanese Industrial Standards (JIS). 2006. Plastics—Determination of Charpy impact properties—Part 1: Non-instrumented impact test. JIS K 7111-1. Japanese Standards Association, Tokyo.

Japanese Industrial Standards (JIS). 2007. Plastics—Multipurpose test specimens. JIS K 7139. Japanese Standards Association, Tokyo.

Pizzi, A. 2006. Recent development in eco-efficient bio-based adhesives for wood bonding: Opportunities and issues. *J. Adhes. Sci. Technol*. 20:829–846.

Reddy, N. and Y. Yang. 2010. Citric acid cross-linking of starch films. *Food Chem*. 118:702–711.

Schwanninger, M., J. C. Rodrigues, H. Pereira, and B. Hinterstoisser. 2004. Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vib. Spectrosc*. 36:23–40.

Shebe, K. A. 2013. Contact dermatitis caused by synthetic glue. *Curr. Allergy Clin. Immunol*. 26(3):152–155.

Tran, R. T., Y. Zhang, D. Gyawali, and J. Yang. 2009. Recent development on citric acid derived biodegradable elastomers. *Recent Pat. Biomed. Eng*. 2:216–227.

Tsao, G. T., N. J. Cao, J. Du, and C. S. Gong. 1999. Production of multifunctional organic acids from renewable resources. *Adv. Biochem. Eng. Biotechnol*. 65:243–278.

Umemura, K. 2009. Composition cured by applying heat/pressure thereto. PCT/JP2009/062182.

Umemura, K., O. Sugihara, and S. Kawai. 2013. Investigation of a new natural adhesive composed of citric acid and sucrose for particleboard. *J. Wood Sci*. 59(3):203–208.

Umemura, K., T. Ueda, and S. Kawai. 2012a. Characterization of wood-based molding with citric acid. *J. Wood Sci*. 58(1). 38–45.

Umemura, K., T. Ueda, and S. Kawai. 2012b. Effects of molding temperature on the physical properties of wood-based molding bonded with citric acid. *Forest Prod. J*. 62(1):63–68.

Umemura, K., T. Ueda, S. S. Munawar, and S. Kawai. 2012c. Application of citric acid as natural adhesive for wood. *J. Appl. Polym. Sci*. 123(4):1991–1996.

Vukusic, S. B., D. Katovic, C. Schramm, J. Trajkovic, and B. Sefc. 2006. Polycarboxylic acids as non-formaldehyde anti-swelling agents for wood. *Holzforschung* 60:439–444.

Yang, C. Q. and X. Wang. 1996. Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: An infrared spectroscopy study. *Tex. Res. J*. 66:595–603.

Yang, C. Q., Y. Xu, and D. Wang. 1996. FT-IR spectroscopy study of the polycarboxylic acids used for paper wet strength improvement. *Ind. Eng. Chem. Res*. 35:4037–4042.