

Application of Citric Acid as Natural Adhesive for Wood

Kenji Umemura,¹ Tomohide Ueda,¹ Sasa Sofyan Munawar,² Shuichi Kawai¹

¹Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho Uji, Kyoto 611-0011, Japan

²Research and Development Unit for Biomaterials, Indonesian Institute of Science, Chibinong, Bogor 16911, Indonesia

Received 15 January 2011; accepted 13 April 2011

DOI 10.1002/app.34708

Published online 22 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The development of natural adhesives derived from nonfossil resources is very important for the future. Besides, it is desirable to be safe adhesives without using harmful chemical substances. In this study, application of citric acid as a natural adhesive was investigated. Citric acid powder and bark powder obtained from *Acacia mangium* were used as raw materials. Citric acid powder was mixed with the bark powder, and the resulting powder mixture was poured into a metal mold. The mold was hot-pressed at 180°C and 4 MPa for 10 min, and a bark molding was then obtained. The specific modulus of rupture and modulus of elasticity values of the molding containing 20 wt % citric acid were 18.1 MPa and 4.9 GPa, respectively. The molding did not decompose during a repeated boiling treatment. To clarify the effect of tannin on the adhesiveness

of molding, bark was separated into tannin and residue. The molding was not obtained while using the tannin due to the marked fluidity, whereas it was obtained while using the residue, the same as while using the bark. It was considered that components other than tannin contributed to the adhesiveness. Based on the results of Fourier transform infrared spectra, the formation of ester linkages between carboxyl groups derived from citric acid and hydroxyl groups in the bark was confirmed. Accordingly, citric acid brought an adhesion by chemical bonding, and it could be used as a safe natural adhesive. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1991–1996, 2012

Key words: adhesives; citric acid; biomaterials; molding; bark

INTRODUCTION

Wood-based materials are renewable and environmentally friendly materials because lignocellulosic biomass, which is renewable resources, is used as a raw material. However, large quantities of synthetic resin adhesives derived from fossil resource are needed when manufacturing wood-based materials in the wood industry. In addition, harmful chemical substances are usually contained in the adhesives. Considering the future global environment, it is desirable to reduce the use of synthetic resin adhesives containing harmful chemical substances.

Many researches have been carried out to investigate ways of reducing the utilization of the synthetic adhesives. For example, there has been reports regarding natural adhesives,¹ binderless board,^{2–4} and chemical surface activation of wood.^{5,6} Natural adhesives use natural polymers derived from plants and animals as raw materials. However, some chem-

ical modification of natural polymers using harmful chemical agents and addition of some synthetic resin are commonly needed for developing the good bonding properties. Binderless board is bonded by the chemical components contained in the raw material without the use of adhesives. This type of board, however, is problematic in that the kinds of raw materials are restricted and the physical properties are not acceptable. Chemical surface activation of wood is a technique in which components such as lignin and hemicellulose of the surface are activated by chemical treatment. In this treatment, some oxidizing agents, strong acids, and alkalis, which are harmful substances, are usually required. Accordingly, further research on a safe and environmentally friendly natural adhesive is important.

In this research, we paid attention to citric acid which is a natural organic polycarboxylic acid containing three carboxyl groups. Citric acid is contained in citrus fruits such as lemons and limes, however, it is commercially produced by fermentation of glucose or glucose- and sucrose-containing materials. Citric acid is widely used in foods, beverages, and pharmaceuticals. In addition, it has been researched as a cross-linking agent to improve the physical and mechanical properties of wood,⁷ plant fiber,⁸ paper,⁹ and starch.¹⁰ However, application of citric acid as a main material of wood adhesive has never been examined. In this study, the possibility

Correspondence to: K. Umemura (umemura@rish.kyoto-u.ac.jp).

Contract grant sponsor: Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Culture, Sports, Science and Technology, Japan; contract grant number: 21580206

TABLE I
Formulation of Moldings

Citric acid content (wt %)	Weight ratio of citric acid to bark matter	Mold for JIS K 7139		Cylindrical mold	
		Bark matter (g)	Citric acid (g)	Bark matter (g)	Citric acid (g)
0.0	10 : 0	10.00	0.00	10.00	0.00
11.1	8 : 1	8.89	1.11		1.25
20.0	4 : 1	8.00	2.00		2.50
33.3	2 : 1	6.67	3.33		5.00
40.0	1.5 : 1	6.00	4.00		6.67

of citric acid as a natural adhesive for wood was investigated by fabricating bark moldings.

MATERIALS AND METHODS

Materials

Acacia mangium bark powder was obtained from Koshii Wood Solutions Co. The powder size was less than 150 μm , and the chemical components were as follows: tannin (methanol extract): 30%, lignin: 44.7%, holocellulose: 20.3%, and ash: 5.0%. Citric acid was purchased from Nacalai Tesque and was powdered to <250 μm . The materials were vacuum-dried at 60°C for 15 h.

Separation of tannin

One hundred grams of the raw bark powder was extracted with 1000 mL of 70% acetone aqueous solution¹¹ for 48 h at room temperature. After filtration, the filtrate containing tannin was vacuum-concentrated using a rotary-evaporator and freeze-dried. On the other hand, the residue after filtration was washed with distilled water and vacuum-dried at 60°C. The dried tannin and residue powders were stored in a desiccator with silica gel.

Making of molding

First, the citric acid and the bark matter were put into a plastic cup. The top of the cup was covered with aluminum foil, and the cup was shaken for a few seconds. The citric acid contents (wt %) were adjusted to 0, 11.1, 20.0, 33.3, and 40.0, giving weight ratios of bark matter/citric acid of 10 : 0, 8 : 1, 4 : 1, 2 : 1, and 1.5 : 1. Details regarding the formulations are shown in Table I. A cylindrical mold with a 70 mm inner diameter and a dumbbell-shaped mold for Japanese Industrial Standards (JIS) K 7139-1966 A type were prepared. The mixture powder was poured into each mold and hot-pressed at 180°C and 4 MPa for 10 min. The molding was obtained and was stored in a desiccator with silica gel.

Evaluation of molding

Both edges of the dumbbell-shaped molding were cut, and a rectangular specimen of 80 \times 10 \times 2–4 mm was prepared. The static three-point bending test was carried out under air-dry condition. The effective span and loading speed were 50 mm and 5 mm/min, respectively. The modulus of rupture (MOR) and the modulus of elasticity (MOE) were calculated. Water immersion treatment at 20°C for 24 h was performed using a rectangular specimen (50 \times 20 mm) cut from the circular molding. After the treatment, weight change was measured under wet condition. The wet specimen was then vacuum-dried at 60°C for 15 h, and the dry weight was measured. A repeated boiling treatment was also performed using the edge (about 20 \times 20 mm) of the dumbbell-shaped molding. The treatment condition was boiling water immersion for 4 h, drying at 60°C for 20 h in an oven, boiling water immersion for 4 h and vacuum-drying at 60°C for 15 h. The specimen weight was measured at each stage.

Fourier transform infrared (FTIR) spectroscopy

FTIR measurements of the moldings were performed. In the case of the repeated boiling treatment, the specimen (about 20 \times 20 mm) was inserted into an extraction thimble, and the top of the thimble was stapled. The thimble including the specimen was treated in boiling water. After the treatment, the specimen was vacuum-dried at 60°C for 15 h. All of the infrared spectra were obtained with an FTIR spectrometer (FT/IR-4200, JASCO Corp.) by using the KBr disk method and were recorded by means of an average of 32 scans at a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

Effects of citric acid content on bending properties

When raw bark powder was molded with citric acid powder, the dark brown molding was obtained. As an example, the molding containing 20 wt % citric

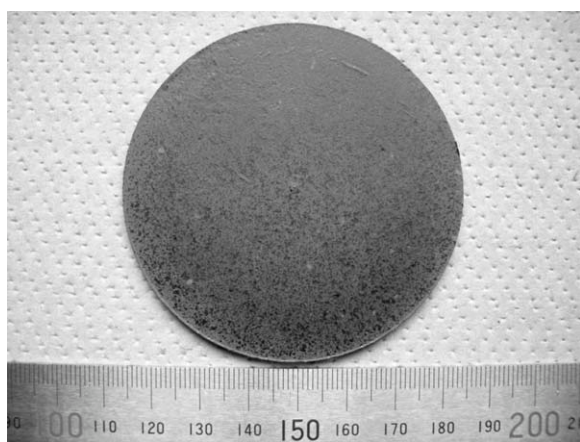


Photo 1 The bark molding with citric acid.

acid is shown in Photo 1. Figure 1 shows the effects of citric acid content on the MOR of the moldings. The obtained molding densities ranged from 0.9 to 1.3 g/cm³. The value of bark-only molding (0 wt %) was 1.5 MPa, indicating that the bark powder developed almost no bonding strength under this molding condition. The value drastically increased as citric acid content increased. The maximum value was 23.4 MPa with a 20 wt % citric acid content. The specific MOR considering the density of the molding was 18.1 MPa. The above 20 wt % content brought a decrease in MOR. Figure 2 shows the effects of citric acid content on the MOE. The value increased with increasing citric acid content up to 20 wt %, reaching a maximum of 6.3 GPa. A further increase in the content resulted in a decrease in the value. The specific MOE also showed a similar trend. Judging from the results in Figures 1 and 2, the addition of citric acid was effective for development of good bending

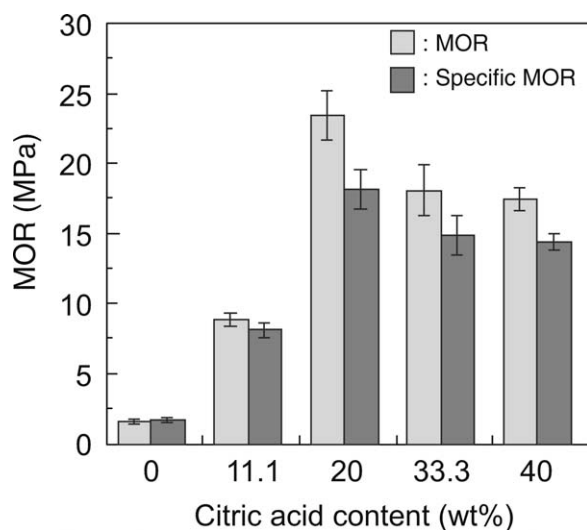


Figure 1 Relationship between citric acid content and MOR.

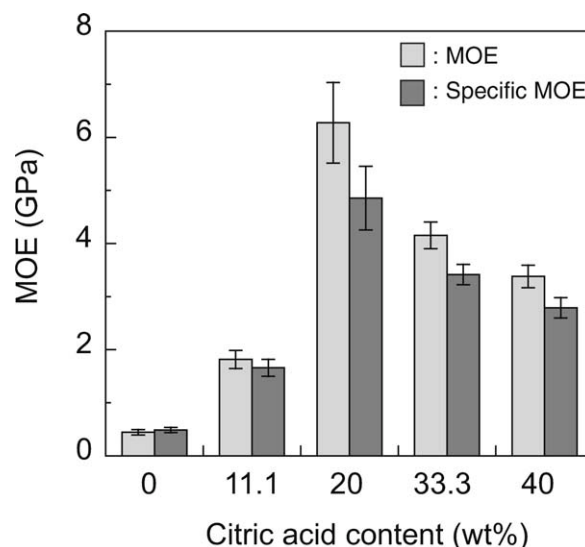


Figure 2 Relationship between citric acid content and MOE.

properties, and the appropriate content of citric acid was 20 wt %. It was confirmed that citric acid acted as an adhesive. The poor bending properties at the high citric acid content would be due to the excess citric acid in the molding.

Effects of citric acid content on water resistance

To investigate the water resistance of the molding bonded with citric acid, weight changes in water immersion treatment were observed. The results were shown in Figure 3. In the case of the bark-only molding, the weight increased to 55.8%. After drying, the weight was recorded as -2.8%. This means that absorption and desorption of water mainly occurred. In the molding bonded with citric acid, the weight increase was inhibited by increasing the citric acid content. The value of the molding

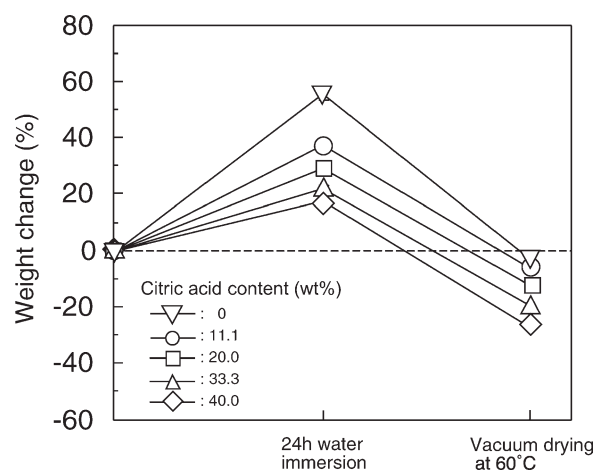


Figure 3 Weight changes of moldings in water immersion treatment.

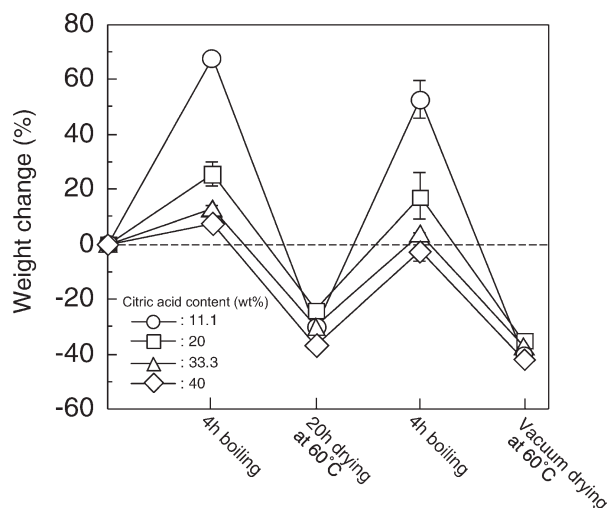


Figure 4 Weight changes of moldings in repeated boiling treatment.

containing 40 wt % citric acid showed 17.6%. However, the weight after drying tended to decrease with increasing citric acid content, and the maximum decrease value was -27.3% . Considering the result of the bark-only molding, the cause seemed to be elution of substances related to citric acid. It is known that citric acid melts at 153°C and dehydrates to give aconitic acid on heating at 175°C .¹² Therefore, citric acid might convert to aconitic acid in this study, and further investigation is required to identify the formation. At least, however both compounds are water-soluble. As the effect of citric acid on water resistance of the molding remained ambiguous in this treatment, a repeated boiling treatment was performed. The results are shown in Figure 4. While the bark-only molding decomposed completely in the first boiling treatment, the molding

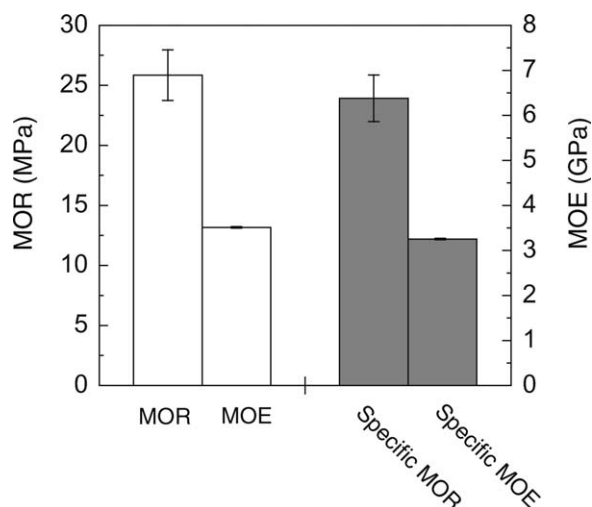


Figure 5 Bending properties of molding with residue and citric acid (wt %).

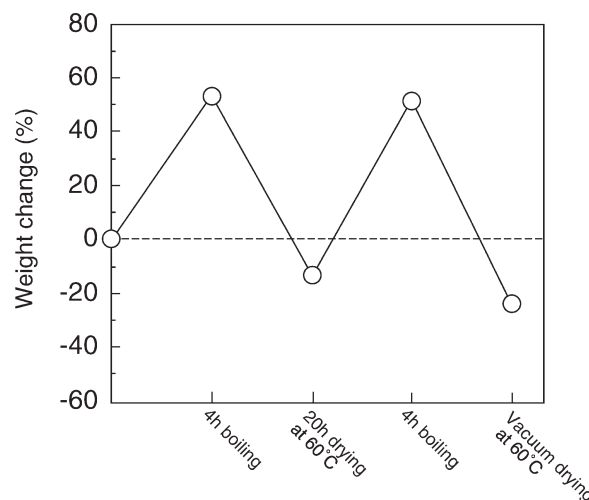


Figure 6 Weight changes of residue molding in repeated boiling treatment.

containing citric acid did not decompose irrespective of the amount of citric acid during the treatment. The weight increase in the first boiling treatment was inhibited with increasing citric acid content. The marked effect was observed in addition of 20 wt % and more. Weight decreases ranging from -25 to -37% were observed in the first drying treatment, indicating that some elution from molding occurred during the first boiling treatment. The trend of weight increase in the second boiling treatment was similar to that of the first boiling treatment. The range of weight decrease in the second drying treatment following the second boiling treatment was -35 to -42% , and marked differences by the amount of citric acid were hardly recognized. Comparing the weight decrease between the first and second drying treatments, a large difference was not observed.

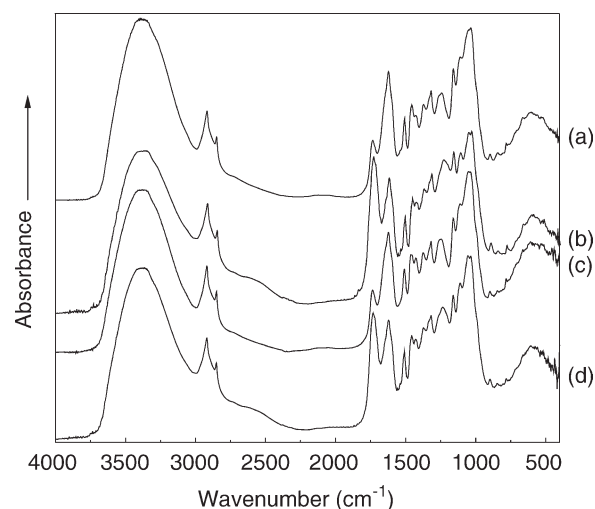


Figure 7 Infrared spectra of (a) bark-only molding, (b) bark molding with citric acid 20 wt %, (c) bark-only molding after repeated boiling treatment, (d) bark molding with citric acid 20 wt % after repeated boiling treatment.

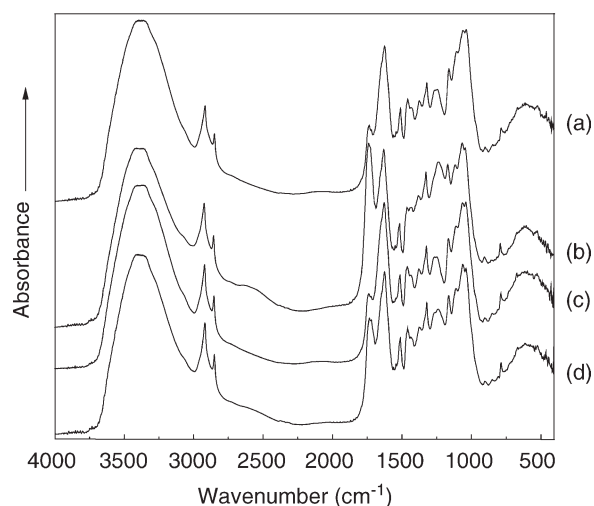


Figure 8 Infrared spectra of (a) residue-only molding, (b) residue molding with citric acid 20 wt %, (c) residue-only molding after repeated boiling treatment, (d) residue molding with citric acid 20 wt % after repeated boiling treatment.

Based on the result obtained, it was clarified that the molding bonded with citric acid had high water resistance although containing some soluble substances. Accordingly, citric acid can be expected as a water resistance adhesive.

Effects of bark component on adhesiveness

The bark of genus *Acacia* has been researched as a raw material for formaldehyde-based resin adhesives^{13–15} because condensed tannin contained in the bark has high reactivity. There is the possibility that the tannin contributes to the adhesiveness of the molding. The tannin was extracted from the bark powder, and the mixture powder of the extracted tannin and citric acid (20 wt %) was molded. However, the molding was not obtained due to the marked fluidity, and the solid after cooling was very brittle. On the other hand, the residue powder was able to fabricate the molding with citric acid, as is the case with bark powder. Consequently, it seemed that some component except for the tannin contributed to the adhesiveness. Figure 5 shows the bending properties of the molding with the residue and citric acid (20 wt %). The values of MOR and MOE were 25.9 MPa and 3.5 GPa, respectively. Compared with the molding with bark in Figures 1 and 2, the MOR value was similar, but the MOE was reduced by approximately half. Figure 6 shows the weight change of the molding in repeated boiling treatment. The weight increased by 53.6% in first boiling treatment and then decreased by –13.5% in the subsequent drying treatment. The weight decrease in the second drying treatment following the second boiling treatment was –23.4%. Compared with the bark

molding in Figure 4, the residue molding absorbed much water during boiling treatment and showed a little elution during dry treatment. This result suggested that the residue molding had some voids and good adhesiveness due to the tannin extraction treatment. As a result, it seemed that the bending properties were also affected.

Bonding mechanism

To clarify the development of adhesiveness by adding citric acid, FTIR measurements were performed. Figure 7 shows the FTIR spectra of bark moldings. Comparing the bark-only molding (a) and the bark molding with citric acid (b), the absorption band at 1734 cm^{-1} of (b) was higher than that of (a). This absorption band was ascribed to C=O stretching derived from carbonyl groups.^{16,17} Considering the difference of citric acid addition, the strong peak in (b) was the carboxyl groups derived from citric acid. The infrared spectrum of the bark-only molding after repeated boiling treatment (c) was very similar to that of (a), indicating that the effect of the treatment on the spectrum were hardly recognized. The infrared spectrum of the bark molding with citric acid after repeated boiling treatment (d) was similar to that of (b), except that the absorption peak at 1734 cm^{-1} was a little small. The cause would be due to the elution of substances related to citric acid. However, the peak was apparently higher than that of (c). Therefore, the peak of 1734 cm^{-1} in (d) was attributed to the formation of ester linkages. This is also borne out by the fact that the molding with citric acid had good bending properties and high water resistances. Figure 8 shows the FTIR spectra of residue moldings. The spectra of (a) and (c) were very similar. This indicated that the change of spectra by the repeated boiling treatment was hardly recognized. In the case of citric acid addition, the strong absorption peak at 1732 cm^{-1} derived from citric acid was observed in (b). The absorption peak decreased by repeated boiling treatment as shown in (d), because the elution of substances related to citric acid occurred. However, the absorption peak of (d) was clearly higher than that of (b). The formation of ester linkages was confirmed even when residue molding. Consequently, the ester linkages between carboxyl groups derived from citric acid and hydroxyl groups of bark component brought adhesiveness causing good physical properties. Further research on using citric acid as an adhesive for wood will be reported in a future article.

CONCLUSIONS

Citric acid was used as a natural adhesive to fabricate the bark molding. The molding obtained had

good bending properties, and the specific MOR and MOE values under the optimum condition of 20 wt % citric acid content were 18.1 MPa and 4.9 GPa, respectively. Based on the results of water resistance tests, the bark molding contained some elution substances related to citric acid. However, the molding did not decompose during a repeated boiling treatment. It seemed that some component except for tannin contributed to the adhesiveness. Judging from the FTIR spectra, the ester linkages between carboxyl groups derived from citric acid and hydroxyl groups of bark were recognized. This means that adhesion by chemical bonding was performed. Accordingly, it was clarified that application of citric acid as a natural adhesive for wood is possible.

References

1. Pizzi, A. *J Adhes Sci Technol* 2006, 20, 829.
2. Ando, M.; Sato, M. *J Wood Sci* 2009, 55, 283.
3. Okuda, N.; Sato, M. *J Wood Sci* 2008, 54, 36.
4. Xu, J. Y.; Widyorini, R.; Yamauchi, H.; Kawai, S. *J Wood Sci* 2006, 52, 236.
5. Halvarsson, S.; Edlund, H.; Norgren, M. *Ind Crops Products* 2009, 29, 437.
6. Young, R. A.; Fujita, M.; River, B. H. *Wood Sci Technol* 1985, 19, 363.
7. Vukusic, S. B.; Katovic, D.; Schramm, C.; Trajkovic, J.; Sefc, B. *Holzforschung* 2006, 60, 439.
8. Ghosh, P.; Das, D.; Samanta, A. K. *J Polym Mater* 1995, 12, 297.
9. Yang, C. Q.; Xu, Y.; Wang, D. *Ind Eng Chem Res* 1996, 35, 4037.
10. Reddy, N.; Yang, Y. *Food Chem* 2010, 118, 702.
11. Makino, M.; Ohara, S.; Hashida, K. *J Trop Forest Sci* 2009, 21, 45.
12. Barbooti, M. M.; Al-Sammerral, D. A. *Thermochim Acta* 1986, 98, 119.
13. Barbosa, A. P.; Mano, E. B.; Andrade, C. T. *Forest Prod J* 2000, 50, 89.
14. Lee, W. J.; Lan, W. C. *Bioresource Technol* 2006, 97, 257.
15. Hoong, Y. B.; Paridah, M. T.; Luqman, C. A.; Koh, M. P.; Loh, Y. F. *Ind Crops Prod* 2009, 30, 416.
16. Labbe, N.; Rials, T. G.; Kelley, S. S.; Cheng, Z. M.; Kim, J. Y.; Li, Y. *Wood Sci Technol* 2005, 39, 61.
17. Schwanninger, M.; Rodrigues, J. C.; Pereira, H.; Hinterstoisser, B. *Vib Spectrosc* 2004, 36, 23.