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A Comprehensive Review of Sustainable Benefit of Cassava Starch and Its Potential in Wood-Based and Lignocellulosic Materials

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Abstract: Cassava starch possesses enormous potential as a versatile and eco-friendly material that extends beyond its primary use in the food industry. Despite its widespread applications in the textile, pharmaceutical, and cosmetics sectors, the wood and lignocellulosic industry has yet to realize its full potential. This review paper provides a comprehensive and detailed analysis of cassava starch-wood-based and lignocellulosic products, highlighting the technical challenges encountered and potential solutions. The review emphasizes the promising applications of cassava starch in bio-based adhesive, and thermoplastic starch (TPS) composite. Moreover, this paper suggests new research areas that must be explored to enhance the practicality and commercialization of cassava starch-based products in the wood and lignocellulosic industry. Cassava starch is an invaluable resource for sustainable and eco-friendly wood-based products, and it is imperative to conduct further research to unlock its full potential.

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1. Introduction

Cassava (*Manihot esculenta*) is a perennial woody shrub native to tropical America. Its sweet, chewy underground tuber is one of the most popular edible root vegetables. Other names for this plant include yuca, manioc, and tapioca. Cassava is mainly grown for its starchy roots, but it also has edible stems, leaves, and petioles that are widely used as food [1]. Approximately 60% of cassava production is for human consumption, 33% for animal feed, and 7% for other industries like textile, pharmaceutical, cosmetics, and paper [2].

Cassava is grown widely around the world, but Africa (57%) and Asia (31%) are the primary producers [3]. For example, according to the Malaysia Department of Agriculture, 2,876 hectares of cassava were grown in Malaysia in 2019, producing about 42,285 metric tonnes of the crop [4]. It is primarily planted in Sarawak (Eastern Malaysia), covering about 600 hectares [5]. The primary industries utilizing cassava in Malaysia are the food, textile, and paper industries. In addition, it is also being used in the production of certain chemicals like acetone, alcohol, and acetic acid [4].

Recently been an increase in interest in utilizing the commercial potential of cassava starch for various applications (Table 1). This is mainly caused by rising cassava production, which increases starch availability and makes it more affordable for industrial operations, ultimately creating new niche markets within the already-existing industry [6]. In addition, cassava starch is biocompatible, biodegradable, stable, low-cost, and non-toxic, making it one of the intriguing additives for researchers to work with [7].

Table 1 - The current research area for cassava plants and their waste

Application	Niche Areas	Source(s)
Biofuels	Bioethanol	[8]–[10]
	Biohydrogen	[11], [12]
	Biobutanol	[13]
Packaging	Food trays	[14]
	Biofilms / bioplastics	[15]–[20]
	Nanocomposite / nanomaterials	[21]–[25]
Medical	Tissue engineering	[26]–[28]
	Drug delivery	[29]–[32]
Bio adsorbents	Metal ions removal	[33]–[35]
	Dye removal	[36]–[38]

Wood and lignocellulosic materials are highly valued for their renewability, potential for carbon sequestration, and ability to support sustainable industries while reducing environmental impact. Wood is a natural material from trees' stems, branches, and roots. It has been used for centuries as a versatile and renewable resource due to its strength, durability, and aesthetic appeal. On the other hand, lignocellulosic material refers to plant biomass containing lignin and cellulose, including wood, agricultural residues, and energy crops grown specifically for fuel production [39].

Malaysia's wood industry has significantly contributed to its economic growth and foreign exchange earnings. However, the wood supply from Malaysia is no longer sustainable, and the natural forest's average log production is decreasing. As a result, the wood industry has shifted its focus from solid wood to wood-based products, such as engineered wood and other lignocellulosic material like bamboo products. These products' innovation allows cassava starch to be incorporated into the wood-based and lignocellulosic material industry.

Therefore, this paper reviewed the properties of cassava starch that could be used in the wood and other lignocellulose material industry. This study is designed to address the following questions:

1. What is the current research in the related field, and what is the limitation and challenge of such an application?
2. Is the application fit for patenting and commercialization, and what should be the research focus?

Thus, this review paper offers valuable insights related to the current research and the future potential of cassava starch in the wood-based industry. This review paper has been divided into three parts. The first part explains the properties of cassava starch that are advantageous for wood-based applications. The second part highlights the past research and attempts to answer the above-stated research questions. Finally, this paper will conclude the opportunities and future outlooks of utilizing cassava starch in wood research.

2. **Properties of Cassava Starch**

Cassava is a plant that converts the most solar energy into soluble carbohydrates per unit of land area. Compared to other starchy crops, cassava produces roughly 49% more carbohydrates than rice and 25% more than maize. The most significant contributor to product yield is cassava starch, which has around two to four times as much as yam bean, taro, and sweet potato combined [40]. The cassava root's typical composition comprises 70% moisture, 24% starch, 2% fiber, 1% protein, and 3% minerals [6].

Starch is a polymer of lengthy chains of glucose molecules joined by glycosidic bonds, which have the chemical formula $(C_6H_{10}O_5)n$. The high molecular weight components of starch, amylose, and amylopectin are principally responsible for the chemical functioning of the substance. In cassava starch, amylopectin makes up 83% of the amylose composition and is accountable for crystallization [41]. The significant characteristics of starch, such as flexibility and mechanical resistance, are influenced by this crystalline area. However, these characteristics are also influenced by the amylose/amylopectin ratio and the component's molecular weight distribution, degree of branching, and conformation process [2].

The starch granules are usually 4 to 35 μm in diameter and insoluble in cold water. However, they will swell extensively if heated in excess water because they absorb water and disintegrate [9]. They would also lose birefringence and crystallinity, and some amylose would leach out. As a result, the starch granules rupture, and a hydrophilic colloidal solution is created, altering the starch mixture's rheological characteristics [43].

The cassava-based products quality is primarily dependent on the starch's quality [44]. The starch content in mature cassava roots is around 15 to 33%, depending on climate and harvest period [43]. The low residual materials (fat, protein, and ash) in cassava starch, low amylose content, and high amylose and amylopectin molecular weights distinguish them from other starches.

The physicochemical properties of starch mainly depend on the amylose and amylopectin ratio [45]. Despite not being soluble in cold water, native starch granules with an amylose and amylopectin molecular order can absorb water because of their semi-amorphous structure. Water plasticizes the amorphous area of hydrated granules, lowering the overall glass transition temperature (Tg) and improving the mobility of biopolymers [46]. The physical characteristics of polysaccharides, or Tg, indicate the temperature at which they change from an amorphous to a viscous condition. Polymers in a glassy, brittle state at Tg became flexible. Unfortunately, it is difficult to measure the Tg of starch since it contains both amorphous and crystalline regions [45].

Cassava starch is used in the production of products based on its constitution, physicochemical makeup, and functional characteristics. Starch functions may differ depending on structural characteristics, starch granule size, crystallinity, level of polymerization, or chain length of amylopectin structures [47]. Because of its chemical and structural composition, starch is a polymer with low shear resistance, low processability, low solubility in water, high susceptibility to humidity, and hydrophilicity [48]. However, these starch-degrading capabilities can be altered depending on the use or requirements.

3. **Potential Utilization of Cassava Starch in Wood-Based and Lignocellulosic Materials Products**

*3.1 **Bio-based adhesive***

The wood-based industry heavily relies on adhesives for load-bearing construction, flooring, and furniture-making. These adhesives are crucial in producing glued wood composite materials and are manufactured in large quantities. It is important to note that the particleboard industry has the highest demand for these adhesives, followed by plywood, laminated veneer lumber, oriented strand products, medium-density fiberboard, and other composites [49].

Although various animal and plant proteins were once utilized to make adhesive, this practice has been supplanted by synthetic polymers made from petrochemical sources, such as phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde, due to the inadequate qualities of natural sources of adhesive [50]. Moreover, the bonding ability and water resistance of adhesives made from fossil sources are excellent. Nonetheless, formaldehyde makes up a significant portion of wood adhesive; for instance, urea-formaldehyde contributes 30% of formaldehyde due to its simplicity of processing, widespread availability, low cost, and strong reactivity. However, formaldehyde has recently been linked to a risk to human health due to its ability to cause cancer and environmental hazard due to greenhouse gas emissions produced during its production. As a result, using formaldehyde is strongly discouraged in all industries [51].

Developing eco-friendly adhesives from renewable biomass to replace synthetic adhesives has garnered significant interest. Starch has found widespread use in the materials industry as an adhesive for various products, including binders, sticking materials, adhesives, and pastes. Among the different types of starch, cassava starch is a desirable option due to its abundance, renewability, accessibility, low cost, ease of processing, strong adhesion, and good film-forming properties. It should also be noted that cassava starch paste boasts higher viscosities and lower retrogradation tendencies than cereal-derived starches like corn starch [52].

However, it has been determined that the hydrogen bonds in the starch-based adhesive are too weak to bind wood, being weaker than chemical bonds [53], [54]. Additionally, the ease of hydroxyl groups to form hydrogen bonds with water molecules can lead to a variety of issues, including poor weather durability as evidenced by low water resistance, low cold resistance, low stability, low drying ability, high affinity for water, and short shelf life [50], [51], [55]. Nonetheless, the starch can be altered physically or chemically to enhance its structure and binding capabilities [56].

Many researchers are currently working on developing green starch modification. For example, Mhaske et al. [57] suggest using different green starch modification types: annealing, ball milling, dry heating, heat moisture treatment, high hydrostatic pressure, microwave, plasma, ultrasound, and enzymatic. Maniglia et al. [58] further suggest that dry heating and ozone treatments are environmentally friendly. However, only ball milling modification and ozone treatment have been done on cassava starch, and both processes are still in the early research stage. Therefore, there is plenty of room for improvement to optimize the treatment or research other methods, as suggested by Mhaske et al. [57] and Maniglia et al. [58]. It is important to acknowledge that green products typically come with a higher price tag. This is because manufacturers may incur additional expenses to make their products environmentally friendly, and thus increase the production costs. As a result, using starch as a low-cost raw material may not be as economically viable as it once was [57].

Once the research is complete, the next step is to commercialize the concept. However, it is essential to examine the storage impact on the adhesive bonding formulation as it is a crucial factor or research opportunity that should be considered before the product is commercially available. During the storage of starch pastes, a molecular restructuring procedure known as retrogradation occurs. This process intensifies the interaction between the long-term amylopectin chains and the amylose chains, resulting in syneresis. This change in visco-elastic characteristics of the pastes shortens the shelf-life of starch-based adhesives [54]. In this regard, this problem needed to be addressed before commercializing the product.

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3.2 *Thermoplastic starch (TPS) composite*

Thermoplastic starch (TPS) is a biodegradable and renewable polymer derived from starch. TPS exhibits thermoplastic behavior, meaning it can be melted and reprocessed multiple times without significant degradation. Examples of applications of TPS are in Table 2.

Table 2 - The application of TPS

Application	Examples
Packaging materials	
Biodegradable plastics	
Agricultural films	
3D printing filaments	

Starch can be transformed into TPS by fracturing its structure under high shear stress and temperature conditions. This causes the starch chains to lose structural integrity and undergo intermolecular rearrangement. Plasticizers can be used for this alteration, including sorbitol, water, urea, glycerine, fructose, glucose, and glycol [59]. The proportion of plasticizer and its chemical nature strongly influence the physical properties of the processed starch in two ways: [1] controlling its destruction and depolymerization and [2] affecting the final properties of the material, such as its Tg and modulus [60]. However, the TPS qualities, like other applications, are still very reliant on the amount of amylose in the starch [61].

Typically, natural starch is processed into TPS using a variety of industrial processes, including injection, extrusion, or a batch mixer coupled with a torque rheometer. TPS has excellent extensibility, good gas barrier qualities, and complete biodegradation. Nevertheless, when exposed to humidity, TPS absorbs moisture, leading to mold. It also has weak mechanical properties and is easily thermally deformed, which restricts its use [59], [62]. However, TPS can be improved by applying plasticization, mixing, and other modification processes [40].

Plasticization techniques are frequently employed to increase the flexibility of TPS. It is by lowering intramolecular hydrogen bonding along polymer chains and hence increasing intermolecular space. Consequently, this contributes to lower Tg and decreased crystallinity with increased molecular mobility [63]. Schlemmer and Sales [64] prepared TPS film from cassava starch with three different vegetable oils of Brazilian Cerrado as plasticizers: buriti, macauba, and pequi. It was found that all three vegetable oils presented a good plasticizing effect with interesting thermal properties. The TPS film obtained from these studies is homogenous and has good properties. Unfortunately, no related works on cassava starch manipulated other ingredients as plasticizers, and no further commercialization activities.

The mechanical properties of TPS-based materials can be enhanced by mixing with other additives such as kaolin, emulsifiers, pectin, plant fibers, and cellulose [61]. However, this review paper will only focus on plant-based fibers. In cassava starch TPS composites, various types of lignocellulosic fibers with different sizes from micro to nanoscale have been used as reinforcement, such as wood pulp [65], [66], sugar palm [67], [68], jute [62], [69], sisal [70], kapok [69], hemp [71], flax [72], [73], kenaf [74], coir [75], and cogon grass [76], [77]. The advantage of using natural fibers is that they are readily available, biodegradable, have good strength with low density, low cost, and are renewable. Apart from natural fiber, agricultural waste can also be used in TPS composite, thus promoting the circular economy. So far, some research has been done on agricultural waste, for example, banana leaf fiber [5], sugarcane bagasse [78], oil palm fiber [79], [80], cassava bagasse [23], [81], and coconut fiber [59].

Edhirej et al. [81] developed TPS films from unmodified cassava starch with cassava bagasse blend with 30% w/w fructose as the plasticizer. It was discovered that the size and concentration of cassava bagasse impacted the film's physical characteristics, increasing the film thickness but decreasing the density. Moreover, a more significant bagasse content marginally raises the moisture content while lowering the film's water solubility. Because of their similar chemical makeup, scanning electron microscope (SEM) pictures of TPS, especially those of films containing small-size bagasse, reveal heterogenous matric composition. The study confirms that natural fiber can alter the TPS film's characteristics. Jumaidin et al. [77] found that the TPS composite of cogon grass fiber and cassava starch decreases thickness-swelling value and water solubility,

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suggesting improved dimensional stability of the TPS composite. However, they observed no significant change in TPS composite moisture content and water absorption behavior. Prachayawarakorn et al. [82] suggest that the changes are related to the hydrophobic characteristics of natural fibers in comparison to the hydrophilic properties of the starch.

Campos et al. [80] studied the mechanical properties of TPS composites from oil palm mesocarp fibers that were prepared using a screw extrusion rheometer. While the elastic modulus of the TPS composite increased to 193% and 153% for maximum stress, the elongation at break remained constant. Moreover, it improved its thermal stability. The silica in the oil palm mesocarp fibers is responsible for the improvement of mechanical and thermal properties. It was discovered that the ideal TPS composite would be made with 10% of oil palm mesocarp fibers. Prachayawarakorn et al. [82] suggest that the increased mechanical strength is due to the chemical similarity of starch and plant fibers.

There are several research opportunities available to investigate the impact of plasticizers on cassava starch TPS. So far, only one relevant article has been discovered. Although the TPS composite with natural fibers has shown promise, further research is necessary to enhance material processing and determine the suitability of the TPS composite matrix. Ramírez et al. [59] suggested three primary research focuses on TPS composite. Firstly, it is to produce green material that does not involve any chemicals in its production so that it biodegrades, is renewable, and does not pollute the environment. However, some properties improvement for TPS composite, such as fire-retardancy is essential for electronics, construction, and transportation, usually involves chemicals [83]. Therefore, it would be important that any specific properties improvement should only be made with natural additives to retain the green properties of the TPS composite.

The second research area is to address the pressing issue of processing techniques for TPS composites. These composites pose significant challenges when it comes to injection molding or extrusion, particularly when a considerable amount of fiber is added or the fiber itself is too hard to be processed via injection. This area of focus is critical as it could have a detrimental impact on the commercialization of TPS composites. To circumvent this issue, wood scientists should research fibers that are easier to process or use smaller fibers (micro to nano). It would be highly advantageous to collaborate with an engineer who can assist with processing and machining to prevent problems early on and make it easier to scale up the process.

The life cycle analysis is the final area of research attention. TPS composite is frequently utilized in consumer devices with limited lifespans that are quickly discarded. However, these materials also can be employed for long-lasting interior applications. Thus, a life cycle study is necessary to further develop the TPS composite application. In addition, to ensure proper handling and recycling of TPS composite, it is also essential to set up a unique composting system; otherwise, this could result in environmental pollution [84].

4. **Summary and outlook**

The cassava starch's characteristics and potential uses in the wood-based sector are outlined in this review. Research and application of cassava starch for the food industry are well-established. Currently, the utilization of cassava starch has been expanding to other sectors such as textile and pharmaceutical. This is due to the expansion of cassava cultivation, especially around Africa and Southeast Asia, owing to their ability to withstand drought.

Cassava starch is crucial for the development of environmentally beneficial products. On the other hand, wood-based and lignocellulosic materials are yet another sustainable and environmentally friendly material. Nevertheless, the utilization of these two materials to produce sustainable products is still limited. This paper discovers two main applications: bio-based adhesives and TPS composite.

However, most studies are still needing further research, especially on commercialization. This is a result of the hydrophilic and poor mechanical qualities of cassava starch, which are limitations of the substance. Several strategies have been researched, including altering the starch in wood adhesives and binders and adding natural fibers to TPS composite. Although some of these approaches, especially in TPS starch, have considerably improved the properties, much work is still required to optimize the process, mainly to produce green products without chemicals. Moreover, this review paper also suggests the research opportunity for each application as the way forward before the application can be patented and commercialized.

Another challenge is to develop a feasible and straightforward method to produce different cassava starch-wood-based products that can be mass-produced. Cassava starch-wood-based or lignocellulosic material products are currently primarily prepared on a limited scale in the laboratory. Thus, developing commercially feasible processing techniques will be crucial for the industry.

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