Effects of Moulding Temperature on the Physical Properties of Wood-Based Moulding Bonded with Citric Acid

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Abstract

Development of natural adhesives that do not depend on fossil resources is very important for the future of wood-based materials. We recently found that citric acid can be used as a natural adhesive for wood-based moulding. In this study, we investigated the effects of moulding temperature on the characterization of wood-based moulding bonded with citric acid. Wood powder obtained from *Acacia mangium* was mixed with 20 percent (by weight) citric acid, and the powder mixture was moulded at a temperature ranging from 140°C to 220°C. The press pressure and heating time were set at 4 MPa and 10 minutes, respectively. The bending properties were affected by the moulding temperature, and the moulding fabricated at 180°C showed excellent values. The average impact strength of the moulding at 180°C was 1.1 kJ/m^2. Water resistance increased with moulding temperature, and good resistance against boiling water was achieved. Thermal properties were also clearly increased with moulding temperature. However, few significant differences were found in the mouldings after a repeated boiling treatment. Based on the results of Fourier transform infrared spectroscopy, ester linkages between wood and citric acid were confirmed, especially at high moulding temperatures.

Considering concerns about the future global environment and the potential shortage of fossil resources, material development based on nonfossil resources is essential. Wood-based materials are considered to be ideal because lignocellulosic biomass, which is a renewable resource, is used as a raw material. However, synthetic resin adhesives derived from fossil resources are generally used when manufacturing wood-based materials. Wood-based materials would become truly ideal if some natural adhesive based on bioresources were used in their manufacture. Although studies on natural adhesives have been carried out using protein, tannin, and lignin as the main adhesive materials (Pizzi 2006), some chemical agent derived from fossil resources was commonly necessary to obtain a satisfactory bond strength (Yang et al. 2006, El Mansouri 2007, Krug 2010, Hoong et al. 2011).

We recently found that citric acid can be used as a natural adhesive for wood-based moulding (Umemura et al. 2012a, 2012b). 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 (Abou-Zeid and Ashy 1984, Tsao et al. 1999). It is widely used in food, beverages, and pharmaceuticals. In addition, citric acid has been researched as a cross-linking agent for wood (Vukusic et al. 2006, Bogoslav et al. 2009), plant fiber (Ghosh et al. 1995), paper (Yang et al. 1996), starch (Reddy and Yang 2010), and bioresource-based elastomers (Tran et al. 2009). In our previous research, the effects of citric acid content on the basic physical properties of wood-based mouldings were clarified under fabricating conditions at 200°C and 4 MPa for 10 minutes (Umemura et al. 2012a). The wood-based moulding showed excellent properties at a citric acid content of 20 percent by weight. However, the effects of moulding temperature on these physical properties remain unknown. In the present study, moulding temperatures from 140°C to 220°C were tested under a constant citric acid content of 20 percent by weight,

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Forest Prod. J. 62(1):63–68.

and the optimum moulding temperature to achieve good physical properties was determined.

Materials and Methods

Materials

A wood block of *Acacia mangium* was pulverized, and wood powder was obtained by using a sieve with a mesh size of 250 μm. Citric acid (anhydrous) was also pulverized into a powder with mesh size of less than 250 μm. These materials were vacuum dried at 60°C for 15 hours. The moisture content of wood powder was 0.82 percent.

Moulding preparation

The citric acid powder was put into a plastic cup with the wood powder. The citric acid content was adjusted to 20.0 percent (by weight), giving a weight ratio of wood:citric acid of 4:1. Details regarding the formulations are shown in Table 1. The top of the cup was covered with aluminum foil, and the cup was shaken vigorously by hand for a few seconds. A cylindrical mould with an inner diameter of 70 mm and a dumbbell-shaped mould (A type) of the Japanese Industrial Standard (JIS) K 7139 (JIS 2007) were used for making moulding. The mixed powder was poured into the moulds and hot pressed at 140°C, 160°C, 180°C, 200°C, and 220°C. The press pressure and pressing time were 4 MPa and 10 minutes, respectively. The diameter of the cylindrical moulding was 70 mm, and the thickness was 2 to 3 mm. The overall length of the dumbbell-shaped moulding was 153 mm with a narrow section 80 mm long, and the width was 20 mm with a narrow section 10 mm. The thickness was 4 to 6 mm. The obtained mouldings were conditioned for about 1 week at 20°C and relative humidity 60 percent.

Bending test

Both edges of the dumbbell-shaped moulding were cut, and rectangular specimens 80 by 10 by 4 to 6 mm were prepared. A static three-point bending test was carried out with a span of 50 mm and a loading speed of 5 mm/min. The test was performed in triplicate, and each average value with standard deviation of the modulus of rupture (MOR) and the modulus of elasticity (MOE) was calculated.

Charpy impact test

According to JIS K 7111-1 (JIS 2006a), a Charpy impact test was performed using a digital impact tester (DG-CD; Toyo Seiki Seisaku-sho, Ltd.). A rectangular 80 by 10 by 4 to 6-mm specimen from the dumbbell-shaped moulding was used, and the impact strength in the flatwise direction without notch was measured. The average value and standard deviation of five specimens was calculated.

Repeated boiling treatment

Weight and thickness changes caused by a repeated boiling treatment were observed using the edge (about 20 by 20 mm) of the dumbbell-shaped moulding. The edge was vacuum dried at 60°C for 15 hours prior to the treatment. The treatment conditions were immersion in boiling water for 4 hours, drying at 60°C for 20 hours in an oven, boiling water immersion for 4 hours, and vacuum drying at 60°C for 15 hours. The experiment was performed in triplicate, and the average value with standard deviation was calculated.

Table 1.—Formulation of the mouldings.

	Wood powder (g)	Citric acid powder (g)
Dumbbell-shaped mould	8.0	2.0
Cylindrical mould	10.0	2.5

Thermal analysis

The obtained moulding was pulverized into a powder with a mesh size of less than 150 μm, and the powder was vacuum dried at 60°C for 15 hours. Thermogravimetric analysis (TGA) was carried out using a TGA 2050 (TA Instruments, Japan). The powder was scanned from room temperature to 550°C at a rate of 10°C/min under nitrogen purging. Differential scanning calorimetric (DSC) measurement was taken using a DSC 2910 (TA Instruments). The powder was encapsulated in an aluminum pan and scanned from room temperature to 350°C at a rate of 10°C/min under nitrogen purging.

FTIR spectroscopy

All infrared spectra were obtained with a Fourier transform infrared (FTIR) spectrophotometer (FT/IR-4200; JASCO Corporation) using the KBr disk method and were recorded with an average of 16 scans at a resolution of 4 cm^{-1}.

Results and Discussion

Mechanical properties

Table 2 shows the effect of moulding temperature on the apparent density of the moulding specimen used for the bending test. The apparent density ranged from 0.73 to 1.18 g/cm^3, and density tended to increase with increasing temperature. The density at 140°C was extremely low because this temperature is lower than the melting temperature of citric acid. The moisture content of the specimen was about 5.73 percent. Figure 1 shows the relationship between moulding temperature and bending properties. The moulding at 140°C developed almost no bending properties. Bending properties were definitely observed, however, at temperatures of 160°C and higher. The maximum average value of MOR was 39.1 MPa at 180°C, and the specific MOR considering the density was 35.0 MPa. The maximum average value of MOE was 6.1 GPa at the same temperature, and the specific MOE was 5.5 GPa. Temperatures above 180°C brought a decrease in bending properties, possibly because citric acid decomposes and evaporates remarkably and small cracks develop in the moulding. Figure 2 shows the impact strength of the mouldings at 180°C and 200°C. The strength at 180°C was higher than that at 200°C, and the average value at 180°C was 1.1 kJ/m^2. Based on the results shown in Figures 2 and 3, the optimum moulding temperature for mechanical properties was 180°C. It was clarified that the mechanical properties of the moulding at 180°C sufficiently met the standard values of JIS A 5741 (wood–plastic recycled composite; JIS 2006b).

Water resistance

Figure 3 shows the effect of moulding temperature on weight change in a repeated boiling treatment. The mouldings at 140°C and 160°C decomposed completely

Table 2.—Density of the mouldings.

	Temperature (°C)				
	140	160	180	200	220
Density (SD) (g/cm^3)	0.73 (0.004)	1.04 (0.011)	1.12 (0.017)	1.18 (0.024)	1.14 (0.042)

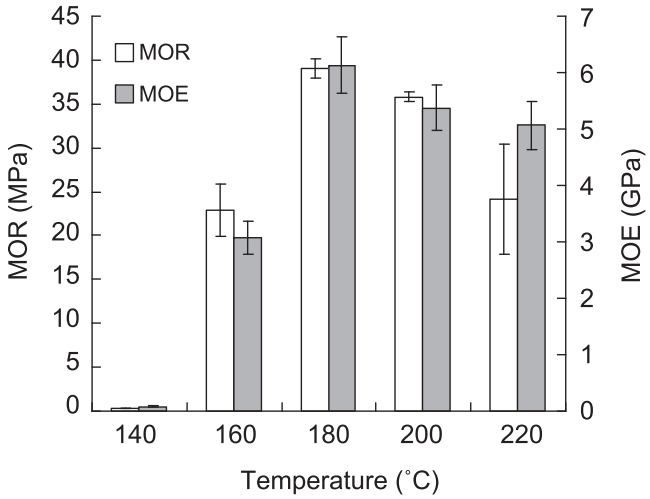

Figure 1.—Bending properties of the mouldings.

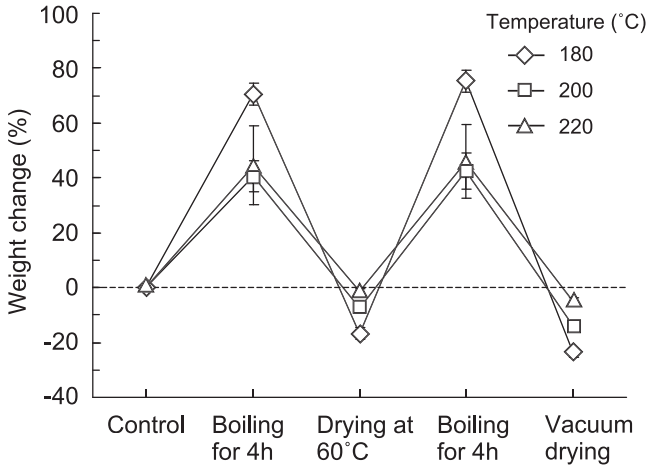

Figure 3.—Weight changes of the mouldings under a repeated boiling treatment.

during the first boiling treatment. The weight change of the moulding at 180°C was large compared with that of the mouldings at 200°C and 220°C. A weight decrease of −24 percent was observed after the second drying treatment, indicating that remarkable elution from the moulding occurred during the treatment. If the mouldings at 200°C and 220°C were compared, the amount of weight decrease in drying treatments was smaller in the moulding at 220°C. Figure 4 shows thickness changes in the treatment. In the case of moulding at 180°C, the change in thickness after the first boiling treatment was 48.9 percent and the value following the second treatment was 54.6 percent. The final dried thickness change was 28.4 percent. Although the moulding kept its form even after the treatment, a remarkable increase in thickness was observed. The thickness change of the moulding at 200°C was greatly suppressed, and the final dried thickness change was only 6.2 percent; the change in the moulding at 220°C was even smaller. Based on the results shown in Figures 4 and 5, it was clarified that the moulding developed water resistance at temperatures above 180°C and that water resistance improved with increasing moulding temperature.

Thermal properties

Figure 5 shows the thermogravimetric (TG) and derivative TG (DTG) curves of the mouldings. The moulding at 140°C exhibited a two-step degradation. The first stage was observed around 200°C and can be attributed to the decomposition of substances derived from citric acid (Umemura et al. 2012a). The second stage was seen around

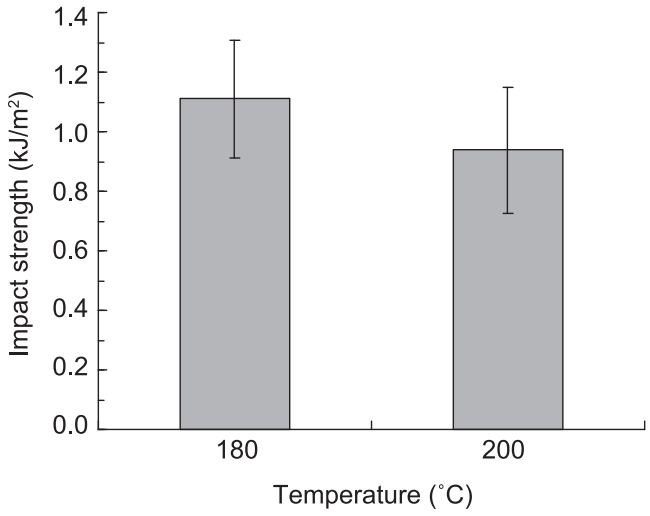

Figure 2.—Impact strength of the mouldings.

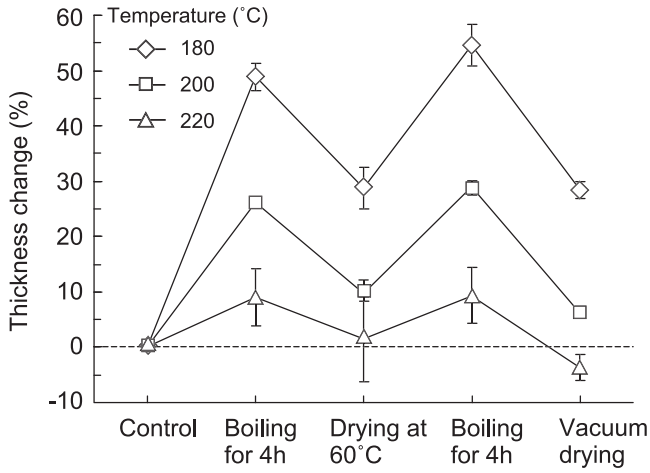

Figure 4.—Thickness changes of the mouldings under a repeated boiling treatment.

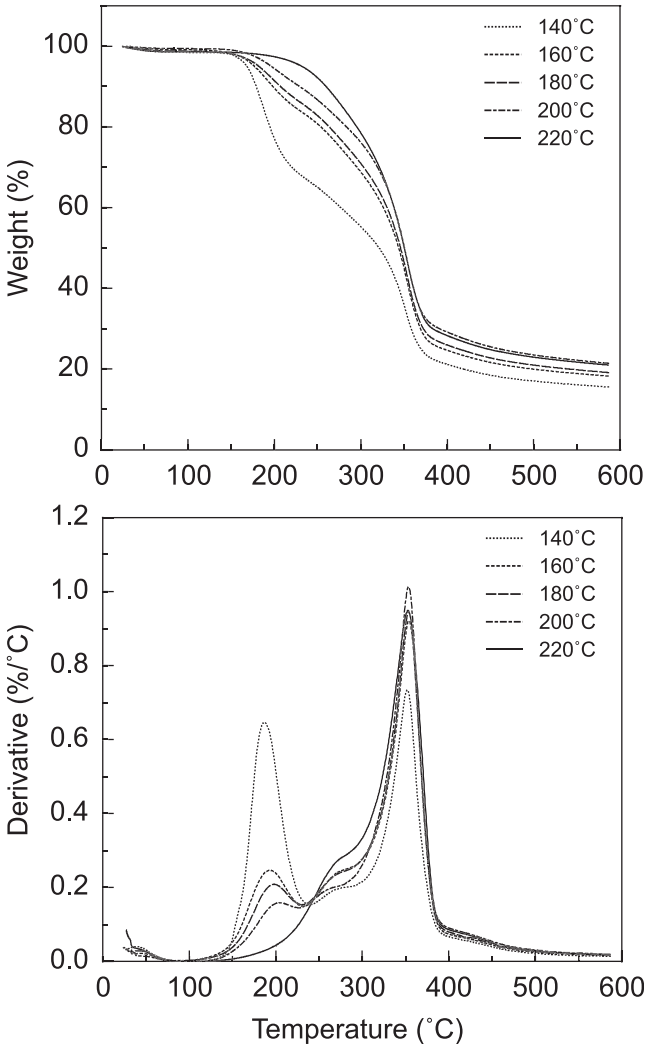

Figure 5.—Thermogravimetric and derivative thermogravimetric curves of the mouldings.

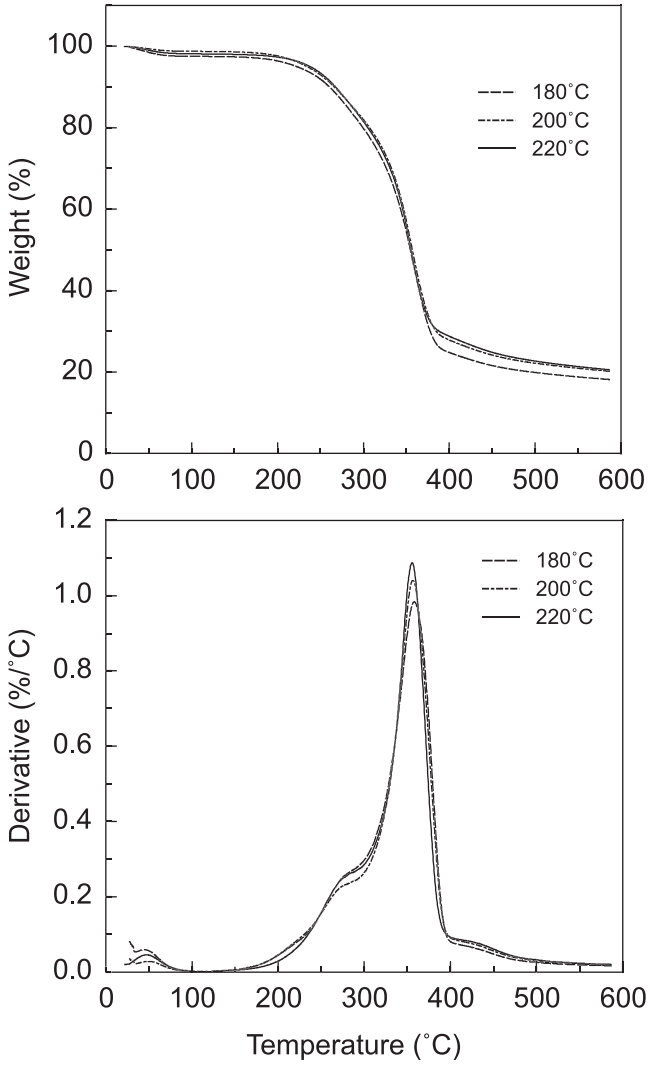

Figure 6.—Thermogravimetric and derivative thermogravimetric curves of the mouldings after a repeated boiling treatment.

350°C and can be attributed to the decomposition of cellulose (Shebani et al. 2008, Umemura et al. 2012a). In the DTG curve, the first peak around 200°C decreased with moulding temperature. The peak was scarcely observed in the moulding at 220°C, suggesting that decomposition and some reaction of citric acid may occur at high moulding temperature. The TGA of the moulding excluding the effect of substances derived from citric acid was performed using the moulding after a repeated boiling treatment. The results are shown in Figure 6. The TGA of the mouldings at 140°C and 160°C yielded no data as a result of decomposition during the treatment. In the DTG curves, no peak was observed around 200°C, indicating that the substances were completely removed in the treatment. The small shoulder around 270°C and the peak around 350°C were observed irrespective of the moulding temperature.

Figure 7 shows the DSC curves of the mouldings. A broad endotherm was observed around 120°C irrespective of moulding temperature. The weight change was scarcely recognized at that temperature, as shown in Figure 5. Therefore, the endotherm was due to the weakening of the hydrogen bonds between carbohydrates (Mehrotra et al. 2010). It is known that citric acid has a sharp endotherm at 157°C and a broad endotherm around 220°C, indicating melting and decomposition, respectively (Barbooti and Al-Sammerrai 1986, Umemura et al. 2012a). In the moulding at 140°C, a sharp endotherm at 153°C attributed to the melting of citric acid was observed; this indicates that the moulding contained pure citric acid. The mouldings heated from 160°C to 200°C showed similar behavior, and the endotherm at 153°C was not observed, probably because of a chemical change in the citric acid during moulding. The endotherm around 210°C would be due to the decomposition of substances derived from citric acid. This endotherm was shifted to a higher temperature in the moulding at 220°C. The curve change at above 250°C was attributed to a marked degradation of wood (Beall 1971, Tsujuyama and Miyamori 2000). Figure 8 shows the DSC curves of the mouldings after a repeated boiling treatment. The DSC measurement of the mouldings at 140°C and 160°C yielded no data as a result of decomposition during the treatment. On the whole, similar behavior was observed irrespective of moulding temperature. Based on the results shown in Figures 6 and 7, the endotherm around 120°C resulted from the weakening of the hydrogen bonds and the endotherm around 240°C was derived from the degradation of the moulding. The thermal

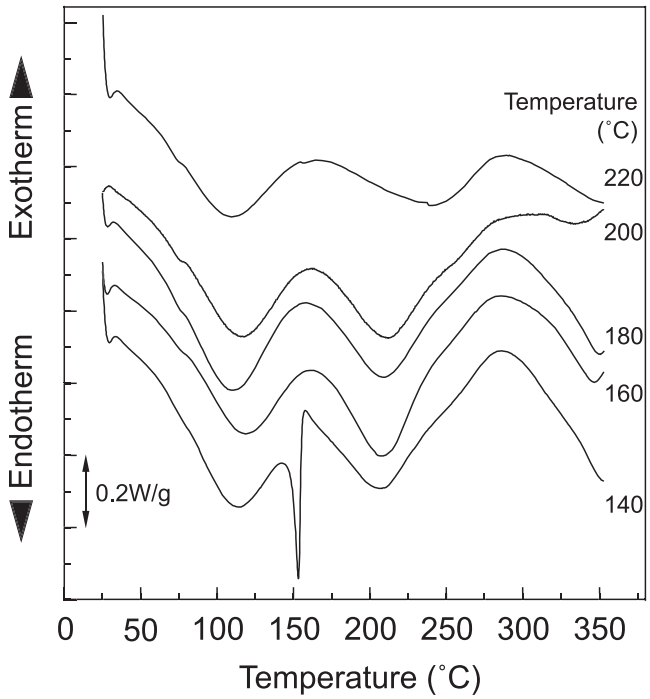

Figure 7.—Differential scanning calorimetric curves of the mouldings.

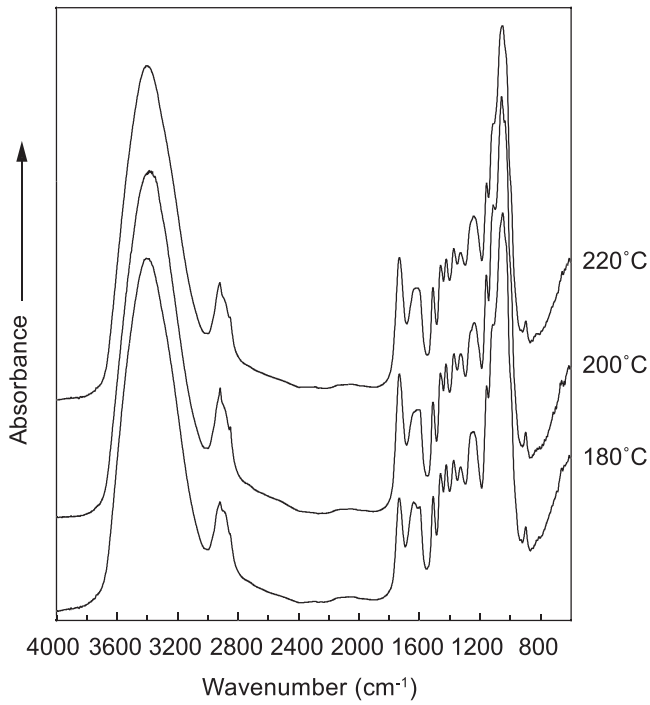

Figure 9.—Infrared spectra of the mouldings after a repeated boiling treatment.

properties of the mouldings at 180°C to 220°C were very similar.

Chemical structure of the moulding

The effect of citric acid content on the chemical structure of the moulding was investigated by FTIR. Figure 9 shows the infrared spectra of the mouldings after a repeated boiling treatment. The peak around 1,733 cm^{-1} is generally attributed to C=O stretching derived from the carboxyl group and/or the C=O ester group (Yang and Wang 1996, Žagar and Grdadolnik 2003). Taking our previous work into consideration (Umemura et al. 2012a, 2012b), this peak suggests ester linkages resulting from the reaction between citric acid and wood. The peak intensity of the mouldings at 200°C and 220°C was higher than that of moulding at 180°C, which implies an increase in ester linkages at high moulding temperatures. If one considers the results concerning mechanical properties shown in Figures 1 and 2, the increase in ester linkages does not necessarily contribute to an improvement in mechanical properties, possibly because of the involvement of morphological influences such as the occurrence of cracks at high moulding temperatures.

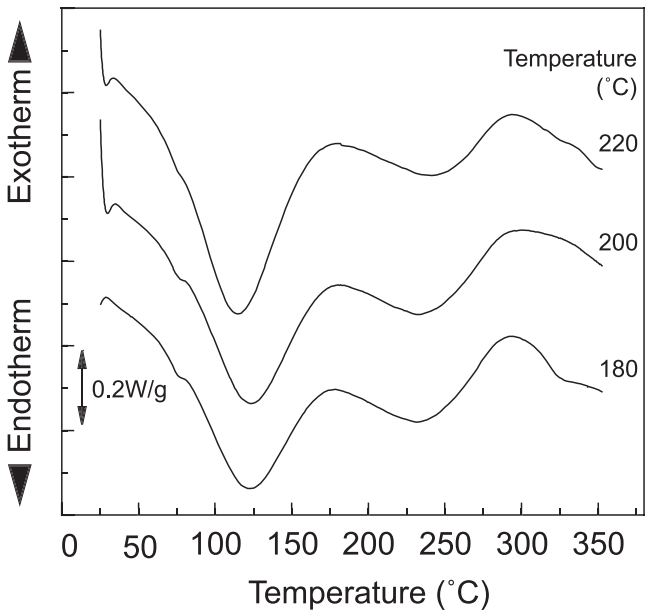

Figure 8.—Differential scanning calorimetric curves of the mouldings after a repeated boiling treatment.

Conclusions

The effects of moulding temperature on the characterization of moulding composed of wood powder and citric acid were investigated. Mechanical properties were affected by moulding temperature, and the moulding fabricated at 180°C showed excellent values. Water resistance increased with moulding temperature, and good resistance against boiling water was achieved. Thermal properties also improved with moulding temperature. In TGA and DSC measurement, a marked peak change derived from citric acid was observed only at 140°C. Few significant differences were found in the mouldings after a repeated boiling treatment, irrespective of moulding temperature. Based on the results of FTIR, ester linkages between wood and citric acid were confirmed, especially at high moulding temperatures.

Acknowledgments

This work was financially supported in part by a Grant-in-Aid for Scientific Research (C; No. 21580206) from the

Ministry of Education, Culture, Sports, Science, and Technology, Japan, and by Special Coordination Funds for Promoting Science and Technology entitled ''Creation of the paradigm of sustainable use of tropical rainforest by the intensive forest management and advanced utilization of forest resources.''

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