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BIOADHESIVES - AN ENVIRONMENTAL FRIENDLY ALTERNATIVE

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Abstract:

Volatile organic compounds, the main constituent of synthetic adhesives have been found to be carcinogenic in nature and practically feature in our daily activities therefore exposure to these poisonous chemicals becomes inevitable. In order to overcome this menace, this study has brought to the fore, bio-adhesives, known globally for its fast-curing capability, reduced environmental effects, low production cost in commercial quantities without affecting food supplies. Through the lens of an in-depth literature, the importance of tannin, lignin, starch and plant protein as viable primary sources of bio-adhesive has been brought to the limelight, showcasing their modifications and prospects. Lignin will show promising reward if the secondary produce from pulp waste is recycled while plant protein and starch may not thrive since their primary produce are major food sources; tannin on the other hand, is an available resource directly from plant and would not disrupt food supply, tannin can therefore be recommended as the best alternative for bio-adhesives production.

Key words*: synthetic adhesive; bio-adhesive; volatile organic compounds; modifications.*

INTRODUCTION

A typical synthetic adhesive is produced through reacting phenol with formaldehyde and this has caused an unprecedented increase in the demand for phenol as this was obtained from (Hexaresearch 2018; Reportbuyer 2018) that as at 2016, close to 12 million tons of phenol was on demand in the phenol market. The very essential market of synthetic adhesives is the building and construction segment utilized mainly for structural purpose as well as for flooring or wall covering, making it a rapidly growing market. Synthetic adhesives are usually made up of component such as polyvinyl acetate, epoxy, phenol-formaldehyde, and polyurethane which are in turn made up of toxic chemicals such as epichlorohydrin, methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), formaldehyde, and other volatile organic compounds (VOCs) (Zhang *et al*. 2017). These chemicals are very expensive and also hazardous to both the safety of living beings and its surroundings, it is compulsory that application procedures are relayed to users stating necessary warnings in order to avoid hazards during the period of application. Allergies and hypersensitivity have been associated with synthetic adhesives overtime. Adhesives such as epoxy adhesives cause skin irritation. Furthermore in 2004, there was a reclassification of formaldehyde to Category 1 – known human carcinogen, which drove the desire of finding the alternative of phenol- formaldehyde based adhesives (Mai *et al*. 2004). Also, in 2018, it was published by some US researchers in the journal science that petroleum-based chemicals in finished products when measured in a group can emit much more pollution than automobiles (Nhat and Thrush 2018). However, it is rather unfortunate that bio-adhesives which are more eco-friendly, with suitable mechanical and chemical properties as well as competitive production costs have been neglected for far too long.

Bioadhesives consist of varieties of substances, but protein, tannin, carbohydrates and lignin derivatives feature particularly for wood adhesive (Pizzi 2006). Bioadhesives are natural polymers; sometimes used more loosely to describe glue formed from biological monomers such as sugars. Polysaccharides are a chemically and structurally diverse class of natural products, some of which have adhesive properties. The basic structural characteristics of polysaccharides for exhibiting adhesive properties mainly include high molecular weight and polar functional groups improving their mechanical

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strength (Patel *et al*. 2013). The polysaccharides with polar and hydrogen bonding functional groups, ethers, hydroxyls, and carboxylates, exhibit superior adhesion to wood and metals that are high surface energy adherends and also serve as possible sites for chemical modification and cross-linking with the aim to improve adhesive property. However, no biological resource can act entirely like phenol hence the need for chemical modifications of their functional groups. With the constraint of rising oil prices, environmental pollution and high price of phenols in mind, several attempts have been made to replace phenol with a natural material having similar structure. This study brings to light an environmental-friendly alternative to synthetic adhesives and its potentials thereby reducing harmful gasses being released into the atmosphere on daily basis and proffers a more economical way of converting waste to wealth.

CHEMISTRY AND UTILIZATION OF BIO-ADHESIVES

Lignin

Lignin, since the beginning of time, has been known as the natural bond in plants. Wood lignin can be isolated by either dissolving lignin or the non-lignin components by solvents while industrially; lignin can be gotten from different paper and pulp processes. Due to its phenolic nature, it has been a center of attraction for researchers over the years as the new face of wood adhesives. The lignin structure is phenolic in nature and can be used as a replacement of phenol in the formation of wood adhesives through the synthesis of phenolic resins. The lignin structure is composed of a highly cross-linked phenylpropane unit (C_6C_3). These units are in turn held together by several ether (C-O) and carbon-carbon (C-C) linkages. Pearl (1967) reported that the functional groups in lignin polymer are also present in its precursors. These functional groups are highly responsible for its reactivity and modifications in the preparation of lignin-based adhesives. This functional group includes methoxyl, phenolic hydroxyl, benzyl alcohol, carbonyl groups and a bit of aldehyde groups. Due to the crowded and complex structure of lignin, its reactive tendency is quite low and brittle during adhesive formulations (Tejado *et al*. 2008) hence the need for modifications.

Kraft lignin is the by-product of kraft pulping derived from cooking wood chips with a sulfur-based chemical. Almost all kraft lignin are burned to generate energy and recover chemicals even with this, only a small amount of the kraft lignin that is produced by the pulp and paper industry is commercially used apart from its use in a wide range of products. It is projected that Kraft process single-handedly produces about 95% of the world quantity of lignin per year and the 55 million tons of lignin co-produced per year are only used as energy source for combustion application (Gosselink *et al*. 2004).

Lignosulphonates is often polar and water soluble because of the presence of sulfonate groups. (Li *et al*. 2013). Delignification in this case occurs due to the ester bond cleaving to the ether bond. Sulfonation occurs primarily at the side chain of the phenyl propane units between the benzyl aryl ether and benzyl alkyl ether linkages (Laurichesse and Averous 2013).

Organosolv lignin could be recovered by distillation reducing water and air pollution usually associated with kraft pulping; gotten though filtration or centrifugation. Filtration due to its time-consuming ability, is most effective while the mixture is yet > 100^0C.The lignin gotten is water insoluble increasing bond durability when used as an additive in PF resins. They are characterized by their hydrophobicity, low glass transition temperature, low molecular weight and narrow molecular weight distribution (Senyo *et al.* 1996*).*

Autohydrolysis occurs when acetyl groups of D-xylan are hydrolyzed at elevated temperatures in the presence of water and is recovered from residue by dissolving the lignin in sodium hydroxide and removal of the insoluble residue, hereafter the lignin was precipitated by hydrochloric acid and subsequently dried to form a fine bulky powder.

Modification of lignin-based adhesives

The best way to conform lignin into a raw material for adhesives is to use it to replace phenol in phenol formaldehyde (PF) resin systems known to bond wood substances over the years. Replacing phenol with lignin must come with an assurance that the lignin takes part in the resin bonding process (Kalami *et al.* 2017). Van der Klashorst, (1989) and Sellers, (2004) have at different times worked successfully on how to replace or add lignin to produce durable adhesive. However, despite its advantages, lignin in its industrial state has been discovered to possess several constraints that can affect this potential. Lignin in its native state is polyphenol in structure and so is similar to formaldehyde resins unlike industrial lignin whose structure and native state has been changed. These industrial lignins have to be additionally cross-linked for them to be replaced as insoluble resins. The type of cross linking used is usually based on the plant species and the type of isolation process employed.

METHYLOLATION: Lignin reacts with formaldehyde under alkaline conditions producing methylol groups at the *ortho* positions of the aromatic ring (Benar 1999). With rise in temperature, these methylol groups in turn react with free and reactive positions of other lignin units to form methylene bonds (crosslinking). Reaction of lignin with formaldehyde, introduces methylol groups at position C_5 of the chain

(Vazquez *et al.* 1997). In the reaction, with hydroxymethyl groups incorporated into the lignin aromatic rings, the reactivity of the molecule is increased (Pizzi 2006).

PHENOLATION: is best for lignosulfonates because of the presence of benzylic hydroxyl groups. Here, the phenolic hydroxyl group is multiplied by reacting the lignin with phenol to produce a methylene linkage (Van der Klashorst 1989). After the condensation of phenol into the lignin aromatic ring, methylene linkages are formed decreasing the molecular weight and improving the flow properties. Hereafter, the phenolated lignin is then reacted with formaldehyde to make novalac or resol resins. If resol resin is made, the medium has to be made alkaline. The reactivity of the phenolated lignin is enhanced because for every reactive position lost to cross linking, two new reactive positions are created (Ysbrandy *et al.* 1992).

DEMETHYLATION: is the process of removing the methyl group from the lignin molecule while replacing it with a hydrogen molecule (Fig. 1). Demethylation is usually facilitated by enzymes called O-demethylases stripping off the –OCH_3 group in lignin giving rise to the phenolic hydroxyls groups and thereby making it more reactive e.g. enzymes such as laccase and fungus such as brown-rot fungi. Demethylation reactions mostly result in the formation of o-quinone structures during kraft pulping. Conclusively, kraft lignins contain little amounts of organically bound sulfur, in the form of thiol compounds (Glasser 2001).

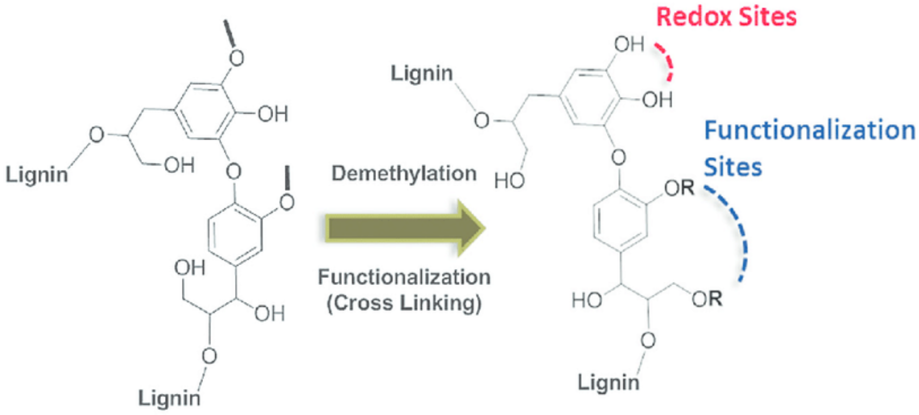

Fig. 1.
Chemical modification of lignin (Davide and Markus 2015).

TANNIN

The name “tannin” is originated from an industrial process of “leather tanning,” in which animal hides are transformed into leather through making them materials of historical origin. Major sources of tannin extraction exist in various parts of plants such as bark, wood, leaves, seeds, roots, and even the plant galls used for various purposes. They have been divided into three main subgroups: (1) hydrolysable tannins, (2) condensed tannins, and (3) phlorotannins. Hydrolysable tannins are highly soluble in water; consisting of a central core of a carbohydrate (D-glucose) with its hydroxyl groups esterified with phenolic compound. Different extraction methods have been used in tannin extractions, the most common ones being maceration, Soxhlet extraction, supercritical CO_2 and percolation. Microwave and ultrasound assisted extraction has also been studied to increase tannin productivity though utilized rarely due to its less efficiency in non-polar tannins and solvents (Wang and Waller 2006).

Tannins are applicable in several industries such as food (packaging; instead of plastic or polyethylene packages which come with environmental contaminants, biological sources such as gelatin, starch and tannins has been introduced), wood (adhesives; wood requires a large amount of coatings, glues and adhesives to hold up a structure but are produced with materials known to be carcinogenic in nature thereby arising for biological sources more eco-friendly), medicine and pharmaceuticals (several synthetic chemicals have been applied to drug molecules to treat threatening diseases but yet leave numerous side effects shifting attention to alternative natural compounds clinically effective with minimum adverse effects) to mention a few. The global tannin market is expanding very rapidly; according to estimation, 1076.3 kilotons tannin was required in 2015 which expected to rise with CAGR of 5.8% from 2016 to 2025 industry (Grandview Research 2017). The demand was mainly in the wine, leather, pharmaceuticals, and wood industries; hence, global market size for tannin related industries may increase up to $3.3 billion by 2025. The applications of condensed tannins are expected to increase up to 424.8 kilotons by 2025 in comparison of 242.9 kilotons in 2015 (Akhlash and Sunil 2019).

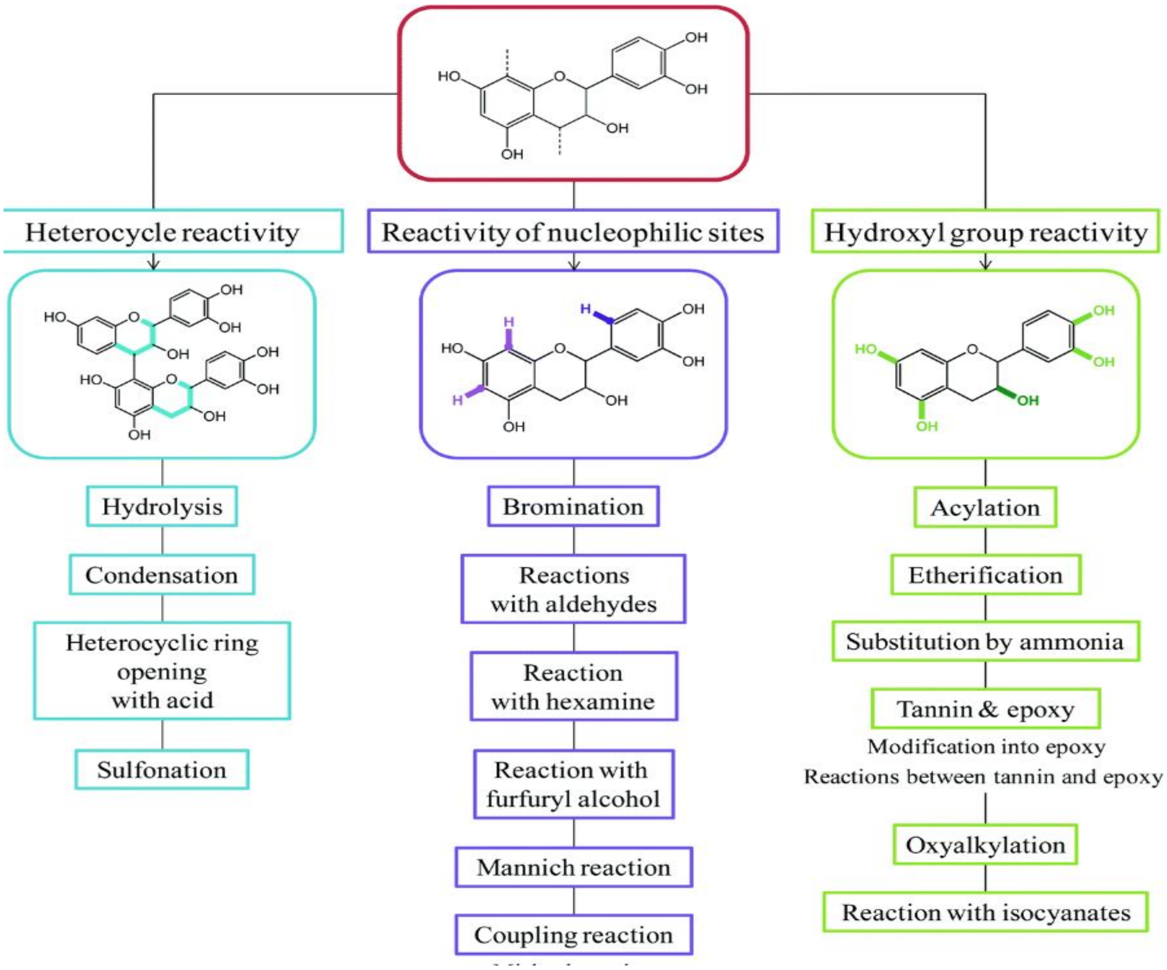

Fig. 2.
Chemical modification of tannin (Arbenz and Avérous 2015a).

As presented in Fig. 2, the chemical modification of tannins can be divided into three main groups; Heterocycle can be opened and can lead to rearrangements of the chemical structure.

Catalyzed rearrangements such as hydrolysis and autocondensation are common reactions for tannins. The cleavage of the interflavonoid bond can also be acid-catalyzed or induced by a sulfonation reaction. Degradation under acidic media leads to the formation of catechins and anthocyanidins or the formed products can autocondense, giving an alkaline condensation (Arbenz and Averous 2015b). Acids such as HCL (Hemingway and Gerald 2007) and Acetic acid (Hemingway and Kreibich 1984) have been used for degradation of tannin. Arbenz and Averous, (2015b) also oxypropylated condensed tannin using KOH as a catalyst and reported that modulating oxypropylation reaction parameters will control the chain length of polypropelene oxide.

Reactivity of nucleophilic sites, created by OH groups present on the aromatic rings, leads to electrophilic aromatic substitutions. In bromination, on the A-ring, C6 and C8 are both activated by the phenol group but preferentially done on the C8 position. Preferential sites usually depend on the flavonoids. Fitzen *et al*. (2016) prepared a tannin–hexamine adhesive as a 40% w/w solution of mimosa tannin in water using sodium hydroxide solution to set the desired pH. When molecules with nucleophilic sites such as tannins are present in the medium, amino-imine groups are formed and react with the phenolic compounds. Basso *et al*. (2017) have reported for the first time a reaction of catechin and polyflavonoid tannins with TEP, leading to polymerization and cross-linking revealing that the reaction takes place mainly on the C3 of the flavonoid heterocycle ring and on the aromatic C4 and C5 carbons of the flavonoid B-ring. Some studies used formaldehyde and furfuryl alcohol to improve the alcohol reactivity. The latter is commonly used, mixed with tannin as a reactive species, to produce foams (Foo and Hemingway 1985).

Reactions can also take place directly with the OH. Phenolic and aliphatic hydroxyl (OH) groups possess reactive functions modifiable to attain some tannin derivatives. Tannin could be modified to increase its chemical reactivity in solvents and its processing. To increase the reactivity site, changing the nature of the reactive sites or increasing the hydroxyl group reactivity is paramount. Acylation is known to increase reactivity sites because they form a strong electrophile when treated with metal catalysts. Solvent such as pyridine, acetone, chloroform etc ensure solubility of tannin. Reacting with acetic anhydride in pyridine ensures the solubility of tannin, with this tannin loses its water solubility.

PLANT PROTEIN

Protein based bio-adhesives include adhesives extracted from plants, several studies have been conducted on the manufacture of protein-based adhesives from different crops such as soy, canola, cottonseed, wheat glutten etc. (Chen *et al*. 2015a; Wang *et al*. 2014, Nordqvist *et al*. 2013). They are either used directly or in combination with a cross-linking agent that forms covalent bonds with the tissue surface.

SOY BASED ADHESIVES

Soy based protein adhesives have been limited due to a general problem of poor water resistance. It is natural to expect that with all these reactive moieties in the soy proteins, it would be easy to develop covalent bonds of the protein subunits and agglomerates with cross-linkers. However, many of these reactive groups are buried inside the globule, making reactions difficult. The polar groups inside the protein form interactions with other polar groups to stabilize the protein structure, making reactions even more difficult with these polar side chains. Several methods such as cross-linking (Liu and Li 2007), enzymatic modification (Kalapathy *et al*. 1995), chemical de-naturation (Kalapathy *et al*. 1995) and addition of additives (Chen *et al*. 2015b) have been employed to improve the performance of soy protein-based adhesives. Lei *et al*. (2014) discovered that cross-linking protein regardless of the cross-linker improves the water resistance. He reacted epoxy and melamine-formaldehyde with hydroxyl (–OH) and amine groups (–NH) of soy protein, respectively. Chen *et al*. (2015a) proposed that adding hydrophilic polyols into soy protein-based adhesives will form intermolecular hydrogen bond improving the wettability and wet adhesion strength by 30%. Although plywood was developed using other adhesives, such as animal protein, it gained commercial significance using soy flour with high pH (>12) conditions (Lambuth 1990). Much of the literature emphasizes the use of basic conditions with sodium salts for solubility and calcium salts for water resistance. This can certainly be true for monovalent cations, but divalent calcium cations should hold the proteins together better. Given that the soy adhesives were manufactured under basic conditions, as are phenol-formaldehyde (PF) adhesives, it occurred to some researchers to combine soy with PF to decrease the cost (Kalapathy *et al*. 1997) but was discovered that it was more viscous in combined adhesives compared with PF alone. To address this problem, the amount of soy is kept low or hydrolyzed to decrease its molecular weight.

COTTONSEED AND CANOLA

Cottonseed is mainly a low-value but abundant by-product. As with several plant proteins, it is currently on investigation as an adhesive for wood bonding. Cottonseed meal protein is fairly typical in composition for plant proteins, but is higher in arginine content. He *et al*. (2016) have looked at the performance of cottonseed protein isolate in wood adhesives, while Cheng *et al*. investigated its performance for producing wood composites (Cheng *et al*. 2013). Canola protein isolate, on the other hand, was used to bond cherrywood veneer at 190^{0}C to give good wet bond strength in two-ply wood bonds. The addition of sodium bisulfite decreased the dimercaptan bonds and viscosity but did not greatly decrease bond strength (Li *et al*. 2012). Given the amount of rapeseed and canola grown and that these are a ready source of protein, it is surprising that more research has not been done on them. Wang *et al*. (2014) grafted glycidyl methacrylate on canola protein via free radical polymerization to make an adhesive (Fig.3).

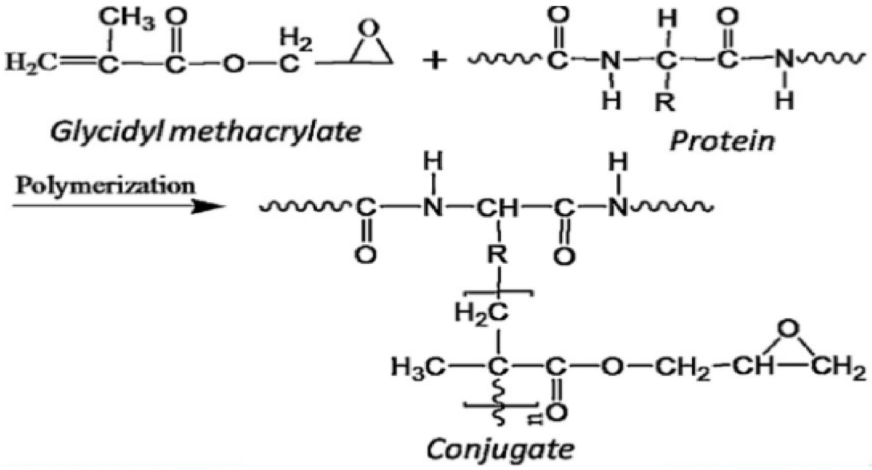

Fig. 3.
Modification of canola protein using glycidyl methacrylate (Fatemah et al. 2017).

WHEAT GLUTEN

With more than 100 different proteins in wheat, they are grouped into categories based on their structure and properties (MacRitche and Lafiandra 1997). Analysis of the proteins by size exclusion high-performance liquid chromatography shows a range of peaks from monomeric to polymeric, making separation of pure proteins difficult. Among the monomeric (single-chain) proteins are the gliadin and albumin groups. The gliadins are monomeric storage proteins with molecular weights of 30-80kpa while the monomeric albumins have weights of 20-30kpa, with many of them being enzymes. In comparison with soy, wheat protein is higher in glutamate plus glutamic acid and proline, and lower in aspartame plus aspartic acid and lysine which makes up the reactive amino acids. The ability of gluten to hold dough together indicates that these proteins may have some utility as an adhesive. It has a large impact on the physical properties of the dough providing wood panels with a better bond strength (Nordqvist *et al*. 2013).

STARCH

Starch is a natural polysaccharide derived from seeds, roots, and leaves of certain plants, such as corn, wheat, potato, rice etc. In the marketing industry, starch is applicable in adhesives, agrochemicals, cosmetics and toiletries, detergents, paper making additives, pharmaceuticals, paints, textiles, water purification and even biodegradable plastics due to its wide range of properties like gelatinization, pasting, retrogradation, absorption capacity, swelling ability, and solubility and mainly its low cost considering other alternatives (Sanderson 1981). Starches, when treated have a viscosity and rheology more appropriate for liquid adhesives, including alkali treatment, acid treatment, and oxidation (Baumann and Conner 2003). Adhesives based on starch and dextrin makes up the single principal category compared to other natural adhesives. They have been extensively used in the packaging industry and easy to apply, hot or cold, from water dispersions. On the other hand, this class of adhesives is known to have a reduced moisture resistance and mold growth. Starch has three hydroxyl groups on C2, C3, and C6 positions in each glucose unit with the ability to form hydrogen bonding. The high affinity of starch to water via hydrogen bonding leads to its poor water resistance and slow drying of starch-based adhesives. Due to these limitations, the direct use of starch in bio-adhesives is not feasible. To achieve this, chemical modifications like esterification, oxidation and cationization could be carried out on starch molecules (Fig. 4).

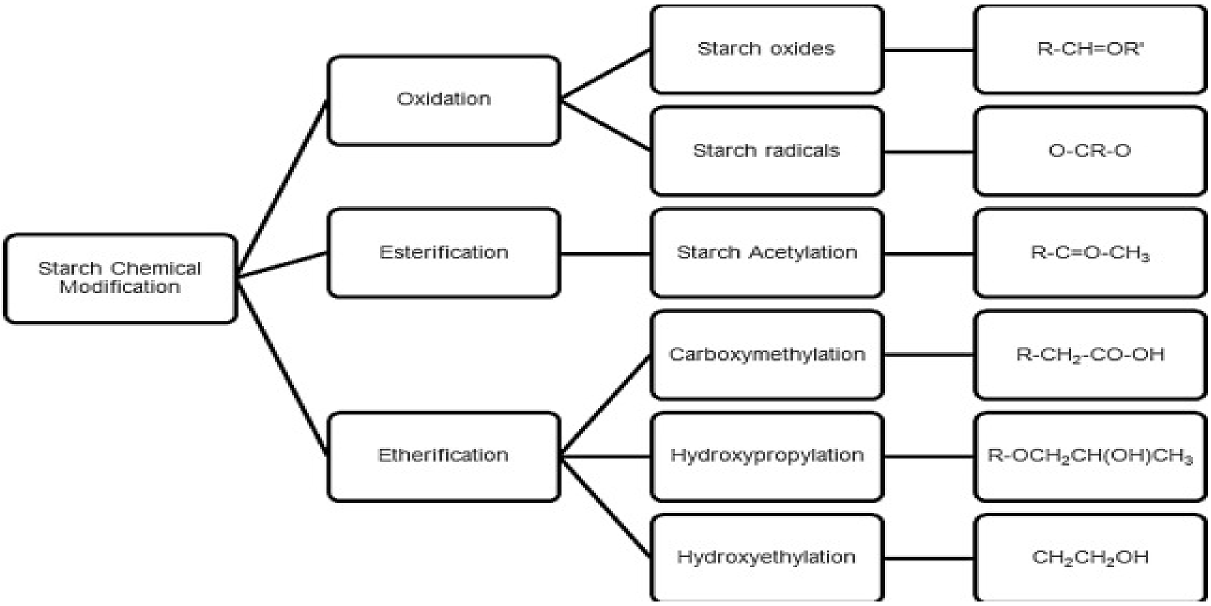

Fig. 4.
Chemical modifications of starch-based adhesive (Nonhlanhla et al. 2017).

Esterification is a typical chemical modification of starch. This is done by converting the hydroxyl groups to esters e.g reacting corn starch with maleic anhydride then cross-linking with polyisocyanate (Qiao 2016). Another modified starch-based adhesive was produced through a chemical cross-linking with polyvinyl alcohol (PVOH) in the presence of hexamethoxymethylmelamine (Imam *et al*. 2001). Wang *et al.* (2012) develop a novel bio-adhesive from grafting of vinyl acetate onto waxy cornstarch by reacting vinyl acetate with the hydroxyl group of the glucose to generate an ester linkage and realized stronger bond strength.

Starch is also chemically modifiable through an oxidation process capable of forming a better reactive binder. Oxidizing reagents such as hydrogen peroxide react with starch at a suitable temperature and pH (Kuakpetoon and Wang 2001) to give oxidized starch.

Cationic modification of starches is usually done with monomers like amino, ammonium, sulfonium, phosphonium and have been developed for ages (Rutenberg and Solanek 1984). The most widely used monomer, however, is probably 3- chloro-2-hydroxypropyltrimethylammonium chloride (CHPTMA) under the trade name of QUAT 188. Della Valle *et al.* (1991) used wheat starch in a twin-screw extruder as a reactor and got a 82% yield in a 24h reaction time. Carr (1994) got an even higher yield of 90% by reacting starch with Q188 in a ZSK 30 twin-screw extruder as reactor while using NaOH as the catalyst. Esan *et al.* (1996) proved that the extractability of potato starches extrudates depends on the penetration of the solvent through the extrudates particles and the diffusion of its soluble substances into the solvent. Their optimum results were achieved by suspending one part ground cationic potato starch extrudate in ten parts of a solvent consisting of 80% ethanol and 20% water (w/w).

FUTURE PROSPECTS OF BIOADHESIVES

Lignin based adhesives: The pulp mill is the main commercial source of lignin. Approximately 50 million tons of lignin is produced worldwide annually, of which 98% to 99% is incinerated to manufacture energy and steam in the pulp mills. Most of the lignin produced in pulp industries as byproduct is burned for energy power with only a small fraction of the lignin, derived mainly from the sulfite pulp mill recovered commercially in a bio-refinery concept. Although, energy power is necessary for industry, burning lignin in order to produce heat is not only harmful to the environment due to the release of certain gases, but also a waste of resource (Bruijnincx and Weckhuysen 2014; Simao *et al*. 2018).

Pulp and paper unavoidably play a vital role in every sector of Africa especially Nigeria; from the educational to political to social and even economic development of the country. In 1969, Nigerian’s first paper mill was built followed by the commissioning of 2 other paper mills in 1986 (Adegbehin and Omijeh 1989). This paper mills thrived for a while but began to fall due to the insufficient supplies of long fibred pulp which was mostly imported at the time. When the country’s population was about 48 -65million people, consumption was estimated to be between 14,000-27,000 tonnes per year (Enabor 1971). Director General of Raw Materials and Development Council (RMRDC), Prof. Hussain Doko, revealed that Nigerian loses over 800 million dollars yearly to pulp and paper importation while the printer’s association quoted 1 million dollars lost annually. These figures are sadly, more than the budget of N10.33 trillion in 2020 (Omiko *et al.* 2020).

Establishing the fact that the pulp mill is the main commercial source of lignin and the non-functionality of the paper mills in Africa, it is quite safe to say depending solely on lignin as an alternative for phenol-based adhesives will not thrive in the ever-moving economic market.

Tannin-based adhesive: Tannin, found in various parts of plants including bark, seeds, stems, roots and leaves, serves as the commercial source of tannin. In 2015, the global tannin market was estimated at 1,076.3 kilotons with the highest demand from the leather and winemaking industry (Fig. 5)(Grandview Research 2017). The technologies of interest remain the new ones either based on no addition of aldehydes, or on the use of hardeners which are non-emitting or non-toxic, primarily to decrease or completely get rid of formaldehyde emissions from wood adhesives. However, this raw material exhibits certain limitations like reactivity, high viscosity, a shorter shelf life and poor weather resistance. These limitations have also got research attention.

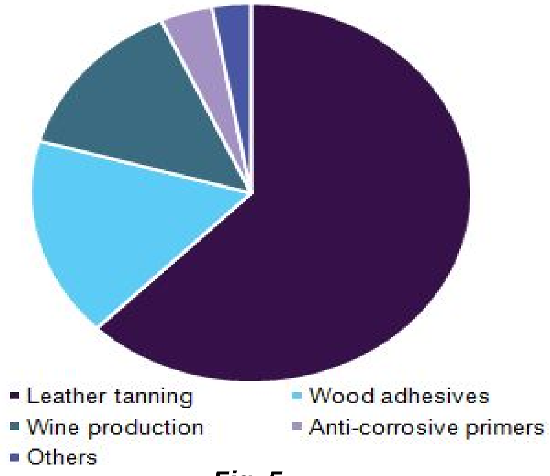

Fig. 5.
Global Tannin Market volume(%) by application (Grandview Research 2017).

Effective methods like acid/alkaline hydrolysis using acid anhydride/ NaOH (Sowunmi *et al*. 2000) OR destruction of heterocyclic either in the tannin molecules through sulfite or bisulfate treatment. To aid the reactivity of tannin, cross-linking tannin with isocyanate assist the participation of the B-ring, thereby increasing the bonding strength of wood products (Pizzi 1980). The pot life of tannin is increased by stabilizing formaldehyde through the formation of hemiacetals $CH_2[OH][OCH_3]$. When the adhesive is cured at a high temperature, the alcohol is given off alongside formaldehyde from the hemiacetal (Xiaojian and Guanben 2019).

The potential world supply of tannins is really massive, however, what is lacking, is a marked increase in the factories extracting them. Also, some new tannin extraction factories have surfaced in the last decade, but competition with other bio-sourced materials already industrially available for adhesives is intense at present (Xiaojian and Guanben 2019).

Protein-based adhesive: Plant protein adhesive is not the ancient protein and bone glues used in carpentry, or blood used as an additive in plywood glue-mixes. Soy adhesives as well as their modifications for wood adhesives after partial hydrolysis have been investigated and produced acceptable results. These products are not used commercially yet, but the use of them can be explored in the future. If decided to be explored in the economic market, its major drawback will be scarcity because so far, only soy adhesives has been intensely worked on except its used alongside other bio-based resins. Secondly, soy bean acts mainly as a food crop and may run at a risk of competition with the food industry. However, if plant protein is subsidized, they work as such and are very environmentally-friendly (Zhong *et al*. 2003).

Starch-based adhesive: The fine, smooth texture and non-poisonous nature of starch makes its use, a desirable choice particularly for domestic and structural material for adhesives (FAO 1983). Cassava starch is the major raw material for starchy adhesives; readily available in large quantities African countries. Nigeria being the largest producer of cassava in the world, cancels out the shortage in availability of major raw material though, the extraction of starch could only come from food crops. Ozemoya *et al*. (2007) proposed the use of the secondary product (cassava starch and milk) from the product of garri for the processing of starchy adhesives. These secondary products which are usually drained off mostly in the rural areas could be processed industrially rather than causing environmental pollution. Using borax as a chemical stabilizer/ viscosity enhancer for a longer pot life and comparing with a commercial adhesive; he concluded that cassava starch could be a good source of readily available adhesives saving the country from expensive importation. With this fact in place, starch-based adhesive can be a suitable go-to plan for adhesive production but must be based primarily on the secondary product of cassava in order to avoid competition between food production and the adhesive industry.

CONCLUSION AND RECOMMENDATION

Production and utilization of bioadhesives have gradually become acceptable in several countries due to the health benefits it poses to the atmosphere however, to widen the markets of bio-adhesives, it is necessary to chemically modify these biopolymers making them as effective as the synthetic wood adhesives and also to improve their bonding strength and water resistance. Industrial lignin promises to be most financial-rewarding owing to the fact that its secondary product is being recycled but is impossible since the industry that could produce these wastes is non-functioning; compared to protein which will not thrive in the ever-growing financial market because its primary sources are mainly used as food. Tannin is an available resource whose present constraint could be easily tackled and exploited compared to starch, which runs at a risk of competing with the supply of food but could be remedied since its primary product is a daily need and is not usually affected by season (Ozemoya *et al*. 2007). Tannin, if placed in the forefront, as a primary source for the adhesive market will thrive most favorably in the world's economic market, invariably creating an environmental-friendly atmosphere and amassing wealth for the economy.

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