

Characterization of Bagasse-Rind Particleboard Bonded with Chitosan

Kenji Umemura, Keiji Kaiho, Shuichi Kawai

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

Received 5 June 2008; accepted 9 November 2008

DOI 10.1002/app.29704

Published online 24 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The development of high-performance non-wood lignocellulosic board without using synthetic adhesives derived from fossils resources is very important for the future. In this study, the characterization of bagasse particleboard bonded with chitosan was investigated. The 4 wt % chitosan-acetic acid solution was sprayed onto bagasse rind particles at a 2–10 wt % chitosan solid content based on the dry particles. Particleboards with target densities of 0.75 and 0.9 g/cm³ were manufactured using a steam-injection press. The steam pressure and total pressing time were 1 MPa (180°C) and 7 min, respectively. The addition of 2–4 wt % of chitosan was the most effective in the bending properties. The

high-density board bonded with a 4 wt % addition of chitosan showed a good result in the internal bond strength test. Furthermore, the board had favorable dimensional stability in dilute acetic acid as well as in a cyclic accelerated aging test. Judging from the analysis of bagasse extract-added chitosan films, it was suggested that chitosan reacted with extract from bagasse during steam-injection pressing. The reaction seemed to contribute to the board's good resistance to dilute acid. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2103–2108, 2009

Key words: bagasse; chitosan; particleboard; physical and mechanical properties

INTRODUCTION

Recently, the preservation of forest resources has been recognized as important due to the decrease of worldwide forest area. Accordingly, the utilization of non-wood lignocellulosic resources, especially plant fiber, has been gradually increasing. Bagasse obtained from sugar cane (*Saccharum officinarum* L.) is a residue produced in large quantities by the sugar and alcohol industries. It is well known as one of the useful non-wood lignocellulosic resources.¹ In the field of wood-based materials, researches on bagasse can be divided into two main groups. One group includes research on the manufacture of boards using synthetic adhesives derived from fossil resources. Most synthetic adhesives are derived from fossil resources that cause environmental problems. Their use will unavoidably decrease in the future due to the exhaustion of the fossil resources. In addition, bagasse contains some residual sugars which may inhibit the curing of some

adhesives. The removal of sugars and the use of suitable adhesives are necessary to produce good quality board. The other group includes research on the manufacture of board without using synthetic adhesives, namely binderless board. Such board utilizes a self-bonding system by chemical components such as hemicelluloses. However, the performance of binderless board is generally very poor when compared with board that uses a suitable synthetic adhesive.² Therefore, the development of high performance board without using synthetic adhesives is very important.

Chitosan is a deacetylated derivative of chitin that is extracted mainly from crab and shrimp shells. Chitin is widely distributed in nature and is one of the most abundant biopolymers. In terms of its general properties, chitosan is a cationic polysaccharide with amino groups and is soluble in dilute acid but insoluble in water. In our previous reports, the interactions of chitosan with wood and wood components were investigated.^{3–6} It was clarified that chitosan has good bonding properties with wood, and reacts with reducing sugars such as glucose and xylose. In this study, bagasse particleboards were manufactured by using chitosan as an adhesive. The effects of the addition amount of chitosan on the physical and mechanical properties of the board were elucidated. The reactivity between chitosan and the sugar component of bagasse was also investigated.

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

Contract grant sponsor: Ministry of Education, Culture, Sports, Science and Technology, Japan; contract grant number: 18580161.

MATERIALS AND METHODS

Materials

The sugarcane (*Saccharum officinarum* L.) bagasse rinds were obtained from a company in Okinawa prefecture. The bagasse rinds were cut to about 5 cm in length, and then were milled to particles by using a knife ring flaker. The particles obtained were dried at room temperature for about 10 days. The moisture content of the dried particles was 9.9%. Furthermore, the particles were screened, and small particles less than 0.15 mm in length were removed. Purified chitosan powder was purchased from Kimica Corp. (Tokyo, Japan). The degree of deacetylation and the molecular weight were about 85% and 35,000, respectively. The chitosan powder was previously vacuum-dried at 50°C for 24 h. An acetic acid, N/400 potassium polyvinylsulfate, and 0.1% toluidine blue indicator solution were purchased from Wako Pure Chemical Industries (Osaka, Japan). The polymeric diphenylmethane diisocyanate (PMDI, COSMONATE M-201W) were obtained from Mitsui Chemicals Inc. (Tokyo, Japan).

Manufacture of particleboards

First, chitosan was dissolved in 1% acetic acid, and 4 wt % chitosan-acetic acid solution was prepared. The solution was sprayed onto the particles in a blender at 2–10% chitosan solid content based on the weight of the oven-dried particles. The chitosan-sprayed particles were dried at 50°C in an oven until the moisture content decreased to about 10%. The particles were mat-formed by using a forming box of 230 mm × 230 mm. The mat was pressed using a steam-injection press, which was sealed with a 12 mm thick stainless steel frame. A fourdrinier screen and a perforated metal plate were previously put inside of the steel frame to control the board thickness to 7 mm. The steam pressure and steam injection time were 1 MPa (180°C) and 6 min, respectively. After that, the steam was discharged and evacuated further by using a vacuum system for 1 min. That is, the total pressing time was 7 min. The size of the manufactured board was 230 mm × 230 mm × 7 mm, and the target densities were at two levels 0.75 and 0.9 g/cm³. As a reference, particleboards bonded with PMDI were manufactured. Ten percent acetone was added to the PMDI, and the solution was sprayed onto the particles in a blender at 6% solid content based on the oven-dried weight particles. The press method and target densities were the same as described above.

Evaluation of board properties

After being conditioned for 1 week under 20°C and RH 60%, the boards were evaluated according to the

Japanese Industrial Standard for particleboard (JIS A 5908, 2003). The static 3-point bending test in dry condition was conducted on specimens of 150 mm × 25 mm × 7 mm from each board. The effective span and loading speed were 75 mm and 5 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 specimens of 50 mm × 50 mm from each board, and thickness swelling (TS) after water immersion for 24 h at 20°C was measured in specimens of the same size from each board. After the above TS test, the thickness changes under cyclic-accelerated aging treatment (drying at 105°C for 20 h, warm water immersion at 70°C for 24 h, drying at 105°C for 20 h, boiling water immersion for 4 h, and drying at 105°C for 20 h) were evaluated. TS after 5% acetic acid immersion at 20°C for 24 h was also measured on specimens of 50 mm × 50 mm. Each experiment was performed in triplicate, and the average value with standard deviation was calculated.

Preparation of bagasse extract-added chitosan film

For the materials of bagasse extracts, two types of particles were used. One material was the bagasse rind particles used for making particleboard, and the other was the particles collected from bagasse binderless particleboard (0.9 g/cm³). Both the particles were pulverized to 30–60 mesh size, and were vacuum-dried at 50°C for 15 h. The dried powders were extracted with warm water at 60°C for 3 h. Each water solution was lyophilized, and then the extracts were obtained. In film preparation, chitosan (0.5 g) and the extract (0.125 g) were dissolved in 25 mL of 1% acetic acid solution. That is, the concentration of the extract was 20 wt %. The solution was stirred at room temperature and then filtered by a glass filter. After the removal of air bubbles *in vacuo*, the solution was poured into a small plastic tray (8 cm × 5 cm) and was dried in an oven at 50°C for about 20 h. The film obtained was immersed in an ethanol/4% sodium hydroxide mixture (7 : 3, w/w) for 1 h to remove residual acetic acid and was washed thoroughly with an ethanol/distilled water mixture (7 : 3, w/w). After the washings showed a neutral pH, the films were dried at the ambient temperature for 30 min. Finally, the films were vacuum-dried at 50°C for 15 h.

Weight increase

The weight increase of the film was determined according to the following equation:

$$\text{Weight increase(\%)} = (W_{c+m} - W_c) \times 100/W_c$$

where W_{c+m} is the film weight of bagasse extract-added chitosan and W_c is the film weight of pure chitosan.

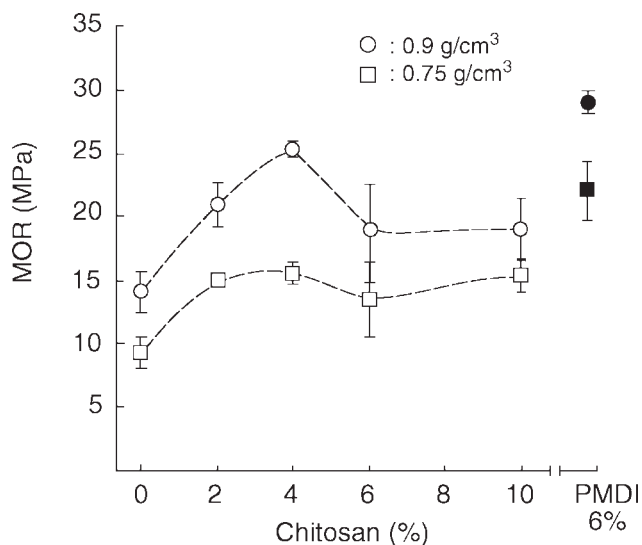


Figure 1 Relationship between the addition of chitosan and MOR.

Free amino group and insoluble matter

The number of free amino groups in the film was determined by the colloidal titration method. Each film (0.20 g) was dissolved in 99.80 g of 5 wt% acetic acid solution for 3h, and the insoluble matter was filtrated by a glass filter. A total of 1.00 g of the filtrate was mixed with 30-mL distilled water. After 2 to 3 drops of 0.1% toluidine blue indicator were added, the filtrate was titrated against N/400 potassium polyvinylsulfate. The insoluble matter was washed with distilled water and vacuum-dried at 50°C for 24 h. The weight change was calculated based on the case of a pure chitosan film, and the FTIR analysis was performed.

Fourier transform infrared spectroscopy (FTIR)

All of the infrared spectra of the films were obtained with an FTIR spectrometer (Spectrum One, Perkin-Elmer) by using the KBr disk method and were recorded by means of an average of 16 scans at a resolution of 4 cm⁻¹. The infrared spectra of the film were collected by passing a beam of infrared light through the KBr disk containing the sample. A Fourier transform instrument attached to the spectrometer is used to measure all wavelengths at once. The spectra obtained reveal details about the molecular structure of the film.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the effects of the chitosan amount on the MOR of bagasse particleboards. At a density of 0.75 g/cm³, the value of the binderless board (0%)

was 9.3 MPa. The value increased with increasing chitosan amount up to 4%, and the maximum average value was 15.6 MPa. The above 4% addition amount hardly affected the MOR value. In the case of 0.9 g/cm³, the value also increased up to 4%, and the maximum average value was 25.3 MPa. The value was 80% higher than that without chitosan (0%). When chitosan was added above 4%, the value clearly decreased. The MORs of the boards bonded with PMDI at densities of 0.75 and 0.9 g/cm³ were 21.9 and 29.0 MPa, respectively. The boards bonded with chitosan indicated about 20% lower values than the boards with PMDI. Figure 2 shows the effects of the chitosan addition on MOE. At a density of 0.75 g/cm³, the maximum MOE value was 2.27 GPa at the 2%. The value was similar even when the chitosan amount increased further. In the case of the high density of 0.9 g/cm³, the maximum value was 3.04 GPa at the same amount. A further increase of the addition amount resulted in a decrease of the value. Regardless of the density, the MOE of the board bonded with PMDI was superior to that of chitosan to some degree.

Based on the results in Figures 1 and 2, the appropriate amounts of chitosan for bending properties were 2–4% based on the particle weight. The poor bending properties at the high addition amounts were due to the decrease of the particle amount contained in the board, and the low tensile properties of chitosan. According to our previous report,⁵ the tensile strength and Young's modulus of the pure chitosan film used in this study were 44.7 MPa and 2.26 GPa, respectively. Figure 3 shows the results of the IB of the board. The value increased gradually with increasing chitosan amount at a density of

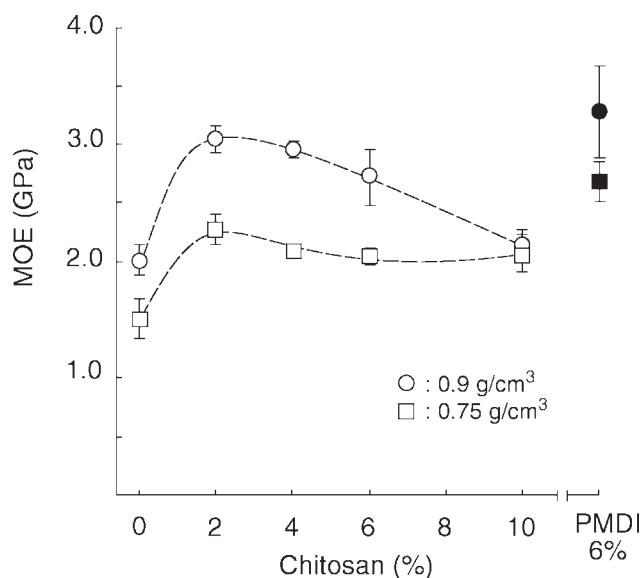


Figure 2 Relationship between the addition of chitosan and MOE.

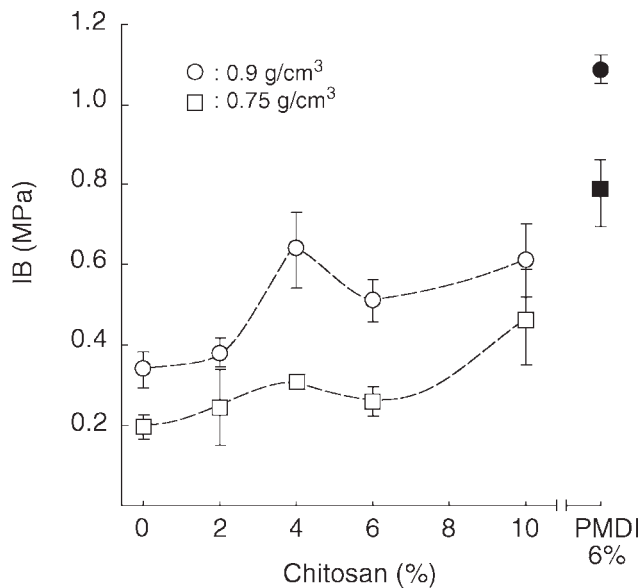


Figure 3 Relationship between the addition of chitosan and IB.

0.75 g/cm³. At the high density of 0.9 g/cm³, the value increased until the additional amount was 4%, and maximum average value was 0.64 MPa. When the chitosan was added at 4% or above, the value did not improve. This means that the increase of chitosan did not necessarily contribute to the IB. The values of the board with PMDI at 0.75 and 0.9 g/cm³ were 0.8 and 1.1 MPa, respectively. Therefore, it was clarified that the adhesiveness of chitosan was inferior to that of PMDI. However, at least, the effect of the addition of chitosan on the bond strength was confirmed. Figure 4 shows the result of the TS of the board. At the density of 0.75 g/cm³, the value decreased drastically to about half with the chitosan

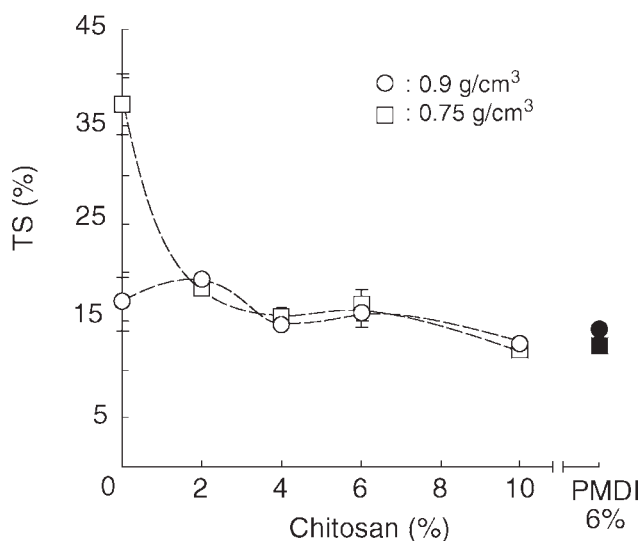


Figure 4 Relationship between the addition of chitosan and TS.

of 2%. The addition of a small amount of chitosan was very effective for the dimensional stability of the board. When the chitosan was added at a level of 2% or above, the value decreased from 18.3 to 11.7%. The TS in high-density board decreased from 16.7 to 12.8% as the amount of chitosan increased. The reason that the change of TS was small degree regardless of the addition amount would be that the test condition was mild for the board. When compared with the board with PMDI, the board with the 4% or higher amount of chitosan showed a similar performance, irrespective of the board densities.

To investigate the detailed dimensional stability of the high density board, a cyclic accelerated aging treatment was performed. The results are shown in Figure 5. With immersion in warm water at 70°C for 24 h, the TS of the binderless board was found to be about 90%. The TS increased further during the immersion of boiling water for 4 h. This increase was caused by the degradation of bonding properties between particles and the swelling of each particle. The board bonded with a 4% of chitosan exhibited excellent stability. The performance was comparable to that of board bonded with PMDI. Chitosan is inherently insoluble in water, and has good adhesiveness for wood in water.^{3,4} The particles are bonded closely to each other in the high density board. As a result, the board with chitosan would have good dimensional stability even under severe treatment. Subsequently, the dimensional stabilities of the boards in 5% acetic acid solution were investigated to observe the effect of dilute acid on chitosan. The results are shown in Figure 6. The binderless board decomposed in 2 h. It was recognized that the dimensional stability in dilute acid was very different from that in water. Asada et al.⁷ reported that some water-soluble organic acids were formed by autohydrolysis of bagasse

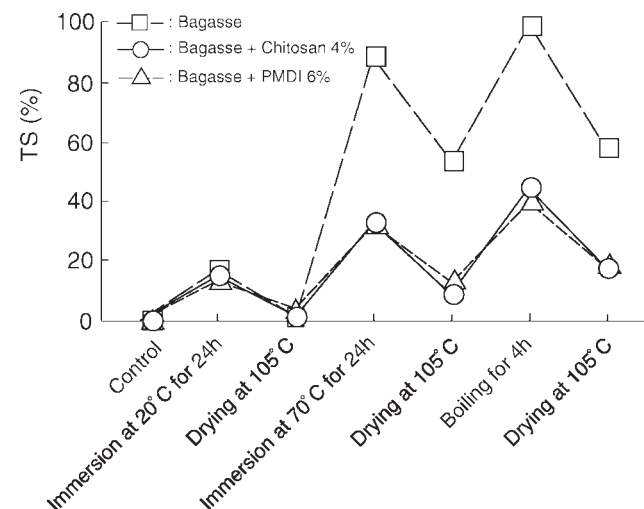


Figure 5 The change of TS in a cyclic accelerated aging treatment.

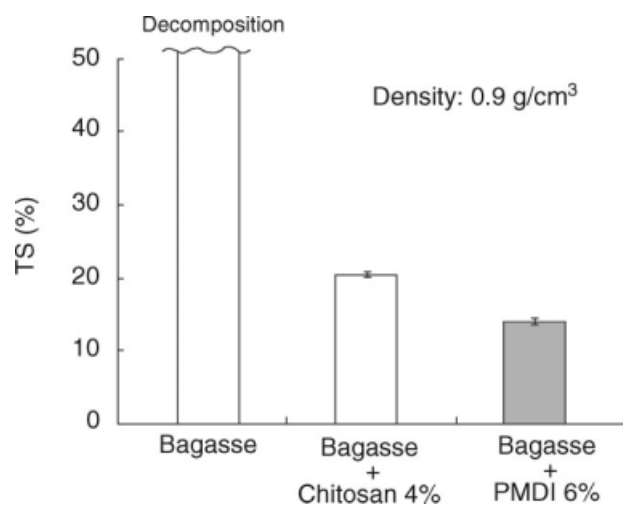


Figure 6 TS of various bagasse particleboards in 5% acetic acid solution.

under steam heating. Therefore, it seemed that hydrolysis and the cleavage of hydrogen bonds were promoted in 5% acetic acid. The TS value of the board bonded with chitosan was about 20%. The value was slightly inferior to that of board bonded with PMDI. The addition of chitosan at least resulted in an inhibition of the TS in dilute acid. Generally, chitosan is dissolved in dilute acid. But, it has been made clear that dry and steam-heated chitosan films exhibit an insoluble property in dilute acid.^{8,9} One reason for this stability would be that chitosan provided this insoluble property in dilute acid during steam injection pressing. Further, bagasse may form some reducing sugars from extract during pressing. It is known that chitosan reacts easily with reducing sugar, which indicates an insoluble property in dilute acid.^{5,6} Therefore, the interaction between chitosan and extracts from bagasse was investigated.

Chitosan film properties

Two types of bagasse extracts were prepared, and the each characterization of extract-added chitosan films was examined. The results are summarized in Table I. When the extract from bagasse rind particles was added to chitosan, the weight increase of the film was 18.5%. The value of insolubility in 5% acetic acid was 0.3%. This indicates that the film obtained was almost dissolved. The relative amount of free amino groups based on that of pure chitosan film was 83.2%. In the case of extract from bagasse binderless board, the weight increase of the film was similar to that of the bagasse rind particles. However, the film indicated insoluble property of 34.5% in acetic acid solution. In addition, the relative amount of free amino groups was clearly lower than that of the bagasse rind particles added. This means that chitosan interacted with the extract. Figure 7 shows the infrared spectra

TABLE I
Characterization of Chitosan-Bagasse Extract Films

	Weight increase (%)	Insoluble matter in 5% acetic acid (%)	Free amino groups (%)
Chitosan + bagasse particle extract	18.5 (0.019)	0.3 (0.015)	83.2 (0.019)
Chitosan + bagasse binderless board extract	16.7 (0.018)	34.5 (0.158)	54.8 (0.131)

Value in parentheses is the standard deviation.

of the extract from bagasse binderless board (a), pure chitosan (b), chitosan + the extract from bagasse binderless board (c), and insoluble matter of the extract added chitosan in 5% acetic acid (d). In the extract from bagasse binderless board (a), strong absorption peaks were clearly observed at 3391 and 1050 cm^{-1} . Small peaks at 1726 cm^{-1} and a small shoulder at

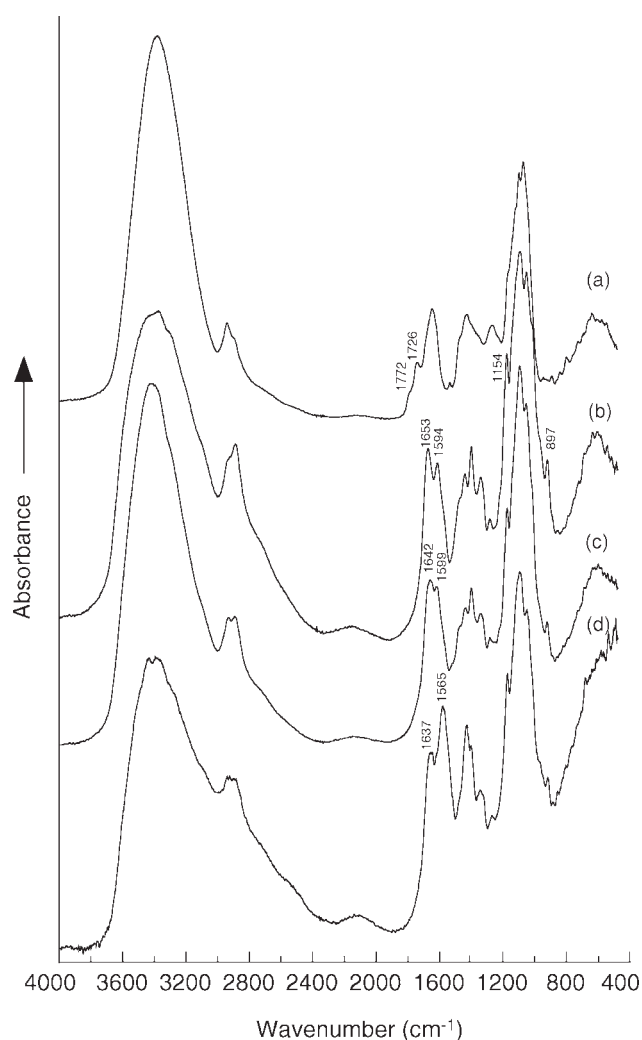


Figure 7 Infrared spectra of (a) bagasse binderless board extract, (b) chitosan, (c) chitosan + bagasse binderless board extract, and (d) insoluble matter in 5% acetic acid.

around 1772 cm^{-1} were also indicated. Geng et al.¹⁰ reported infrared spectra of water-soluble hemicellulose in bagasse. The absorption peaks at around 3436 , 1043 , and 897 cm^{-1} were assigned to the hydroxyl group, ether in the sugar unit, and β -glycosidic linkages between sugar units, respectively. The shoulder at 1745 cm^{-1} was assigned to the acetyl, uronic, and ferulic ester groups of the polysaccharides. According to these assignments, the peaks at 3391 and 1050 cm^{-1} were attributed to the hydroxyl group and ether in the sugar unit, respectively. The absorption bands at 1726 and 1772 cm^{-1} would be derived from the carbonyl groups containing ester groups. The absorption peak at around 897 cm^{-1} was very small in this study. Regarding the infrared spectrum of pure chitosan (b), the assignments of several peaks have already been clarified. The characteristic absorption bands between 4000 and 2500 cm^{-1} are 3480 – 3440 cm^{-1} , 3260 – 3270 cm^{-1} , and 2960 – 2878 cm^{-1} for the OH, NH, and CH stretching regions, respectively.¹¹ The adsorption at around 1650 cm^{-1} , around 1560 cm^{-1} , and around 1310 cm^{-1} are assigned to amide I,^{11,12} amide II,^{11,12} and amide III,¹² respectively. In this study, the absorption peak at 1594 cm^{-1} that is attributed to the primary amino group was observed. The adsorption at around 1154 cm^{-1} and 897 cm^{-1} have been assigned to the C–O stretching and the β -D-configuration, respectively.^{11,13,14} When the extract from bagasse binderless board was added to chitosan (c), the absorption peaks at 1653 and 1594 cm^{-1} were shifted to 1642 and 1599 cm^{-1} , respectively. Considering the results shown in Table I, the peak changes were caused by the interaction between chitosan and the extract. However, no other remarkable peak changes were observed. The reaction product was analyzed on the basis of a spectrum of insoluble matter in 5% acetic acid (d). Adsorption at around 1637 and 1565 cm^{-1} were clearly identified. Generally, bagasse suffers hydrolysis under high-pressure steam, and yields low molecular weight substances.^{7,15} In particular, monosaccharides such as xylose and glucose are formed in quantity in the presence of dilute acid.^{16,17} In our previous researches, the reactions between chitosan and some reducing sugars such as xylose and glucose were studied.^{5,6} The Maillard reaction occurred easily between them, and the reaction products were insoluble in 5% acetic acid. The whole peak pattern of this study was very similar to those of the insoluble matters of 10 wt % glucose and xylose added-chitosan films in 5% acetic acid.^{5,6} Judging from the assignments of the insoluble matters of 10 wt % glucose and xylose added-chitosan films in 5% acetic acid, the peak at around 1637 cm^{-1} would be attributed to the overlap of the C=O group and the C=N linkage, and the peak at 1565 cm^{-1} would be a secondary amine. According to the results, chitosan reacted with extract containing reducing sugars that were produced by

hydrolysis during pressing. It is possible that a similar reaction occurred when the particleboard with chitosan was made. This would in part contribute to its resistance to dilute acid.

CONCLUSIONS

Characterization of bagasse rind particleboard bonded with chitosan by using a steam-injection press was investigated. In the bending properties of the board, the 2–4 wt % addition amount of chitosan was the most effective. The bending properties were about 20% lower when compared with those obtained of using PMDI. The IB of the board was improved by the addition of chitosan. The high-density board bonded with a 4 wt % addition of chitosan had an especially good value. The TS of the board was improved by the addition of chitosan. The high-density board with the 4 wt % addition of chitosan had excellent dimensional stability, equivalent to that of board made using PMDI. In addition, the TS in dilute acetic acid was almost equal to that in water. Based on the characterization of extract-added chitosan films, it was suggested that chitosan interacted with the extract from bagasse binderless board. The progress of the Maillard reaction was expected from the results of the IR spectra. The reaction seemed to contribute to the board's good resistance to dilute acid.

References

1. Rowell, R. M.; Young, R. A.; Rowell, J. K., Ed.; Paper and Composites from Agro-Based Resources; Lewis publishers: New York, 1996.
2. Widyorini, R.; Xu, J. Y.; Umemura, K.; Kawai, S. *J Wood Sci* 2005, 51, 648.
3. Umemura, K.; Inoue, A.; Kawai, S. *J Wood Sci* 2003, 49, 221.
4. Umemura, K.; Iijima, Y.; Kawai, S. *J Adhes Soc Jpn* 2005, 41, 216.
5. Umemura, K.; Kawai, S. *Carbohydr Polym* 2007, 68, 242.
6. Umemura, K.; Kawai, S. *J Appl Polym Sci* 2008, 104, 2481.
7. Asada, C.; Nakamura, Y.; Kobayashi, F. *Biotechnol Bioprocess Eng* 2005, 10, 346.
8. Lim, L.-Y.; Khor, E.; Ling, C.-E. *J Biomed Mater Res* 1999, 48, 111.
9. Lim, L.-Y.; Wan, L. S. C. *Drug Dev Ind Pharm* 1995, 21, 839.
10. Geng, Z. C.; Sun, J. X.; Liang, S. F.; Zhang, F. Y.; Zhang, Y. Y.; Xu, F.; Sun, R. C. *Int J Polym Anal Charact* 2006, 11, 209.
11. Japanese Society for Chitin and Chitosan, Ed.; Chitin and Chitosan Handbook (in Japanese); Gihodo Shuppan: Tokyo, Japan, 1995; Chapter 8.2.
12. Sannan, T.; Kurita, K.; Ogura, K.; Iwakura, Y. *Polymer* 1978, 19, 458.
13. Hirano, S. *Agric Biol Chem* 1978, 42, 1939.
14. Hirano, S.; Matsuda, N.; Miura, O.; Tanaka, T. *Carbohydr Res* 1979, 71, 344.
15. Kaar, W. E.; Gutierrez, C. V.; Kinoshita, C. M. *Biomass Bioenergy* 1998, 14, 277.
16. Markus, N.; Herbert, D.; Christiane, T.; Bamusi, S.; Rudolf, B. *Appl Biochem Biotechnol* 2002, 98–100, 49.
17. Aguilar, R.; Ramirez, J. A.; Garrote, G.; Vázquez, M. *J Food Eng* 2002, 55, 309.