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Characterisation of tannin resin blends for particle board applications

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Abstract

Tannins and cashew nut shell liquid (CNSL) are groups of natural resins that are receiving wide attention as substitutes to synthetic binders in the production of biocomposites. In this work, blends of hydrolyzed tannin, CNSL, and urea formaldehyde (UF) have been tested to determine their mechanical and physical properties for particle board applications. The blending of hydrolyzed tannin with UF resin has been found to reduce the formaldehyde emission levels significantly. A blend of hydrolyzed tannin and CNSL has been found to possess better dimensional stability. Tannin-blended resins cure faster, i.e. have shorter pot life, and result in composites with better water and moisture resistance when compared to UF. Thermal analysis by differential scanning calorimetry has shown that tannin blends exhibit better thermal stability and have a higher glass transition temperature than UF resin. Generally, it was found that particle boards made from coffee husks, and bonded using the tannin resin blend that include UF and CNSL, possessed superior properties to those made using UF alone. The mechanical and physical properties of coffee husk-particle boards produced using this new resin blend are presented and discussed.

Keywords: Tannin; Cashew nut shell liquid; Urea formaldehyde; Phenol formaldehyde; Coffee husks

1. Introduction

Developing countries, especially in Africa face an increasing demand for building materials due to fast growing urban populations and subsequent need for better shelters. The rising cost of wood and timber products, and the concern for conservation of natural forests, is creating a dilemma for the majority in the population. Moves to utilize agricultural wastes for making particle boards that would replace wood products, are receiving notable attention. However, the cost of these boards remain high due to the high cost of the resin or binding glues, that have to be imported from developed countries. As such, large quantities of agricultural wastes such as rice husks, coffee husks, etc., which have great potential for producing particle boards remain underutilized, and the bid to reduce timber and wood consumption, especially for construction, requires new innovations in this direction.

For some time now, researchers have been working on natural resins, derived from local plants, so as to replace synthetic resins in board manufacture. One such potential resin is cashew nut shell liquid (CNSL), which can be condensation polymerized using formaldehyde to produce a temperature resistant, fast curing resin [1]. Recently, there have been growing interest on tannin-based resins [2]. This is because the availability of tannins is more widespread, and they are cheaper than CNSL. Tannins are naturally occurring phenolic compounds, which have been a subject of extensive research leading to development of a wide range of industrial applications. Tannins have traditionally been used for converting animal hides to leather, 'tanning', due to their ability to interact and precipitate proteins found in animal skin. The term 'tannin' comes from the ancient Celtic word for oak, which still remains a popular source for tannins used in converting animal skin into leather (tanning). Today, in addition to oak (*Quercus* sp.), there are many other plant species that are being used to produce commercial tannin. These include plants such as *Acacia* sp.

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(wattle), *Eucalyptus* sp., *Mirtus* sp. (myrtle), *Acer* sp. (maple), *Betula* sp. (birch), *Salix Caprea* (willow), *Pinus* sp. (pine), etc.

Chemically, tannins are made up of complex phenolic compounds of high molecular weight, ranging from 500 to 20,000. There are two main categories of tannins: (a) hydrolysable tannins (HT) and (b) condensed tannins (CT). Generally, tannins are soluble in water, with exception of some very high molecular weight compounds.

HT are readily soluble in water, making it possible for them to react with other substances to yield a wide range of water-soluble chemicals such as gallic acid (-gallotannins) or ellagic acid (-ellagitannins) [2]. Fig. 1 shows the chemical structures of simple phenols obtained in HT.

CT (Proanthocyanidis) posses a condensed chemical nature, even though they are still capable of undergoing further condensation reactions. They have complex chemical structures made of flavonoid units, with variations on the sites at which the flavan bonds are created. In general, CT possess rigid carbon–carbon bonds that cannot be broken easily by hydrolysis. Fig. 2 shows the chemical structure of wattle tannin (*Acacia mearnsii*) flavonoids according to Pizzi [2].

Tannins have found a wide range of other industrial applications, in addition to their widespread use in tanneries. These include use in the manufacture of inks, for dyeing of textiles, and as a corrosion inhibitor. In Chile and Brazil, a variety of products have been developed from tannin [3]:

- Anti-corrosive primer, sold under brand name-Nox Primer for treatment of rusted steel surfaces prior to painting.

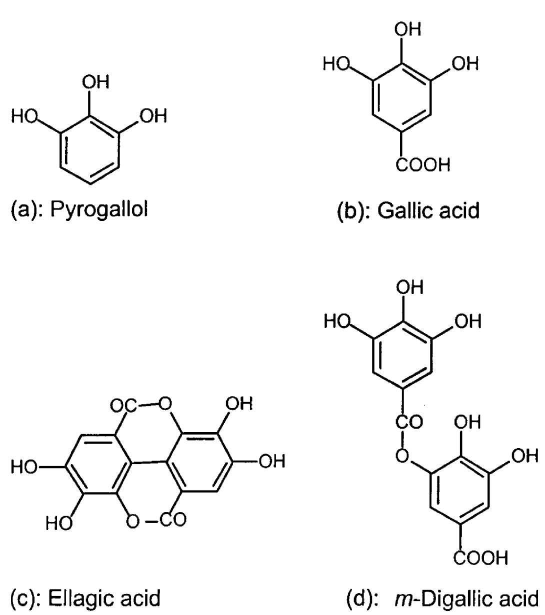

Fig. 1. The chemical structures of some phenols synthesized from HT.

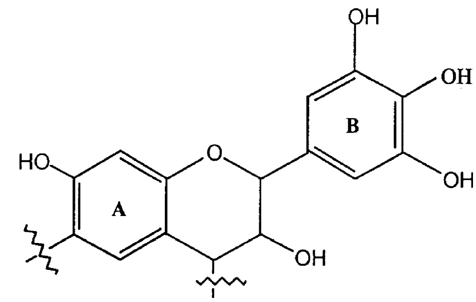

Fig. 2. The chemical structure of wattle tannin (*Acacia mearnsii*) flavonoids.

- Rust converter to transform oxidized steel into a smooth sealed surface.
- Wood adhesives for bonding wood chips in producing particle board building materials.
- Rust inhibitor where tannin is added to mineral oil to protect cold rolled steel from corrosion during transportation or storage.

In the USA, a commercial product for corrosion protection is now available from HALOX, a division of Hammond Group Inc. [4].

Following the oil crisis of the 1970s, interest in plant based polymeric resins increased, and significant research developments on tannin-based resins were achieved in South America, Australia and South Africa [2,3,7]. As a result, a wide range of tannin-based adhesives constituting a variety of combinations with synthetic resins, have been commercially developed, to meet specific needs. Vazquez et al. [5] developed a tannin resin from *Pinus pinaster* bark, and found that the resin was superior to commercial phenol formaldehyde (PF) resins as regards to moisture tolerance and bond strength. It has also been found [6] that the production of particle and ply-boards using tannin-based resin required less press time, leading to higher productivity. There has been growing concern over formaldehyde emissions in urea formaldehyde (UF) and PF bonded particle board and ply-boards. It is now known that adhesives produced from tannin, if properly cured, give nearly zero formaldehyde emission.

Much of the work on tannin-based adhesives, has been focused on developing resins for exterior applications as well as lowering formaldehyde emission levels. Hemingway [7] has reported that the properties of tannin-based adhesives combined with di-isocyanates, such as methyl di-isocyanate (MDI) are superior to those formed by blends of tannin, melamine and formaldehyde.

In Tanzania, the demand for wood adhesives, mostly UF, is estimated at just about 1000 tonnes per year [6]. However, with the restoration of a market economy, there are several new ply-board and particle board factories in the pipeline. The challenges facing the emerging manufacturers in most developing countries include reducing the fraction of imports in the locally made products, while increasing the local component. This paper, presents an attempt by researchers in Tanzania to develop a new blend of resin based on tannin and CNSL for the ply-board and particle board industries. The resins have been tested using coffee-husks as an alternative to wood particles, an attempt to reduce the deforestation by using agriculture wastes. This work will in future be extended to other types of agricultures wastes, such as bagasse, coir, rice husks, etc.

2. Experimental methods

2.1. Resin preparation

(i) Tannin resin blend:

Dry tannin powder from barks of wattle trees was supplied by Tanganyika Wattle Company in Njombe, Tanzania. For its hydrolysis, accordingly, 100 g of 44% tannin in water dispersion, 7.6 g of 33% sodium hydroxide and 0.13 g castor oil were stirred for 3 h at about 90 °C. The solution was then cooled to 70 °C and 4.0 g of 99.5% acetic acid was added, after which the mixture was cooled to 25 °C. This was to stop any cross-linking reaction in the resin.

For every 1800 g of hydrolyzed tannin, 160 g of Urea were added to assist break hydrogen bonds, and 320 g of formaldehyde (40%) were added for condensation reaction. In addition, 160 g of CNSL were added as an emulsifier. The mixture was thoroughly stirred, and its pH adjusted to 5 by adding small amounts of acetic acid and sodium hydroxide. The latter also acted as a catalyst to the condensation polymerization reaction.

(ii) UF:

Urea formaldehyde powder was weighed and dissolved in water to give a resin with 35% solid contents. The viscosity of the adhesive was between 180 and 350 cP.

(iii) PF:

The PF resin was supplied in liquid form, and before use, a 3% by weight hardener was added and the mixture thoroughly stirred.

2.2. Particle board production

Tanzania produces about 50,000 tonnes of coffee for export annually. In the processing of the coffee, significant amount of waste, estimated at about 20,000 tonnes, in the form of coffee husks is generated. Pre-determined amounts of *Arabica* coffee husks from the Moshi Coffee Curing Mill, were blended in the resin in a rotary blender. The resin was either UF or hydrolyzed tannin blend. The mix was hand laid in a mould, placed between hot platens of an electrically heated 50-ton press, set at 180 °C, then pressed for 5 min.

2.3. Mechanical tests

Flexural tests were carried out in accordance with ASTM standard D1037-93 part A. A Lloyd universal testing machine LRX5K was used. Five samples of 315 mm length, 75 mm width, and an average thickness of 11.76 mm were used in three point bend tests. The three point bending tests were conducted at a cross-head speed of 6 mm/min and the loading span was 250 mm. The flexural strength and the flexural modulus of the particle boards were evaluated.

2.4. Water absorption and thickness swelling tests

The water absorption and thickness swelling of the particle boards were determined in accordance with ASTM D1037-93 on test samples measuring 76 mm × 76 mm. The samples were fully immersed in distilled water at 25 °C for 1 h.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was done using a TGA2950 Du Pont instrument. Nitrogen gas was set to run at 60 ml/min to provide a controlled combustion environment. TGA was carried out in the temperature range of 40–450 °C. The curves obtained were analyzed using a TGA v5.1A Du Pont 2200 programme. Different states of raw tannin were analyzed, i.e. powder, solid and hydrolyzed. Also three resins were tested i.e. UF, PF and hydrolyzed tannin.

2.6. Differential scanning calorimetry

A Du Pont instrument was again used for this test, and was run simultaneously with the TGA test described above. Samples weighing between 5 and 22 mg were used. Nitrogen gas was set to run at 60 ml/min, and the temperature limit was set at 200 °C/min. The cooling air supply line value was kept open and the pressure adjusted to 689.5 kPa. The absolute and differential enthalpies were recorded continuously, and analyzed using General V4.1C Du Pont 2200 programme.

3. Results

The thermogravimetric behaviour of the various forms of tannin was analyzed, and the results are given in Fig. 3. It is observed that the behaviour of solid and

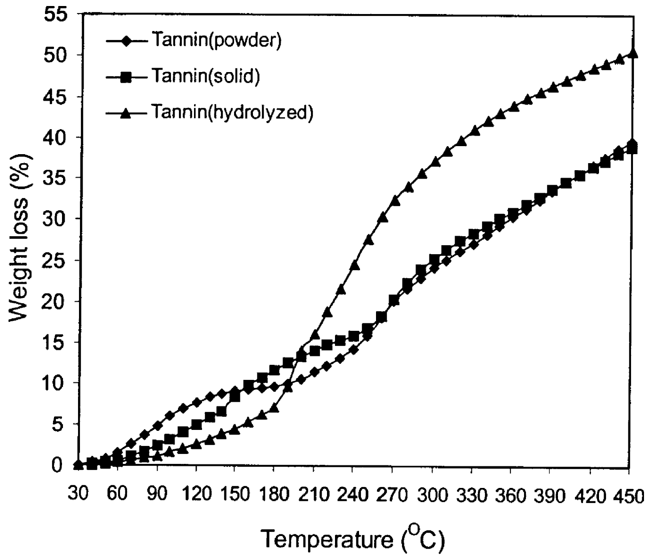

Fig. 3. TGA analysis of different forms of tannin.

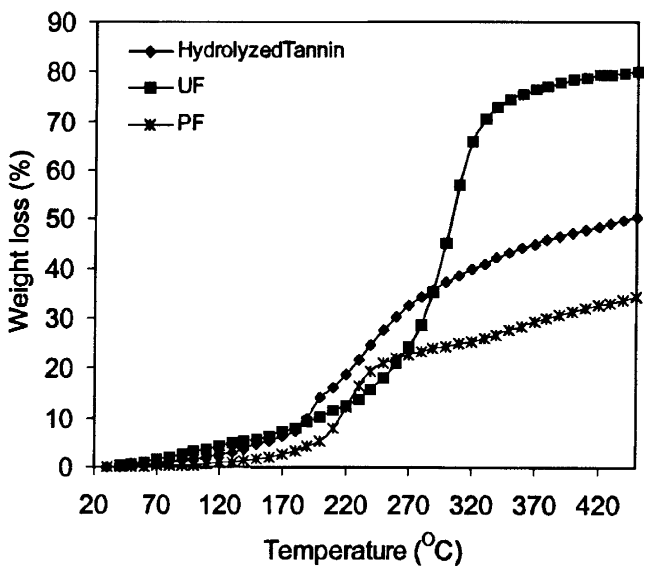

Fig. 4. TGA analysis of hydrolyzed tannin, UF and PF.

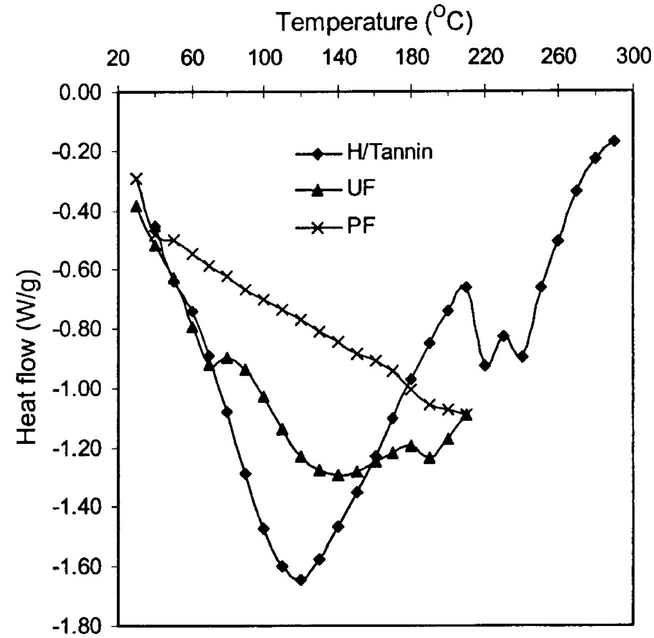

Fig. 5. DSC analysis of PF, UF and hydrolyzed tannin resins.

spray dried forms of tannin are identical. The results show that tannin, in any form had lost up to 10% of its weight by the time it reached 200 °C. Fig. 4 shows the results of thermogravimetric analysis of hydrolyzed tannin blend (HT), UF, and PF. Beyond 270 °C, UF showed the least thermal stability, while HT was intermediate.

The differential scanning calorimetry (DSC) monographs for the three resins are shown in Fig. 5. In all cases, the curves are endothermic. The first point of instability on the curve has been taken as the glass transition temperature T_g. From Fig. 5, the T_g for PF, UF and Tannin are estimated as 40, 40 and 50 °C, respectively. This estimation is debatable because the points of instability are not very pronounced. The more pronounced transformations, represented by the turning points on the DSC curves in both Figs. 4 and 5, have more to do with the chemical breakdown or evolution of moisture and formaldehyde in the resins.

The results from flexural tests are summarized in Table 1. From these results, it is noted that hydrolyzed tannin gives particle boards with slightly higher flexural strength and modulus compared to UF. The water resistance and thickness swelling characteristics of hydrolyzed tannin bonded particle boards are also better.

Table 1
Some mechanical and physical properties of coffee husk particle boards

Particle board composition	Density of boards (kg m^{-3})	Resin weight fraction (%)	Flexural modulus (MPa)	Flexural strength (MPa)	Water absorption in 1 h (%)	Thickness swelling in 1 h (%)
Coffee husk—UF	1032	11.0	1089	5.15	24.3	20.2
Coffee husk—hydrolyzed tannin	1035	14.0	1216	6.53	8.4	5.9

4. Discussion

Currently, UF is the commercial resin popularly used for making particle boards and plywood boards in Tanzania. Under tropical conditions, the boards are sometimes subjected to extremely high temperatures and moisture contents. They also must meet their mechanical strength requirements.

Although the flexural strengths of coffee-husk particle boards made using UF and tannin resins are nearly the same as shown in Table 1, the flexural modulus of the later is slightly superior. Since the amount of resin retained in the particle boards was not same for these two biocomposites, it may not be fair to give credit to the tannin resin for the superior mechanical properties of the tannin board.

It has been verified [8] that tannin resin bonded coffee husk boards have better moisture resistance than those made using UF. According to Fig. 3, hydrolyzed tannin exhibits better thermal stability than solid and powder tannins at temperatures below 180 °C. At higher temperatures, powder and solid tannins have similar thermal characteristics. So far we cannot offer any explanation to this observation.

From DSC studies, both resins appear to exhibit fairly low glass transition temperatures. However, since the glass transition temperature is a variable parameter that strongly depends on degree of cure and cross-linking, it may not be the best decisive criteria for comparison. The heat flow curves shown in Fig. 5 show clearly that hydrolysable tannin had the lowest endothermic point at 120 °C. This is likely the temperature at which residual formaldehyde and water vapour are driven off from the resin. Such a reaction appears to occur in UF at a little higher temperature. Hence, if similar curing conditions were applied to both resins, there would be lower residual formaldehyde content in hydrolyzed tannin resin than in UF. Similar findings have been confirmed by Calve et al. [6]. Further heating of the resin has been seen to result into the cleavage of the methylene linkages in the cured resin's polymer network. This phenomenon appears to occur more rapidly in UF than in tannin (see Fig. 4). In practice, it has been noted that hydrolyzed tannin resin blends cure better and faster than their UF and PF counterparts. The mechanical properties of hydrolyzed tannin bonded particle boards are slightly superior to UF bonded particle boards. They also have better resistance to thickness swelling and water absorption. Vasquez et al. [5] have made similar observations when they compared tannin-based resins with PF.

There are other researchers, who have observed the performance of resins blended from UF, PF and tannin extracts. Calve et al. [6] and Coppens et al. [9], were able to produce reactive adhesives that exhibited attractive exterior grade properties from tannin-UF and tannin-formaldehyde resin blend. These hybrid resins were also found to possess lower formaldehyde emissions compared to UF. Some of the challenges that have to be overcome to make tannin resins more user friendlier, include dealing with tannins' high viscosity and short pot life. Previous work that was done by Pizzi [10] shows that the viscosity of tannin can be significantly reduced by heating it in the presence of sodium hydroxide.

There is also need to extend this work to include other types of biocomposites. Current focus is to investigate the performance of biocomposites made from agricultural wastes such as rice husks, peanut shells, coir, bagasse, maize cobs, and sisal waste. Successful development of such composites would reduce the need for wood-based particle boards. This research is however hampered by lack of research facilities. Investigations on bonding mechanisms and related interfacial phenomena may be possibly done using dynamic mechanical thermal analysis techniques and SEM fractography. These facilities are not at the disposal of researchers in Tanzania. Since these biocomposites are being proposed for application in tropical countries, there is also need to assess their resistance to biodegradation and attack in the presence of micro-organisms such as fungi and insects such as termites.

5. Summary and conclusions

In this paper, the performance of tannin-based resin blend has been evaluated in comparison with UF on coffee husk particle boards. Results show that the tannin-based resin gives particle boards with improved resistance to water and moisture resistance, while exhibiting slightly superior thermal and mechanical properties.

It can be concluded therefore that tannin-based resin blends have great potential to replace UF resin in particle board applications, such as those employing agricultural wastes like coffee husks. However, it is the economics and aesthetics that will dictate the choice between locally produced tannin resin glue and imported UF resin, for the particle board industry. UF resins tend to result into clear boards while tannin bonded boards have the characteristic brownish colour of phenolics.

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