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INNOVATOVE ECO-FRIENDLY WOOD ADHESIVE FORMULATIONS: EXPLORING THE EFFICACY OF GELATINIZED CASSAVA STARCH AND POLYVINYL ALCOHOL CROSSLINKED WITH CITRIC ACID

(Formulasi Pelekat Kayu Mesra Alam: Inovatif Meneroka Keberkesanan Pati Ubi Kayu Bergelatin dan Alkohol Polivinil Berpaut Silang dengan Asid Sitrik)

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Abstract

In an effort to develop eco-friendly bio-adhesives for wood applications, this study explores the effect of citric acid as a new cross-linking agent on the properties of a cassava starch/polyvinyl alcohol (PVA)-based wood bio-adhesive. The bio-adhesive was synthesized in a three-step process: first, the hydrolysis of cassava starch using hydrochloric acid, followed by the oxidation of cassava starch with ammonium persulfate, and finally, the polymerization of starch and PVA with citric acid. The reaction was conducted for 100 min in a three-neck flask, using a mercury stirrer at 70°C under atmospheric pressure. The amount of citric acid added to the adhesive was calculated based on the dry weight of the cassava starch, with percentages ranging from 0%, 0.5%, 1%, 1.5%, to 2%. The adhesive characteristics were then evaluated in line with the ASTM D906 wood adhesive standard. Tests were conducted to measure adhesive viscosity, solid content, dry and wet shear strengths, thermal stability, and surface morphology. Molecular changes resulting from the addition of citric acid were analyzed using Fourier transform infrared spectroscopy. This research demonstrated that the addition of citric acid improved the adhesive properties. Specifically, the addition of 2% citric acid (AD-CA2.0) produced optimal results across several analyses. These included a high viscosity reading of 2910 cP, dry and wet shear strengths of 1.21 MPa and 0.89 MPa, respectively, and high solid content of 36%.

Keywords: bio-adhesive, cassava starch, polyvinyl alcohol, citric acid, polymerization

Abstrak

Sebagai pengiktirafan mendapatkan bio-pelekat mesra alam untuk aplikasi kayu, kajian ini meneroka kesan asid sitrik sebagai agen penghubung silang baharu ke atas sifat-sifat bio-pelekat kayu berasaskan kanji ubi kayu/polivinil alkohol (PVA). Bio-pelekat disintesis melalui tiga langkah: hidrolisis kanji ubi kayu dengan asid hidroklorik (HCl), pengoksidaan kanji ubi kayu dengan ammonium persulfat ($(NH_4)_2S_2O_8$), dan pempolimeran kanji dan PVA dengan asid sitrik. Tindak balas dijalankan selama 100 minit dalam kelalang leher tiga dan pengacau merkuri pada suhu 70 °C dan tekanan atmosfera. Berdasarkan berat kering kanji ubi kayu, peratusan asid sitrik yang ditambahkan pada pelekat berbeza antara 0%, 0.5%, 1%, 1.5%, dan 2%. Selaras dengan piawaian pelekat kayu ASTM D906, kelikatan pelekat, kandungan pepejal, kekuatan ricih kering dan basah, kestabilan terma dan morfologi permukaan telah diuji. Perubahan molekul telah dianalisis menggunakan spektroskopi Fourier Transform Infrared (FTIR). Penyelidikan ini menunjukkan bahawa penambahan asid sitrik meningkatkan ciri pelekat. Penambahan 2% asid sitrik

(AD-CA2.0) mempunyai hasil yang optimum untuk beberapa analisis seperti kelikatan tinggi pada 2910 cP, kekuatan ricih kering dan basah pada 1.21 MPa dan 0.89 MPa, dan kandungan pepejal tinggi pada 36%.

Kata kunci: bio-pelekat, kanji ubi kayu, polivinil alkohol, asid sitrik, pempolimeran

Introduction

The global rise in human population has led to an escalating demand for wood furniture, which in turn has increased the consumption of wood adhesives, a pivotal component in the wood industry [1]. Numerous studies have underscored this trend, highlighting a significant annual increase in the demand for wood adhesives [2]. In industry, the capacity of an adhesive to combine two materials in a short amount of time is preferred because it is practical and simple [3, 4].

Wood adhesives are commonly produced by chemical reactions [5], with two main types being utilized in the industry: conventional and natural adhesives [6]. Conventional adhesives are typically derived from petroleum, a nonrenewable resource. Formaldehyde was one of the earliest standard adhesives used to bind wood pairs [7]. It continues to dominate the production of wood-based adhesives owing to its effectiveness, stability, and cost-efficiency [8]. For instance, the urea-formaldehyde adhesive, known for its superior water resistance, is commonly used for interior products, while the phenol-formaldehyde adhesive is preferred for exterior applications [9].

Empirical evidence supports the health risks associated with the use of conventional adhesives. Formaldehyde, a known carcinogen that is used to treat human organ systems [10], poses potential threats not only during the manufacturing process but also in the final products. This is because formaldehyde naturally occurs in wood products and its emissions are generated by the residual formaldehyde content of the resin. Exposure to formaldehyde can induce skin and lung irritation, genotoxicity, and cancer [11]. Additionally, formaldehyde emits volatile organic chemicals that cause significant risks to both humans and the environment [12].

Various investigations on bio-adhesives have been conducted as potential substitutes for petroleum-based adhesives in wood bonding. The objective is to mitigate the adverse effects of synthetic adhesives on both human health and the environment [13]. The raw ingredients for bio-adhesives are abundant and inexpensive resources found in nature. These included materials such as soy, tannins, lignin, gelatin, wood fibers, plant polymers, and starch [14, 15].

Cassava starch, a material rich in amylose and amylopectin, has been utilized as a raw ingredient for bioplastic and paper adhesives [16]. This suggests that cassava starch could potentially serve as a raw material for bio-adhesive production. However, wood panels constructed entirely of starch are currently too fragile for practical use [17]. The hydroxyl groups in starch chains are hydrophilic, causing the starch to quickly interact with water, resulting in poor moisture tolerance. Moreover, when exposed to sufficient moisture and heat, the starch undergoes gelatinization, absorbing water and swelling [18].

A solution to this issue is the addition of PVA to the bio-adhesive, which reduces the rate of water absorption and decreases starch swelling. In the meantime, to ensure effective binding between starch and PVA, a cross-linking agent is required. Previous studies have investigated the influence of cross-linking agents like PTSA and bio-oil on the quality of bio-adhesive materials [19], [20]. However, these agents have been found to reduce adhesive quality, highlighting the need for the development of improved cross-linking agents.

Citric acid, with its three functional carboxyl groups, holds promise as it can potentially form bonds with the hydroxyl groups in starch and PVA. Its incorporation as a cross-linking agent in cassava starch bio-adhesives has demonstrated improved water resistance and mechanical qualities [21]. Despite these promising results, no studies have been conducted to analyze the effects of citric acid on the adhesive properties of starch. This investigation, therefore, sought to fill this research gap by focusing on the performance of cassava starch and polyvinyl alcohol (PVA) using citric acid as the cross-linking agent. A range of tests were

carried out to assess the physical properties and structural changes of the bio-adhesive, including viscosity, dry and wet shear strengths, solid content, thermogravimetry, and Fourier transform infrared (FTIR) analyses.

Materials and Methods

Materials

This study utilized cassava starch purchased from PT. Budi Acid Jaya. PVA and sodium dodecyl sulfate (SDS) procured from CV. Gudang Kimia, Yogyakarta. Hydrochloric acid (HCl, 37%) and citric acid were obtained from the Chemical Reaction and Catalyst Laboratory, UGM, Yogyakarta. Ammonium persulfate ($(NH_4)_2S_2O_8$) was provided by the LPPT UGM (Yogyakarta). Wooden boards (*Tectona grandis*) were purchased from UD. Makmur Jaya, Yogyakarta.

Bio-adhesive synthesis

The bio-adhesive was prepared by dissolving 50 g of cassava starch in 100 mL of 0.5 M HCl. The solution was stirred for 15 min to ensure homogeneity, before being placed in a batch reactor for gelatinization. In this study, the reactor, designed using a three-necked flask and a mercury stirrer, was maintained at a temperature of 70 °C and 1 atm pressure. The stirrer was set to a speed of 500 rpm. After 10 min of gelatinization, 0.4 grams of $(NH_4)_2S_2O_8$ were added to the solution. In addition, 1 gram of SDS was added to the solution after the process had run for 30 minutes. Approximately 15 g of PVA dissolved in 50 mL of distilled water was added to the reactor. The process continued with adding citric acid at a certain concentration, and the reaction was carried out for 1 h. All procedures were repeated with citric acid concentrations of 0%, 1%, 1.5%, and 2% based on the weight of cassava starch. The schematic of bio-adhesive is provided in Figure 1.

Viscosity analysis

The viscosity of the adhesive was analyzed using the ASTM D1084 standard [22]. Approximately 200 mL of the adhesive solution was poured into a glass beaker for this experiment. The adhesive viscosity was measured using a DV-E Brookfield Viscometer. The solution viscosity results were displayed on the monitor.

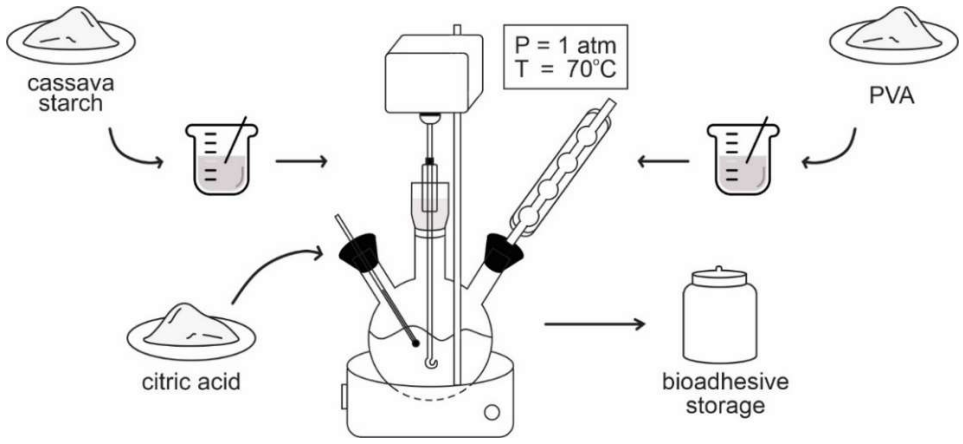


Figure 1. Schematic diagram of cassava starch bio-adhesive synthesis

Dry shear strength analysis

The dry shear strength was measured according to ASTM D906 [23] guidelines. Wood pieces measuring $30 \times 25 \times 2$ mm^3 were attached to the bio-adhesive and pressed under 3.27×10^{-2} N/mm^2 for 24 h before being stored at room temperature for seven days. The maximum bonding strength of the sample was determined at a speed of 2 mm/min using a universal testing machine in the Department of Chemical Engineering UGM. The shear strength of the adhesive was estimated using Equation (1).

$$\sigma_t = \frac{W}{A \times 1000} \quad (1)$$

Where σ_t is the shear strength of the adhesive (MPa),

W is the maximum force load (N), and A is the bonding area of the wood (mm^2). Dry strength analysis was conducted five times.

Wet shear strength analysis

The wet shear strength of the adhesive was calculated using the ASTM D1183 standard [24]. Identically sized wood pairs, already analyzed for dry shear strength, were bonded, and compressed under a pressure of 3.27×10^{-2} N/mm^2. After a day, the sample was submerged in distilled water for 24 h. Following this, the sample was dried and stored at room temperature at a relative humidity of 50%. Using a universal testing machine, we measured the maximum load of the sample at a testing speed of 2 mm/min. We used Equation 1 to calculate the wet shear strength. To ensure accuracy, we repeated this analysis five times and calculated the average of the results.

Solid content analysis

The solid content of the adhesive was determined according to ASTM-D2369 [25]. One gram of bio-adhesive was initially placed in a petri dish and heated at 110 °C ± 2.5 °C for an hour. After stabilizing the sample temperature using a desiccator for 10 min, we weighed the samples. We then used Equation 2 to determine the solid content of the adhesive.

$$S = \frac{w_2 - w_0}{w_1 - w_0} \times 100\% \quad (2)$$

Where S denotes the solid content of adhesive (%), w_0 signifies the mass of the petri dish (gram), w_1 is the mass of petri dish and sample before heating (gram), and w_2 is the mass of petri dish and sample after heating (gram). The solid content analysis was repeated three times.

Fourier transform infrared spectroscopy

The change in the functional groups in the adhesive because of the reaction process was investigated using a spectrophotometer FTIR Nicolet Is10 Mb 3000 from LPPT UGM in Yogyakarta, Indonesia. The spectral range of this study was between 650 and 4000 cm^{-1}, and 32 scans were recorded.

Thermogravimetry Analysis

Thermogravimetric analysis was performed at the Chemical Instrument Analysis Laboratory using a thermogravimetric analyzer (TA Instruments), housed in the DSC-60 Plus Shimadzu, Department of Chemical Engineering, Gadjah Mada University. The sample was dried in an oven at 60 °C for 3 h to obtain an adhesive powder with a size of 200 mesh or finer. The sample was placed in an alumina crucible, and another empty alumina crucible was used as a control. In an N_2 environment, the sample was gradually heated to 600 °C at a rate of 10 °C per min.

Adhesive morphology analysis

To analyze the morphology of the newly prepared adhesive, we used a Dino-Lite microscope AM8917 from the Department of Chemical Engineering, UGM and a scanning electron microscope (SEM) JSM-6510LA from LPPT, UGM. For the Dino-Lite microscope analysis, we placed the sample on a clean transparent glass. The light of the Dino-Lite microscope was turned on, and the magnification was adjusted to 500×. An image of the adhesive morphology was then captured for further analysis.

Results and Discussion

This study investigated the effects of citric acid addition on the quality of bio-adhesives made from cassava starch and PVA. The experiment varied the addition of citric acid between 0%, 0.5%, 1%, 1.5%, and 2%, based on the mass of cassava starch. The samples were labeled as AD-CA0 (blank sample), AD-CA0.5, AD-CA1.0, AD-CA1.5, and AD-CA2.0, according to their respective citric acid content. The experiment was conducted in a batch reactor system at 500 rpm.

In general, the synthesis of cassava starch bio-adhesives using citric acid involves a three-step process. The initial step involves hydrolysis and gelatinization of cassava starch using HCl. This process, carried out at 70 °C and 1 atm of pressure, breaks the glycosidic linkages in the starch to create an acid-thinned starch. The starch was then oxidized with ammonium persulfate $(NH_4)_2S_2O_8$) to produce carboxyl groups (–COOH). hydrolysis and oxidation mechanisms are shown in Figure 2.

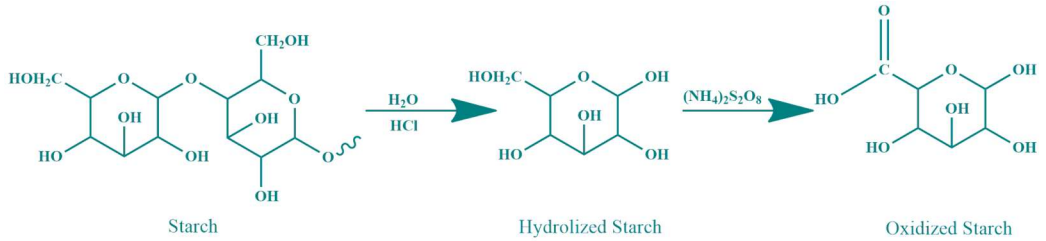


Figure 2. Reaction mechanism of cassava starch hydrolysis and oxidation

The carboxyl group of oxidized starch can form a bond with citric acid, which acts as a cross-linking agent. This bond formation gives rise to ester-starch. In addition, this oxidized molecule can induce retrogradation following gelatinization, a process where gelatinized starch reverts to its original form. Figure 3 illustrates the mechanism by which starch, and citric acid generate ester-starch.

Moreover, starch and PVA have the potential to form a bonding molecule known as ester starch/PVA. Figure 4 depicts the formation of bonding molecules between the starch and PVA using citric acid.

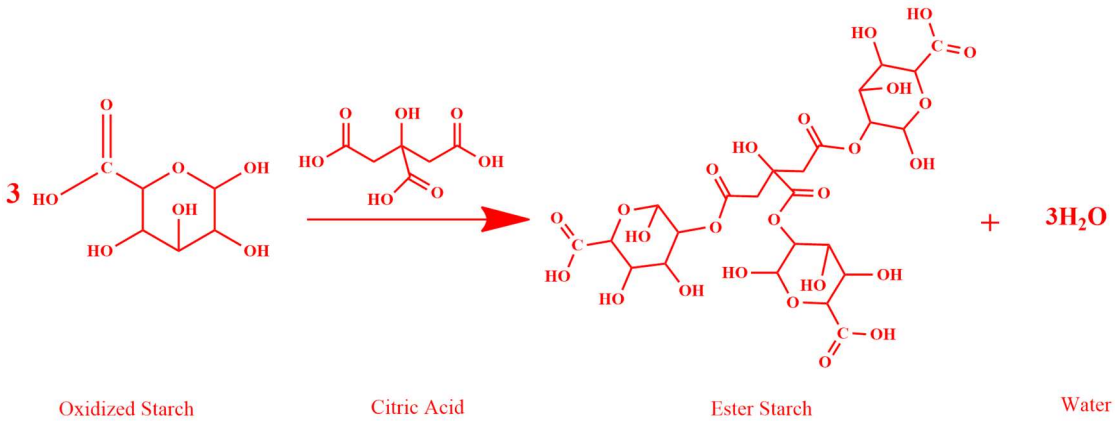


Figure 3. Reaction mechanism of ester starch synthesis

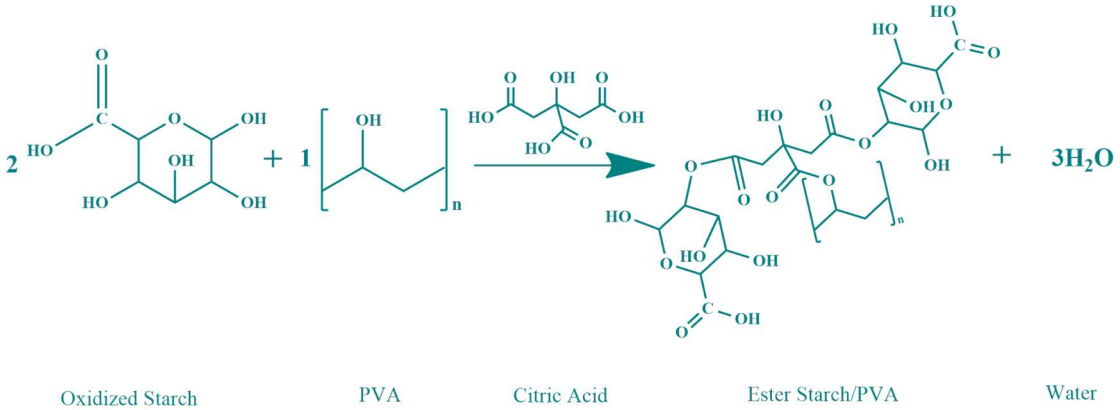


Figure 4. Reaction mechanism of ester starch/PVA synthesis

Viscosity analysis

The viscosity of each adhesive was measured to determine its physical properties. This characteristic is necessary as it greatly affects the adhesive capacity to coat wood surfaces. If the adhesive is too thick, it struggles to penetrate the wood pores, resulting in poor bonding. Conversely, a liquid adhesive fails to bond two pieces of wood together because it is rapidly absorbed by the wood pores. Figure 5 provides a visual example of this explanation.

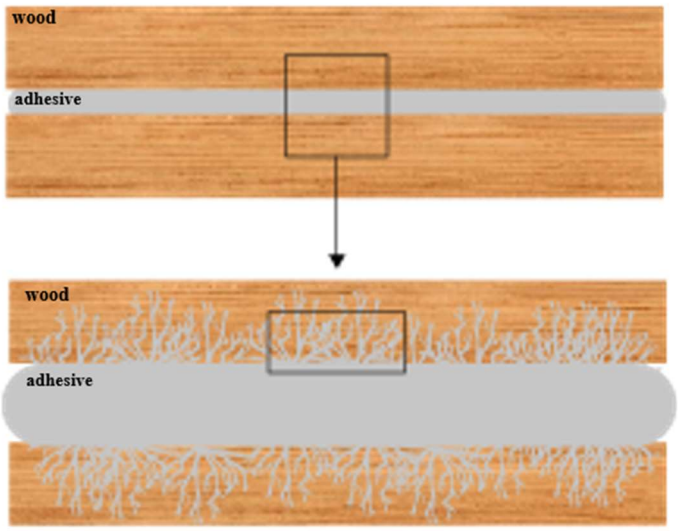


Figure 5. An illustration of bio-adhesive adsorption into the wood pores

In this experiment, viscosity was examined using a Brookfield Viscometer spindle. Given the nature of the adhesive as a non-Newtonian fluid, whose thickness fluctuates over time, the spindle was adjusted from its smallest to largest size and from its slowest to the fastest speed [26].

As shown in Figure 6, the adhesive viscosity increased with the addition of citric acid. The viscosity of AD-CA0, the reference sample without citric acid, was recorded at 1137 cP. Upon inclusion of 0.5% citric acid, the viscosity of AD-CA0.5 steadily increased to 1222 cP. The adhesive viscosity dramatically increased to 2312 cP and 2882 cP at concentrations of 1% (AD-CA1.0) and 1.5% (AD-CA1.5), respectively. Finally, adding 2% citric acid resulted in an adhesive viscosity of 2910 cP (AD-CA2.0).

This progressive increase in viscosity with the addition of citric acid underlines its role as a potent cross-linking agent that significantly influences adhesive properties. This is because the addition of citric acid to the adhesive greatly enhances the interaction of starch, PVA, and the cross-linker forming a polymer [27]. Citric acid, endowed with three carboxyl groups, functions as a bridging agent to enhance the number of hydrogen and covalent bonds between molecules. When citric acid is added to the mixture, its carboxyl groups react with the hydroxyl groups on starch and PVA to form a stable ester and reduce the mobility of the polymer chains. This polymerization process contributes to a denser solution, making the adhesive thicker and heavier. Therefore, higher concentrations of citric acid result in a more viscous adhesive.

Our results align with those of Kang et al. [28] and Wang et al. [29], who found that the addition of a cross-linking agent significantly increased polymer viscosity and enhanced adhesive mechanical properties. A comparison of our findings showed the consistency of cross-linker addition to the viscosity of the polymer. This finding also indicates that the concentration of citric acid as the cross-linker significantly contributes to the viscosity properties of the adhesive.

Dry and wet shear strength analysis

The shear strength of an adhesive is a crucial component that significantly influences its overall performance. The objective of this assessment was to determine the adhesive capacity to join two wood pieces. Additionally, we sought to determine how environmental factors affect the adhesive quality. Each sample was analyzed five times to confirm the accuracy of the data collected during this study. According to Figure 8, the adhesive strength was greater under dry conditions than that under wet conditions because water and starch share the same similar polarity properties. Therefore, the adhesive tends to dissolve in water easily, thereby reducing its bonding strength. The illustration of adhesive, wood, and water is shown in Figure 7.

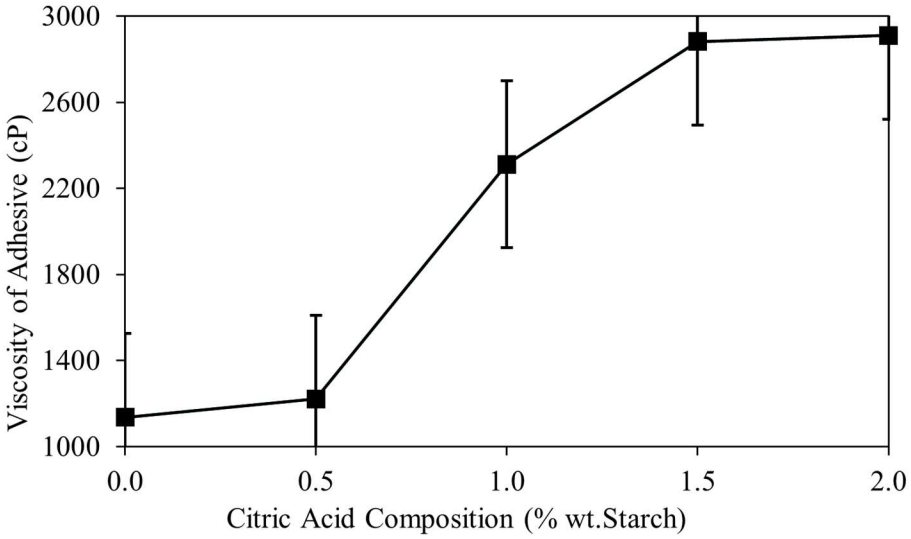


Figure 6. The viscosity of adhesive in various percentages of citric acid concentration

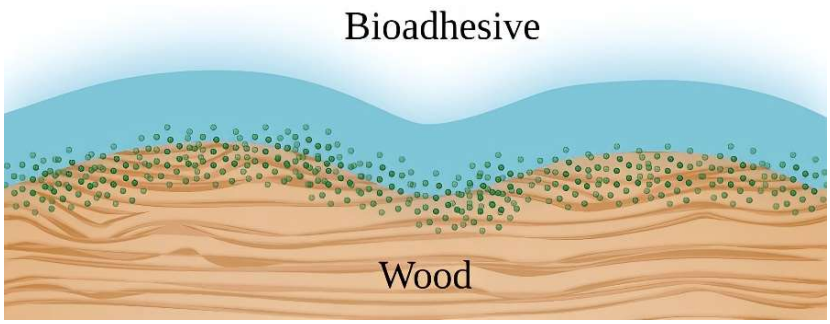


Figure 7. Illustration of the interaction between adhesive and water

An analysis of the shear stress demonstrated that the addition of citric acid significantly enhanced the adhesive's strength. In dry conditions, the reference sample (AD-CA0) exhibited a shear strength of 0.66 MPa. With citric acid addition, the shear strengths of samples AD-CA0.5, AD-CA1.0, and AD-CA1.5 increased progressively to 0.86 MPa, 1.02 MPa, and 1.16 MPa, respectively. AD-CA2.0 reached the highest dry shear strength with a value of 1.21 MPa. By contrast, under wet conditions, the reference sample (AD-CA0) recorded the lowest shear strength at 0.54 MPa. The shear strengths of samples AD-CA0.5, AD-CA1.0, and AD-CA1.5 reached 0.68 MPa, 0.70 MPa, and 0.84 MPa, respectively. The sample AD-CA2.0 demonstrated a maximum shear strength at 0.89 MPa.

Our findings echo those of Zhao [30] and Widyorini [31], who demonstrated that the addition of citric acid enhances polymer strength. The cross-linking reaction between citric acid and starch/PVA lowers the number of hydroxyl groups in the starch, thereby reducing the adhesive affinity for water and enhancing its resistance to moisture. However, when the adhesive is immersed in water, its bonding capability weakens owing to its similar polarity with water, making it more soluble and less resistant in wet conditions.

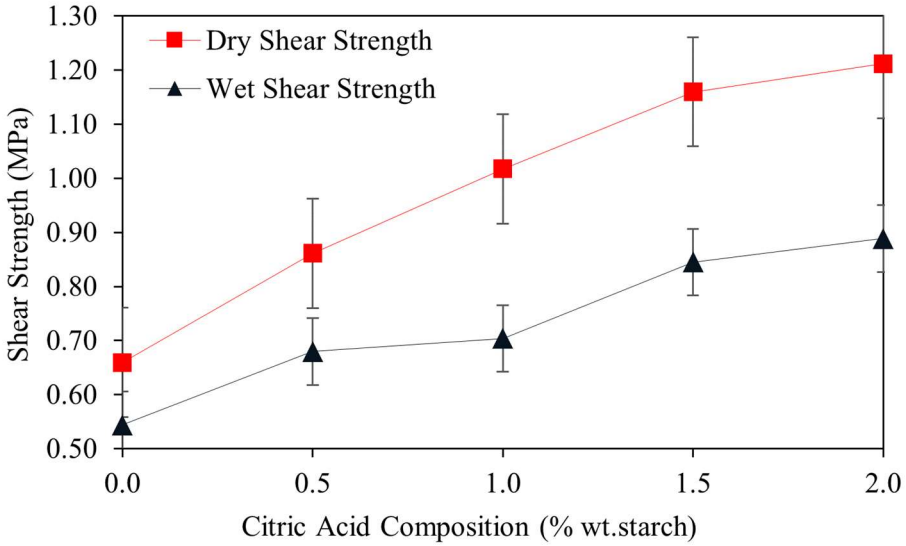


Figure 8. Dry and wet shear strength of adhesive in various percentages of citric acid concentration

Solid content analysis

The measurement of the adhesive's solid concentration is a critical step in determining the proportion of solid components. This analysis aids in evaluating the adhesive homogeneity and its ability to coat the substrate during the gluing process. Furthermore, determining the solid content provides insight into the adhesive's volatility level. This is crucial because high volatility can adversely affect the health of users. A well-balanced mixture of solid materials in the adhesive results in superior performance in terms of homogeneity and volatility [32].

In this study, we examined the solid content of the adhesive according to the ASTM D2369 standard. As illustrated in Figure 9, the addition of citric acid increased the adhesive's solid content. The solids made up 29% of the reference sample (AD-CA0). Upon adding citric acid, the percentage of solids rose to 33%, 34%, and 35% for samples AD-CA0.5, AD-CA1.0, and AD-CA1.5, respectively. Sample AD-CA2.0, with a 36% proportion of solids, included the highest percentage of solids.

This increase in solid content can be attributed to the bonding formed between cassava starch and polyvinyl alcohol owing to the addition of citric acid, thereby reducing the number of volatile components. Consequently, the reaction between citric acid and cassava starch/PVA increases the number of solid components. This observation aligns with a study conducted by Marquez [33], who discussed the potential of citric acid to modify adhesive properties and enhance the molecular solid weight of the adhesive. However, a high percentage of solids can hinder the adhesive performance owing to difficulties in application on wood. To ensure robust wood bonding, the adhesive needs to quickly coat the surface of the wood pores.

Fourier transform infrared spectroscopy

FTIR spectroscopy was performed to understand the structural modifications of the chemical molecules during the reaction. The molecular structures of

cassava starch, the 0% citric acid sample (AD-CA0), and the 2% citric acid sample (AD-CA2.0) were analyzed for comparison. Figure 10 illustrates the results of the analysis.

Figure 10 shows the alteration peak at 994 cm^{-1}. This implies that the strength of the C–O bonds in cassava starch was lower than that in the reference sample (AD-CA0). Additionally, the strength of the peak at 3262 cm^{-1} increased, indicating that the number of hydroxyl groups in each molecule of hydrolyzed starch increased. These modifications explain why cassava starch underwent hydrolysis during the procedure. Furthermore, the peak intensity at 1639 cm^{-1} for sample AD-CA0 increases, indicative of the creation of carboxyl functional groups (C=O) owing to oxidation. At 2942 cm^{-1}, the peak intensity increased as the fraction of carboxyl groups in AD-CA2.0 increases. This indicates that the sample underwent greater oxidation during polymerization.

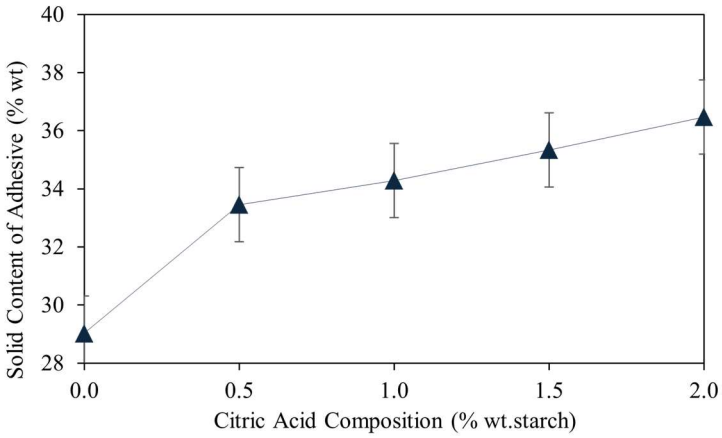


Figure 9. The solid content of adhesive in the various percentages of citric acid addition

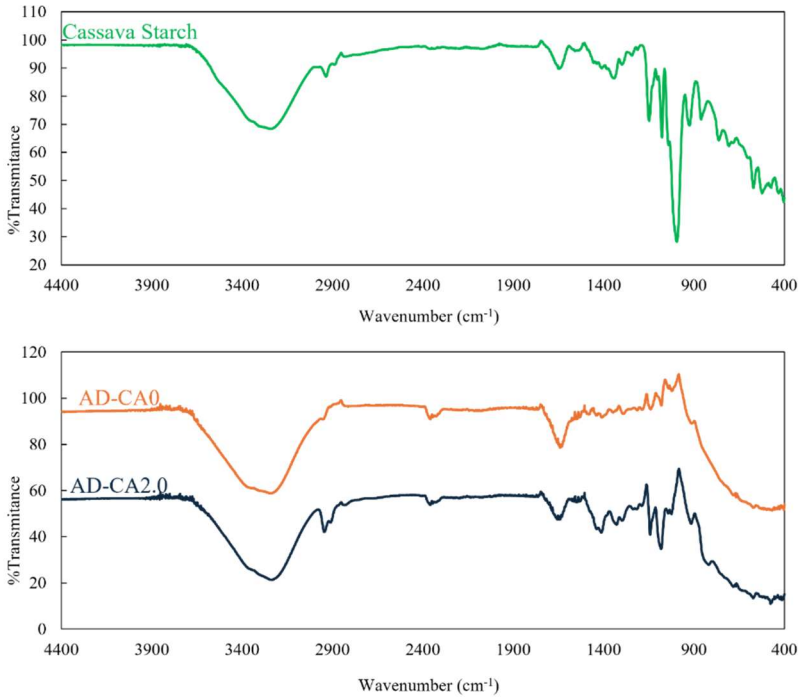


Figure 10. Infrared spectra of cassava starch, AD-CA0, and AD-CA2.0

Thermogravimetry analysis

Thermogravimetric analysis was performed to determine the thermal stability of the material. The thermal stabilities of both the reference sample (AD-CA0) and the sample with citric acid addition (AD-CA2.0) were examined across a temperature range between 0 °C and 600 °C. Figure 11 shows the results of thermogravimetric analysis. The mass loss of the reference sample (AD-CA0) and citric acid sample (AD-CA2.0) was separated into two stages based on this curve.

For the AD-CA0, the initial temperature degradation stage ranges from 0 °C to 100 °C, whereas the second stage spans from 100 °C to 600 °C. In the first stage, the sample experienced a weight loss of approximately 5%. This is attributed to the evaporation of water and monomers present in the adhesive. During the second stage, owing to the breakdown of hydrogen and covalent bonds in the adhesive, the weight progressively decreases until it reaches 600°C.

For the sample containing citric acid (AD-CA2.0), the first step of degradation occurred between 0 °C and 142 °C, and the second stage occurred between 142 °C and 600 °C. The initial stage saw a weight loss of about 7%, consistent with the evaporation of water and monomers as temperature increased. Owing to the dissolution of covalent bonds in the adhesive and the degradation of the adhesive leftovers, the mass loss rate decreased steadily during the second stage. This data suggests that the addition of citric acid can indeed enhance thermal stability of the adhesives.

Morphology analysis

A Dino-Lite microscope and a SEM were used to analyze adhesive surface morphology. This experiment was conducted to investigate the homogeneity of the adhesives. The adhesive morphology before (AD-CA0) and after (AD-CA2.0) citric acid addition was compared. As illustrated in Figure 12, the adhesive's surface became smoother with citric acid introduction. SEM analysis confirmed an increase in the adhesive's homogeneity following citric acid addition (Figure 13). This can be attributed to citric acid enhancing the likelihood of a reaction between cassava starch and PVA which made the homogeneity of adhesive increase.

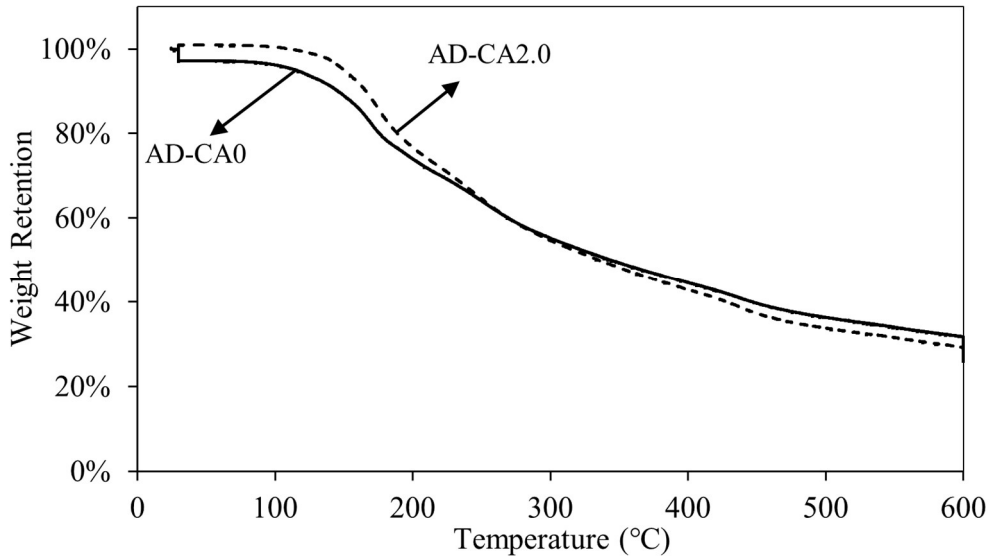
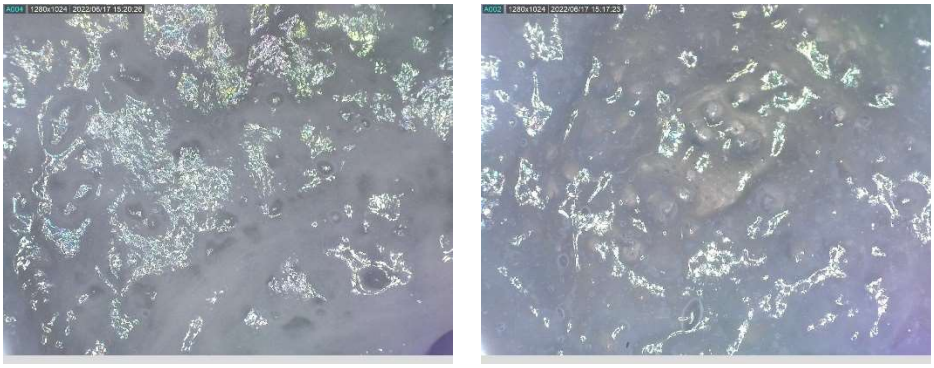


Figure 11. Thermogravimetric curves of citric AD-CA0 and AD-CA2.0



a b

Figure 12. The morphology of cassava starch/PVA adhesive before (a) and after (b) citric acid addition using dino-lite microscope

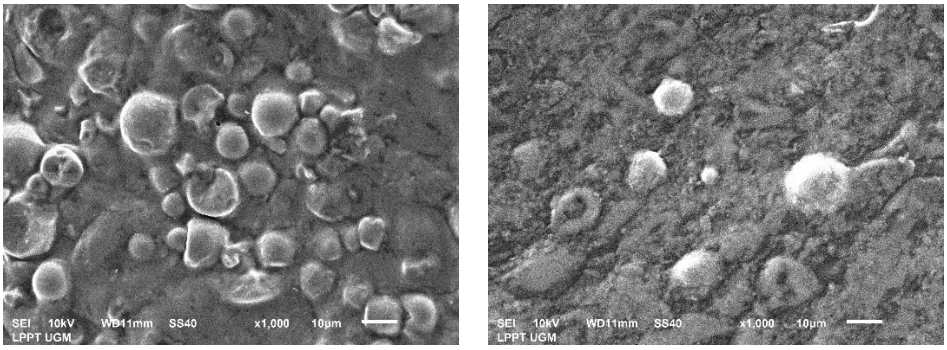


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Figure 13. The morphology of cassava starch/PVA adhesive before (a) and after (b) citric acid addition using scanning electron micrograph

Conclusion

Incorporating citric acid as a cross-linking agent considerably improved the quality of the cassava starch bio-adhesive. The physical attributes of the adhesive, such as viscosity, solid content, and dry and wet shear strengths, were improved with citric acid addition. Sample AD-CA2.0, with 2% citric acid, demonstrated the highest bond quality in this experiment, recording a viscosity of 2910 cP, and dry and wet shear strengths of 1.21 MPa and 0.89 MPa, respectively. Furthermore, the solid content of this sample was 36%. The adhesive underwent hydrolysis, oxidation, and polymerization according to FTIR measurements. Furthermore, the morphological study revealed that citric acid addition improved adhesive uniformity. These findings have opened up new avenues for further research to explore the long-term durability and environmental sustainability of cassava starch bio-adhesives modified with citric acid. Future studies could investigate the aging behavior of adhesive bonds under various environmental conditions, such as temperature and humidity fluctuations, to assess their performance over extended periods.

Acknowledgement

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