Low Density Sugarcane Bagasse Particleboard Bonded with Citric Acid and Sucrose: Effect of board density and additive content

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The development of natural adhesives derived from non-fossil resources is very important for the future. In this study, by taking sugarcane bagasse as the raw material, without using any synthetic resin but adding some eco-friendly additives (citric acid and sucrose), low density particleboards were successfully developed. The effects of board density and additive contents on the physical and mechanical properties of the boards were investigated. The bonding mechanism was observed by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The results showed that the low density bagasse particleboard had good mechanical properties and dimensional stability relative to its low board density. The modulus of rupture (MOR) and the thickness swelling (TS) values increased with increasing board density. The board with a density of higher than 0.40 g/cm^3 and manufactured at 15% additive content can meet the requirements of the Chinese national forestry industry standard LY/T 1718-2007 (2007). Based on the results of the FTIR spectra, the additive not only increased the hydrogen bond but also the molecular linkage force (C-O-C). X-ray diffraction showed the relationship between crystallinity of cellulose and the strength of particleboard.

Keywords: Low density; Bagasse particleboard; Citric acid; Sucrose

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INTRODUCTION

Bagasse, a waste product of sugarcane processing, is rich in sugar-containing compounds, which makes it a good raw material for particleboard manufacturing. Widyorini *et al.* (2005) developed bagasse particleboard by using a steam-injection pressing at the temperature of 190 °C, and they claimed that the bagasse pith particles provided better board properties than bagasse rind particles.

At present, large quantities of synthetic resin adhesives derived from fossil resources are utilized when manufacturing particleboard. Harmful chemical substances, which cause health disorders and environmental problems, are usually contained in the adhesives. In order to refine the global environment and to establish a sustainable society, it is very important to develop a novel natural adhesive without harmful chemical substances. To resolve these serious problems, some studies about binderless (Gao *et al.* 2011) or natural adhesives, such as citric acid and sucrose, have been conducted. Citric acid is an organic polycarboxylic acid, which contains three carboxyl groups and has been considered as a cross-linking agent for wood (Vukusic *et al.* 2006) and plant fiber.

The effects of citric acid content on the physical properties of wood-based mouldings were clarified by Umemura *et al.* (2012) under fabricating conditions of 200 °C and 4 MPa for 10 min. The physical properties of the manufactured board with a density of 0.80 g/cm³ at 200 °C satisfied the type 18 requirements of the Japanese industrial standard for particleboard (JISA 5908) (Umemura *et al*. 2012, 2015).

At present, many studies have been done on the development of low density particleboard (Kawai *et al*. 1986; Subiyanto 1991; Sellers *et al*. 1993; Rowell *et al*. 1995; Kawasaki *et al*. 1998; Korai H *et al*. 2001; Wang and Sun 2002; Mo *et al.* 2002; Xu *et al.* 2004). Kawai developed a low-density board with a density of 0.40 g/cm³ using isocyanate compound adhesive. Some people use low density raw material for manufacturing low-density board. For example, Sellers used kenaf core to make phenol-formaldehyde (PF) particleboard with a board density as low as 0.26 g/cm³. Xu *et al.* (2004) developed a low density (0.20 g/cm³) binderless particleboard from kenaf core using steam-injection pressing. The results showed that the low-density kenaf binderless particleboards had good mechanical properties and dimensional stability relative to their low board densities.

However, using natural adhesive to make low density particleboard has seldom been reported. In this study, low density particleboards were developed by using bagasse as raw material. Such products are suitable for sound absorption and thermal insulation. In addition, the products are free from formaldehyde emissions and are especially suitable for interior use. The effects of board density and additive content on the physical properties of the particleboards manufactured with citric acid/sucrose-additives were investigated. The effects of functional groups on the strength of particleboard were revealed by Fourier Transform Infrared Spectroscopy (FTIR), and the relationship between cellulose crystallinity and the strength of particleboard were characterized by X-ray diffraction.

EXPERIMENTAL

Materials

Sugarcane bagasse particles, obtained from Xingxiang Co. Ltd., Hunan, China, were crushed by a knife ring flaker. After air drying, the moisture content of the bagasse particles was 10% to 13%. Citric acid and sucrose were purchased from Xilong Chemical Company. Table 1 shows the size composition of bagasse particles based on mesh analysis by screening test.

Table 1. Distribution of Particle Size Based on Mesh Analysis

Mesh No.	Mesh opening(mm)	Weight percentage (%)
> 10	> 2.00	24
10 to 30	2.00 to 0.60	42
30 to 80	0.60 to 0.18	28
< 80	< 0.18	6

Manufacture of Particleboards

The dimensions of the particleboards were 320×320×7 mm. The weights of the particles were measured according to their target board densities which were set at 0.30, 0.35, 0.40, 0.45, and 0.50 g/cm³. Citric acid and sucrose were dissolved in water under a ratio of 1:1, and the concentration of the solution was 30 g citric acid and 30 g sucrose /100 g solution. The solid additives (citric acid and sucrose) that accounted for 5%, 10%, 15%, 20%, 30%, and 40% of the oven-dried particles were used as an adhesive and sprayed onto the particles. The moisture content of the particles was then increased to 28-30%. The particles were hand-formed into homogeneous single-layered mats using a 320 × 320 mm forming box. Then the mats were hot-pressed for 8 min at the temperature of 180 °C. The board thickness was controlled by 7 mm-thick distance bars.

Evaluation of Board Properties

Prior to evaluation of the mechanical properties, dimensional stability, and thermal insulation, the low density boards were conditioned at room temperature for about 7 days until equilibrium moisture content was reached (6 to 8%). The properties and thermal conductivity of boards were evaluated in accordance with the Chinese national forestry industry standard LY/T 1718-2007 (2007) (Table 2) for low density fiberboard.

The modulus of rupture (MOR) test was conducted with four 200×50×7 mm specimens that were cut from each board using a three-point bending test over an effective span of 150 mm at a loading speed of 5 mm/min. Four test specimens of 50×50 mm were prepared from each sample board for the purpose of thickness swelling (TS) tests (2h immersion in 20 °C water). The thermal conductivity of the low density particleboards were tested with another two 300×300×7 mm specimens.

Table 2. The Chinese National Forestry Industry Standard LY/T 1718-2007

Board type	Density (g/cm³)	MOR (MPa)	2 hTS (%)	Thermal conductivity (W/m.K^{-1})
Normal type	$0.35 \leq \rho < 0.45$	≥ 3.0	≤ 10	
	$0.25 \leq \rho < 0.35$	≥ 2.0	≤ 12	
	$\rho < 0.25$	≥ 1.1	≤ 15	
Functional type	$0.35 \leq \rho < 0.45$	≥ 3.0	≤ 10	0.05 to 0.10
	$\rho < 0.35$	≥ 2.0	≤ 12	

Fourier Transform Infrared Spectroscopy (FTIR)

The particleboards converted to powder through a grinder, and the powder obtained was dried with a dryer at 102 °C for 24 h. All of the infrared spectra were obtained with an FTIR spectrometer (IRAffinity-1, Shimadzu, Japan) by using the KBr disk method and were recorded by means of an average of 32 scans at a resolution of 4 cm^{-1}. The samples contained particleboards with 0% additive content (blank) (A), 15% additive content (B), and 30% additive content (C).

X-Ray Diffraction (XRD)

X-ray diffraction was used to determinate the crystallinity of the bagasse cellulose with different treatments. The testing samples including particleboards with 0% additive content (blank) as sample A, 15% additive content as sample B, and 30% additive content as sample C. X-ray diffraction data were obtained by a XD-2 X-ray instrument from Beijing Pukinje General Instrument Co., Ltd., and the samples were ground powders which passed through 250 mesh screens and were dried at 102 °C for 24

h. CuKα radiation generated at a voltage of 36 KV and current of 20 mA was utilized, and the X-ray scattering data were collected in the 5° to 55° 2θ range at a scan speed of 2°/min.

The relative crystallinity was calculated as Eq. 1, based on Segal Crystallinity Index (CI) (Segal *et al.* 1959), where I_{002} is the height of the highest diffraction peak around 2θ = 22°, I_{am} is the height of the minimum intensity between the two major peaks around 2θ = 18°, and CrI is the relative degrees of crystallinity.

$$CrI = \frac{I_{OO2} - I_{am}}{I_{OO2}} \times 100\% \tag{1}$$

RESULTS AND DISCUSSION

Effects of Additive Content on the Board Properties

The effects of additive content on the properties of the particleboard with a density of 0.45 g/cm³ were investigated. Figure 1 shows the relationship between additive content and MOR of low density bagasse particleboard. It can be seen that, as additive content increased from 0% to 40%, the MOR first increased drastically then decreased slightly and became steady at last. When the additive content attained 5% or more, the MOR of the particleboard met the requirement of the national forestry industry standard. The average MOR value of the control particleboard (0%-additive content) was 2.3 MPa. However, the maximum average MOR value, 6.2 MPa, was obtained with a 15% additive content, which was about 170% higher than that of the control particleboard. When the additive content ranged from 15% to 40%, increasing additive content brought a decrease in the MOR. A further addition of additive did not contribute to the enhancement of the strength.

The observed trends can be explained as follows: the particleboard strength was determined by bonding strength among particles and the strength of the particles themselves. Under high temperatures, the additive would react with the functional groups of particles and enhance the bonding strength of the particleboard. The MOR of the particleboard thus increased when the additive content increased from 0% to 15%. However, when a board density was fixed, the amount of particles would be reduced with the increasing of additive content, which induced the decrease of board strength. This explained the MOR of the particleboard decreasing with a further increase in the additive content to more than 20%.

Figure 2 shows the relationship between additive content and thickness swelling (TS) of low density bagasse particleboard with water immersion treatment for 2 h. The TS decreased with the increasing of additive content. The TS was 28% for the control particleboard, whereas the TS of the particleboard with 15% additive content was only 7.9%. The reason was that the amount of ester linkage that resulted from the connection between citric acid and –OH of cellulose increased with the increasing of additive content, weakening the expansion of the particles, which contributed to the decrease of TS of particleboard. With further increasing the additive content, no more ester linkage could be formed, thus the TS basically kept steady. The board with the additive content of 15% or higher met the standard requirement.

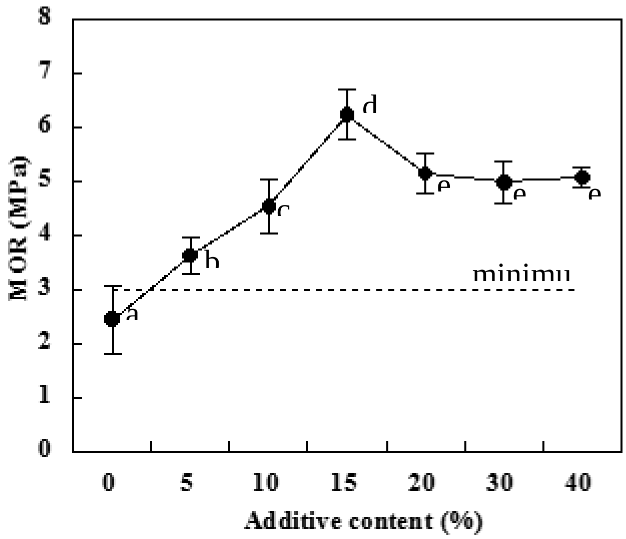

Fig. 1. Relationship of low density bagasse particleboard between additive content and MOR at 0.45 g/cm³ density. Error bars indicate standard deviations. Different letters in the figure indicate that means are significantly different（$p<0.05$）

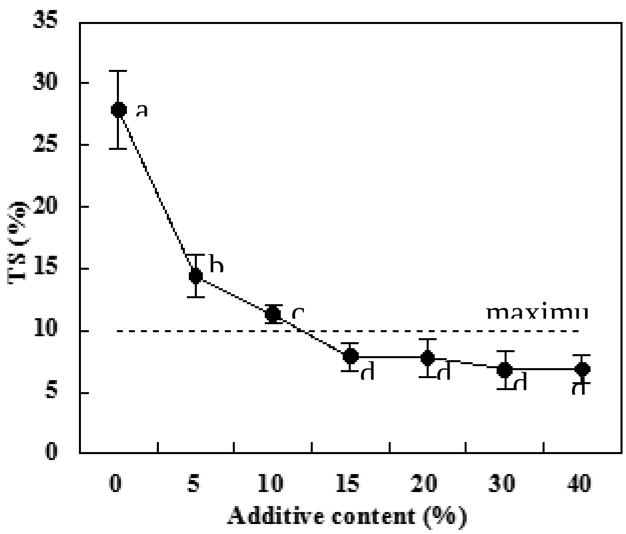

Fig. 2. Relationship of low density bagasse particleboard between additive content and TS at 0.45 g/cm³ density. Error bars indicate standard deviations. Different letters in the figure indicate that means are significantly different（$p<0.05$）

Effects of Board Density on the Properties

Figure 3 shows the relationship between board density and modulus of rupture (MOR) of low density bagasse particleboard. The additive content of all the boards was 15%. It can be seen that there was a positive linear correlation between board density and MOR. When the board density was set at 0.30 g/cm³, the average test value of MOR was 1.17 MPa, which does not meet the requirement of the Chinese National Forestry Industry Standard LY/T 1718-2007 (2007) (3 MPa). However, the board with a density higher than 0.40 g/cm³ was comparable to the standard. Higher density board has a larger amount of particles per unit volume than that of lower density board; thus it shows higher MOR due to the superior bonding among the tightly packed particles.

Figure 4 shows the relationship between board density and thickness swelling (TS) of low-density bagasse particleboard. It can be seen that the TS had a positive liner correlation with density in the range of 0.30 to 0.45 g/cm³. However, the TS decreased slightly when the density further increased from 0.45 g/cm³ to 0.5 g/cm³.

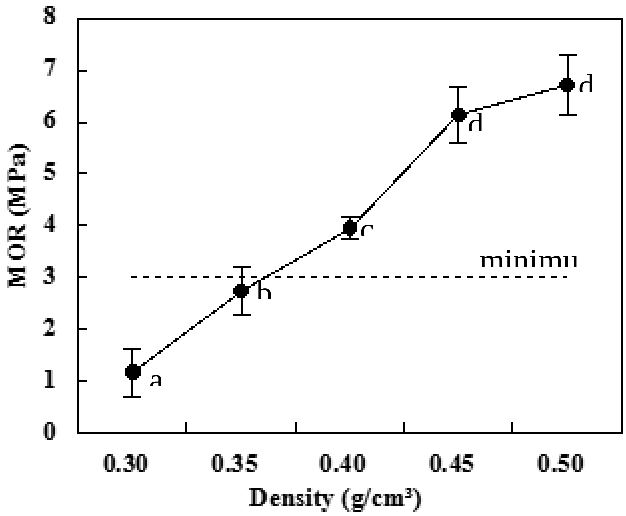

Fig. 3. Relationship between density and MOR of low density bagasse particleboard at 15% additive content. Error bars indicate standard deviations. Different letters in the figure indicate that means are significantly different（$p<0.05$）

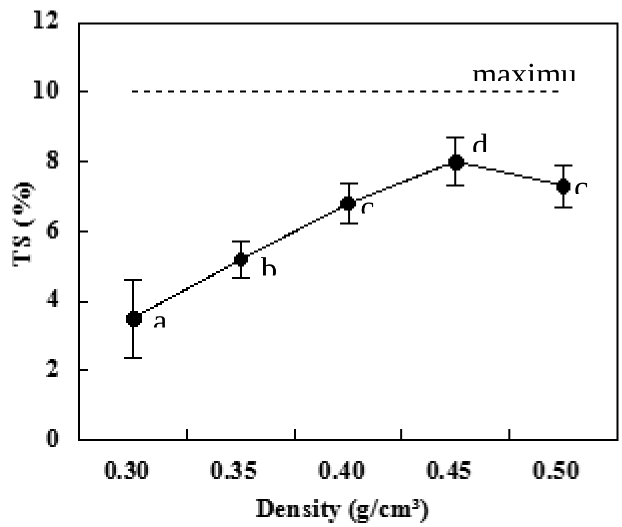

Fig. 4. Relationship between density and TS of low density bagasse particleboard at 15% additive content. Error bars indicate standard deviations. Different letters in the figure indicate that means are significantly different（$p<0.05$）

The reason for the maximum in the value of TS seemed to be that there are two major factors affecting the TS of the board. One is the springback due to stress release, whereas the other is the bond strength of particles (Xu *et al*. 2004; Sonderegger and Niemz 2009). The boards with higher density had a high compression ratio when pressing the board, which might have led to high springback after soaking in water. On the other hand, higher density boards would have large amounts of particles and small porosity per unit volume. Thus, the particles bonded closely with each other, obtained high bonding strength, and couldn't be easily penetrated by water. The interaction of these two factors caused the TS to first increase with the board density and then decrease. However, all the particleboards showed excellent water resistance properties; they were lower than 10%, the requirement of the standard.

Thermal Conductivity

The effects of density on the thermal conductivity coefficient of low density bagasse particleboard are shown in Fig. 5. The thermal conductivity coefficient of lighter particleboards was lower than that of heavier particleboard. The thermal conductivity values were 0.0709 and 0.09796 W/(m·k) at the densities of 0.35 and 0.50 g/cm³, respectively. All particleboards were able to meet the requirement of the standard. Thermal conductivity is an important parameter to show the material's capability of transmitting heat. The density of board has a direct positive correlation with its thermal conductivity. The higher the board density is, the greater will be the thermal conductivity (Xu *et al*. 2004, 2005; Lin *et al.* 2014). This is because the lighter board contains a large number of voids fill with air, which is a poor conductor (0.0239 W/(m • k).

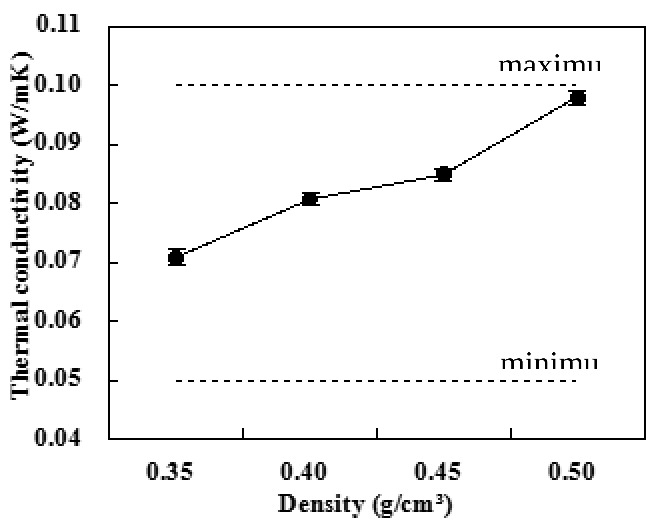

Fig. 5. Effects of density on thermal conductivity coefficient of low density bagasse particleboard. Error bars indicate standard deviations

Fourier Transform Infrared Spectroscopy (FTIR)

The effect of additive content on the chemical structure of low density bagasse particleboard was investigated by FTIR, and the results are shown in Fig. 6. It can be seen that the peaks of B and C were similar to that of A, which means that the types of functional groups in boards were unchanged after having been treated with additives.

However, the band intensity and peak position of the absorption band for -OH around the wave number of 3400 cm^{-1} had changed. Compared with A, the band absorption of B and C decreased, indicating the reduction of free -OH in the samples, while the shift of the peak position to a lower wave number was due to the increase of bonding -OH in the board. The -OH absorption peak of samples A, B, and C were 3443, 3412, and 3433 cm^{-1}, respectively. Moreover, the -OH on cellulose molecules reacted with citric acid and sucrose, forming ester linkages (Fig. 7) and hydrogen bonds (Umemura, K. *et al.* 2015). Thus, the amount of free -OH was reduced, which reinforced the strength of the board.

The peak of samples B and C at around 1734 cm^{-1} was clearly higher than that of sample A. The peak is generally attributed to C=O stretching derived from carboxyl group and C=O ester linkage (Yang and Wang 1996; Žagar and Grdadolnik 2003). Citric acid was added to produce more oligosaccharide by promoting the degradation of hemicelluloses. In addition, the added citric acid has carboxyl group, which caused the absorption intensity of -C=O to be strengthened.

The absorption peak at 1047 cm^{-1} resulted from C-O-C stretching vibration of hemiacetal. As the additive content was increased, the absorption of C-O-C became stronger, which resulted in citric acid undergoing esterification with cellulose, hemicelluloses, and sucrose, respectively. In summary, the additive not only increased the hydrogen bond but also the molecular linkage force (C-O-C). This explains why the properties of particleboards with additives were stronger.

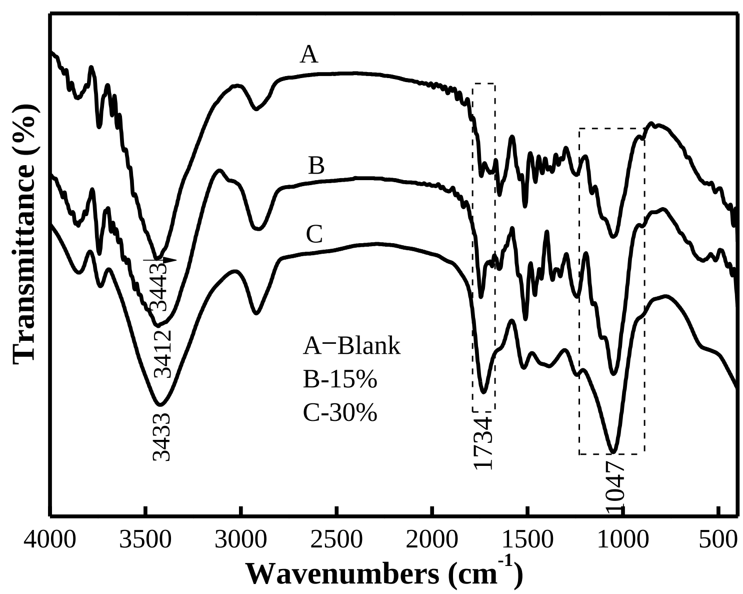

Fig. 6. FTIR spectrum of low density bagasse particleboard with different additive contents

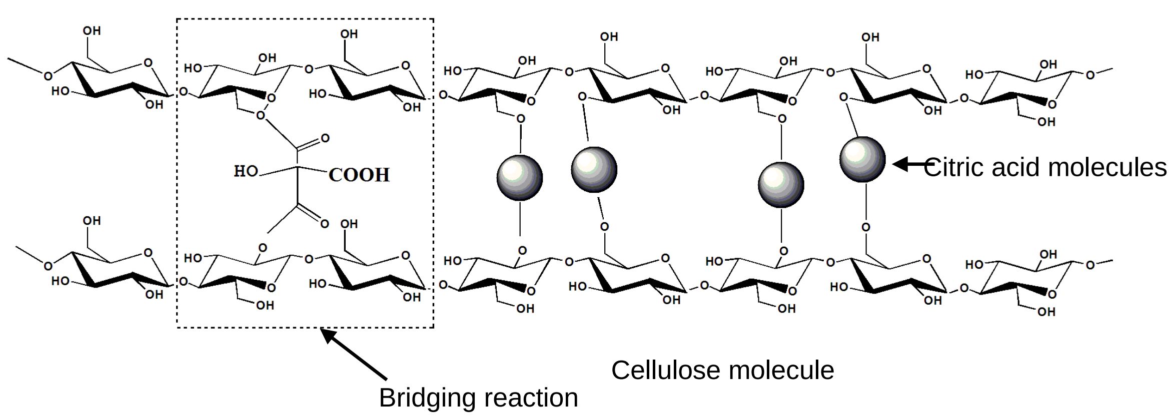

Fig. 7. The reaction between citric acid and cellulose molecule

X-ray Diffraction (XRD)

Figure 8 shows the X-ray diffraction spectra of low density bagasse particleboards with different additive contents. The degrees of crystallinity of different samples are shown in Table 3. The crystallinity of cellulose increased first, then decreased with the increasing of additive content. The degree of crystallinity of B was 48.2%, which was 5.2% higher than A, whereas an additive content of 30% brought about a decrease in the crystallinity of cellulose to 40.9%, which was 10.6% lower than A.

The cellulose molecule chain of wood is composed of crystalline regions and amorphous regions (Zhao *et al.* 2006). When the additive and water were added into lignocelluloses materials, they went into the amorphous regions first, in which the citric acid would esterify with the -OH in cellulose molecules to form the ester linkages (Fig. 7). The newly formed ester linkages acted as bridges, making the molecule chain in amorphous regions rearrange regularly to increase the crystallinity degree of bagasse cellulose, contributing to the enhancement of board strength. A further addition of additive content caused the increasing concentration of citric acid, which led to a stronger cellulose swelling (Navard *et al.* 2006). The enhanced cellulose swelling might damage the crystalline regions of cellulose to some degree, resulting in the reduction of cellulose crystallinity. This might be another reason why the board strength was weakened when the additive content was increased from 15% to 30%.

Table 3. Crystallinity of Samples

Sample	Mesh (screen)	Additive content (%)	I_{am}	background	I_{002}	background	Crystallinity (%)
A	250	0	483	170	752	175	45.8
B	250	15	487	174	792	184	48.2
C	250	30	517	177	760	184	40.9

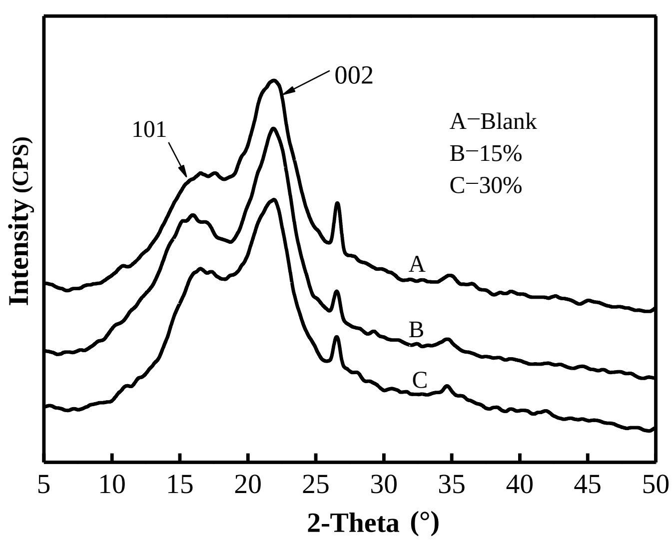

Fig. 8. X-ray diffraction spectra of low density bagasse particleboard with different additive content

CONCLUSIONS

1. The properties of low density bagasse particleboard can be improved by adding citric acid and sucrose during board manufacture. The board with a density of 0.40 g/cm³ or higher manufactured at 15% additive content can meet the requirements of the Chinese national forestry industry standard LY/T 1718-2007 (2007).
2. Low density bagasse particleboard showed good thermal insulation properties. It is a promising building material for thermal insulation applications.
3. Based on the results of the FTIR analysis, citric acid promotes the formation of hydrogen bonding and esterification (C-O-C), which contributes to improving the properties of particleboard.
4. The cellulose molecule and citric acid were found to undergo a bridging reaction with the formation of ester linkages, which were favorable to increase the crystallinity degree of celluloses. The increasing of crystallinity is conducive to the enhancement of properties of the particleboard.

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