MAJOR PROJECT

STUDY ON PLANT-BASED ADHESIVES AND ITS APPLICATIONS IN PLYWOOD INDUSTRIES

A Major Project Report submitted in partial fulfillment for the award of the degree of

MASTER OF SCIENCE (M. Sc.)

In

CHEMISTRY

Submitted by

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CANDIDATE'S DECLARATION

We, **Divya Garg** (2K21/MSCCHE/15) and **Sanya Gulati** (2K21/MSCCHE/41), hereby certify that the work which is being submitted in this major project report entitled **"Plant-Based Adhesives and its Applications in Timber and Wood Industry"** in the partial fulfillment for the award of the degree of Master of Science at **Delhi Technological University** is an authentic record of our own work carried out by us under the supervision of **Dr. Roli Purwar** (Professor, Department of Applied Chemistry, DTU).

We further declare that the project report has not been submitted previously to any other Institute/University for the award of any degree or diploma associateship, Fellowship, or other recognition or any other purpose whatsoever. Also, it has not been directly copied from any source without giving its proper reference or citation.

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CERTIFICATE

This is to certify that **Sanya Gulati** and **Divya Garg** students of the degree of Master of Science of Applied Chemistry department at **Delhi Technological University** have submitted their major project report entitled **" Plant-Based Adhesives and its Applications in Timber and Wood Industry "** for the year 2022-2023 in partial fulfillment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the students under my supervision.

they have taken proper care and shown utmost sincerity in completion of this project. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to any university or elsewhere, and certify that this project is up to my expectations and as per the guidelines provided by the university.

Place: Delhi **Supervisor's Signature**

Date:

ABSTRACT

In this presented work, we report the modelling and development of an environmentally friendly adhesive obtained from the wattle-tannin and cornstarch. The manufacturing of wood composites is typically focused on formaldehyde-based and petrochemical-based adhesives for example phenol formaldehyde (PF), urea formaldehyde (UF), and melamine urea formaldehyde (MUF), which can aggravate health and environmental issues under certain conditions. Here, we describe a formulation of high-volume biorefinery byproducts used as formaldehyde-free glue as well as the adhesion characteristics of this formulation as measured by ultimate shear stress and wood failure rates. We demonstrate that adhesives exhibit the same advantageous qualities as formaldehyde-based resins, such as water tolerance, quick restoring, and equivalent performance in terms of adhesion. It would be necessary to develop and deploy suitable replacements for formaldehyde-based adhesives, such as urea formaldehyde, in the wood processing industry in light of prospective and even stricter future restrictions on its usage. The main objective of this project is to demonstrate the performance of cornstarch- wattle tannin-based adhesive in the plywood manufacturing. Plywood panels were glued together and mechanical properties were investigated to evaluate the mechanical performance of an optimal cornstarch-wattle tannin-based adhesive. The laboratory findings indicate that particleboards bonded well with our adhesive derived from cornstarch and wattle tannin.

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Divya Garg & Sanya Gulati

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CHAPTER 1 INTRODUCTION AND OBJECTIVES

1.1 GENERAL

Increased building development brought about due to growth of the human population has intensively increased call for wood-based goods like wood panels, laminates for packing, fiberboards, plywood, particleboards, oriented strand boards, etc. Furthermore, a range of wood products are heavily consumed by the sectors that produce furniture. The stiff joining of these wood samples is important for ensuring the durability and better performance of different products in furniture industry [1]. Adhesives have played a significant part in the effective use of wood resources as well as the expansion and development of the forest products industry. Modern wood products that are practical and useful, whether they are used for building, furniture, or other purposes, are produced by adhesively connecting solid wood and wood particles of varying sizes [2]. Wood adhesives offer thermal and moisture protection while forming powerful, long-lasting bonds between various wooden components and panels. Numerous biomass materials have been used as renewable feedstock to create bio-based wood adhesives, including lignin [4–6], starch [7-8], plant proteins [6-9], tannin [10], bark [11–12], and vegetable oils [13].

1.1.1 SYNTHETIC ADHESIVES

Synthetic adhesives are composed of prepolymers or polymers generated from petrochemical raw materials. In laboratories, these are also created using chemicals and synthetic compounds. The synthetic adhesive binder is made up of synthetic resin, synthetic rubber, or a copolymer or mechanical combination of these materials. Some of the known examples for this type of adhesives are cello tape, amino resins, phenolic resins, latexes or poly (vinyl alcohol), epoxy resins, and isocyanates [3]. Synthetic glues can be odourless, and we can pick between a tacky synthetic glue and one that dries thoroughly. Synthetic

glues may only require application to one of the surfaces, saving our time throughout the manufacturing process.

The primary disadvantage of synthetic glues is that they are non-renewable hydrocarbon resources. Hazardous emissions from formaldehyde-based synthetic adhesives such as free formaldehyde and free phenol can harm the human body during their manufacturing, storage, transit, and use [4]. Additionally, these resins rely on depletable fossil fuels. These facts have prompted increased worries about resource sustainability and environmental protection, which has compelled the creation of biobased polymer materials from a wealth of renewable biomass resources.

1.1.2 NATURAL ADHESIVES

Natural adhesives are derived from organic materials present around the globe. Natural adhesives including starch, animal glues, and plant resins have been used for ages and are still commonly used today for packaging and wood joining [5]. Many naturally occurring ingredients, including proteins such as gelatin, starch, and cellulose, can be used to make glue. Some of the most common adhesives used in the paper and packaging sectors are starch and dextrin glues since they are widely available and relatively simple to make, they are among the least priced adhesives for paper packaging. Natural adhesives can bond with a variety of materials to meet your requirements.

Along with various advantages, these types of adhesives also have certain shortcomings on a larger picture [6]. Natural adhesives cannot match with synthetic adhesives in terms of grip and hold between the woods. Natural adhesives are preferable for applications that do not require a long lifespan [7]. They could be ideally used for general packaging, for example. To make a solid binding between wood particles of varying sizes, natural glues should be applied to both the surfaces, only then it can be effective for longer duration.

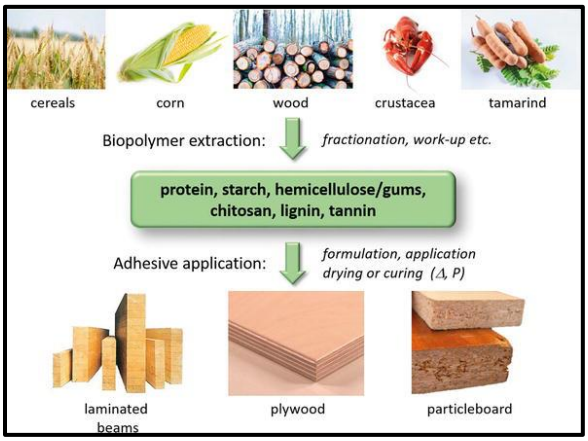

Fig1. Adhesives application in wood industries

1.2 OBJECTIVES

- The main goal of the project is to determine whether comparable results could be obtained using raw cornstarch instead of extracted starch based on results with starch adhesives.

- It includes the preparation of the bio-based adhesive, its optimization, and characteristics including rheological and thermal analysis, for use as a wood adhesive using FTIR and TGA data.

- Particleboards joined with adhesives based on cornstarch flour/NaOH were tested with external force and checked if the glue can be effective for longer timespan.

- Additionally, the goal of the current study is to use this cornflour- tannin based adhesive in the manufacturing of particleboard by replacing UF resins as much as possible by adding cornflour and wattle tannin extracts [14].

CHAPTER 2 LITERATURE REVIEW

2.1 INTRODUCTION

Adhesives have played a significant part in the effective use of wood resources as well as the expansion and development of the forest products industry, and they will continue to do so. Modern wood products that are practical and useful, whether they are used for building, furniture, or other purposes, are produced by adhesively connecting solid wood and wood particles of varying sizes. Since the 1930s, synthetic adhesives with strong bonding capabilities, such as urea-formaldehyde resin, phenol-formaldehyde [PF] resin, and melamine-urea-formaldehyde resin, have been used extensively in the wood industry [30]. These synthetic adhesives' benefits include their large range of types, outstanding durability, good performance, and average resistance to heat and/or moisture. However, hazardous emissions from formaldehyde-based synthetic adhesives such as free formaldehyde and free phenol can harm the human body during their manufacturing, storage, transit, and use [78]. Additionally, these resins rely on depletable fossil fuels. These facts have prompted increased worries about resource sustainability and environmental protection, which has compelled the creation of biobased polymer materials from a wealth of renewable biomass resources. Adopting formulations with catalysts or scavengers to quench unreacted formaldehyde during processing is one method of reducing formaldehyde emissions. The search for alternatives to formaldehyde-containing adhesives has also been motivated by formaldehyde's harmful effects on human health [31].

The development and usage of petroleum-based adhesives, however, has had a detrimental effect on the environment and human health [32]. They mostly come from finite, non-renewable fossil fuel sources and release low molar mass hazardous chemicals during the production, distribution, and usage of the final product. An interest in more environmentally friendly adhesives based on biopolymers derived from renewable resources has been

sparked by the growing environmental concern. Natural bio-based raw materials such as starch, protein, and tannin have been used as adhesives for centuries [33].

Several review papers published on the biobased adhesives. The ability to use more forms of lignin depends on the formulation's inclusion of water in particular. The grind-mix-apply method produces a resin that functions similarly to formaldehyde resins and might potentially be used as a drop-in substitute [79]. We predict that greater lignin supply brought about by government mandate15 and more scalable, less expensive processing of cellulosic biomass favored the economics of a lignin-based glue with numerous uses, ranging from the fabrication of engineered wood to the manufacture of furniture [34]. Tannin replaced PF up to 10, 20, and 30% with phenol, causing tannin phenol formaldehyde [PFT] to have higher viscosity, a shorter gel time, and a lower pH. PFT resins have been successfully used as an eco-friendly surface bonding glue in the production of particleboard [35]. It was reported that to achieve the desired bond strength, water resistance, and good industrial and high-tech applicability by incorporating thermal acid treatment, protein crosslinking, and thermal alkali degradation, a novel soybean protein adhesive was produced. The adhesive showed good potential for commercial use in structural wood composites [80]. The primary characteristics of soybean protein adhesives were significantly influenced by the crosslinker species, and the aqueous modified polyamide was the most effective crosslinker [36]. This review paper is focused on the research carried out in last twenty years plant-based wood adhesive.

2.2 PLANT-BASED WOOD ADHESIVE

2.2.1 TANNIN

Tannins are naturally procured water-soluble polyphenols that are present in numerous plants, including fruits, leaves, barks and woods [1]. The antimutagenic and anticarcinogenic properties of tannin are very well documented. In contemporary polymer industries, they become increasingly functional because tannins have unique features such as antioxidant, antimicrobial and anti-inflammatory properties [2]. The growth of many fungi, yeasts, bacteria, and viruses is inhibited by tannins. Extensive studies on the wood

adhesives with tannin incorporation have been evaluated since past decade [71]. Tannins are usually graded as condensed and hydrolyzed compounds in two major classes [3]. The structure of molecule present in tannin i.e., Tannic acid is shown in fig1. The main benefit of employing tannins in wood adhesives is their chemistry-based crosslinking behaviour with phenol and formaldehyde. Condensed tannins are polyphenolic substances that typically consist of oligomeric flavonoid-type structures that can be primarily found in the heart wood or bark of various tree species. The final extract used for making of adhesives is usually composed of 70–80% active phenolic groups [8]. By introducing tannins into the adhesive formulation, formaldehyde emissions have been shown to be reduced without affecting the mechanical performance of the adhesives [72].

The chemical coupling of tannins in Phenol-formaldehyde and Melamine-urea-formaldehyde systems is based on their affinity for methylol groups, performing condensation reaction with methylol groups present on Urea formaldehyde (UF) or phenol-based adhesive species serving as the mechanism for tannin synthesis, coupling, crosslinking, and rehabilitate with these substrates. Other formulation strategies for tannin-based adhesives have been tried, such as encouraging tannin auto-condensation, which is said to produce an admissible adhesive bond through a distinct aspect of condensed tannin chemistry in which the oligomers of tannin are encouraged to self-polymerize, leading to formation of crosslinked polyphenolic networks. This method differs from traditional adhesive condensation chemistries [9].

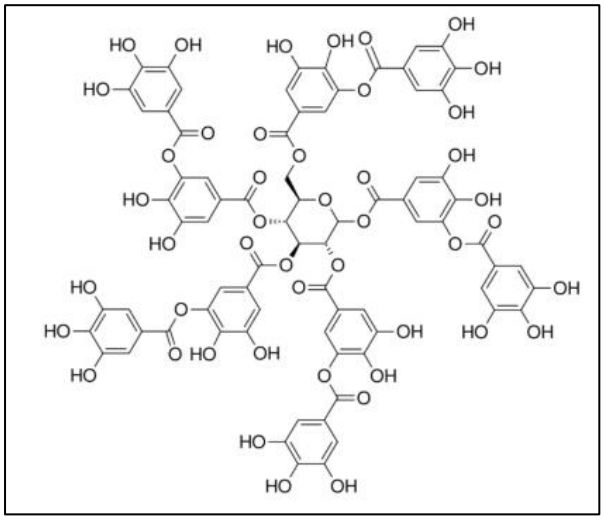

Fig2. Chemical structure of tannic acid, a tannin

Gonultas in 2018 created and tested adhesive compositions for woods and particleboards making, which are made using various hardeners and tannin powder from Turkish red pine bark. Özacar in 2006 investigated a thermosetting tannin-based wood adhesive system from formaldehyde which reacts with both condensed and hydrolysable tannin for adhesive formation [73]. Nath et al. in 2018 have investigated the characteristics and potential uses of mangrove-based tannin-based glue for the manufacturing of particleboards, and Cui et al. infused tannin-based adhesives with cellulose nanofibers for manufacturing of particleboard with a considerable amount of improvement in the mechanical characteristics of fabricated panels [17].

S. No.	Name of Plant resource	Method of adhesive preparation	Properties of adhesive
	Tannin extracted from Natural vegetables	Distilled water was combined with various amounts of defatted soy flour (SF) using a mechanical stirrer. The soy slurry was mixed with the tannic acid solution (5, 10 and 15 wt% based on soy dry weight), and the mixture was agitated for 30 minutes. The content of tannic acid in the water solutions was 45 weight percent. The urea solution (50 wt%) was added to the soy slurry and tannic acid solution after they had been thoroughly mixed. Hexamine was utilised as a hardener at 6.5 weight percent; the amount was calculated using the dry weight of tannic acid. The adhesives received a 40% aqueous hexamine solution addition. The pH was lastly brought down to 7 with a 50 weight percent NaOH water solution before hardener was applied. [26]	Tannic acid was added to the adhesive to reduce its pH and viscosity. It is challenging to apply soy-based adhesives on veneer surfaces due to their high viscosity. These problems contribute to plywood's weak bond strength. The soy protein structures are better at unfolding and

			denaturing due to tannic acid's lower pH [74].
	Mimosa tannin (Acacia mearnsii)	By combining tannin and glycerol diglycidyl ether (GDE) together in a straight mixture at room temperature, mimosa tannin-based wood glue was created. A particular quantity of Mimosa tannin was taken and placed in a 100 mL plastic bottle. Then some distilled water was added, and enough hand stirring was done to create a uniform tannin mixture. Following that, a weight of GDE was gradually added to the tannin mixture, and the mixture was manually stirred until it was uniform. [27]	With an increasing proportion of GDE, the tannin-based wood adhesive's heat stability gradually increased. A excellent bonding performance and water resistance are also provided by this adhesive as a result of the existence of non-hydrolyzable ether bonds that are created by the reaction between tannin and GDE [75].
	Tannin powder extracted from Turkish red pine (Pinus brutia) barks	A glass reactor containing the 40% solids tannin solution was filled, and the reactor also contained a hardener. The mixture was then agitated for 20 minutes at room temperature and for an additional 20 minutes at 60 °C. The mixture was subsequently chilled at 25 °C. [28]	The adhesive formulations exhibited substantially greater thermal resistance traits, a lesser mass loss value, and a higher beginning

			degradation temperature [76].
	Chestnut (Castanea sativa) shell	In a 10L Pyrex glass reactor with mechanical stirring and temperature control, the extraction tests were conducted. For chestnut shell and bur, the solid/liquid ratio was 1/10 (w/w), whereas for eucalyptus bark, it was 1/15 (w/w). As extraction agents, sodium hydroxide and sodium sulphite aqueous solutions were utilised. At room temperature, the material and water were combined. After heating, the alkali was added, and the contact time started to run. After one hour, the suspension was vacuum filtered; the solid residue was then thoroughly washed with water to produce a nearly colourless filtrate; this filtrate, together with the initial water washings, was then concentrated by spray-drying. This extract was made into a 40% (w/w) aqueous solution, to which the chosen hardener (paraformaldehyde) was added, and the mixture was then done. [29]	Adhesives produced from condensed chestnut shell tannin possess the additional benefit of being fully free of formaldehyde. Particleboards were given the E0 formaldehyde emission classification, which was a significant advancement in getting them past the board industry's increasingly demanding environmental regulations [77].

Table1. Different sources of extracting tannin and properties of formulated adhesives

2.2.2 CASTOR OIL

Contrary to what its name would imply, castor oil is not a legume; its botanical name is Ricinus communis and it belongs to the Eurphorbiacae purge family. It is typically a kharif season crop. Esters of 12hydroxy-9 octadecenoic acid (ricinoleic acid, 89%), linoleic acid, 4.2%, oleic acid, 1%, palmitic acid, 1%, dihydroxystearic acid, 0.7%, 0.3%, and 0.3% eicosanoic acid, 3%, are included in it [101-103]. These lengthy pendant chains and fatty acids are structurally composed of hydroxyl groups, which provide the network an effective thermosetting nature, flexibility, high strength elasticity, and hydrolytic resistance. Their unsaturation component functions as grafting centres during the manufacture of polymers. Such triglycerides can be used to investigate the broad range of polymers in foams, coatings, adhesives, elastomers, and sealants. In tropical and subtropical regions, castor plants can be found. Castor seed oil was extracted mechanically, which involved crushing the seeds and then reheating them in a steam-jacketed container to reduce their moisture content. Castor oil that has been cold-pressed has a slightly higher saponification value than oil that has been extracted using a solvent. Chemically speaking, it is an oil that is viscous, lighter in colour, nonvolatile, and nondrying. It also has a bland flavour and is occasionally used as a purgative. It tastes mildly acidic and gives off a little distinctive odour that makes you queasy. It has a good shelf life in comparison to other vegetable oils and does not grow rancid until exposed to a lot of heat [27].

2.2.3 RICE BRAN (RB)

Rice Bran is a by-product of rice milling and mass-produced from brown rice through abrasive milling to produce pure polished rice [4]. The likely composition of rice bran is 12–15% protein, 15–20% fat, 36% starch, and other inorganic materials [5]. In the production of adhesives, defatted RB flour is very useful as a raw material. For the formation of adhesive, defatted rice bran powder is added to dilute water and to maintain its pH to 6-9, dilute H_2SO_4 or NaOH solution is added. The mixture is heated and materials like PVA or formaldehyde are added to form a gelatinized adhesive [6]. Chemical treatment in alkaline conditions has significantly improved performance of adhesive and has proved to be an

effective method for preparation of the rice bran adhesives with better strength. It has faster gel formation ability than any synthetic material-based adhesives [37]. The physical and mechanical properties of these types of adhesives-based particleboards are also higher when the pH is higher.

The Strength of Proteins in rice bran is determined by their capacity to disperse in water as well as the interactions of the proteins' non-polar and polar groups with the substrate. The bulk of these groups are inaccessible in native proteins due to internal linkages. To break these interactions and uncoil or "disperse" protein molecules, a chemical change is necessary. This shift is accelerated by hydrolysis or by raising the pH, which can be performed by exposing the material to heat, acid/alkali, organic solvents, detergents, and urea (Lambuth, 1977 [55]; Hettiarachchy *et al*., 1995) [56]. Zhong *et al*., 2002 [57] denatured soy proteins using guanidine hydrochloride and developed a fiberboard adhesive. Similarly, Mo *et al.*, 2001 [58] modified soy protein for particleboard bonding with sodium hydroxide, urea, and dodecylbenzene sulfonic acid. Kreibich (2001) hydrolyzed commercial soybean protein fractions with acid and alkaline catalysts to provide a mixture of oligomeric polypeptides and amino acids with viscosity and reactivity properties suitable for incorporation into phenolic wood adhesives [59]. The dry bonding strength of pure RB adhesive turns out to be quite satisfactory when alkali treatment or Toluene 2,4-diisocyanate (TDI) cross linking agent is used [7]. Water resistance of adhesive also improved significantly when TDI was added as a crosslinking agent. In Fig3, a block diagram of such an adhesive formed using RB is shown [38].

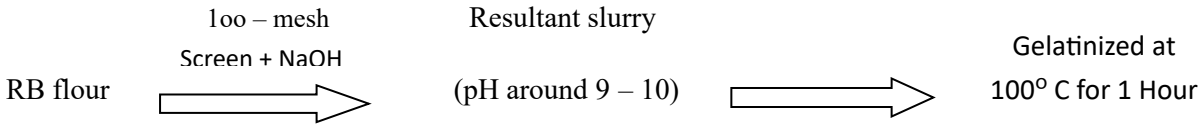

Fig3. Schematic diagram for preparation of Rice bran adhesive

2.2.4 CITRIC ACID

A novel tissue adhesive consisting of citric acid derivative (CAD) as a cross-linker was developed in 2004. The main sources of Citric acid are plants. Lemons, limes, and other citrus fruits are the predominant natural sources of citric acid [39]. Other fruits that contain much smaller amounts of it include certain berries, cherries, and tomatoes. Citric acid is a natural organic polycarboxylic acid containing three carboxyl groups [60]. In addition, citric acid has been researched as a crosslinking agent for plant fiber [61], starch [62], paper [63], wood [64, 65] and bio-based elastomers [66]. The mass production of citric acid in years 2019, 2020 and 2021 respectively are shown in Fig4. The suitable mixture of sucrose and citric acid is utilized as an adhesive for the manufacture of different particleboards [40]. The resulting particleboards met the criteria of JIS A 5908 standard and enhanced mechanical characteristics and water resistance of particleboards. The synthesis of carbonyl groups between citric acid and the composition of wood was thought to be the reaction mechanism [15]. A naturally occurring disaccharide, sucrose (-d-fructofuranosyl-d glucopyranoside), made from sugar beet or sugarcane, is also utilized in adhesive formation with citric acid in recent literatures. According to studies on the chemistry of sucrose, heating can cause sucrose to become amorphous and increase the viscosity of the solution. Acidic chemicals typically serve as catalysts for this reaction [16]. The application of citric acid with bark powder has great ability to work as an adhesive when mixed with metal mold. The results of Fourier transform infrared spectra also confirmed that the formation of ester linkages between carboxyl groups derived from citric acid and hydroxyl groups in the bark [41]. The cross-linkage of Collagen molecules with citric acid derivatives is depicted in Fig5.

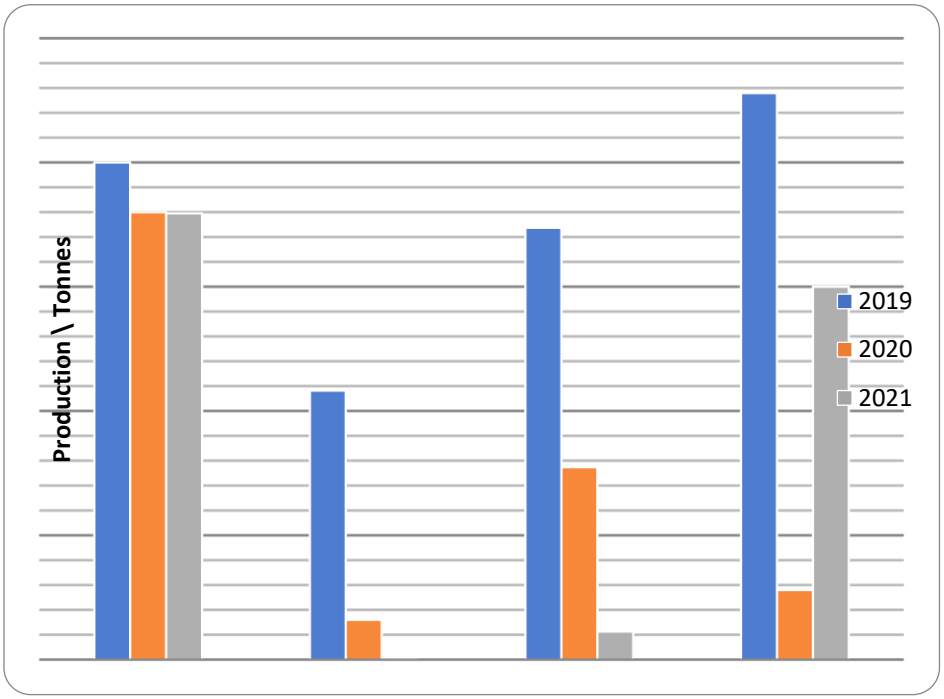

Fig4. Production of tonnes of Citric acid in recent years

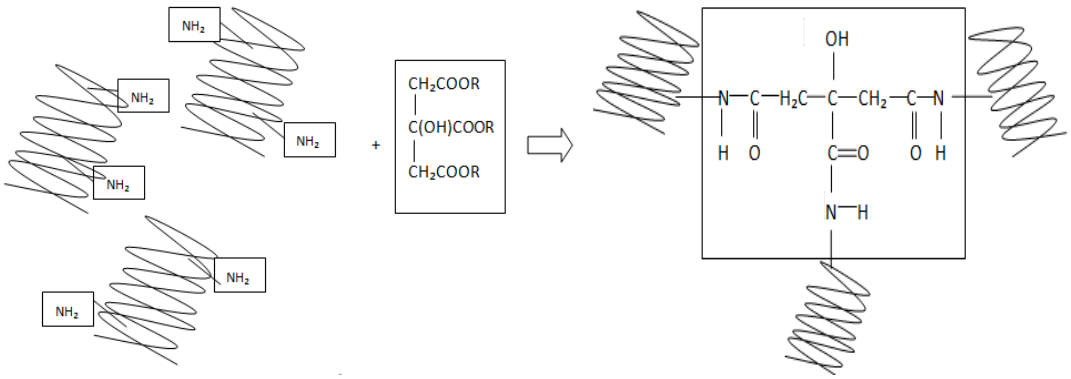

Fig5. Cross-linking collagen with CAD

2.2.5 WHEAT GLUTEN (WG)

Wheat gluten (WG) is a by-product of the production of wheat starch. Eighty percentage of wheat protein makes up the complex mixture known as wheat gluten; the remaining 20% is made up of lipids, polysaccharides, and minerals. With an isoelectric point of roughly 7, gluten wheat contains a lot of hydrophobic amino acids [41]. The glutenin fractions of wheat gluten are linked to its elastic qualities, whereas gliadins are involved in its viscous properties [10]. The most significant use of WG is in enhancing the thermal stability of the linkages in particleboard by the inclusion of the modified WG.

While maintaining the adhesive qualities of the wood joint, Lagel *et al.* used up to 30% of hydrolyzed wheat gluten in the production of phenol-formaldehyde resin [11]. In a different method, hydrolyzed gluten was combined with formaldehyde, glyoxal, tannin/hexamine resin, or polymeric diphenylmethane diisocyanate (pMDI) to create an adhesive that included between 90 and 95 weight percent and between 70 and 80 weight percent of renewable materials, respectively [42]. The bonding strength of the two formulations was sufficient for interior grade particleboards [43].

2.2.6 SOY PROTEIN

One of the most common plant proteins that is utilized to replace synthetic resins in wood adhesives is soy protein. Poor water resistance property is only downside that limits its use [44]. The performance of soy protein-based adhesives has been enhanced using a variety of techniques, including cross-linking, enzymatic modification, chemical denaturation, and the inclusion of additives, to address this issue [12]. Addition of hydrophilic polyols like ethylene glycol and diethylene glycol to soy protein-based adhesives, enhanced its wettability and wet adhesion strength by 30% due to the intermolecular hydrogen bond formation [45]. Lei *et al.* tried solving the issue by inculcating soy-based adhesives' cross-linking nature with epoxy resin, melamine-formaldehyde, and a combination of both [13]. Soya bean is high in triglyceride oil and edible proteins. The oil-free soya meal includes a significant amount of protein, ranging from 35 to 55% [104-106]. Many attempts have been made in recent years to use this abundant plant protein to create wood adhesives with better

strength and/or water resistance [67, 68]. It is also a fact that the soya-based adhesives gives a better flexural strength to the plywood.

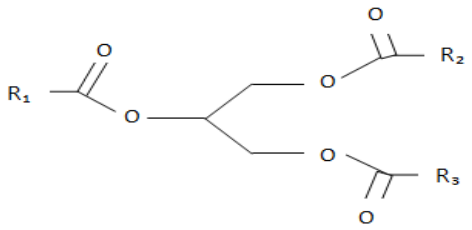

Fig6. Structural representation of molecules in Soybean oil

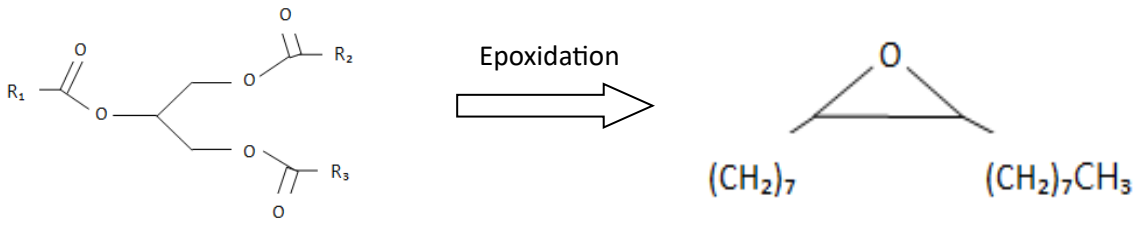

Fig7. Epoxidation of Soyabean oil molecule for formation of epoxy-linkage

The chemical reaction between epoxy and melamine-formaldehyde with hydroxyl (–OH) and amine groups (–NH) of soy protein, turned out to be very effective. Rice husk (RH) as wood chips were employed by Ciannamea *et al.* to improve the performance of the created medium-density particleboards with soy proteins [46]. For the removal of silica from RH, lignin, and hemicelluloses from rice husk, bleaching was done with sodium hydroxide. According to Khosravi *et al*., soy protein can only be utilised as a binder when it is in a dispersion condition and not when it is in a powder state [107-110]. It was discovered that the dispersion time had a substantial impact on the final product's mechanical and water resistance [14]. Lignin residue is extracted using Soyabean flour, which is taken as raw material for preparation of soyabean-based adhesive as described in Fig8 [47].

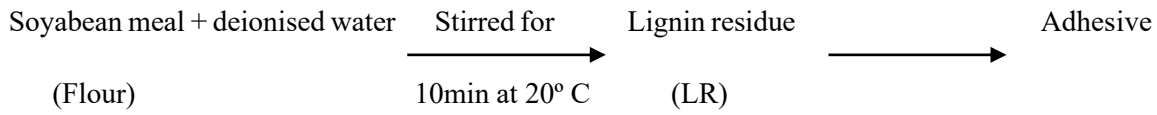

Fig8. Block diagram representation of adhesive formation using Soyabean flour

2.2.7 LIGNIN

Due to the many benefits of lignin, the development of lignin-based wood adhesives has received a lot of attention in recent years. Lignin is the only non-petroleum source of renewable aryl compounds in nature and the second most prevalent natural polymer in the cell walls of biomass [18]. Mainly, lignin is extracted by pulping black liquor and isolating it. Due to its many benefits, lignin has been used as the foundation for formaldehyde-free resins [48]. It is not toxic, to begin with. Second, several of the same desired characteristics of (Formaldehyde based resins) FBRs as wood adhesives are represented by the physiological benefits lignin provides plants, such as mechanical strength, water resistance, and chemical stability. Third, using lignin as a substitute for FBRs offers a chance for upcycling because it is produced in large quantities as a by-product of industrial processes [19]. The lignin-based epoxy resin formulation displays flexibility of the substrate (wood type) and feedstock (lignin and crosslinker) [81]. The ability to use more forms of lignin depends on the formulation's inclusion of water in particular [49]. The primary issue with lignin adhesives is their incredibly poor reactivity, which results in extended press times and higher production costs in the panel manufacturing industry [20].

Types of lignin	**Properties**
Kraft Lignin	Lignin units produce new carbon-carbon bonds, which results in new oligomeric structures. Caustic or organic solvents can dissolve kraft lignin. Since kraft lignin is not very water soluble, it can be purified by removing the water-soluble parts, leaving behind a product with a

	low ash level of under 3%. Typically, the number-average molecular weight ranges from 1000 to 3000 g/mol. Low residual sulphur content—typically less than 2%—and a significant concentration of phenolic hydroxyl groups are present in the structures. Modern technology allows for the separation of 20–25% of kraft-lignin from black liquor without impairing recovery boiler performance [82].
Lignosulfonate	Up to 8% of the sulphur in lignosulfonates is present as sulfonate groups on the aliphatic side chains. They are water soluble, have an average molecular weight of 15.000–50.000 g/mol, and only have a few phenolic hydroxyl groups in their structures. Lignosulfonates are the salts of lignin sulfonic acid [8062-15-5] and have the CAS values [8061-52-7] for calcium, [8061-51-6] for sodium, and [8061-53-8] for ammonium. Up to 25% of the mixture may contain ash [83]. The most common use of lignosulfonates is as concrete water, while they have many other uses as well. The largest manufacturers collectively produce 1.1 106 t/a by having a capacity of more than 1.4 106 t/a of various lignosulfonates.
Organosolv Lignin	As adhesives for the manufacturing of wood particleboard, organosolv lignins derived from the bark and wood of sugar maple were investigated. The findings revealed that wood lignin has a larger weight-average molecular mass than bark lignin. The investigated organosolv lignins were utilised to make particleboards both in their recovered form and in mixtures with glyoxal or isocyanate. It was discovered that sugar maple bark lignin, either unaltered or treated with isocyanate, performed better as an adhesive than wood [84]. Contrarily, the combination of glyoxal and organosolv wood lignin proved a more effective adhesive than bark alone. The sugar maple bark organosolv lignin was shown to have the best adhesive ability of all the tested lignins when combined with isocyanate.

Table2. Types of lignin and its properties

2.2.8 CASHEW NUT

A viscous, reddish-brown liquid known as cashew nut shell liquid (CNSL) is shaped like the honeycomb structure of cashew nuts that are gathered from cashew trees [50]. Cardanol is a phenolic lipid that is produced from anacardic acid, the main ingredient of cashew nutshell liquid (CNSL), a byproduct of the processing of cashew nuts [85-87]. The cardanol is used for decarboxylase derivatives produced by the thermal breakdown of any anacardic acid that occurs in nature [51]. Given that the side's chemical makeup contains many compounds, this includes chain's level of unsaturation varies. cardanol tri-unsaturated is the main element (41%) and the remaining of the cardanol is 2% saturated, 22% bi-unsaturated, and 34% mono-unsaturated [52]. Cardanol molecules typically have two double bonds in their side chains that are unsaturated, which facilitates cross-linking and gives paints made from its good progressive drying and baking qualities [88]. Cardanol Varnishes have a unique structure that gives them a high level of electrical insulation, increased resistance to water and chemicals, and superior flexibility [21].

2.2.9 STARCH

People like starch as a bioresource because it is renewable, non-toxic, safe, and less expensive; it is used extensively in food, medicine, textiles, paper, pharmacy, and agriculture. To store energy, the majority of plants produce the carbohydrate starch [53]. It is preserved as spherical granules within cells that are 2 to 100 m in size. The majority of starches found in foods sold in markets come from cereals like corn and wheat as well as tubers like potatoes and tapioca [54]. Chemically modified starch broadens the variety of physical qualities available for many applications since they have good physicochemical properties that differ significantly from their parent starch [69]. These grains and tubers often contain between 60 and 90% of their dry weight in starch, making them rich in starch [22]. Starches are commonly utilised in the adhesives industry (Kennedy, 1989), their bonding capacity is insufficient for glueing wood [70]. Because of its poor stability and weak adhesive properties, native starch without modification is typically not appropriate for use as an adhesive [89-91]. As a result, numerous studies involving physical, chemical, and

biological methods—such as hydrolyzation, gelatinization, oxidisation, crosslinking, and grafting—were conducted to change starch [23]. In applications involving wood and wood composites, environmentally friendly starch adhesives can also completely replace UF adhesives [92-94]. It is possible to achieve water resistance, extremely low formaldehyde emission, and comparable performance properties by adding cross-linkers like iscoyanates and Melamine formaldehyde [24].

MODIFICATIONS OF STARCH

Modification of Starch	Properties
Using different type of crosslinkers	Extremely low formaldehyde emission, water resistance, and equivalent performance characteristics
By acid	At high relative humidity, minimise moisture sorption, molecular movement, and swelling.
Addition of emulsion	increasing the medium density fiber's mechanical and physical characteristics
Blending with biopolymer	Zero formaldehyde emissions eco-friendly system. Glyoxal and dioxal, two aldehyde hardeners, can be employed to improve characteristics.

Table3. Modifications of starch

2.2.10 PALM OIL

The oil palm's fruit pulp is used to make palm oil, which has a 10% diunsaturated, 39% monounsaturated, and 49% saturated fatty acid composition. A liquid and a solid fraction of palm oil can be separated [95]. There have been reports of palm oil-based polyester and polyether polyols being used to make polyurethane adhesives. The commercial polyether and polyester polyols were combined with the palm oil-based polyol (up to 15%) to react

with toluene diisocyanate and create a flexible polyurethane [25]. The advantage of PU adhesives made from polyester polyol derived from palm oil is that there is no need for a volatile organic solvent during the preparation process, and polyester polyol is made from sustainable and renewable resources [96-98]. When compared to the typical PVAC wood adhesives sold on the market, the PU adhesives created from toluene 2,4-diisocyanate (TDI) and polymeric 4,4′-methylene diphenyl diisocyanate (pMDI) both displayed greater mechanical strength [99-100]. It was a good product choice for sticking big wood surfaces because it also showed high chemical and thermal resistance and had a long enough pot life [26].

CHAPTER 3 EXPERMENTAL ANALYSIS

3.1 MATERIALS AND EXPERIMENTAL METHOD

3.1.1 MATERIALS

Unaltered commercial grade cornstarch was procured from the store; Sodium hydroxide, NaOH (Molecular weight = 40.00 g/mol) was taken from Loba Chemie Pvt. Ltd. Commercial flavonoid, wattle tannin (Wattle OP) was supplied by Loba Chemie Pvt. Ltd. The hardener, hexamine 99% extra pure, was provided by Loba Chemie Pvt. Ltd.

3.1.2 PREPARATION OF CORNSTARCH-TANNIN ADHESIVE

To produce 200 g of adhesive, 65% (p/v) cornstarch water solution was produced by dissolving 52 g of cornstarch in 80 ml of deionised water and stirring at a room temperature, then adding 5.2 g of wattle tannin. The hardener content was 5% hexamine by weight on the tannin extract solids content. Before adding it to the cornstarch-tannin solution, the hexamine was dissolved in water to form a 30% solution. After mixing the solution, 40 ml of sodium hydroxide (33%) was introduced [111]. The resulting adhesives were mixed at room temperature for 45 minutes before being used to bond plywood pieces.

Fig9. Adhesive formulation on mixing cornstarch and tannin

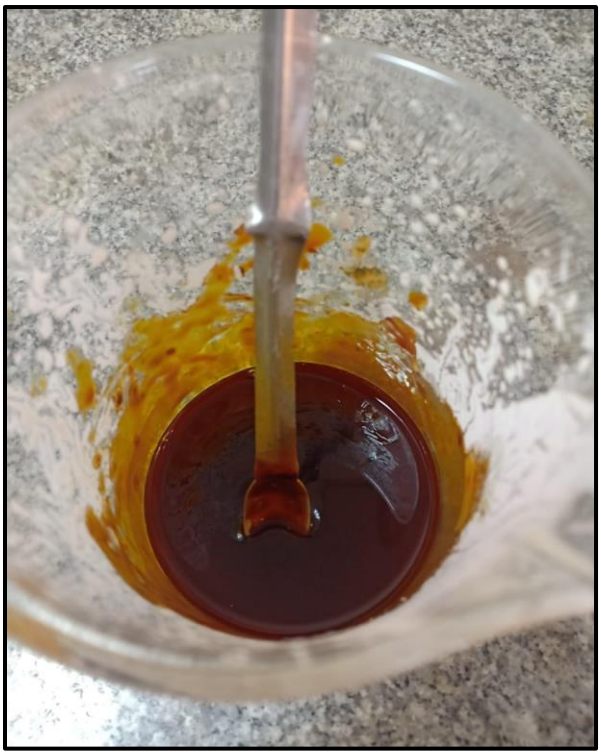

Fig10. Viscous adhesive formation on addition of NaOH

3.2 PLYWOOD PREPARATION AND TESTING

Five plywood panels of dimension 165 x 165 mm^3 were prepared from 3 mm thick plywood with a moisture content of 4% at a glue mix spread of 150 g/m^2 single glueline on each panel [112]. In the case of cornstarch-tannin adhesives, hot pressing was done at 13 bar pressure and 170 °C for 5 minutes press time (optimal conditions).

Fig11. Plywood panels adjoined together using our adhesive

3.3 PREPARATION OF FOUR DIFFERENT ADHESIVES WITH CERTAIN VARIATIONS IN COMPOSITION

Later we experimented with concentration of NaOH added to the adhesive and saw variations in the viscosity of adhesives. Hardener i.e., hexamine content was also varied to check its response to the thickness of adhesive [113]. Four adhesives were prepared and various tests were run on them to check the physical, mechanical properties and viscous nature of these adhesives. Firstly, two adhesives were prepared with similar content

proportions, Adhesive A and Adhesive B, wherein the Adhesive A was prepared with the hardener (Hexamine) and Adhesive B was prepared without any hardener content. A second set of adhesives was prepared with half the concentration of NaOH i.e., 20 ml wherein Adhesive C contain hardener and Adhesive D was without hardener content. Characterization techniques like TGA (Thermogravimetric analysis), FTIR (Fourier transform infrared) and Rheometer were undertaken to analysis the strength of our adhesives.

3.4 CHARACTERIZATION TECHNIQUES

TGA (Thermogravimetric analysis) is an analytical technique used to measure a substance's thermal stability and volatile component percentage by monitoring the weight change that occurs while the substancee is heated at a constant pace [114]. These devices can measure water loss, solvent loss, plasticizer loss, decarboxylation, pyrolysis, oxidation, breakdown, weight percentage filler, the quantity of metallic catalytic residue left on carbon nanotubes, and weight percentage ash. For TGA analysis, the sample size should be between 2 and 50 mg [115].

FTIR (Fourier transform infrared) is the most popular type of infrared spectroscopy. All infrared spectroscopies work on the idea that when infrared (IR) radiation passes through a sample, some of the radiations are absorbed and the remaining radiations are recorded [116]. It produces an infrared absorption spectrum for recognition of chemical bonds in a molecule. The spectra generate a sample profile, a unique molecular fingerprint that may be used to scan samples for a variety of components. It determines how much light is absorbed by a sample at each wavelength. FTIR spectrometers are typically utilized for measurements in the mid and near infrared ranges. The mid-IR area is 5,000-400 cm^{-1} [117]. Shorter near-IR wavelengths, 10,000-4,000 cm^{-1}, necessitate a higher temperature source, often a tungsten-halogen lamp. The absorption of the quartz enclosure limits the long wavelength output of these to roughly 2,000 cm^{-1}.

A rheometer is a laboratory equipment used to measure how a viscous fluid (a liquid, slurry or suspension may be) flows in response to applied forces and so comprehend a material's flow/deformation properties [118]. Thixotropy, viscoelasticity, yield stress, creep compliance, extensional viscosity, and stress relaxation behaviors are some of the most essential qualities that may be determined with a rheometer [119]. We can acquire three types of rheological measurements: extensional flow, dynamic shearing, and steady-state shearing [120].

CHAPTER 4 RESULT AND DISCUSSIONS

Firstly, the physical properties of cornstarch-tannin adhesives were identified for example viscosity of cornstarch-tannin adhesives, stability of adhesives, optimization of reaction time and temperature of the reaction were studied. Secondly, the mechanical properties of plywood prepared with cornstarch-tannin adhesives were studied.

4.1 PHYSICAL PROPERTIES OF FORMULATED ADHESIVE

The cornstarch-tannin adhesive was formulated without any employment of formaldehyde; which was substituted by a nonvolatile and nontoxic aldehyde, (hexamine) yielding good mechanical properties for the plywood. At laboratory levels, wattle tannin hardened with hexamine has shown to be a good formaldehyde-free system. This beneficiary effect is completely based on the double mechanism of slow hexamine decomposition to reactive imino-amino methylene bases, and their subsequent reaction (very fast) with the wattle tannin. Many researches are still in progress for further improvement in cornstarch-tannin adhesive formulations by employing other non-toxic, nonvolatile and aldehyde hardeners like- glyoxal or dioxal. Our formulated adhesive was brownish-viscous liquid having good glue strength.

4.2 RHEOLOGICAL EXPERIMENTS

Four different rheological experiments were conducted using a parallel plate rheometer in laboratory. After calibration of rheometer, a certain amount of adhesive was placed between the two plates (approx. 0.25 mL or 0.12 mL). The resultant viscosities ranged from 10 to 5000000 m-Pa s. Fig. 11 shows the viscosity–shear rate data with both increasing shear rate (from 1 to 100 1 /s) for Adhesive A and B. Fig. 12 shows the variation of viscosity with

increasing shear rate for Adhesives C and D. The resultant viscosities ranged from 10 to 3000000 m-Pa s. Fig. 12 shows the viscosity–shear rate data with both increasing shear rate (from 1 to 100 1 /s) for Adhesive C and D. All the tests were conducted within 5 days the adhesives were prepared. The decreasing shear rate viscosity data were lower according to observations, indicating a thixotropic behavior.

Out of the four adhesives considered, Adhesive D exhibits rheological characteristics distinct from other Adhesives with better properties according to data collected. It shows the lowest fluid consistency index and the highest flow behavior index. Adhesive B and Adhesive D have low viscosity compared to other two adhesives and show better strength.

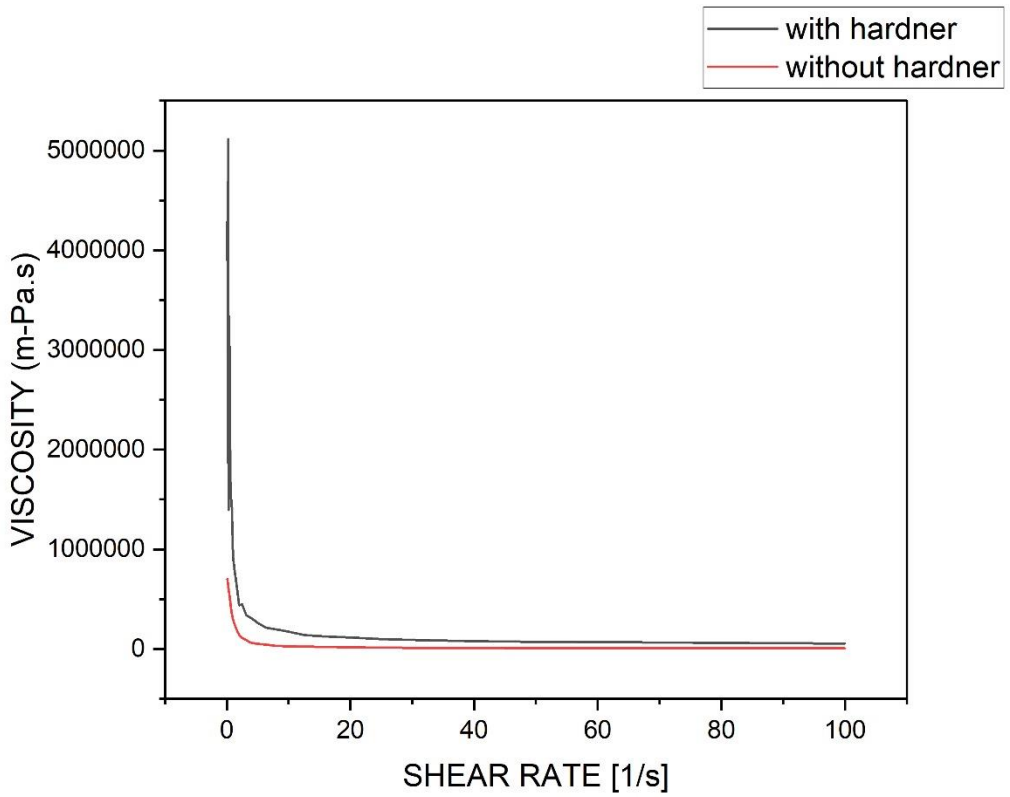

Fig12. Viscosity–Shear rate data of cornstarch–wattle tannin Adhesives A, B observed when tested to various maximum shear rates at 25 °C

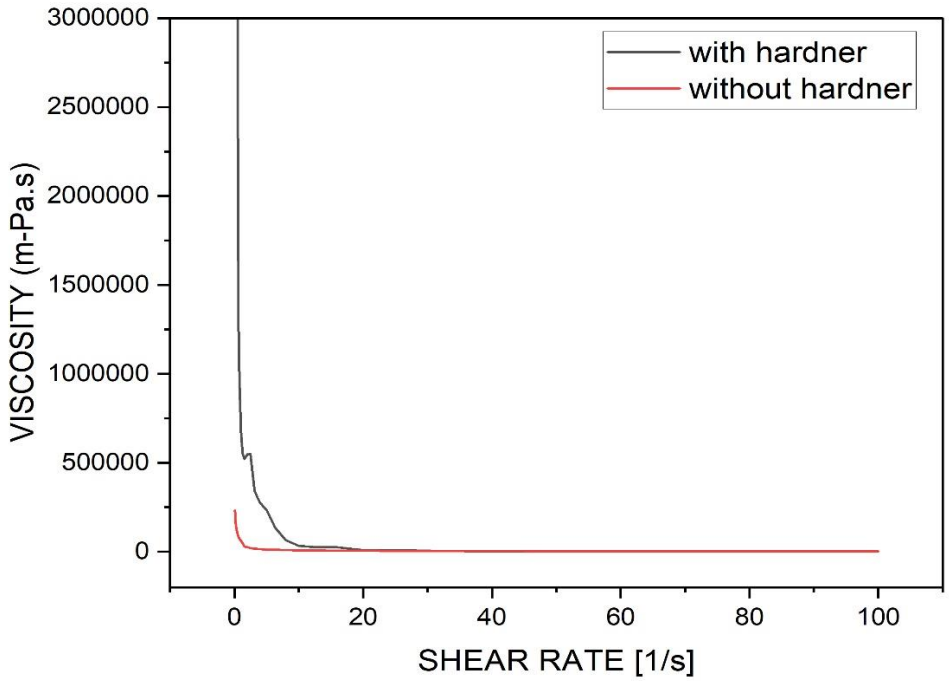

Fig13. Viscosity–Shear rate data of cornstarch–wattle tannin Adhesives C, D observed when tested to various maximum shear rates at 25 °C

4.3 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis (TGA) was done for the determination of the thermal stability and degradation of optimal adhesive. Using TGA, we checked the thermal stability and thermal decomposition of the adhesive. Fig. 13 shows the TGA curve of the optimal cornstarch–wattle tannin adhesives prepared. TGA curve reveals the weight loss of the sample in relation to the temperature of thermal degradation. The curve shows that there are three obvious mass losses at 176.03°C, 248.2°C and 311.76°C. The decomposition of adhesive in general started at 176.03°C. The decomposition of cornstarch commenced at 248.2°C according to data, whereas lastly the decomposition of the wattle tannin started at about 311.76°C. The curve also exhibits that thermal degradation began only after the substances have absorbed certain amount of heat energy. The heat simultaneously initiated the degradation processes and the breaking down of the structure by giving rise to molecular

chain ruptures. The results obtained with thermogravimetric analysis confirm that around 130°C they risk no degradation of wattle tannin and cornstarch.

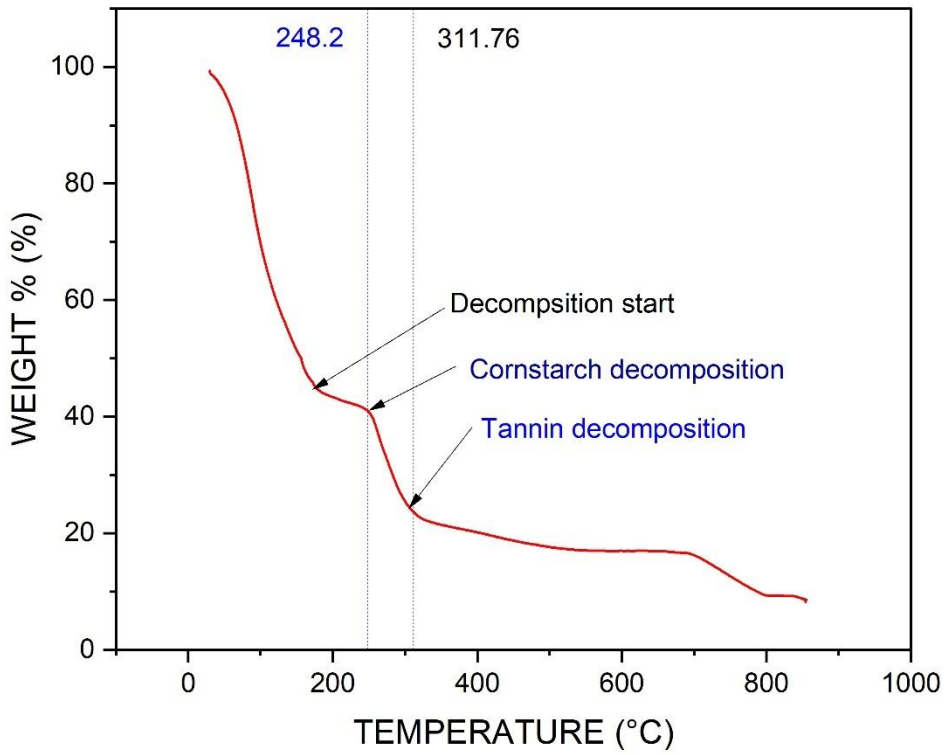

Fig14. TGA curves of cornstarch–wattle tannin adhesives

4.4 FTIR ANALYSIS

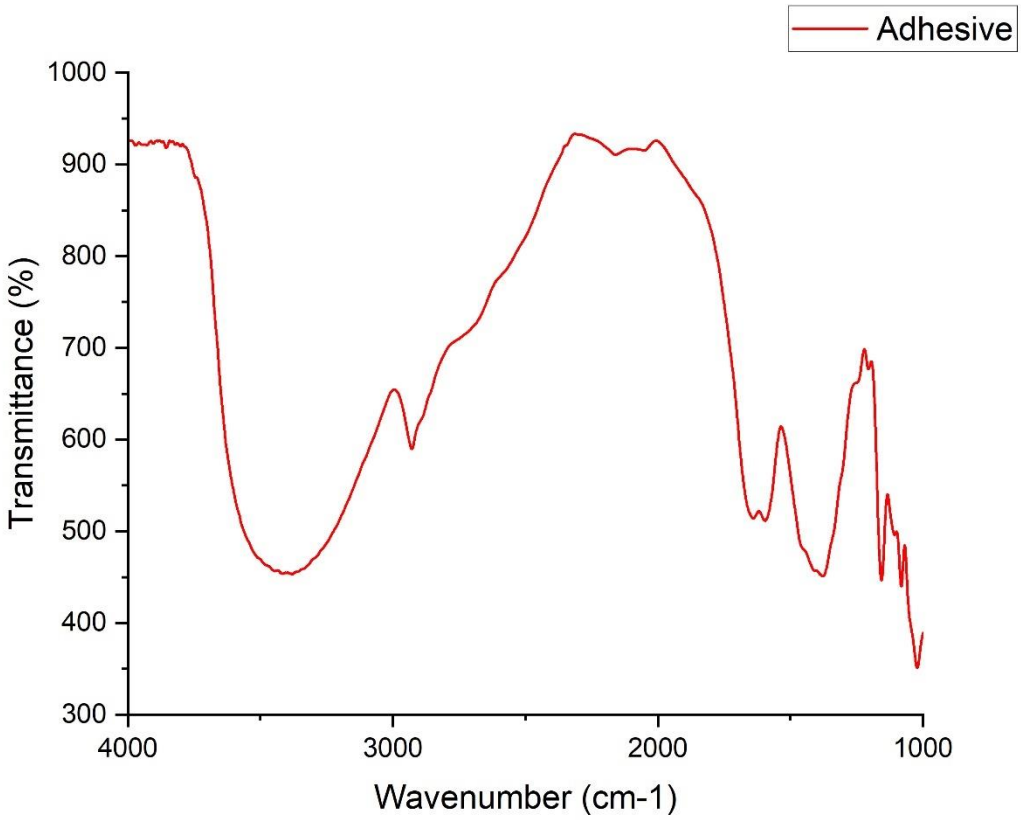

Fig15. FTIR spectrum of cornstarch–wattle tannin adhesives

Bands (cm^{-1})	Assignments
3433	Stretching vibrations of O-H groups
2994, 2930	C-H stretching vibrations ascribed to (CH_2) groups
2323	Stretching vibrations of phosphine groups
2171	Assigned to the (C≡C) stretching vibration
1373	C-H bending vibrations ascribed to (CH3) groups
1225	Stretching vibrations of COOH groups
1158, 1138	Assigned to the secondary alcohol groups (2°)
1068	Assigned to the primary alcohol groups (1°)
1020, 1000	Stretching vibrations of (R-O-R') ether groups

Table4. FTIR absorption bands and assignments of the sample adhesive

FTIR measurements were performed in this work with a view to identify the functional groups present in Adhesive D. Fig. 14 represents the FTIR spectrum and Table. 4 summarizes the bands and their corresponding assignments. Sample of Adhesive D was scanned between 4000–1000 cm^{-1}. As it could be seen from Table. 4, the broad band spectrum is visible around 3300-3400 cm^{-1} related to the hydroxyl groups. Besides, a new peak at 2323 cm^{-1} which was ascribed to the phosphine group. Also, it can be derived from that the carboxyl groups and ester groups were detected in the FTIR spectrum of the adhesive. These observations confirm that an esterification reaction occurred between the carboxylic groups and hydroxyl groups of tannin. Besides, the new peak at 2994 cm^{-1}, 1373cm^{-1} were detected according to FTIR spectrum, which were respectively ascribed to C-H stretching vibrations of (CH_2) groups and C-H bending vibrations of (CH3) groups. In addition, spectra of the primary alcohol groups (1°) and the secondary alcohol groups (2°) was also visible at 1068 cm^{-1} and 1158 cm^{-1}, respectively.

CONCLUSION

One of the most significant problems in the production of wood-based panels is formaldehyde emission. Consumers and manufacturers of wood-based panels are more aware of the dangers involved as health concerns have grown over time. Due to its high toxicity, existing classification, and potential future complete ban of usage, formaldehyde must thus be reduced or eliminated from the production of many types of products. One of the greatest ways to deal with the issue of formaldehyde being present in finished products in the free/unbound form is to remove it from resin composition. There are numerous applications for the benefits that bio-based adhesives offer. High functionalities can speed up curing and enhance the adhesive bond, as is the case, for instance, with lignin. Vegetable oils' lengthy alkyl chains can be employed to increase water resistance. Many bio-based materials can be recycled more easily because of their inherent biodegradability, and their lower toxicity and improved environmental compatibility can reduce the need for additional environmental testing and save money when future environmental laws are anticipated. Additionally, by incorporating bio-based components, additional capabilities can be added to adhesives. A new adhesive was created, and it demonstrated good promise for commercial use in structural wood composites by providing the requisite binding strength, water resistance, and technological adaptability. The primary characteristics of protein adhesives were significantly influenced by the crosslinker species, and the aqueous modified polyamide was the most effective crosslinker. The prepared adhesives for plywood panels bonded with cornstarch and tannin showed better properties to those of plywood panels bonded with commercial PF in industries. There is a relationship between increased addition of NaOH and hardener in bond strength properties. However, it has been demonstrated that cornstarch and wattle tannin are a perfect blend to replace the PF resins used to bond wood panels and furnitures, without adversely causing effect on bond properties. Petrochemical PF can also be partially substituted in resols in industrial applications by addition of cornstarch and wattle tannin extracts.

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