Physical-Mechanical Properties and Bonding Mechanism of Corn Stalks Particleboard with Citric Acid Adhesive

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Abstract

As a natural fiber and agricultural by-product, corn stalks (*Zea mays saccharata*) is considered as an alternative raw material to produce particleboard. Corn stalks is a good source of lignocelluloses, renewable and low cost. This research was aimed to investigate the characteristics of corn stalk particleboard with citric acid as adhesive. This study also evaluated bonding mechanism particle with citric acid and the bonds between celluloses derived corn stalk with citric acid. The boards were manufactured under the hot pressing temperature 200 ^{o}C for 10 min. The citric acid concentration was varied in 0, 15, 20 and 25 wt%. The board size and target density were (25 x 25 x 0.9) mm^3 and 0.8 g.cm^{-3}. Results showed that the physical properties of particleboards improved with increasing citric acid concentration up to 20 wt%. At the optimum citric acid content of 20 wt% could provide particleboards with the modulus of rupture, modulus of elasticity and internal bonding satisfied the requirement of the 13 type of the JIS A 5908 (2003) standard. Infrared (IR) spectral analysis from board which manufactured from isolated cellulose was mixed citric acid and pressed on temperature 200 ^{o}C showed the presence of ester linkages that the carboxyl and hydroxyl groups of citric acid had reacted with the hydroxyl groups of corn stalk cellulose.

Keywords : citric acid, corn stalk, concentration, particleboard, adhesive

Abstrak

Sebagai serat alami dan produk samping pertanian, batang jagung (*Zea mays saccharata*) dianggap sebagai bahan baku alternatif untuk menghasilkan papan partikel. Batang jagung adalah sumber lignoselulosa yang baik, terbarukan dan biaya rendah. Penelitian ini bertujuan untuk mengetahui karakteristik papan partikel batang jagung dengan asam sitrat sebagai perekat. Penelitian ini juga mengevaluasi mekanisme ikatan partikel dengan asam sitrat dan ikatan antara selulosa yang berasal dari batang jagung dengan asam sitrat. Papan dibuat pada suhu 200 ^{o}C selama 10 menit. Konsentrasi asam sitrat bervariasi dalam 0, 15, 20 dan 25%. Ukuran papan dan kerapatan target adalah (25 x 25 x 0,9) mm dan 0,8 g.cm^{-3}. Hasil penelitian menunjukkan bahwa sifat fisik, mekanik papan partikel meningkat dengan meningkatnya konsentrasi asam sitrat hingga 20%. Pada kandungan asam sitrat optimum 20% mampu menghasilkan papan partikel dengan nilai keteguhan patah (MOR), keteguhan lentur (MOR) dan kuat rekat internal (IB) yang memenuhi persyaratan JIS A 5908 (2003) Tipe 13. Analisis spektra inframerah (IR) dari papan yang dibuat dari pencampuran isolat selulosa dengan asam sitrat dan dikempa pada suhu 200 ^{o}C menunjukkan adanya ikatan ester dimana gugus karboksil dan hidroksil asam sitrat telah bereaksi dengan gugus hidroksil dari selulosa batang jagung.

Kata kunci : asam sitrat, batang jagung, konsentrasi, papan partikel, perekat

Introduction

Particleboards are fibrous panels made up of lignocellulosic materials joined together with synthetic binder. Particleboards are among the most popular materials used in interior and exterior applications in floor, wall, ceiling panels, office dividers, bulletin boards, cabinets, furniture, counter, and desk tops. With depleting wood resources, the wood industry struggles to obtain sufficient amount of raw material for particleboards production. High demand for wooden materials and rises in agricultural areas and forest fires also increased the importance of particleboards instead of using solid woods. This condition encourage many studies on the possibility of using natural fibers or agricultural by-products as materials in place of wood materials for particleboards. Various studies investigated properties of particleboards made from natural fibers or agricultural by-products such as corn stalk and leaves (Theng *et al*. 2015), rice husk (Kumagai & Sasaki 2009), rice straw (Zhang & Hu 2014), kenaf core (Okuda & Sato 2008), bagasse (Widyorini *et al*. 2005), and oil palm trunk (Baskaran *et al*. 2013).

Agricultural fibers, such as straw and plant stalks, have been considered as renewable alternatives for making particleboard, which would ease the huge demand for wood. As a natural fiber and agricultural by-product, corn stalk is considered as a potential raw material to produce particleboard. Limited information is available for corn stalk particleboard, which may have potential application in insulation, furniture, packaging, or lightweight core materials. Particleboard performance is mostly related to the properties of adhesives and their compatibility with particle. Urea formaldehyde (UF) and phenol formaldehyde (PF) has been the major adhesives for particleboard. Therefore, various investigations were carried out to evaluate characteristics of particleboard made from corn stalk particle and citric acid as adhesive.

The main goal of the current study is to confirm the feasibility of using corn stalk particle as alternative raw material for particleboards with citric acid as adhesive, which, to our knowledge, has not been thoroughly investigated before. The objectives of study are; (a) to investigate the effect of different concentration of citric acid on the physical-mechanical properties of particleboards and, (b) to study the bonding mechanism corn stalks particle with citric acid and the bonds between isolated celluloses derived from corn stalks with citric acid.

Materials and Methods

Fresh corn stalk were collected from field at Cibeureum, Darmaga region Bogor. They were washed by fresh water and cutted using a knife ring flaker into smaller particles about 1.5 to 2.5 cm. Particles were dried to 8 percent moisture content. Technical citric acid was purchased from chemical distributor of Setia Guna (Bogor, Indonesia). Citric acid was dissolved in water at a ratio 1:1, and this solution was used as adhesive.

Chemical composition from corn stalk also were analysed based on TAPPI T method. Corn stalks particle was blended with citric acid solution. Based on oven dry particle weight, 10, 20, and 25% citric acid resin were applied for particleboard, respectively. In this research also was made particleboard without from corn stalks without citric acid as control. Particleboards samples were made with length x width x thickness (25 x 25 x 0.9) cm^3. Hand formed mats were pressed in a hydraulic hot press at a temperature of 200 ºC, a pressure of 2.5 MPa for 10 minutes with a target density of 0.8 g cm^{-3}.

Particleboards were conditioned for about two weeks at room temperature. Test samples were prepared and cutted by circular saw than tested based on JIS A 5908:2003 (JSA 2003) particleboard standard for physical and mechanical properties.

Results and Discussion

The chemical composition of corn stalks shown in Table 1. Corn stalks has the potential as a source of lignocellulose material because it has high levels of α-cellulose, holocellulose, hemicellulose and lignin. The chemical content of corn stalk similar to those of other agricultural by-products and annual fiber plants that are commonly used an alternative raw materials to manufacture particleboard such sorghum, rice straw, bamboo, kenaf stalk, ramie, jute, coconut fiber and palm oil trunk.

As an information, production of corn in Indonesia reach 19.03 million ton at 2014 (BPPKP 2015). They reported also that the annual local corn production of Indonesia grows 6 percent per year (BPPKP 2015). Therefore corn stalks fiber as a waste from agricultural by-products was generated abundantly.

The data in this study showed the solubility of corn stalks in 1 wt% content of NaOH and in high hot water. The high solubility in hot water indicates high levels of simple carbohydrates and simple phenolic compounds, which can occur due to weathering due to hydrolysis.

Figure 1 and 2 shows the effect of the citric acid concentration on the thickness swelling (TS) and water absorption (WA) of particleboards which manufactured from corn stalks particle and citric acid as adhesive. The samples were soaked in water for 24 h. Both reveal similar trends of swelling and water uptake in all types of boards. The TS value of particleboard from corns stalks and citric acid fulfilled JIS A 5908:2003 standard for particleboard, maximum of 12%. Moreover, the TS value of corn stalks particleboards better than particleboards from sweet sorghum (Kusumah *et al.* 2016) and bamboo (Widyorini *et al.* 2014) was also used citric acid as adhesive with same concentration (20 wt%). However, particleboard without citric acid from corn stalks particle not fulfilled the particleboard standard.

The TS and WA value from corn stalks particleboard with citric acid also were higher than 100 wt% corn stalks particleboard bonded urea formaldehyde (25.55 and 63.39%) that researched by Guler *et al.* (2015). Particleboards made from corn stalks particle with bonded citric acid 20 wt% gave the lower TS value (2.92%) and WA value (33.45%) among all boards. This result indicates that 20 wt% citric acid content be an optimum adhesive concentration that produce particleboard with good dimensional stability properties.

Table 1 Chemical composition of corn stalk particle

Chemical component	Content, %
α-Cellulose	32.4
Holocellulose	55.6
Hemicellulose	23.2
Klason lignin	16.3
Solubility in hot water	27.6
Solubility in NaOH 1%	55.7
Ash	8.1

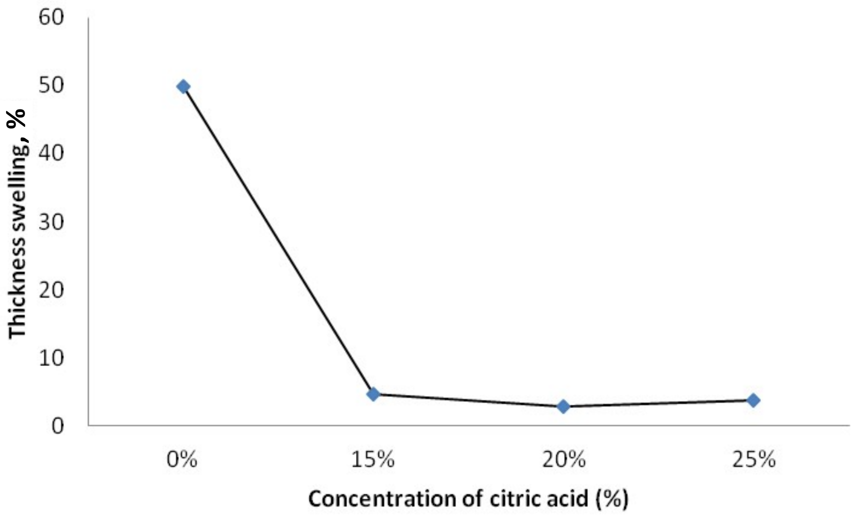

Figure 1 Thickness swelling value of particleboard.

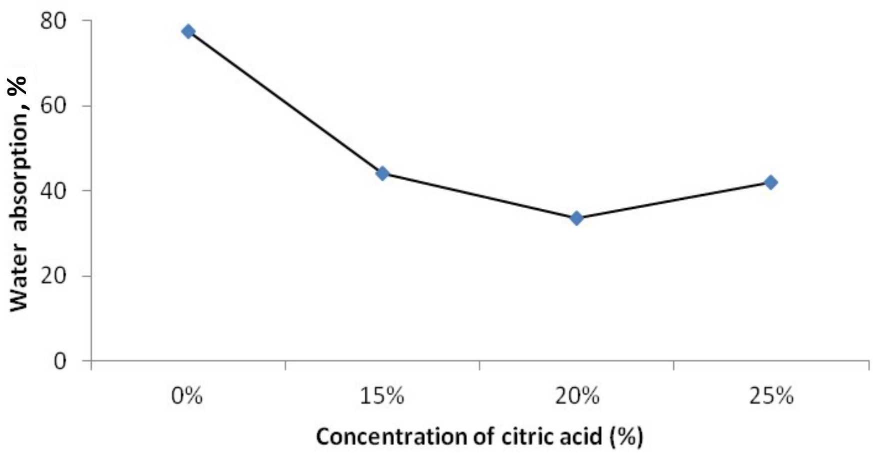

Figure 2 Water absorption value of particleboard.

The mechanical properties of the particleboards are shown in Figures 3-5. Mechanical properties of the particleboards also followed similar trend. The modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond (IB) values of the particleboards increased as the citric acid concentration was increased from 0 to 20 wt% and then slightly decreased.

The maximum average MOR and MOE values of corn stalks particleboard were 14.71 MPa and 4.96 MPa at 20 wt% citric acid, respectively. The MOR and MOE values of the particleboard fulfilled JIS A 5908:2003 requirements of Type 13 Particleboard and were higher than particleboard from corn stalks and 9 wt% UF adhesive by Guler *et al*. (2016).

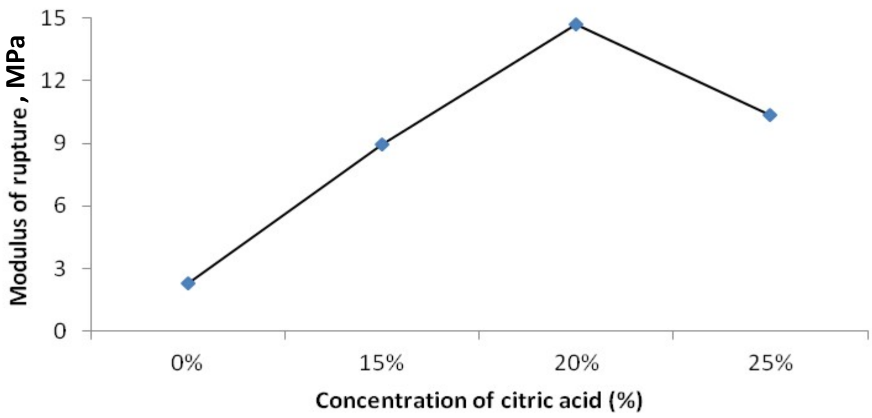

Figure 3 Modulus of rupture from particleboard.

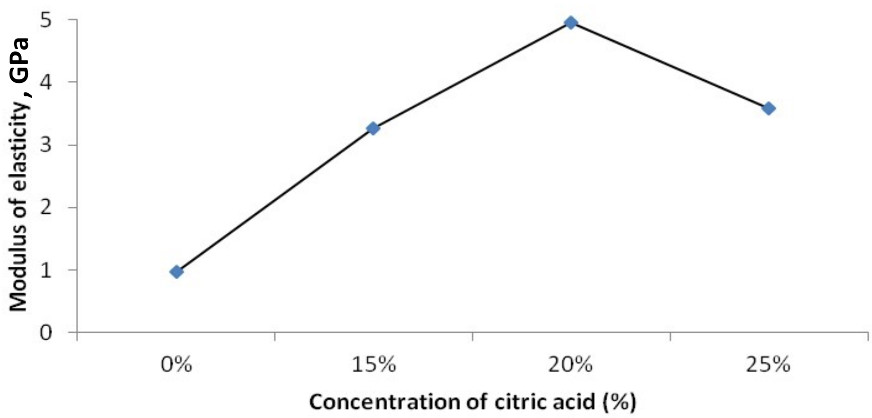

Figure 4 Modulus of elasticity from particleboard.

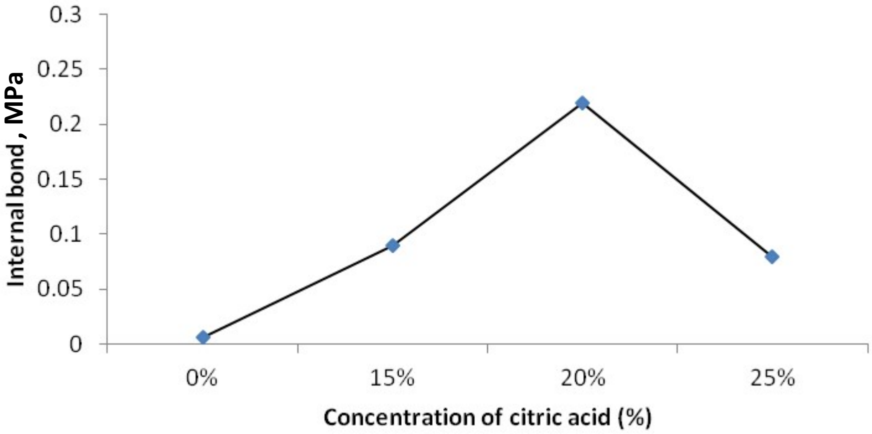

Figure 5 Internal bond values of particleboard.

The internal bond (IB) of particleboards were relatively middle value, ranging from 0.08 to 0.22 MPa. The IB strength of particleboards bonded with 20 wt% citric acid greater than those of board bonded with 0, 15, and 25% wt citric acid, respectively. Only the IB value of particleboards bonded with citric acid at 20 wt% fulfilled JIS A 5908:2003 requirement of Type 8 Particleboard, minimum of 0.15 MPa, moreover requirement of Type 18.

Bonding mechanism

The bonding mechanism properties of citric acid as adhesive for corn stalks particleboard that pressed with temperature of 200 ºC for 10 min can be observed using FTIR spectroscopy. Figure 6 shows FTIR analysis of particleboard without adhesive and particleboard with citric acid adhesive. Peaks in the range of 1700 cm^{-1} can be attributed to stretching C=O derived from carboxyl groups or ester groups (Yang *et al*. 1996, Zagar *et al*. 2003). The peak at 1190 cm^{-1} was caused by the C-O stretching of the carboxyl group. This figure indicates that the addition of 20 wt% citric acid as an adhesive gives the intensity of the carbonyl group higher than the addition of 15 and 25 wt% citric acid. Establishment of ester bonds could be colored during the forging process. The occurrence of ester bonds between carboxyl groups derived from citric acid and the hydroxyl group of corn stalks components causes an increase in both physical and mechanical properties.

This bonding mechanism is the same as that researched in wood particleboards bonded with citric acid adhesive (Umemura *et al*. 2014), sweet sorghum (Kusumah *et al*. 2016) and bamboo (Widyorini *et al*. 2014). The carbonyl group is present because of the reaction of the hydroxyl group from the lignocellulosic material and the carboxyl group of citric acid (Umemura *et al*. 2011).

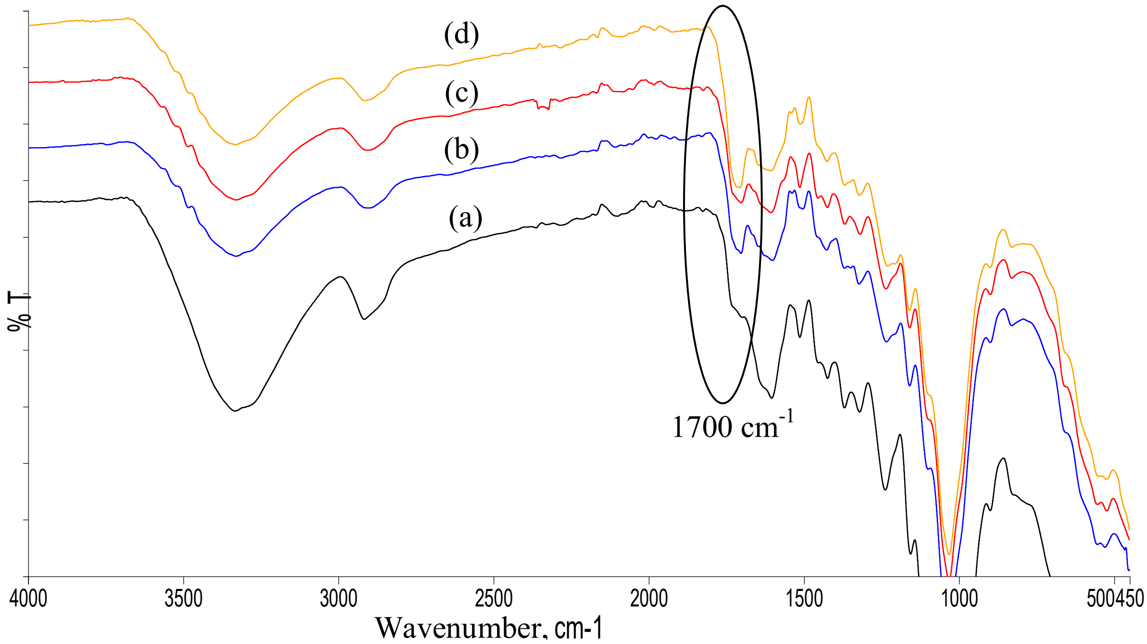

Figure 6 Fourier transform infrared spectra of corn stalks particleboard without adhesive (i), particleboards bonded with 15 wt% citric acid (ii), 20 wt% citric acid (iii), and 25 wt% citric acid (iv).

In this research, corn stalks also were isolated in cellulose for further evaluation of their bonds with citric acid. The expected bond is a covalent bond, the ester bond between the alcohol functional groups in carbohydrates with carboxylic groups in citric acid. The mixture between cellulose and citric acid that pressed on mold at temperature 140 and 200 ºC than investigated using FTIR spectroscopy. The FTIR spectra was used to prove the formation of a new functional group, ester. In this study, cellulose isolates showed a low residual lignin, as well as the loss of the peak for aromatic rings in the range 1600-1610 cm^{-1} and 1505-1515 cm^{-1}. Figure 7 on cellulose isolates added citric acid prior to washing shows spectra with typical ester wavelengths in the range of 1700 cm^{-1} (Paukszta *et al.* 2014). The sample spectra with addition of citric acid after pressing at 140 °C but before washing showed a sharp peak at 1708-1718 cm^{-1}, but the peak was lost after the sample was washed. These symptoms indicate there is no covalent bond between cellulose and citric acid. Establishment of the surviving ester after fresh washing occurs that pressed at temperature 200 °C (Figure 8). However, the peak at 1250 cm^{-1} indicating symmetric strain in C-O and 1168 cm^{-1} for asymmetric strains in C-O could not be distinguished because cellulose isolates also have peaks at these wavelengths.

The ester bond is successfully formed on cellulose. This results in line with the facts that obtained by Vukusic *et al.* (2006), which evaluated the adhesion between cellulose and some organic acids using specimens of cypress wood (*Abies alba*) and beech (*Fagus sylvatica*) chemically modified using polycarboxylic acid (PCA), one of which is citric acid.

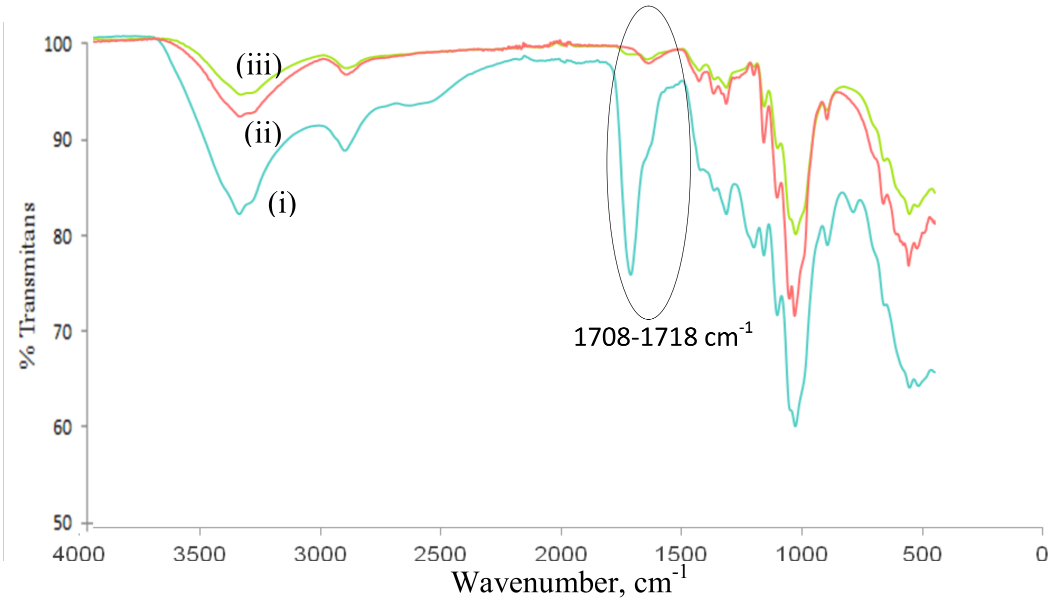

Figure 7 Infrared spectra of cellulose isolate mixed citric acid that pressed at temperature of 140 ºC (i), cellulose isolate mixed citric acid that pressed at temperature of 140 ºC after washing (ii) and cellulose isolate (iii).

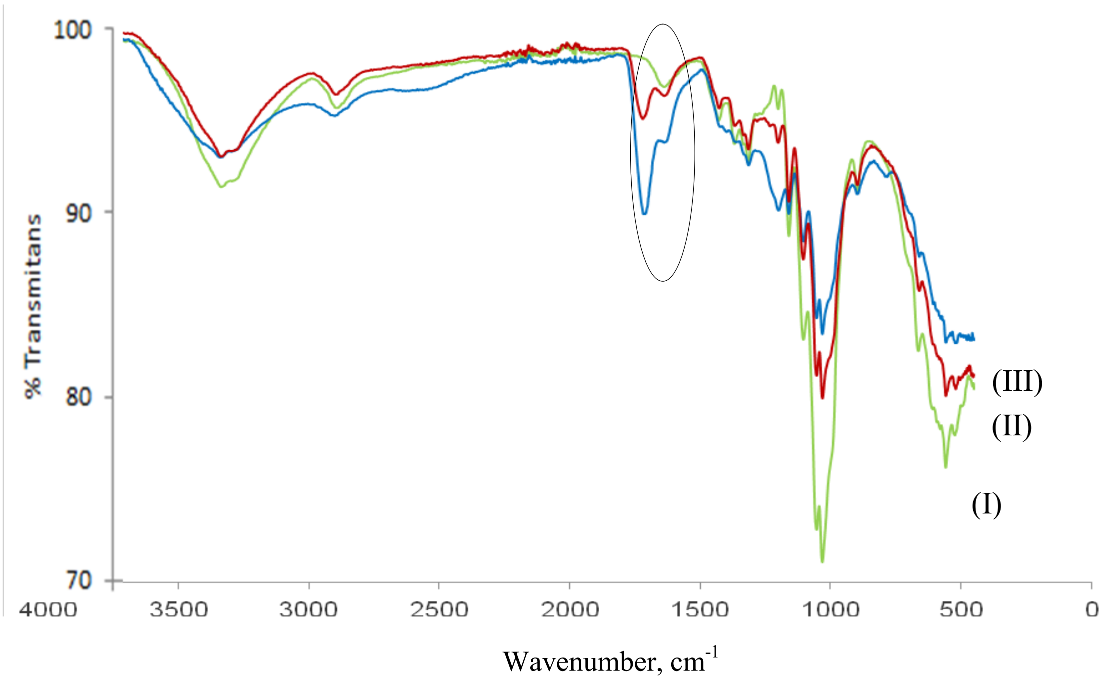

Figure 8 Fourier transform infrared spectra of cellulose isolate (i), cellulose isolate mixed citric acid that pressed at temperature of 200 ºC after washing (ii) and cellulose isolate mixed citric acid that pressed at temperature of 200 ºC (iii).

Conclusion

The results indicated that it is possible to produce particleboards from corn stalks by using citric acid adhesives. Citric acid content has influence on the physical-mechanical properties of corn stalks particleboards. Based on the results obtained in this study, the particleboard bonded with 20% wt citric acid had the best physical-mechanical properties that fulfilled the requirement of the 13 type of JIS A 5908:2003 standard. The addition of 20 wt% citric acid as an adhesive gives the intensity of the carbonyl group higher than the addition of 15 and 25 wt% citric The ester bonds were successfully formed on board from isolated cellulose and citric acid powder that molded and pressed at temperature 200 ºC, as evidenced by the formation of ester groups in cellulose derived from corn stalks. The formation of this covalent bond, which also indicates the formation of crosslinks by citric acid effect on the physical-mechanical properties of corn stalks particleboards.

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