

# Glycerol-based Liquefied Palm Kernel Shell Product and its Blend with Citric Acid as Bio-based Wood Adhesive

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Concerns for the environment and for human health have become critical factors that motivate creating bio-based wood adhesives. Therefore, this study proposes replacing toxic chemicals with alternative adhesives. In the first step, glycerol was added to the natural phenolic compounds from liquefaction of palm kernel shell (PKS), having a high content of lignin. The obtained glycerol-based liquefied PKS, and its blend with citric acid, were tested for bonding in a study on the effects of hot-pressing conditions (temperature and time). The results revealed that the liquefaction system in this study achieved an 83% conversion of the PKS components into glycerol-based liquefaction. According to the Fourier transform infrared and carbon-13 nuclear magnetic resonance analyses, the glycerol-based PKS contained lignin derivatives and furan products. This accounted for its great performance in bonding rubberwood veneers. The tensile shear strength was improved by blending with 15% citric acid, especially when applying the high 190 °C pressing temperature for 15 min.

DOI: 10.15376/biores.18.4.7877-7888

*Keywords:* Palm kernel shell; Glycerol; Citric acid; Bio-based wood adhesive; Liquefaction product

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## INTRODUCTION

Formaldehyde emissions are a critical problem associated with wood-based composites. Especially plywood, particleboard, medium-density fiberboard, and oriented strand board that are fabricated with adhesives containing formaldehyde-based resins, such as urea-formaldehyde, melamine-formaldehyde, or phenol-formaldehyde, are of concern. The formaldehydes released during production and utilization of these products have negative effects on the environment and on human health. Therefore, bioproducts either from plants or from animals for creating bio-based adhesives would be of great interest (Pizzi *et al.* 2020; Mi *et al.* 2021). Citric acid has been claimed to be a non-toxic chemical that shows a good performance in bonding wood veneer or wood particles on making wood composites. Interestingly, it enhances the water resistance of the board, addressing the weak point of many other bio-based adhesives, such as starch-based adhesives (Lin *et al.* 2022).

According to a literature review, the hydroxyl groups in wood polymers, carbohydrates, and lignin are capable of forming ester links with citric acid's carboxyl groups (Ando and Umemura 2021). In the presence of heat, the esterification process is likely initiated through the dehydrative transformation of the citric acid, resulting in the

formation of an intermediate anhydride ring, giving water as a byproduct. Subsequently, this anhydride ring undergoes esterification with a hydroxy group, leading to the opening of the ring and the production of the final ester product (Nguyen and Pham 2020). The anhydride ring of citric acid can be formed at its melting point around 153 °C (Noordover *et al.* 2007). DSC analysis results employing a heating rate of 10 °C/min reveal that citric acid exhibits a peak melting temperature at 154 °C and experiences maximum decomposition at 225 °C (Barbooti and Al-Sammerra 1986). Hence, citric acid can be a standalone bonding agent, or it can be blended with other materials before application as a wood adhesive (Choowang and Luengchavanon 2021; Wibowo *et al.* 2021). A 59% aqueous solution of citric acid was found to give a great shear strength to white jабon plywood when applying the pressing temperature of 190 °C for 10 min under the low 1.3 MPa pressure (Sutiawan *et al.* 2022). Meanwhile, Santoso *et al.* (2020) prepared solutions with sucrose and citric acid in various ratios for bonding Nipa frond particles. They found that the thickness swelling and water absorption of Nipa frond particleboard were positively reduced upon increasing the citric acid proportion, while the mechanical properties tended to be degraded with a high ratio of citric acid. Oktay and co-workers (2021) used citric acid as a hardener by adding 50% based on solids content of resin mixed from cornstarch and wattle bark tannin. Three carboxyl groups in citric acid structure are cross-linked with hydroxy groups of cornstarch or wattle bark tannin, as well as with a transformed glucose product, 5-hydroxymethylfurfural (5-HMF). This network reaction provides excellent bonding in particleboard. The carboxyl groups of citric acid esterify with the -CH<sub>2</sub>OH groups at the C6 position of carbohydrate polymers. This esterification also occurs within lignin's structure, involving either the -CH<sub>2</sub>OH groups on the side chains of the aliphatic segments or the free -OH groups on the aromatic rings (Menezzi *et al.* 2018; Ando and Umemura 2021). 5-HMF contains two types of functional groups: aldehyde and hydroxyl groups, which can condense with citric acid molecules through ether and ester linkages, respectively (Sun *et al.* 2019; Zhao *et al.* 2019). The utilization of a citric acid and glycerol mixture also demonstrates the potential to serve as a binder in wood composite production, enhancing the water resistance of the boards (Segovia *et al.* 2020; Nitu *et al.* 2022). The binder prepared from an aqueous solution of mixed citric acid and glycerol, heated at 100 °C for 60 min in a hot water bath, showed a remarkable ability to produce jute stick particleboard when subjected to a high pressing temperature in range of 180 to 200 °C. An increase in temperature has the effect of promoting the reaction between glycerol and citric acid, thereby enhancing bond strength. However, the internal bonding drops after hot compression at 220 °C for 8 min (Nitu *et al.* 2022). Zhao *et al.* (2019) also observed that freeze-dried citric acid, prepared from an 80 wt% aqueous solution of citric acid heated at 100 °C for 2 h, exhibits endothermic peaks at 155 and 212 °C, corresponding to its melting point and decomposing temperature.

Glycerol is a low-cost and non-toxic chemical that can function as a plasticizer, providing an alternative for the generation of bio-based adhesives (Milotoskyi *et al.* 2019; Azerêdo *et al.* 2022). Unfortunately, pure glycerol gives a low shear strength bonding of wood (Mamiński *et al.* 2011). It must be combined with other chemicals, such as citric acid mentioned above. Remarkably, the addition of phenolic compounds such as condensed tannin to the solution of glycerol and citric acid is beneficial for improving the mechanical properties and bond strength in wood composites. Tannins bond with the glycerol structure to form ether linkages (Segovia *et al.* 2020; Oktay *et al.* 2021). Similar to glycerol, other polyhydric alcohol-based liquefaction products need to be combined, for good performance, with isocyanate-based chemicals such as hexamethylene diisocyanate (HDI)

or polymeric methylene diphenyl diisocyanate (pMDI), for the effective production of wood adhesives (Mamiński *et al.* 2011; Jiang *et al.* 2021). The composition of liquefied biomass products depends on the chemical composition of the biomass itself and the specific type of liquefying reagent used (Jiang *et al.* 2022), and the liquefaction process is a great way to introduce natural phenolic compounds into glycerol. Considering the chemical composition, palm kernel shell (PKS) has plentiful lignin in the range from 43 to 53% by dry weight (Babinszki *et al.* 2021). Lignin is a network of phenolic compounds. The molecules formed from glycerol during liquefaction may be helpful in bonding rubberwood veneer without a crosslinking reagent. Lignin has been interested in being used as a green filler to improve the properties of polymer composites, as well as a curing agent for glycerol (Ortiz *et al.* 2019).

The aim of this study was to investigate the bonding ability of a glycerol-based liquefied PKS product and its blends with citric acid as a non-toxic crosslinking reagent. The efficiency of glycerol to convert PKS to liquor products was studied in the first step. This was evaluated by Fourier transform infrared spectroscopy (FTIR) and by solid state  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy (NMR). The thermal properties of glycerol-based liquefied PKS product, and its blends with citric acid, were tested for the effects of pressing temperature. The effects of pressing temperature and pressing time on bonding of both bio-adhesives were studied in the final step.

## EXPERIMENTAL

### Materials

The PKS were collected from the oil palm industry in Surat Thani province, in southern Thailand. The ground kernel shells were passed through a 0.10-mm sieve before use in this study. The rubberwood veneers were of dimensions 350 x 350 x 1.5 mm<sup>3</sup>. Analytical grade glycerol and sulfuric acid (98% H<sub>2</sub>SO<sub>4</sub>) were used without further purification.

### Glycerol-based Liquefied PKS Preparation

Glycerol was used as the liquefaction reagent to convert PKS powder into liquor form. The dried PKS powder was added into the thermally acidified solution of glycerol in the ratio of 1:4 (w/w). The liquefaction reaction was carried out in a 500-mL three necked flask immersed in a hot oil bath, equipped with a thermocouple and a magnetic stator. The reaction was activated with the constant temperature of 180 °C and 2% of sulfuric acid (98%, w/w)-based on the amount of glycerol reagent. After the designated 30 min reaction time, the flask reactor was quickly moved into a cool bath to quench the liquefying reaction. The sticky liquefied product was separated from the residue (or not reacted PSK) by dissolving in 80% aqueous ethanol solution, before it was stirred and filtered through a filter paper with vacuum assist. The residue was oven-dried at 103 °C until constant weight. The yield of glycerol-based PSK liquefaction product was calculated as follows,

$$\text{Glycerol-based liquefied PSK yield} = [1 - (m_f / m_b)] \times 100 \quad (1)$$

where  $m_f$  is the oven dry weight (g) of residue content after liquefaction reaction and  $m_b$  is the oven-dry weight (g) of palm kernel shell used. The diluted liquefied PKS product was dried in a vacuum rotary evaporator with temperature in the range from 50 to 60 °C, for

removing water and ethanol. The liquefied PKS product was stored in a brown glass reagent bottle and kept in a refrigerator until use.

### Glycerol-based Liquefied PKS Product Characterizations

The method to separate what is soluble and what is insoluble in water followed the description in Choowang *et al.* (2019). The crude glycerol-based liquefied PKS product was added with 10-fold amount of distilled water and stirred for 1 h. After that it was left at room temperature for one night before it was filtered through grade 1 filter paper (Whatman, UK). The solid residue was dried at 60 °C in a hot air oven. The water in the liquor part was removed by using a vacuum rotary evaporator at 50 to 60 °C. The chemical components of crude glycerol-based liquefied PKS and its two parts, soluble and insoluble in water, were assessed by Fourier transform infrared spectroscopy (FTIR) with a PerkinElmer (Waltham, MA, USA), and by solid state <sup>13</sup>C solid nuclear magnetic resonance spectroscopy (NMR) using a Bruker ascend model 400 WB (Fällanden, Switzerland).

### Thermal Behavior Analysis

A differential scanning calorimeter (DSC) was used to investigate the thermal behavior of crude glycerol-based L-PKS and its blends with 15% citric acid. The samples were added into an aluminum pan before placing in the DSC instrument (Mettler-Toledo, Switzerland). After that, the samples were heated from 50 to 300 °C at a heating rate of 10 °C/min. The analysis was run with nitrogen flushing at a flow rate of 20 mL/ min.

### Bonding Performance Tests

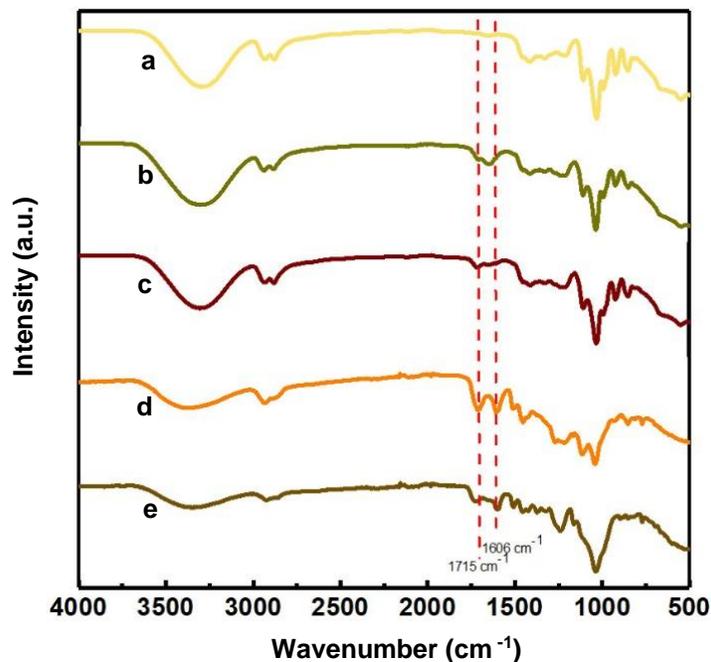
Three-ply rubberwood veneer was prepared for bonding ability tests. Firstly, a 100 g sample of crude glycerol-based liquefied PKS was loaded into a 500-mL beaker before adding citric acid for 15% based on the liquefied PKS amount (Choowang and Luengchavanon 2021). Then, the mixture was stirred until the grains of citric acid were completely dissolved. The glycerol-based liquefied PKS and its blends with citric acid were applied on both sides of rubberwood veneer, 150 g/m<sup>2</sup> per side, before covering with rubberwood veneer. The assembled 3-ply veneer was compressed with a laboratory hot press at the pressing temperatures of 150 °C, 170 °C, and 190 °C. Each pressing temperature was run with the maximum pressure of 5 MPa held for 10 or 15 min. All the boards were kept at 20 ± 3 °C room temperature in 65 ± 5% relative humidity until their use.

For preparing the tensile shear strength specimens, all 3 plies of plywood bonded with both bio-adhesives were cut into tensile shear strength specimens according to ISO 12466-1 (2007) and ISO 12466-2 (2007) standards. Each specimen was fixed to crossheads of a universal testing machine (10ST, Tinius Olsen, UK) with 5 kN loadcell, and then a constant extension speed of 3 mm/min was applied. The maximum load (N) and shear support area on the sample were recorded to further calculate the tensile shear strength. The shear strength was estimated in both dry and wet conditions. For dry conditions, specimens were directly tested after they were conditioned in a room at 20 ± 3 °C temperature and 65 ± 5% relative humidity, while other specimens were soaked in cold water at 20 ± 3 °C for 24 h before testing to assess the wet conditions. The wood failure was assessed for all the tested specimens.

## RESULTS AND DISCUSSION

### Glycerol-based Liquefied PKS Yield, and its Characterizations

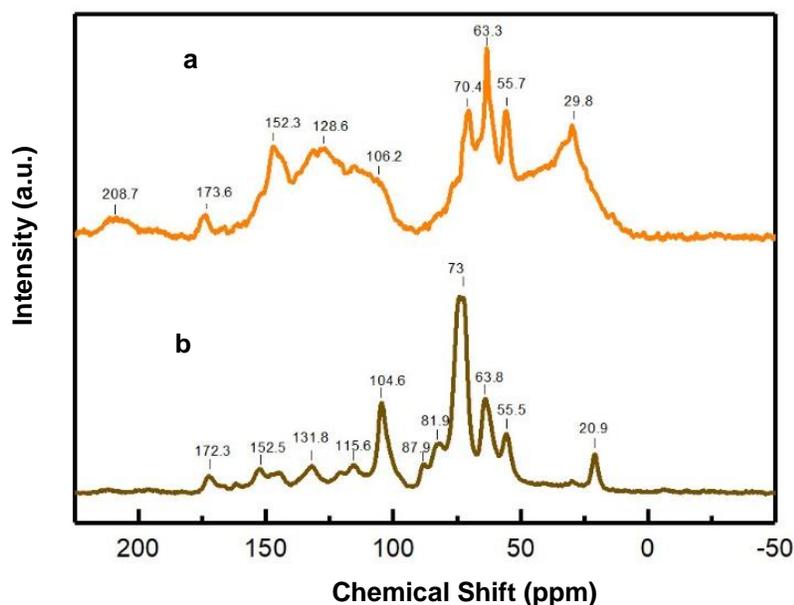
The amorphous polymers lignin, hemicellulose, and amorphous cellulose in the lignocellulose, when in a thermal acid solution of various polyhydric alcohols, typically turn into liquor earlier than the crystalline chemicals such as cellulose (Jiang *et al.* 2021). Hence, PKS with plentiful lignin showed an 83% liquefaction yield when it was reacted with glycerol in the ratio of 1:4 (w/w) and activated by 2% sulfuric acid based on the amount of liquefaction reagent, at 180 °C for 30 min. This result is related to the previous study of Cruz-Lopes *et al.* (2020). Chestnut shells that contained 47% lignin gave a liquefied yield of 91% when the process was run with acid catalyzed solution of glycerol and ethylene glycol (1:1 w/w) at 190 °C for 30 min. During the liquefaction, lignin in PKS was first removed by glycerol. Meanwhile, the decomposed sugars from carbohydrate components were intermediately converted to furan products such as furfural or 5-HMF. Some furan products can cross-link with lignin and its derivatives as well as the glycerol reagent, to form higher molecular weight substrates that precipitated after diluting in water (Choowang *et al.* 2019). The results from this study demonstrate that the water insoluble part of glycerol base liquefied PKS was 33%, based on the oven-dry weight of PKS raw material.



**Fig. 1.** The FTIR spectra of glycerol (a), crude glycerol base liquefied PKS (b), water soluble part (c), water insoluble part (d), and PKS raw material (e)

According to the FTIR spectra in Fig. 1, the FTIR spectrum of PKS that exhibited the C=O stretching vibrations of hemicellulose and lignin around 1724 cm<sup>-1</sup> shifted to 1715 cm<sup>-1</sup> in the FTIR spectra of the water-insoluble components. The peak at 1715 cm<sup>-1</sup> corresponds to the C=O stretching vibrations of carbonyl or carboxyl groups, which are found in organosolv lignin extracted from sugarcane bagasse (Muller *et al.* 2019). This suggests the polymerization of lignin with dehydration products of carbohydrate polymers during the liquefaction process. The C=O stretching vibrations of carbonyl groups in the

structure of furan products are observed around  $1715\text{ cm}^{-1}$  (Choowang *et al.* 2021). The FTIR spectra of PSK revealed C=C stretching of aromatic skeleton of lignin around  $1606\text{ cm}^{-1}$ . This peak was clearly observed in the spectrum of the insoluble part, and also as a tiny peak for the water-soluble part. Furthermore, the peak around  $1606\text{ cm}^{-1}$  possibly overlapped with C=C stretching of the furan ring. The bonding of lignin with other substrates was confirmed by the peak around  $1508\text{ cm}^{-1}$  (Wrzeczionek *et al.* 2021), which shifted in the spectrum of PKS to  $1506\text{ cm}^{-1}$ . Therefore, it can be presumed that the crude glycerol-based liquefied PKS had a high content of aromatic compounds from lignin and its derivatives. This fact was also confirmed by the solid-state  $^{13}\text{C}$  NMR spectra shown in Fig. 2.

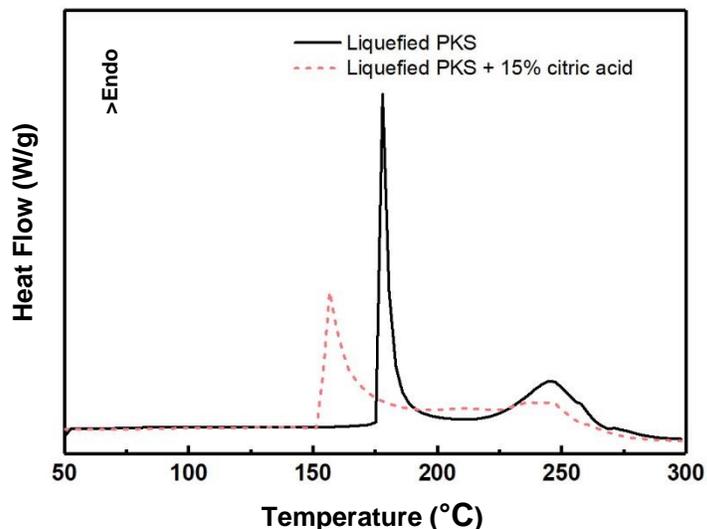


**Fig. 2.** The  $^{13}\text{C}$  NMR spectra of water insoluble part of glycerol-based PKS liquefaction product (a), and of PKS raw material (b)

Figure 2 indicates the chemical shift of PKS raw material and the water insoluble part. The signal of the water insoluble part had the methoxy group ( $-\text{OCH}_3$ ) and the aromatic carbon atoms in the lignin at 56 ppm, and 110 to 160 ppm, respectively. Furthermore, the water insoluble part had lost the signals of carbon atoms in cellulose, which were clear in the chemical shift pattern of PKS at 73 ppm (C-2, C-3, and C-5 atoms) and 104.6 ppm (C-1 atom). Moreover, the signals of water insoluble part around 70.4 ppm and 63.3 ppm corresponded to glycerol. The higher peak at 63.3 might have overlapped from the aliphatic carbon atom of lignin. In addition, the carbonyl group (C=O) was also found in the chemical shift of water insoluble part around 173.6 ppm (Choowang *et al.* 2019). The signal around 29.8 ppm corresponds to the carbon site of furan ring.

### Thermal Behavior of Glycerol-based Liquefied PKS, and its Blend with 15% Citric Acid

The DSC analysis results of the crude glycerol-based liquefied PKS product and its blend with 15% citric acid are presented in Fig. 3.



**Fig. 3.** The DSC responses of crude glycerol-based L-PKS and its blend with 15% citric acid

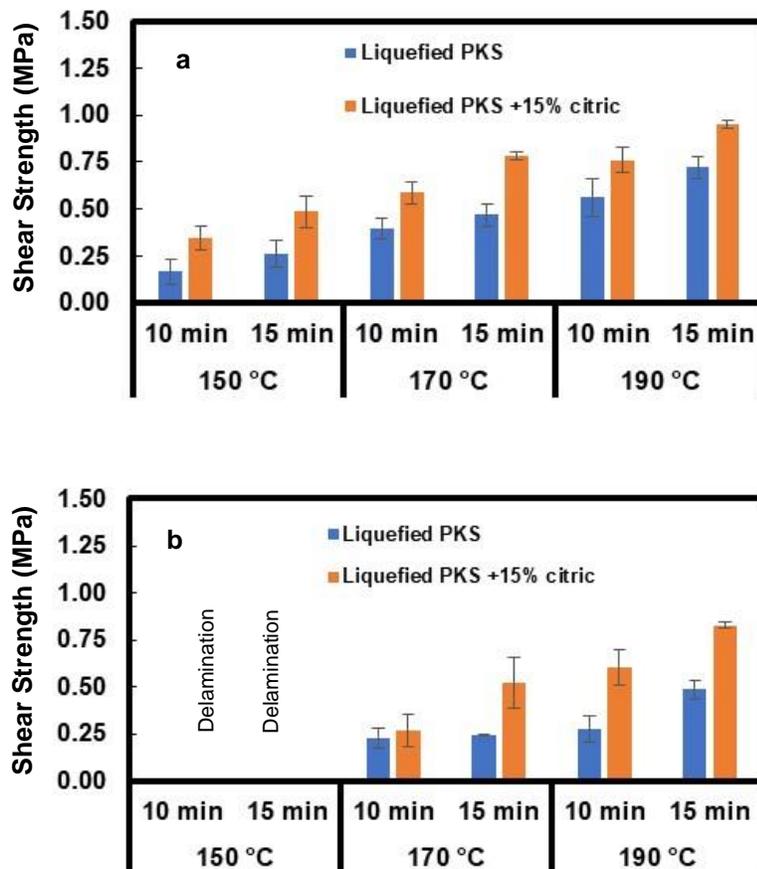
These results reveal two endothermic peaks. The sharpest peak of the crude glycerol-based liquefied PKS appeared at 177 °C but shifted to 155 °C in the blend with 15% citric acid. Both types of binder exhibited similar broad endothermic peaks, extending approximately from 220 to 260 °C. This temperature range is related to the degradation of polymers generated from citric acid and glycerol (Kudahettige-Nilsson *et al.* 2018). It seems that citric acid reduces the curing temperature of a crude glycerol based liquefied PKS product. Citric acid was dehydrated to form cyclic anhydrides with water as byproduct, before further crosslinking with the free hydroxy groups within glycerol-based liquefied PKS products through esterification, which requires a low reaction energy (Nguyen and Pham 2020). Consequently, the total energy consumption for curing crude glycerol-based liquefied PKS was reduced from 159 J/g to 148 J/g on adding 15% citric acid.

### Bonding Performance

The bond strengths of both bio-based adhesives in this study, a crude glycerol-based liquefied PKS, and its blend with citric acid, are shown in Fig. 4. The shear strength increased with pressing temperature and pressing time. Addition of 15% citric acid into the glycerol-based liquefied PKS enhanced the shear strength in both dry and wet conditions, and pressing at 190 °C for 15 min gave the highest shear strengths of 0.95 MPa and 0.83 MPa for the dry and the wet conditions, respectively. These shear strengths satisfy the requirements for plywood bond strength as per ISO 12466-2 (2007). However, they exhibited only a low areal percentage of wood failures (less than 20%), because the bond strength of the adhesive zone is lower than that of the wood interphase zone.

The main components of glycerol-based liquefied PKS were glycerol derivatives with degraded and transformed products from PKS, such as furfural, 5-HMF, and lignin. Some of those components were condensed together to form the high molecular weight substage compounds (Choowang *et al.* 2019). They crosslinked with the free hydroxy groups of rubberwood polymers to fix the board during the hot pressing. The bond strength and its water resistance were promoted by the cross-linking agent, citric acid. Ando and Umemura (2021) have demonstrated that the primary hydroxy groups of the wood polymer are esterified with citric acid under the condition of hot compression at 180 °C for 10 min,

which is related to the previous report by Sutiawan *et al.* (2021). They found that citric acid esterifies with the chemical components of white jaboron wood during plywood production under pressing at 190 °C for 10 min. Therefore, the increases in bond strength and its water resistance for plywood were probably promoted by esterification and network formation by the three functional groups of citric acid with various hydroxy groups of rubberwood and/or the glycerol-based liquefied PKS through a five-structured cyclic anhydride, which is formed as an intermediate product. The cyclic anhydride of citric acid can be generated closely to its melting point (Noordover *et al.* 2007).



**Fig. 4.** The tensile shear strength for dry (a), and wet condition (b) of 3-ply plywood, bonded with a crude glycerol-based liquefied PKS product and its blend with 15% citric acid

Furthermore, the changes of rubberwood components during hot pressing also enhance bond strength and water resistance of the board. This enhancement is attributed to the degradation of carbohydrate polymers, notably starch, hemicellulose, and cellulose. Some sugar monomers are subsequently transformed into furan products, especially furfural and 5-HMF. Meanwhile the heat activated lignin generates free radicals, which subsequently undergo condensation reactions themselves, to furan products and others degradation products. This improved the hydrophobic properties of rubberwood. Especially at the interphase zone of rubberwood and binder, the rubberwood veneers were further crosslinked with various components of glycerol-based liquefied PKS as well as citric acid to form the bonding network (Börcsök and Pásztor 2021; Oktay *et al.* 2021).

The dehydration reaction is instrumental in forming a C-O-C bonds between citric acid and furan products (Zhao *et al.* 2019). Lastly, a network substage was cured to create a thermoset polymer fixed in wood cells and bond area (Ando and Umemura 2021; Kurkowiak *et al.* 2023). Unfortunately, the plywood boards delaminated after soaking in water, in case the low 150 °C pressing temperature was used (Fig. 4a). This might be due to incomplete curing of both glycerol-based liquefied PKS adhesives, according to the DSC analysis. A low pressing temperature needed a longer pressing time.

## CONCLUSIONS

1. The components in liquefaction products of lignocellulose were found to mainly depend on its chemical composition and the liquefaction reagent. Therefore, choosing the type of lignocellulose with a high proportion of lignin, such as palm kernel shell (PKS), is a way to increase the aromatic components in the glycerol based liquefaction. The glycerol-based liquefied PKS had 33% of water insoluble substances: crosslinking products of lignin, furan products, and liquefied reagent according to the FTIR and <sup>13</sup>C NMR analysis. Therefore, it can be proposed as a bio-adhesive for bonding wood veneer.
2. The bond strength of glycerol-based liquefied PKS was improved by adding citric acid. Citric acid is proposed to function as a non-toxic crosslinking reagent to form a polymer network bonding the rubberwood veneer, enhancing the shear strength. However, the properties of adhesives need further study to improve the bonding performance, especially regarding the percentage of wood failures.
3. The hot-pressing conditions are also key factors on curing bio-based adhesives, for good bond strength in rubberwood veneer. In this study, a 190 °C pressing temperature with 15 min pressing time were the best conditions tested for curing glycerol base liquefied PKS and its blend with 15% citric acid.

## ACKNOWLEDGMENTS

This research was financially supported by the Prince of Songkla University, Surat Thani campus, 2021, Grant No SIT6403002S

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Article submitted: June 28, 2023; Peer review completed: August 19, 2023; Revised version received and accepted: September 25, 2023; Published: October 4, 2023.  
DOI: 10.15376/biores.18.4.7877-7888