A Study of Rice Straw Composites Based Adhesive System Using Agriculture Waste

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Abstract- The objective of this research is to explore the feasibility of producing high-performance composite materials using rice straw and ecopolyalcohol polymers-based adhesives. By utilizing rice straw, which is typically considered a waste product, we can create bio composites of superior quality. This approach offers several advantages, including increased economic value, reduced environmental impact through waste management, and the potential for cost-effective alternatives to commercial artificial wood panels. The study focused on optimizing the composition of the adhesive, the type of starch used, as well as the bonding temperature and time. Comparative analysis was conducted to assess the adhesive's bonding strength against a commercially available thermosetting resin. Furthermore, the mechanical and physical properties of the resulting composites were evaluated. The research also investigated the influence of water resistance co-additives (paraffin wax and polyester) on the mechanical properties of the rice straw-based composites. The newly developed adhesive system demonstrated superior performance compared to the traditional urea-formaldehyde resin, achieving a bonding strength of 9.8 N/mm^2 and MOR, IB, and TS values of 31 N/mm^2, 0.49 N/mm^2, and 20%, respectively, in the rice straw-based composites. The findings of this study present a potential solution for utilizing undesirable rice by-products and corn starch as industrial raw materials, which would greatly benefit farmers. Additionally, the modified starch adhesive with a low percentage of polyvinyl alcohol shows promise as a replacement for urea-formaldehyde resin and polymethylene polyphenyl isocyanate commonly used in the wood industry or pMDI in rice straw-based artificial wood. This substitution helps to avoid formaldehyde emissions and toxic gases when exposed to burning, while also reducing dependence on petroleum-based products.

Keywords – Composite materials, Raw materials, Rice, Adhesives, Rice straw, Agro-composites.

I. INTRODUCTION

In Egypt, the forested areas cover approximately 72,000 hectares, which accounts for only 0.1 percent of the total land area, as reported by the Food and Agriculture Organization of the United Nations (FAO, 2009). This represents a relatively small proportion of land available for wood industry applications, especially considering the increasing population and growing pressure from environmentalists to manage and conserve natural resources. To address this challenge, there has been a shift towards utilizing various woody and non-woody materials such as bagasse, rice straw, and cotton stalks as alternative raw materials for producing lignocellulosic composites like particle boards, fiber boards, and plywood. This approach aims to explore alternative sources of materials for the wood industry while reducing the reliance on traditional forest resources.

Formaldehyde-based adhesives, particularly urea-formaldehyde adhesives, are widely utilized worldwide in the production of interior lignocellulosic composites. These adhesives are favored due to their effective adhesion properties and affordability. When formaldehyde-based adhesives, especially urea-formaldehyde adhesives, are subjected to hot pressing during the curing process, a portion of the free formaldehyde undergoes reactions with various chemical components of the lignocellulosic materials. This results in some formaldehyde being incorporated into the adhesive polymers, while a portion is released into the surrounding air as off-gassing. Additionally, the Cannizzaro reaction, which converts formaldehyde into methyl alcohol and formic acid, contributes to the breakdown of formaldehyde. It is worth noting that even during the storage or use of lignocellulosic composites, particularly when exposed to high humidity or temperatures, there is a possibility of measurable levels of free formaldehyde being generated due to hydrolysis, isomerization, and decomposition of the formaldehyde-resin bond [13].

Previous research conducted by the main authors of this paper has demonstrated the enhanced bondability of sugar-cane bagasse fibers when organic and inorganic materials, particularly nitrogen-containing starch derivatives acting as formaldehyde (HCHO) scavengers, were added to commercial urea-formaldehyde (UF) resin [3,4]. Another effective derivative that showed improved results was the inclusion of acrylamide-containing starch. In terms of utilizing rice straw for composite materials [8] found that particle boards made from wheat straw using UF resins exhibited sub optimal properties, particularly in terms of internal bond (IB) strength and thickness swelling (TS). Straw could be used for high-quality surface layers in particle boards when bonded with polymeric diphenylmethane diisocyanate (pMDI) resin or a combination of UF and pMDI [18]. It successfully produced sound-absorbing composites using a combination of rice straw and wood particles, demonstrating that rice straw could substitute up to 20 percent of the wood particles without compromising bending strength [31]. The impact of silane coupling agent (SCA) level and ethanol-benzene (EB) treatment on the properties of reed and wheat boards, revealing improved physical properties [19,20]. To improved bonding ability of wheat straw through enzyme pretreatment [33]. The compression and tensile strength of low-density straw-protein particle boards, finding that the highest mechanical strength was achieved with modified soy protein isolate at 40 percent initial straw moisture content, and with methylene diphenyl diisocyanate (MDI) at 10 percent moisture content [26].

A study on the production of fiberboard using bamboo and rice straw, focusing on its overlaying properties [21]. Their experimental findings indicated that low-quality bamboo and rice straw could be effectively utilized to manufacture value-added fiber boards. To composite boards made from rice straw and waste tire particles exhibited superior flexural properties compared to wood particle boards, insulation boards, fiber boards, plywood, and various other construction materials [32]. All the composite boards demonstrated higher bending modulus of rupture (MOR) values than the insulation board. In our previous research conducted in this field, it was demonstrated that the particle size of straw plays a significant role in the performance of straw particle boards [23,24]. The static bending and internal bonding strength of boards bonded with polymethylene polyphenyl isocyanate (pMDI) resin initially increased and then decreased with decreasing particle size. These results were also compared with pMDI resin-bonded panels. Additionally, it was reported that steam treatment and short duration of oxalic acid (OA) treatment led to notable improvements in the mechanical properties and dimensional stability of rice straw particle boards, particularly in terms of internal bonding (IB) strength. Panels treated with steam exhibited slightly higher performance compared to those treated with OA. The duration of OA treatment had a negative impact on the performance of the panels, while the effect of temperature on the performance of OA-treated panels was not found to be significant.

This current study focuses on the development of an adhesive system using a combination of natural and synthetic polyalcohol polymers, specifically starch-polyvinyl alcohol blends. The objective is to create a simple and cost-effective approach without the need for expensive cross linkers like Cymel 323, which has been reported to potentially have harmful or irritant properties. The adhesive system investigated in this research is considered environmentally friendly as it aims to produce bonded composites from rice straw without the presence of free formaldehyde (HCHO) or other harmful substances. The optimization of synthesis conditions for the starch-polyvinyl alcohol adhesive, as well as its potential to replace environmentally unfavorable urea-formaldehyde (UF) and methylene diphenyl diisocyanate (MDI) adhesives, is also evaluated. It is important to maintain a higher proportion of inexpensive starch in order to achieve an economically viable application of this investigated adhesive system, while the relative amount of polyvinyl alcohol (PVA) should be comparatively lower due to its higher price.

II. MATERIALS AND EXPERIMENTAL PROCEDURE

The corn starch utilized in this research was obtained from Miser Co., a supplier of starch and glucose based in Dora, Egypt. The corn starch had the following characteristics:

A. Chemical composition:
- Maximum humidity percentage: 14%.
- Maximum protein percentage: 0.40%.
- pH range: 5.0-7.0.
- Maximum sulfur dioxide (SO_2) concentration in parts per million (ppm): 300.
- Maximum ash percentage: 0.20%.

B. Heavy metals:
- Maximum arsenic concentration in ppm: 1.0.

- Maximum copper concentration in ppm: 5.0.
- Maximum lead concentration in ppm: 0.5.

C. Microbiological values:
- Maximum total mesophilic aerobic bacteria count (colony per gram): 100,000.
- Maximum yeast count (colony per gram): 500.
- Maximum mold count (colony per gram): 500.
- Salmonella presence: Not detected.
- Staphylococcus aureus presence: Not detected.

As for the polyvinyl alcohol (PVA), also known as Mowiol, it was purchased from Hoechst Co. The PVA had a degree of hydrolysis of 98%, indicating a high level of conversion from its precursor. For comparison, the commercial urea-formaldehyde used in the study was procured from Speria Co., Egypt, and its specifications were as follows:
- Density: 1.25 g/cm^3.
- Viscosity: 350 cP.
- Solid content: 60.5%.
- pH: 8.5.
- Gel time: 108 seconds.
- Free formaldehyde (HCHO): 0.34%.

2.1 Synthesis of polyalcoholic polymer-based wood adhesives

A wood adhesive made by combining corn starch, a natural polyalcoholic polymer, with varying percentages (17-67%) of polyvinyl alcohol (a synthetic polyalcohol polymer) was synthesized at a temperature of 75 ^{0}C. To enhance the performance of the starch-based adhesive, the corn starch was pre-hydrolyzed using different concentrations of HCl (0.5-1.5M) for 2 hours at 60 ^{0}C. The adhesive solutions mentioned above were applied to two pieces of beech wood using a brush, creating a coating with a thickness of 0.1mm. The two coated pieces of birch wood were then joined together, forming an overlap area of 20 x 2.5 mm^2. A load of approximately 5 kgf was applied to the joint and maintained for 24 hours. After curing, the wood joints were conditioned at room temperature (23 ^{0}C) and 60% relative humidity (RH) for one day. These wood joints were subjected to lap shear tests using an Instron 555 Universal Test Machine, following the ASTM D906-98 (2011) standard.

2.2 Rice straw-based composites preparation and testing

Three different sizes of rice straw particles were prepared using a knife mill and passing them through various perforated metal plates. The particle sizes obtained were 4.75 mm, 2.63 mm, and 1 mm. These rice straw particles were then mixed with polyalcohol polymers-based adhesive (St/PV) in two different mass percentages (12% and 16% adhesive to the oven dry weight of rice straw particles). The mixture was used to form laboratory boards through hot pressing at a pressure of 140 bars and a temperature of 130 ^{0}C for 7 minutes. The resulting RS composites had a thickness of approximately 8mm and densities ranging from 905 to 1,001 kg/m^3. To assess the performance of the adhesives, the properties of the boards made from binding the treated RS with the investigated adhesives were compared to those made using a commercially available UF adhesive with environmental impact. The boards were tested for modulus of rupture (MOR), internal bond strength (IB), and thickness swelling (TS) according to the ASTM D1037-06a (2006) standard using an Instron 555 universal testing machine. Water absorption (WA) and thickness swelling (TS) were measured after immersing the boards in distilled water at 20 ^{0}C for 24 hours. Each measurement reported in this study represents the average value of four specimens. Additionally, the study examined the impact of adhesive formulation (starch to PVA ratio), pre-hydrolyzed starch, and the application of water resistance co-additives (paraffin wax and polyester resin) on the binding ability of the produced adhesive.

2.3 Thermogravimetric analysis

Thermogravimetric analyses (TGA and DTGA) were conducted on the RS-based composites using a Perkin Elmer Thermogravimetric Analyzer (TGA7). The analysis was carried out under non-isothermal conditions with a heating rate of 10°C/min and a nitrogen flow rate of 50 cc/min.

III. RESULT AND DISCUSSION

3.1 Synthesises and optimize the starch-based non-toxic adhesive system

In preliminary experiments, the impact of the mass percentage of added PVA to native and hydrolyzed starch on the bonding strength of the produced adhesive was investigated. Additionally, the effects of pressing time and pressing temperature were examined. The results of these experiments are presented graphically in Figs. 1-3. The purpose of this study was to optimize the adhesive composition, as well as determine the optimal bonding temperature and time for future application in the preparation of composites. Furthermore, this research aimed to assess the economic viability of using the investigated adhesive, with the potential to replace commercial HCHO-based adhesive (UF) and expensive pMDI in the production of high-performance straw-based composites that meet the high-grade requirements outlined by ANSI standards.

The results indicate that the addition of PVA to starch up to 17% resulted in increased bond strength values for the adhesive system (St/PV). This value was higher by approximately 5% compared to the bond strength of the commercial UF adhesive (Fig. 1). However, for higher PVA incorporation (20-67%), the trend was reversed, and the bond strength decreased. The viscosity of the modified UF adhesives also appeared to impact the bond strength, as shown in Fig. 1. Increasing the percentage of starch in the adhesives led to higher viscosity, which is attributed to the increased solid content of the adhesive ranging from 13% to 36% when the starch content in the adhesive increased from 33% to 86%. A decrease in the solid content resulted in relatively higher water content, making the specified temperature and time for bonding the beech wood strips less suitable. In accordance with [22], starch-based adhesives exhibit excellent affinity for polar materials like cellulose. This means that starch-based adhesives effectively wet the polar surface of cellulose, penetrate crevices and pores, and ultimately form strong adhesive bonds.

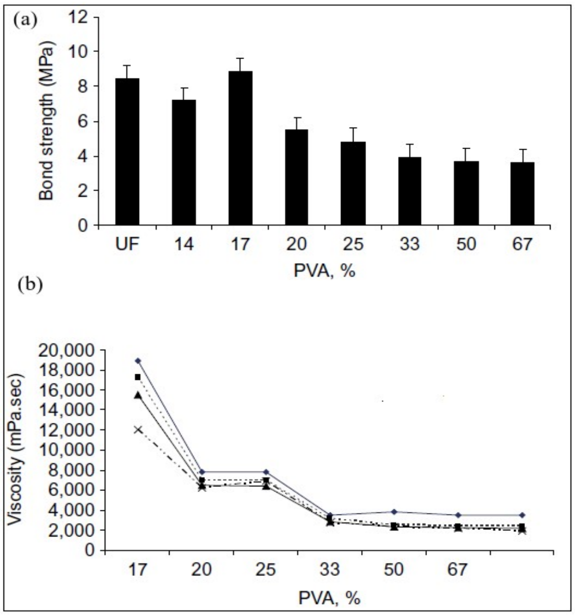

Figure 1 (a) Effect of mass percentage of PVA on bond strength and (b) viscosity of St/PVA adhesive system [10]

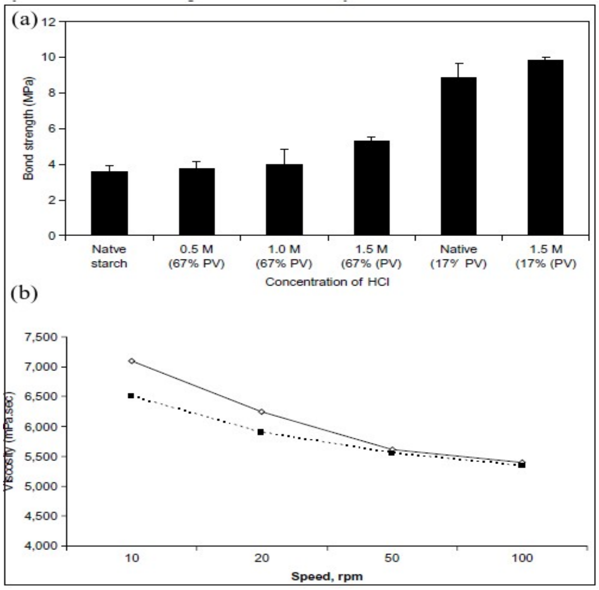

Figure 2 Effect of prehydrolysis of starch on bond strength of ST/PVA adhesive system [13]

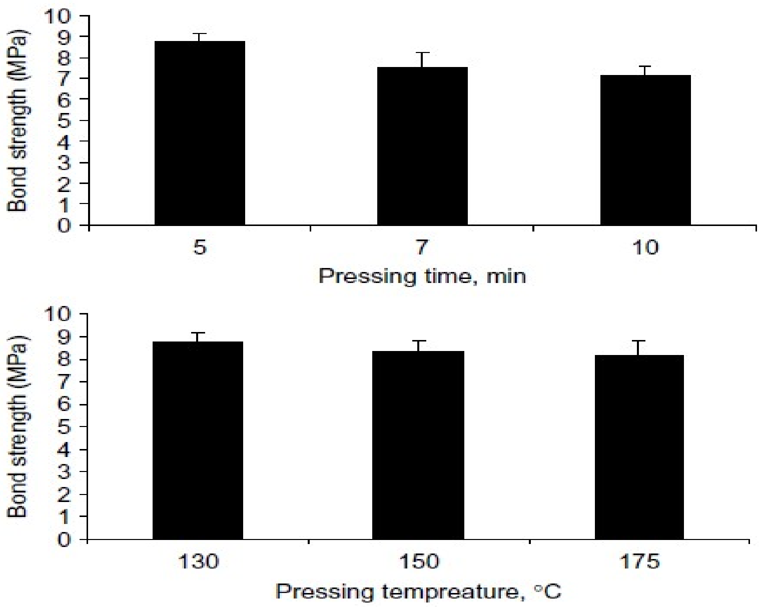

Figure 3 Effect of pressing time and temperature on binding behavior of St/PV adhesive system [17]

The results indicate that prehydrolyzing the starch with HCl had some advantages in terms of bond strength for the St/PV adhesive system containing 67% PVA. However, the bond strength value did not reach the optimum level achieved when incorporating 17% PVA into native starch (8.85 MPa). The concentration of the acid (0.5-1.5M) used for starch hydrolysis had a slight effect on improving the bond strength of the St/PV adhesive (6.1-7.6 MPa) as shown in Fig. 2. On the other hand, prehydrolyzing the starch and incorporating 17% PVA resulted in an improved bond strength of 9.8 MPa. This improvement can be attributed to the decrease in viscosity of the prehydrolyzed starch from 6,200 to 5,800 mPa.s at a speed of 20 rpm, despite the solid content of the produced adhesives being around 34.7%. The decrease in viscosity facilitated the penetration of the adhesive into the beech wood, resulting in a strong bond strength. Regarding the effect of pressing time and pressing temperature on the bond strength of the high-performance St/PV adhesive composition (17% PVA), Fig. 3. demonstrates that a pressing time of 7 minutes and a pressing temperature of 130 ^{0}C provided relatively higher bond strength.

3.2 Performance of polyalcohol polymers-based adhesive on properties of rice straw composites

Based on the bond strength data presented, it can be concluded that increasing the percentage of corn starch in the polyalcohol polymers-based adhesive system was effective in serving as an adhesive for rice straw. Adhesives synthesized with 83% corn starch and 17% PVA showed a significant improvement in bond strength. This adhesive system was then utilized for the preparation of composites. In order to maintain control over the preparation conditions, two factors were examined as part of a preliminary study: the effect of pressing pressure at 130 ^{0}C for 7 minutes (which yielded the optimum bond strength) and the amount of adhesive applied (12% and 16% based on the dry weight of the ground rice straw as a whole).

The results of the study are presented in Figs. 4 and 5. It was observed that increasing the applied pressure from 70 to 140 bars and the amount of adhesive from 12% to 16% led to improvements in the mechanical properties (MOR and IB) as well as the water resistance (TS) of the RS-based composites. Notably, the St/PV adhesive system, which is free from HCHO, demonstrated higher properties compared to the commercial urea formaldehyde adhesive, which is considered environmentally unacceptable.

The observed enhancement in the properties of the RS-based composites resulting from increased applied pressure can be attributed to the high compression of the fibers, leading to a reduction in voids and porosity in the boards. This subsequently increases the density and water resistance of the composites. Furthermore, the higher pressing pressure also resulted in elevated pressing temperatures, promoting stronger fiber-to-fiber and fiber-adhesive-fiber bonds. The improved fiber-to-fiber bonding may also be attributed to the chemical transformation of the hemicelluloses in the rice straw, which undergoes furfural resinification. These optimal conditions were employed for further investigations.

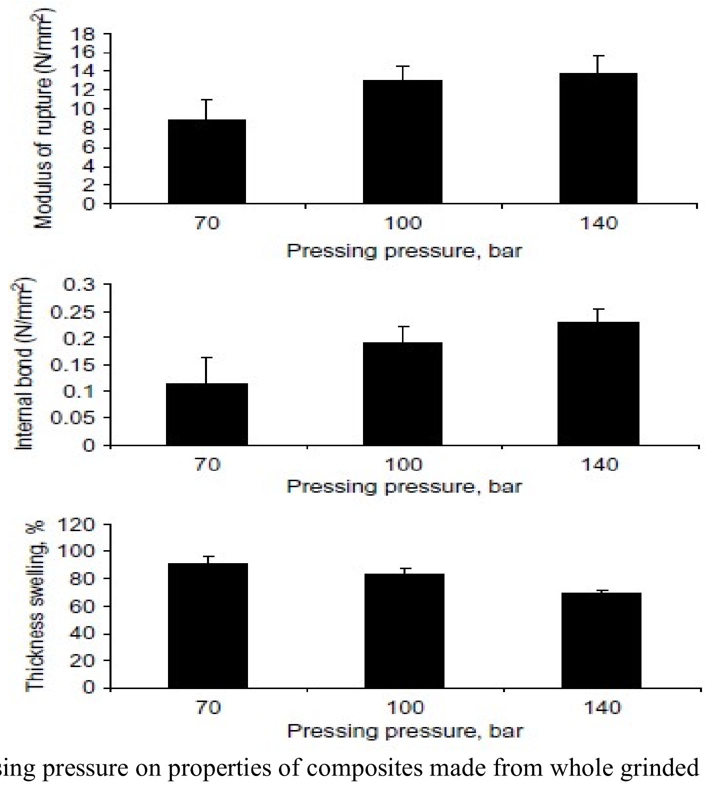

Figure 4 Effect of pressing pressure on properties of composites made from whole grinded RS and 16 per cent St/PV adhesive system [20]

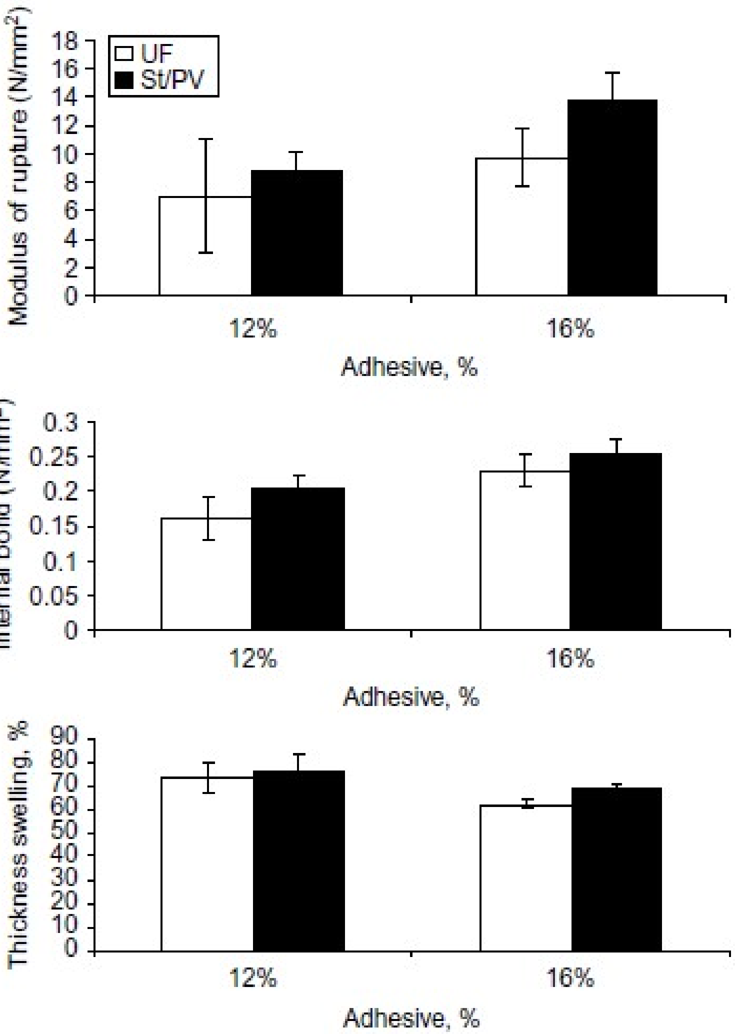

Figure 5 Effect of amount of adhesive systems on of composites made from whole grinded RS and UF, St/PV adhesive system [23]

3.3 Effect of particle size of rice straw on composite properties

The results presented in Fig. 6. confirm the significant influence of rice straw particle size on the quality of the composites, which aligns with our previous findings when using UF and MDI adhesives [20]. Screening the knife mill ground rice straw proved to be effective in producing high-performance RS-based composites compared to using the ground rice straw as a whole. The particle size fractions of 2.63 < RS < 4.76 mm and 1 < RS < 2.6 mm exhibited relatively higher properties. Specifically, the MOR strength of the composites produced from these particle size fractions increased from 13.8 N/mm^2 to 21.8-25.4 N/mm^2, IB increased from 0.25 N/mm^2 to 0.33 N/mm^2, and TS decreased from 69% to 40-55% compared to using the whole RS. This can be attributed to the thin waxy/silica layer that covers the outer surface of rice straw cells, which reduces the wettability of the straw with water-based resins and results in weak fiber-resin bonding. Mechanical treatment through cutting, grinding, and screening of the rice straw fibers allows for partial separation of silica, enabling better resin penetration into the RS fibers and the formation of strong bonds. The relatively larger particle size fractions also exhibited lower ash content compared to the smaller ones. The ash content of the whole RS (16.6%) decreased to 13.2-3.8% upon screening to particle size fractions of 2.63 < RS < 4.76 mm and 1 < RS < 2.6 mm.

However, when the fraction size was further increased to 4.76 mm, a slight improvement was observed, despite its lower ash content compared to the 1 < RS < 2.6 mm fraction. This trend has also been reported in previous studies involving wood flake boards and wheat straw particle boards [8,19,25,30]. The primary reason behind this observation could be attributed to the increase in contact area between the resin and the rice straw particles as the particle size decreases, as well as a reduction in unsplit rice straw particles within the mat. It is challenging for the resin to penetrate the internal surface of unsplit particles, and therefore, by decreasing the proportion of unsplit particles in the mat, the IB strength can be improved. Regarding straw particles, a previous study mentioned that the crushing of straw resulted in a cracked epidermis, which facilitated better resin penetration inside the stem [30].

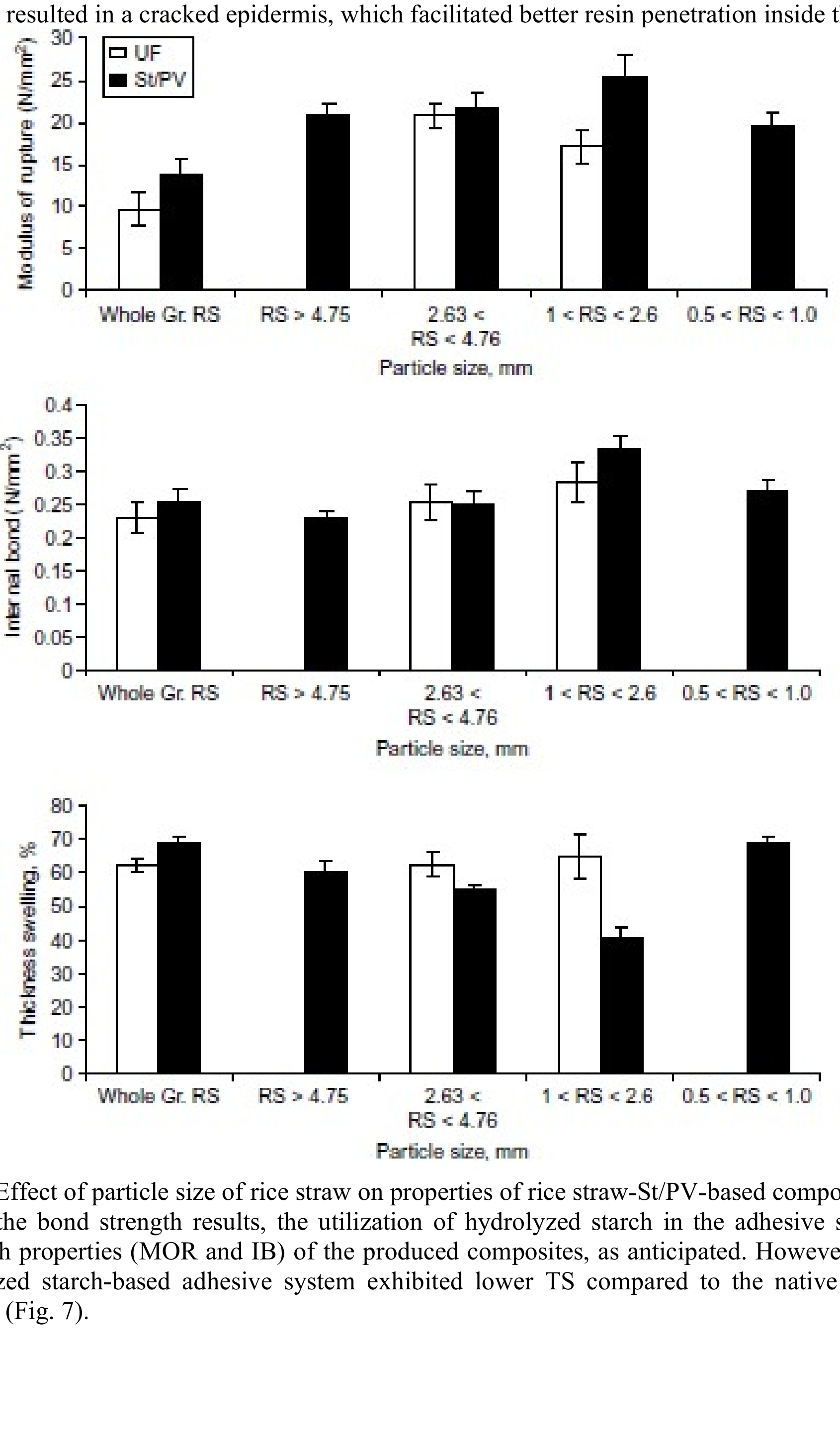

Fig. 6. Effect of particle size of rice straw on properties of rice straw-St/PV-based composite [27]

Consistent with the bond strength results, the utilization of hydrolyzed starch in the adhesive system resulted in improved strength properties (MOR and IB) of the produced composites, as anticipated. However, it was observed that the hydrolyzed starch-based adhesive system exhibited lower TS compared to the native starch/PV or UF adhesive systems (Fig. 7).

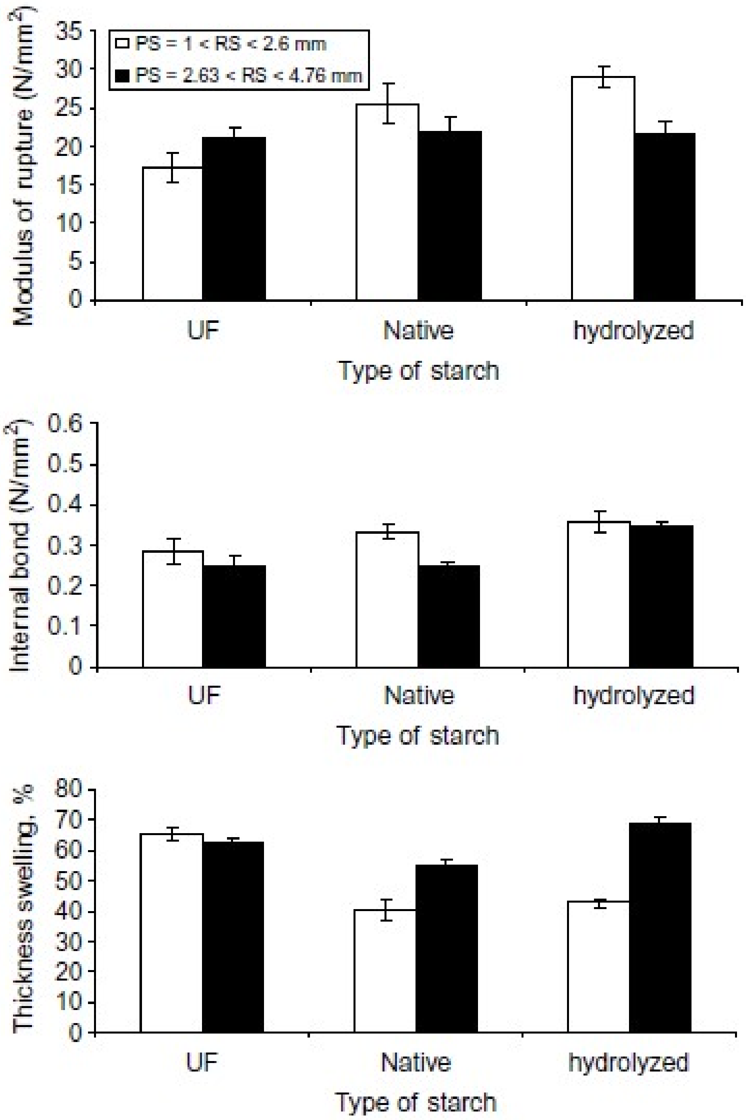

Figure 7 Effect of type of starch used on properties of St/PV-rice-straw based composites [29].

3.4 Effect of water resistance additives on composite properties

Based on the results obtained, it can be concluded that using a rice straw fraction with a particle size ranging from 1.0 to 2.6 mm was effective in producing RS-based composites with relatively higher mechanical properties (exceeding the values specified in ANSI A208.1; MOR > 17MPa, IB > 0.5, MOE > 2,700). However, the water resistance property (TS; > 47%) was found to be very poor, indicating that it does not meet the requirements of standard specifications. Therefore, further research is necessary to enhance the water resistance property of the investigated composites. Acetylation, steaming, and wax-sizing are three commonly employed methods for improving the water resistance of wood-based composites [9,10,11]. In the case of acetylation, the fibers undergo acetylation prior to the formation of the mat. This treatment has shown significant reductions in TS (thickness swelling), WA (water absorption), and LE (linear expansion). Furthermore, the mechanical properties of the modified boards were generally superior to the control group, although wheat straw boards were an exception to this trend.

Regarding steam treatment [11], demonstrated that pretreating hemlock fibers with steam at a pressure of 1.55MPa for 10 minutes resulted in improved dimensional stability and enhanced mechanical properties when used in the production of hard boards. Wax-sizing, on the other hand, has long been utilized for achieving dimensional stability in wood and agro-fiber composites [10]. Paraffin wax, in particular, shows promise as a widely applicable solution in industrial settings, as it is often more cost-effective compared to acetylation and steaming methods.

In this study, the researchers utilized polyester resin and paraffin wax as cost-effective co-additives to enhance the water resistance of the rice straw composites. These additives were mixed with the adhesive and rice straw to create a mat. The results, depicted in Fig. 8, indicate that the amount of co-additives added had a substantial impact on the properties of the composites. The inclusion of paraffin wax and polyester as co-additives led to improvements in both the mechanical properties and the TS property of the composites. Particularly, the proportion of polyester incorporated showed a significant correlation with the enhancement of board properties. The addition of 5 percent polyester resulted in composites with higher MOR, IB, and TS values, with improvements of approximately 25 percent, 39 percent, and 48 percent, respectively.

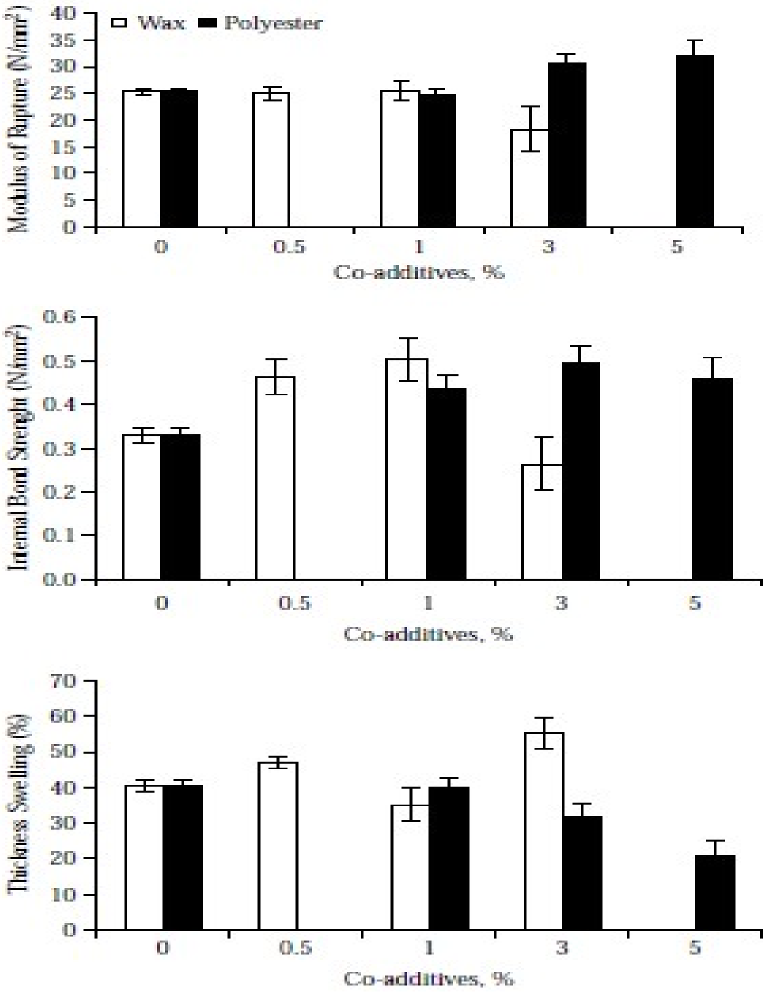

Figure 8 Effect of co-additives on properties of composites produced [31]

In contrast, the addition of only 1 percent paraffin wax resulted in noticeable improvements in IB and TS properties, with percentage improvements of approximately 39 percent and 13 percent, respectively. However, the incorporation of paraffin wax did not show significant positive effects on the bending strength (MOR) of the RS-composite. Nevertheless, the MOR values of the boards produced with optimal polyester (PE) and wax contents met the standard specifications for particle boards of grade H-3 according to ANSI. Moreover, the water swelling property of the boards improved with the incorporation of PE, although it still exceeded the standard value outlined in ANSI A208.1. To further enhance the water resistance behavior of the RS-composite when exposed to moisture, potential solutions such as incorporating a small amount of pMDI with the St/PV adhesive system or utilizing a less toxic and cost-effective cross linker are currently being investigated. These ongoing experiments represent the primary objective of the study.

The enhancement of mechanical properties by incorporating moderate percentages of paraffin wax can be attributed to its lower melting point (52-74 ^{0}C), which likely acts as a plasticizer and carrier for the adhesive, facilitating its penetration into the fibers. This, in turn, improves the flexibility of the fibers during the pressing process. However, when the wax content is relatively high, it may have a negative impact on water resistance. This can be attributed to difficulties in achieving uniform wax distribution on the RS particles. Additionally, when the wax melts and forms a barrier on the particles during heating, it can hinder bond formation and weaken board properties. On the other hand, the added polyester contains functional groups such as hydroxyl and carbonyl groups, which can enhance adhesion properties and promote bond formation between the adhesive mixture and RS particles. This can be supported by the knowledge of polyester's viscosity and elasticity characteristics, which facilitate the interpenetration of the adhesive system into the RS fibers.

The positive impact of adding polyester on the strength properties of the final composite product, compared to boards produced using UF adhesive and starch-PV, is supported by non-isothermal thermogravimetric analysis. The TGA and DTGA curves shown in Fig. 9. provide insights into the thermal degradation behavior of the three composites. In the main degradation step (190-322 ^{0}C), it is observed that the onset temperature and peak maximum of the DTGA curve are higher for the composite produced using starch-PV adhesive system compared to the commercial UF adhesive. Furthermore, the addition of polyester improves the thermal stability of the St-PV-RS-straw composite, as indicated by a slower pyrolytic degradation (broader curve) and a higher onset temperature compared to the UF-RS composite.

IV.CONCLUSION

Based on the obtained results regarding the mechanical and physical properties of the produced composites, it can be concluded that the use of a starch-PVA blend as a polyalcohol polymers adhesive allows for the production of high-performance RS-based composites. The MOR values achieved in this study exceeded the standard requirements, while the IB values were comparable to those of other composites. The strength properties of the composites were further supported by analyzing their thermal stability using a non-isothermal technique. However, it should be noted that the TS values of all boards were higher than the standard limit. To address this issue, future research could explore the potential benefits of incorporating a portion of pMDI with the adhesive and using a less toxic and cost-effective cross linker to improve the water resistance behavior of RS-based composites when exposed to moisture. This study's findings will be the main focus of the forthcoming manuscript to be submitted.

Conflicts of interest: No conflicts of interest

Author contributions: No details for author contribution

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