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Fillers in Wood Adhesives

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Abstract

The introduction of a second component to polymers has been presented; this component is often used to modify the characteristics of the products and to acquire new polymer materials with improved properties. Composite materials have a pivotal role in industries that are now considered the most progressive worldwide. At present, synthetic adhesives based on formaldehyde such as phenol-formaldehyde (PF), urea formaldehyde (UF), and melamine formaldehyde (MF) are predominantly used for wood composite production, and these adhesives are commonly used in the wood panel industry. These adhesives have some advantages and disadvantages. The use of PF adhesives is as important as UF adhesives in the wood panel industry. However, their application is still limited because of its brittleness, brown color, high curing temperature, long curing time, and toxicity due to liberation of phenol and formaldehyde. A variety of methods have been used to improve the performance of UF and PF adhesives as well as to expand their use. These methods are widely used in the industry; they include the simple addition of fillers. Moreover, the addition of fillers could reduce shrinkage and alleviate the stress on the glue line, which improves the hardness and durability.

Keywords: bonding strength, PF, wheat flour, tannin adhesive, organoclay

1. Introduction

The introduction of a second component to polymers has been presented; this component is often used to modify the characteristics of the products and to acquire new polymer materials with improved properties. Composite materials have a pivotal role in industries that are now considered the most progressive worldwide. Generally, the term "composite" is given to materials made of more than one component. Polymer composites are a mixture of polymers with inorganic or organic additives that have certain geometric forms (spheres, flakes, fibers, and particulates). A wide range of polymer characteristics can be improved by composite technologies, such as their mechanical, thermal, barrier, flame retardant, magnetic, optical, and electrical properties and durability, chemical stability, corrosion resistance, and biodegradability [1–4].

Wood adhesives now represent a vital aspect of the wood-based panel industry, and synthetic condensation resins have become widely used. The synthetic resins used can be classified into four varieties, and all these adhesives are based on formaldehyde. These resins are urea formaldehyde (UF), phenol-formaldehyde (PF), resorcinol formaldehyde (RF), and melamine formaldehyde (MF). The PF resin is used in wood adhesives, thermal insulation materials, coatings, molding compounds, and other applications. The high stability of the C-C linkages between the aromatic ring and methylene bridge and the resistance to hydrolysis make it a favorite resin for
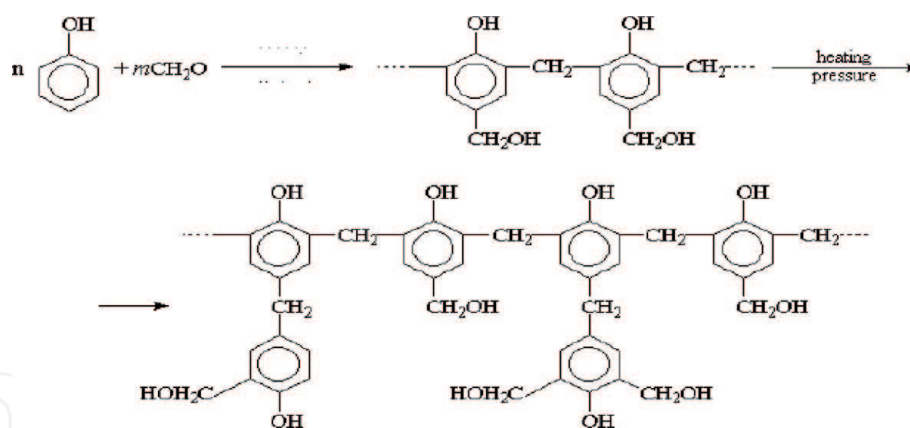
Figure 1.
Synthesis of phenol-formaldehyde resins by polycondensation of phenols, in excess of formaldehyde developed by Baekeland.

glue lines as well as boards, such as weatherproof plywood, oriented strand boards (OSB), medium-density fiber boards (MDF), or particleboards for use under exterior weather conditions. The global demand for PF resin (resol, novolac, and others) continues to increase; recent reports expect this demand to grow at an annual rate of 5.7% from 2014 to 2019 by $19.31 billion. This increased demand is associated with the increased construction in developing regions [5]. The resol phenolic resin accounted for more than 75% of the global market in 2013. This market is expected to grow at a healthy rate of 4.1% until 2019. The PF resin is obtained via condensation reactions between phenol and formaldehyde in the presence of an acid or a base to produce novolac or resol, respectively. Resol-type PF resins (**Figure 1**) [6] have been widely used for decades to manufacture wood adhesives due to their high performance in terms of the mechanical and thermal properties as well as its water resistance.

The concern regarding crude oil supplies and the toxicity of the raw materials extracted from the fossil fuels has grown as they can cause climate change. According to findings conducted by the National Cancer Institute (NCI) on a group of workers who were exposed continuously to formaldehyde, a high possibility of cancer was diagnosed, prompting the World Health Organization to the reclassification of formaldehyde to group I. Wood-based panel industry relies heavily on this material, making it difficult to impose an outright ban on the use of formaldehyde.

Recently, the development of natural or green-based wood adhesives as successful substitutes for synthetic resins has become of interest because of the unwarranted increase in the prices of fossil fuels as well as environmental and health concerns. Lignin and tannin are materials rich in phenolic compounds; both were found to be successful alternatives for phenol in the manufacturing of bio-based PF resins.

2. Fillers

Fillers are substances that can be added to various polymer systems to reduce the cost or improve their properties [7, 8]. This material can be added as a solid, liquid, or gas. For example, the use of a minimal percentage of clay loading can lead to significant improvements in the mechanical and thermal properties [7, 8]. In general, the fillers used to modify the properties of polymers can be classified into two categories: inert fillers and active fillers. Inert fillers come from inorganic mineral powders, such as kaolin, diammonium phosphate, porcelain clay (which is frequently used), sodium silicate, and magnesium oxide. These fillers are used to reduce cost. These mostly hydrophilic materials can be dispersed in adhesives. Active fillers are organic compounds, which swell when dissolved in a solution.

These fillers include the cellulose-type fillers (wood powder, bark powder, etc.), protein-type fillers (soy protein, blood powder, etc.), and starch-type fillers (wheat flour, etc.). These materials have the ability to react with resins.

Clays are one group of the additives that have been widely used in the preparation of polymeric composite materials. Recently, increasing attention has been given to the development of polymer/clay nanocomposites because of their dramatically improved properties as compared with conventional fillers after the addition of very low portions of the filler [9]. Clay minerals are used in soil science and sedimentology to refer to particles formed by the combination of tetrahedral and octahedral aluminosilicate ($[SiO_4]^{4-}$ and $[AlO_4]^{5-}$) layers that are 1 nm thick with 200–300 nm lateral dimensions, as shown in **Figure 2** [10]. Clay minerals are important materials that are mainly hydrated aluminosilicates with neutral or negative charges [11]. The internal and external cations can be changed by inorganic or organic cations [10, 12].

The hydrophilic nature of clays makes them poorly suited for mixing with most hydrophobic polymer materials [13]. In addition, the poor physical interaction between the organic components in polymeric materials and the inorganic components in clay leads to their separation and the formation of discrete phases. Therefore their mixtures have poor properties, and this incompatibility prevents the dispersion of clay layers within polymer matrix, thereby leading to weak interfacial interactions [14–16]. Moreover, electrostatic forces tightly link the clay platelets with each other. Only some hydrophilic polymers are miscible with layers of clay; these materials are used in the preparation of polymer-clay composites such as poly(vinyl alcohol) and poly(ethylene oxide) [8].

For these reasons, clay requires pretreatment before it is used as filler in polymer composites. These piles of clay platelets have dimensions much larger than 1 nm. Therefore, untreated clay would be ineffective during use because most of the clay would be trapped inside and unable to react with the polymer matrix. Generally, the intercalation of clay with different organic species is the basic condition for compatible composite materials to ensure the interaction between the clay surfaces and the polymeric components. The intercalation or surface modifications decrease the surface energy of clay layers and match their surface polarity with polymer polarity. The low surface energy of organoclays is more compatible with organic polymers and can intercalate with the interlayer space under specific experimental conditions.
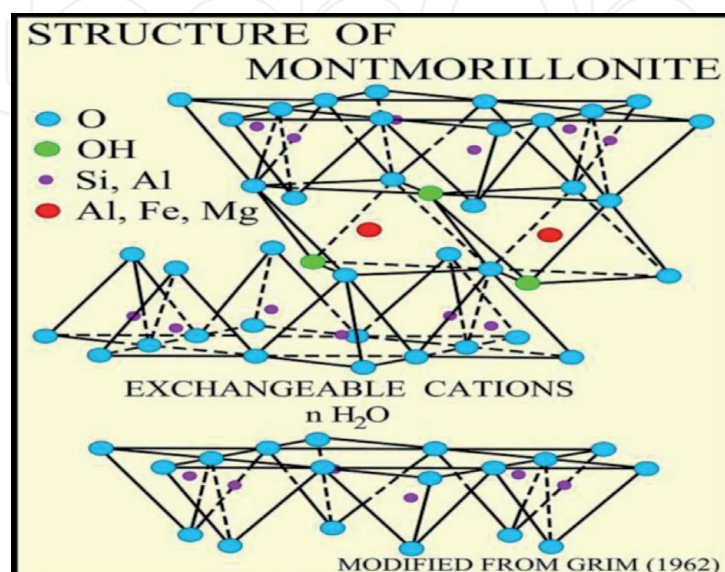

Figure 2.
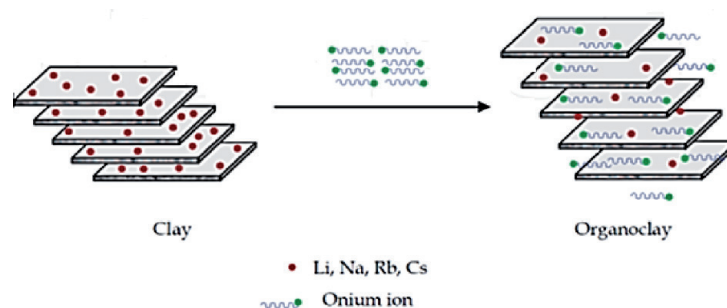*Montmorillonite structure.*

Figure 3.
Scheme of the modification of clay layers by organic onium cations.

This spacing of organoclays is affected by a variety of factors, including the chemical structure of the surfactant, the degree of cation exchange, and the silicate layer thickness [17]. Organically modified clays have been extensively studied in various practical applications in the field of organic-inorganic hybrids, composites, and nanoscale composites [15]. The surface modification of clay layers can be performed through an ion exchange process via the replacement of cations, such as sodium and calcium, in the interlayer space by ammonium or phosphonium surfactants, which usually include benzyl groups and short aliphatic chains [18]. In addition to modifying the surface and increasing the hydrophobicity of clay layers, the introduction of alkylphosphonium ($R_4P^+X^-$) and alkylammonium ($R_4N^+X^-$) cations into the clay layers increases the distances and spacing of the clay layers, which facilitates the intercalation of the polymer chain during the preparation of nanocomposites [19]. Moreover, the cations ($R_4N^+X^-$) and ($R_4P^+X^-$) can provide the necessary functional groups that have the ability to interact with the polymer chains or to initiate polymerization processes, thereby increasing the interfacial interactions, as shown in **Figure 3**.

3. Modification of wood adhesives using fillers

At present, synthetic adhesives based on formaldehyde such as PF, UF, and MF are predominantly used for wood composite production. These adhesives have some advantages and disadvantages. For example, UF adhesives have advantages such as the lack of color in the cured polymer, low price, good mechanical properties, and so on. Consequently, these adhesives are commonly used in the wood panel industry. However, UF resin can only be used as an interior adhesive because of its poor water resistance. The use of PF adhesives is as important as UF adhesives in the wood panel industry. The good water resistance of PF adhesives allows them to be used under more stringent conditions than UF adhesives; thus, PF adhesives can be classified as exterior adhesives. However, their application is still limited because of its brittleness, brown color, high curing temperature, long curing time, and toxicity due to liberation of phenol and formaldehyde [20]. A variety of methods have been used to improve the performance of UF and PF adhesives as well as to expand their use. These methods are widely used in the industry; they include the simple addition of fillers. A variety of resin properties can significantly improve their performance as wood adhesives by the addition of fillers, which are most important for their lower cost. The mechanical performance of the resin is also improved in most cases. Moreover, the addition of fillers could reduce shrinkage and alleviate the stress on the glue line, which improves the hardness and durability. The flow of the adhesive and its smooth flow on the wood surface will be improved because of the penetration of water into the glue in the presence of a filler. The moderate permeability of the glue between the wood components has good mechanical effects by

physically interlocking the wood surface with the curing agents; thus, the bonding strength between the wood products is improved.

Wheat flour is an activated filler, which is most commonly used in factories for the production of UF resins. The addition of approximately 10 to 20% of the wheat flour to the total solid resin can increase the weather resistance of the resin because this filler can reduce the shrinkage of the glue line [21]. According to Ma [22], the use of oxidized starch as a filler with UF resin at proportions of 5–10% will decrease the free formaldehyde emission from 3–7% to 0.2–0.5%. The hydroxyl group reacts with starch molecule chains and liberates formaldehyde to form acetals, thereby reducing the free formaldehyde emission. Compared with wheat flour, oxidized starch as a filler can further increase the bonding strength and water resistance of UF resins [23].

Mosiewicki et al. [24] studied the mechanical and thermal behavior of a composite formulated from a natural quebracho tannin adhesive with pine wood flour as well as the effect of moisture on its adhesive properties. The results showed that the mechanical and thermal properties of composite materials of wood flour/tannin adhesives have sufficient values for use in some industrial applications in terms of its higher stiffness, which is an important requirement. However, this composite material can be used in the dried state alone and must be avoided in humid atmospheres.

Kargarfard and Jahan-Latibari [25] used recycled polyethylene with UF to reduce swelling fish and water absorption during particleboard production, thereby improving its performance in terms of weather resistance. In this work, different amounts of recycled polyethylene (5%, 10%, and 15%) were mixed with the lowest amount of UF resin (4%). Their results revealed that 5% of recycled polyethylene in the surface layer could improve the weather resistance of particleboards. The modulus of rupture (MOR) and modulus of elasticity (MOE) properties were marginally increased when the percentage of recycled polyethylene was increased to 5% in the surface layer. However, when 15% recycled polyethylene was added to the surface layer, the increased MOR was almost doubled, and the MOE was increased by approximately 50% as compared with the control boards.

Du et al. [26] used the synergistic effect of mineral filler (MgO and SiO_2) with UF adhesives for the production of plywood. Plywood has better performance with mineral fillers as compared with the absence of filler or with wheat flour fillers. These results can be attributed to two reasons. (i) The (MgO and SiO_2) filler prevents the glue from excessive permeation into the wood substrate and reduces the internal stress caused by the shrinkage. (ii) The oxygen from silicate and magnesium may be linked with the hydroxymethyl groups of the UF adhesive, thereby improving the durability and weather resistance of the resins.

Another newly developed type of mineral fillers are the nanomaterials, which differ physically and chemically from the normal fillers in terms of their thermal, light, radiation, and mechanical characteristics, among others [27]. Polymer nanocomposites have attracted considerable attention from researchers, especially in research related to polymer-layered silicate (PLS). This interest is attributed to the fact that the addition of small amounts of these materials often significantly improves the mechanical and thermal properties of polymers.

Some researchers have tried to use the nanomaterial fillers in wood adhesive systems, such as nano-SiO_2, nano-$CaCO_3$, and nano-montmorillonite (MMT) [28–31]. Their results showed that the adhesive bonding strength, gel time, and free formaldehyde emission were affected by the addition of nanomaterials. In most cases, the emission of free formaldehydes was significantly reduced.

The exfoliated nano-MMT was used by Zhang et al. [32] as a nanomineral filler with polymeric MDI to modify degraded soybean protein (DSP) and improve its water resistance and technical applicability. The DSP adhesives with MDI as a cross-linking agent showed improved water resistance and bond strength, but their shelf

life is very short. After the modification of MDI-modified DSP by nano-MMT, the produced adhesive had a much longer shelf life but slightly lower bonding strength.

Various PLSs have been successfully used with various types of resins, such as epoxy [33], polyacrylic ester, polyurethane [34], and even PF [35]. However, research on the feasibility and the mechanism of wood adhesive modification with MMT is rather limited.

4. Preparation of water-resistant wood adhesives

Glyoxalated lignin-tannin (GLT) adhesives are good candidates for the replacement of formaldehyde-based adhesives because of health and environmental concerns. Although glyoxalated lignin-tannin resins are low cost and have environment-friendly properties, these types of adhesives do not meet the fundamental required bonding strength and water resistance [36]. In addition, poor water-resistant property has limited their application. Ease of hydrolysis makes this adhesive useful for interior applications only. Consequently, appropriate measure must be taken to overcome the problem and to improve the water resistance of adhesives. In this work, we tried to develop and improve the properties of glyoxalated lignin-tannin resin to meet the fundamental requirement of bonding strength and water resistance.

4.1 Preparation of green wood adhesives using modified tannin and hyperbranched poly(amine-ester)

Due to the unique structure, chemical and physical characteristics, and various industrial applications, hyperbranched polymers (HBPs) have become the focus of considerable interest to chemists, biochemists, biologists, and biomedical experts [37]. This is due to high solubility, reduction of melt and solution viscosity, and abundance of functionalities as a result of the large number of reactive terminal groups within a molecule, nearly spherical molecular shape and the absence of chain entanglement [38]. These characteristics make dendrimers and hyperbranched polymers (HBPs) applicable as drug delivery agents, catalysis, Mitchell mimics, and nanoscale building blocks to artificial cells and coatings [39]. Both dendrimers and hyperbranched polymers are three dimensional and highly branched macromolecules. In this work, oligomeric precursors of poly(amine-ester) were synthesized, and then they were used to modify the tannin to improve the water resistance and mechanical properties of glyoxalated lignin-tannin (GLT)-based wood adhesives. **Figure 4** shows the synthesis of hyperbranched poly(amine-ester).

Previous studies by Lei [21] indicated the use of GL/PF/pMDI formulation with calcium lignosulfonate, and it turned out that the molecular mass decreased significantly during thermal treatment at 170°C for 90 min and pH of 12.7. This has been done to reduce the molecular mass of the lignin. Some linkages of lignin are broken by thermal treatment, and positions that are more reactive will be obtained. This indicates that the thermal treatment will make the material more suitable for such reactions. In this work, the two types of low molecular mass lignins extracted from oil palm empty fruit bunch were used. These are (i) kraft lignin and (ii) organosolv lignin. The adhesive resin properties are shown in **Table 1**.

The quality of wood and how the resin penetrates through the wood surface are important factors that affect the assessment of the adhesive joint in plywood. The bonding strength formed by TGKL and MTGK adhesives was studied via tensile strength test on wood substrates. For a comparative study, the same test was implemented for synthetic commercial phenol-formaldehyde resin. The data is displayed in **Table 2**.
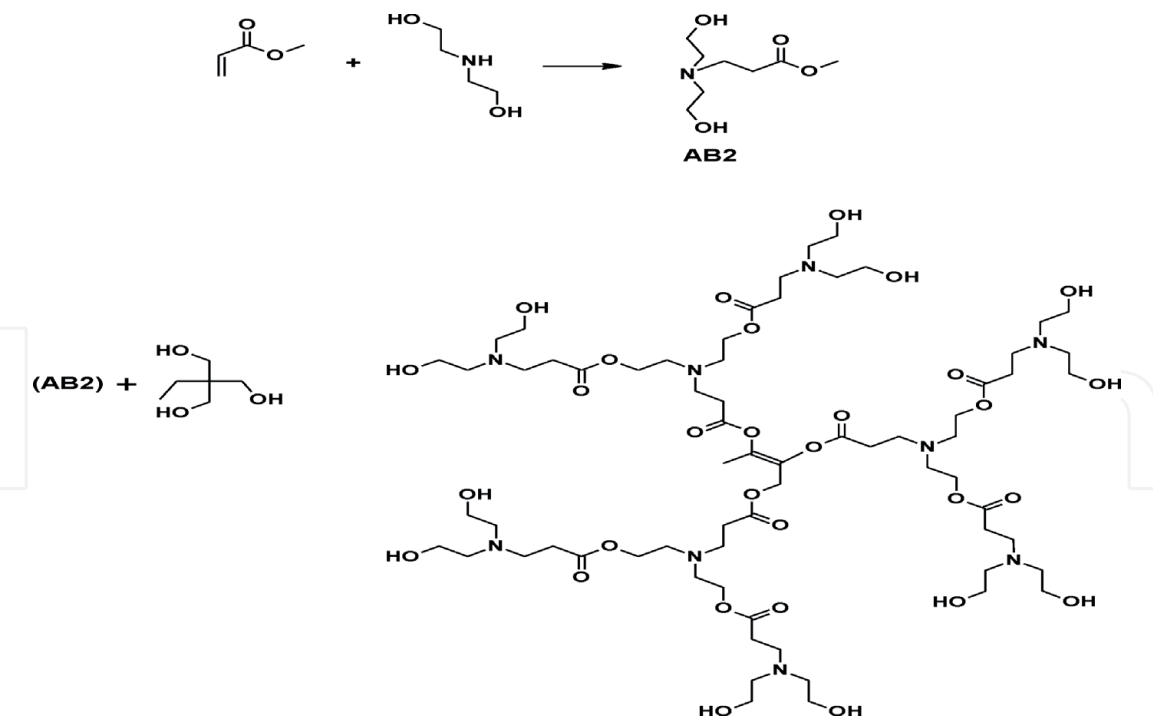
Figure 4.
Synthesis of hyperbranched poly(amine-ester).

Resin type	Viscosity at 30°C, 100 rpm (cP)	Solid content[a] (%)	pH	Gel time at 100°C (s)
CPF	190	59.80	11.30	480
TGKL	65	39.26	9.46	164
MTGKL	108	53.08	9.30	235

[a]*Solid content of the resins was determined by measuring the weight before and after removing the solvent by heating at 105°C to constant weight.*
%Solid content = (weight of the solid resin/weight of the solution) × 100.

Table 1.
Variation of the physical properties of CPF, TGKL, and MTGKL resins.

The maximum load, tensile strength, elastic modulus, and elongation at break of panels are direct measures of the performances. From **Table 2**, the trend shows that the dry MTGKL resin has the tensile strength of 39.72 MPa and elongation at break of 21.91%. This result indicates that MTGKL resin is stronger than that of the CPF resin. TGKL has the tensile strength of 28.79 MPa and elongation at break of 20.61%. That is also stronger than that of the CPF resin but lesser than MTGKL resin. The results of MTGKL and TGKL resins are within the requirement of the relevant international standard as per British Standard for dry tensile strength of plywood (≥0.35 MPa) [40].

Interestingly when comparing TGKL with MTGKL resins, the water resistance of MTGKL resin is improved after modification with poly(amine-ester). This is evident in the results of tensile strength (2.72 MPa) after soaking the plywood samples of MTGKL resin in tap water for 24 h at room temperature, where no delamination occurred in any of the specimens. However, delamination was observed in the plywood samples of TGKL resin after soaking in water for a period not exceeding 1 h, indicating the lack of water resistance for TGKL resin when it was used to bond plywood. This suggests that the modification of tannin by adding oligomeric precursors (hydroxyl-terminated) of a hyperbranched poly(amine-ester) is successful to boost the network structure of natural phenolic resin to prepare a water-resistant resin.

Resin type	Tensile strength, MPa			Elastic module, MPa	Elongation at break (%)
	DRY	Cold water soaking, 24 h	Boiling water soaking, 2 h		
CPF	1.39	---	---	56.61	12.45
	---	1.25	---	41.10	15.84
	---	---	1.01	26.78	17.29
TGKL	2.89	Delamination	---	125.27	20.61
MTGKL	3.97	---	Delamination	185.30	21.91
	---	2.72	---	143.66	18.20

Table 2.
Tensile strength, elastic modulus, and elongation at break of plywood using CPF, TGKL, and MTGKL resins.

The improvement of water resistance of MTGKL resin is assumed to be due to the reaction of the terminal units of glutaraldehyde with the hydroxyl groups of tannin and with $-NH_2$ and $-COOH$. Other exposed groups lead to an increase in the cross-linking density within the resin in the hot pressing process, and consequently, there will be an increase in the mechanical properties. In addition, the presence of furfuryl alcohol as a cross-linking agent and its participation in increasing the cross-linking reaction help to improve the water resistance of MTGKL-based wood adhesives. The whole process is represented in **Figure 5**.

4.2 A combination of lignin polyol-tannin adhesives and polyethylenimine (PEI) as fillers

Protein adhesive, which was secreted via marine mussels, called marine adhesive protein (MAP), is a good example of a renewable resource and free formaldehyde adhesive [42]. MAP has the ability to form strong linkages on wet surfaces and thus could be used as a strong and water-resistant wood adhesive [42]. However, they are costly and not readily available. MAP contains two functional groups (catechol and amino groups). The different reactions between the catechol group and the amino group lead to the cross-link and solidification of the MAP, thereby converting the MAP to a very strong and very water-resistant adhesive [42].

Condensed tannins and lignin are one of the few natural polymers containing a catechol moiety [43]. Previous studies showed the possibility of using a combination of condensed tannins or lignin and polyethylenimine to synthesize wood adhesives. **Figure 6** shows representative structures of polyethylenimine. This adhesive has high shear strength and exhibits significant water resistance [43]. In this work, the wood adhesive system, which consists of a tannin-glyoxalated lignin polyols (TGLP) and PEI, was evaluated for plywood and compared to plywood produced with a glyoxalated lignin/tannin and conventional phenol-formaldehyde resin.

It was observed that an increase in the total solid content of the TGLP-PEI adhesives leads to an increase in its viscosity. Moreover, when the total solid contents in adhesives reached 55%, the TGLP-PEI adhesives became too viscous. It can clearly be seen from **Figure 7** that the total solid contents increased from 48.54 to 56.92% when the ratio of PEI was changed from 10 to 20% in TGLP resin. The tensile strengths (dry, WSAD, and BWT/dry) of wood composites bonded with the adhesives have revealed a dramatic increase in its values (63.04, 59.48, and 53.53 MPa), respectively, and a linear relationship among all values. The TGLP-PEI
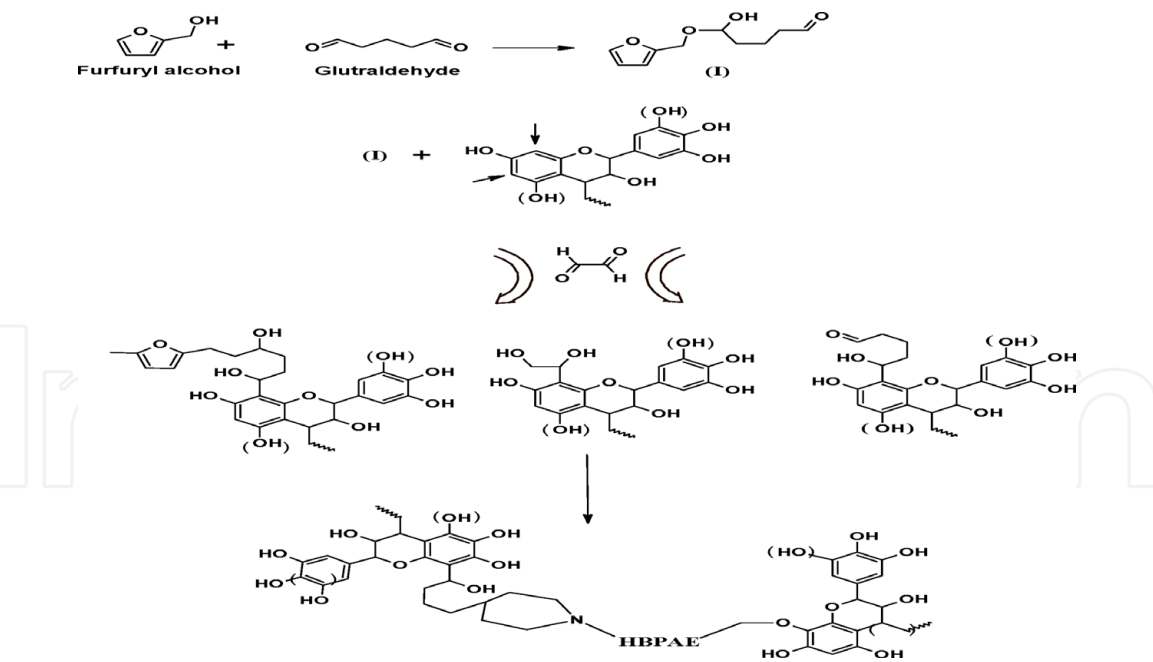
Figure 5.
Proposed mechanism for the participation of formulation components in cross-linking reactions and improvement of water-resistant properties for the resulting modified tannin-glyoxalated lignin [41].
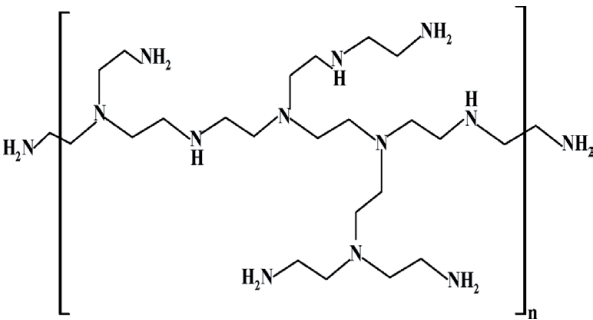

Figure 6.
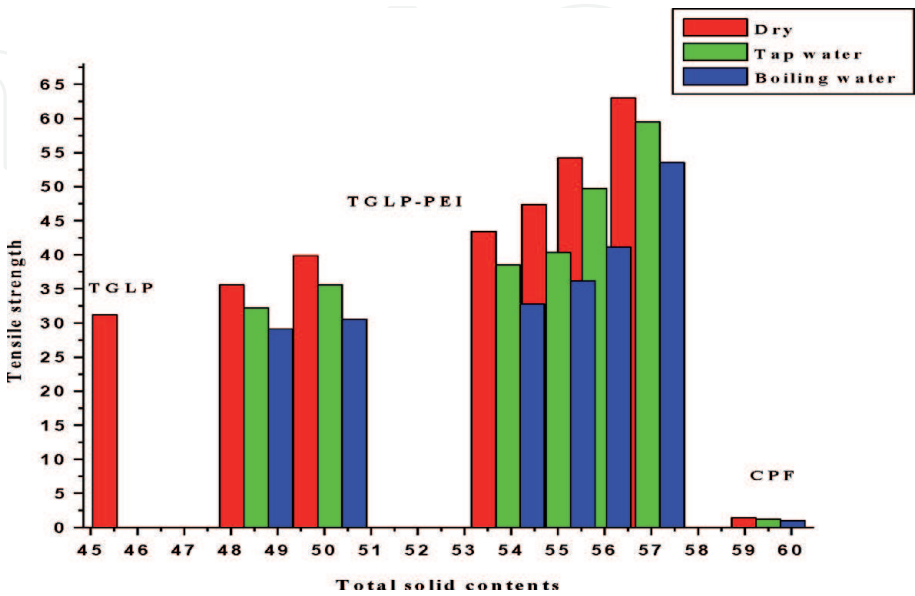*Representative structures of polyethylenimine (PEI).*

Figure 7.
Effect of total solid content of TGLP-PEI adhesives on tensile strength (dry, tap water soaking for 24 h, and boiling water soaking for 2 h) in comparison with TGLP and CPF.

adhesives with total solid contents (56.92%) were applied to plywood and used in subsequent experiments.

The production of wood composites does not favor the use of wood adhesives with low solid contents due to higher energy consumption and comparatively longer time of water evaporation through hot press. In the current study, a significant amount of the total solid contents of adhesives (56.92%) was obtained during the modification of lignin polyol-tannin resins with polyethylenimine. There was a substantial difference in the solid contents of modified (56.92%), unmodified adhesives (45.82%), and the commercial phenol-formaldehyde (59.50%) under the same experimental conditions. The solid content of the TGLP resin (45.82%) was lower than the solid contents of the CPF resin (59.50%). However, the solid contents of the TGLP-PEI resins were almost comparable to the CPF resin, especially when the ratio of PEI was 20% in TGLP-PEI resin. It is known that CPF resins contain large amount of urea, and for this reason, the solid content value is very high [44].

To date, the reactions between lignin and tannin and PEI are not fully understood. Some of the proposed potential reactions are given in **Figure 8**. The nature of TGLP-PEI resin curing mechanisms is comparable to the quinone-tanning methods as reported elsewhere. Moreover, the reaction mechanisms between lignin and PEI are mostly similar to the possible reactions between tannin and PEI. At elevated temperatures, the catechol moiety (2) in the demethylated lignin is highly vulnerable to oxidation process, leading to the formation of quinones (3). This occurs at higher temperatures (140°C) using a hot press during the formation of wood composites. The quinones (3) possibly react with the amino groups present in PEI structure, thus forming Schiff bases (4 and 5). Some other possible reactions between quinones and amino groups of PEI (such as Michael addition reaction) may also occur to form (6) further Schiff bases (7 and 8). A similar kind of reaction occurs during the oxidation process to form phenolic hydroxide in lignin structure during hot press, which further results in the formation of quinone. It further supports the increase of the reactions with amino groups of PEI to form Schiff bases.
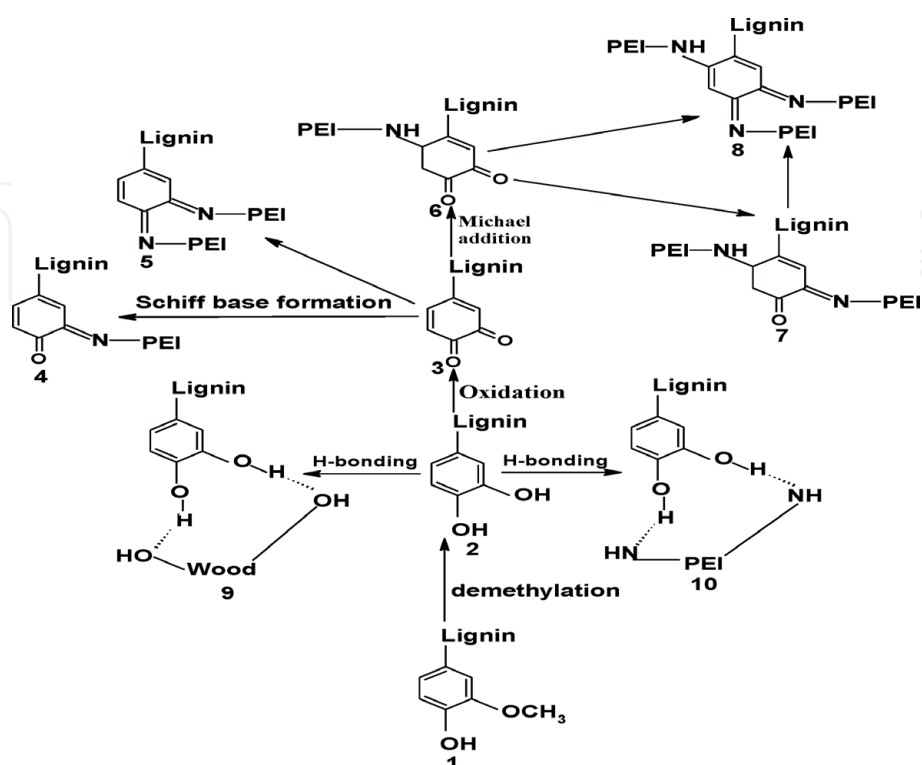

Figure 8.
Some possible reactions between tannin and PEI.

It is well known that wood has lignin, which contains phenolic hydroxyl groups, and these groups can be oxidized to quinone during the hot press; hence they cannot be excluded from the covalent bond formation between TGLP-PEI adhesive and wood. In addition to the reaction of the quinone, the catechol moiety can react with the amino groups of PEI and form strong hydrogen bonds. Furthermore, it can also form strong hydrogen bonds with the hydroxyl groups in the wood components (see a representative structure 9 and 10 in **Figure 8**). It can be inferred from these reactions that the curing reactions through the hot press process lead to the formation of highly cross-linked TGLP-PEI network polymers, as well as water-resistant adhesives. These results are in close agreement to mechanical tests and proven through soaking plywood samples bonded with TGLP-PEI adhesives in the tap water and boiling water.

4.3 Influence of bentonite (BT) clay on lignin

Improving the polymer properties through incorporating a second component such as fillers to obtain new materials has become common. Inorganic additives are frequently used in the wood adhesive industry that improves the mechanical and thermal properties of resins [36]. Recently, the utilization of the montmorillonite to modified phenolic resin attracts significant interest of researchers to improve some properties such as stiffness and toughness [45]. In this work, wood adhesive system, consisting of a tannin-glyoxalated lignin polyol, (TGLP) was modified using bentonite and organo-bentonite clay and then evaluated on plywood.

Scanning electron microscope (SEM) is a significant technique used to interpret changes in morphology of bentonite during a modification process by surfactants. SEM micrographs of bentonite before and after modification with octadecylamine (ODA) as well as the SEM images of composites with adhesive are shown in **Figure 9**. The corresponding elemental analysis data are summarized in **Table 3**. It is worth mentioning that there are no substantial differences in morphology between natural and organic bentonite.
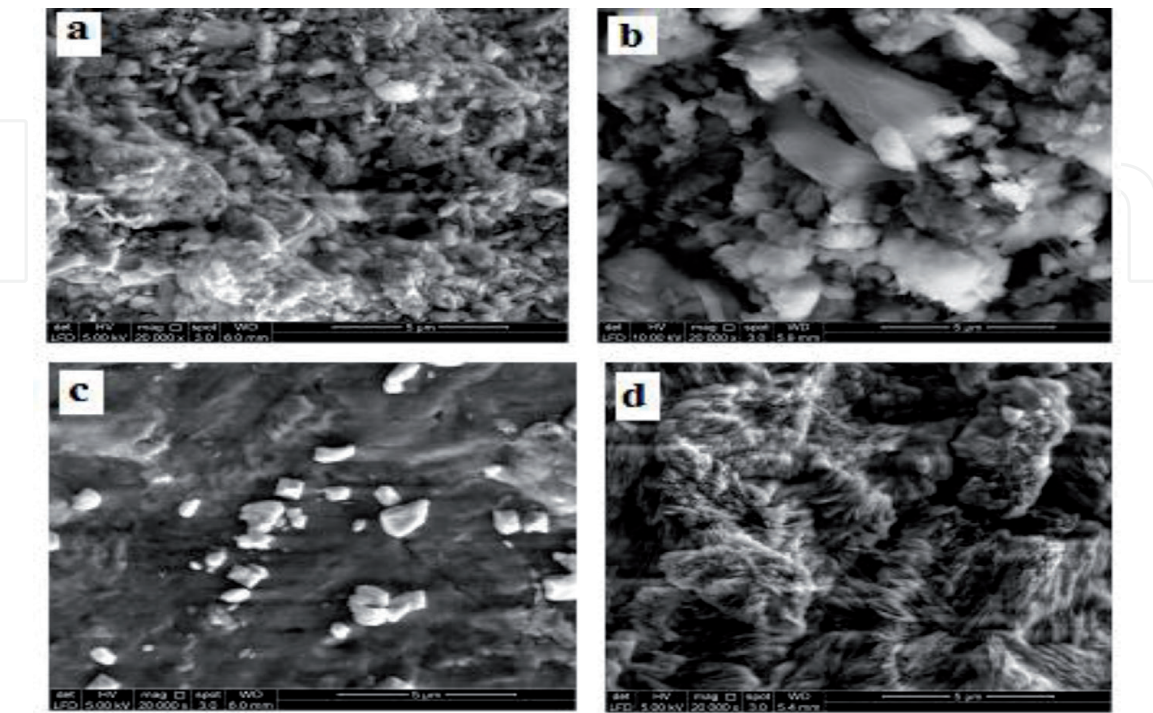

Figure 9.
SEM micrographs of (a) unmodified BT, (b) ODA-modified BT, (c) TGLP-BT, and
(d) TGLP-ODA-BT composites.

Sample	C (w%)	O (w%)	Si (w%)	Al (w%)
BT	12.79	61.05	17.96	5.73
ODA-BT	21.12	68.84	6.22	1.97
TGLP-BT	22.42	67.14	3.95	1.21
TGLP-ODA-BT	23.22	66.39	0.72	0.64

Table 3.
EDX elemental analysis of unmodified BT, ODA-BT, and composites.

The unmodified bentonite (**Figure 9a**) demonstrated huge aggregated morphology with large-sized particles in the structure. Some fragments of small-sized particles in BT structure were relatively regular. This may be due to the interactions of face-to-face and face-to-edge of particles. Comparing with the unmodified BT, the BT-ODA (**Figure 9b**) showed smaller particles and irregular shapes as well as more severely aggregated particles than BT. In addition, the SEM images also revealed the expansion that took place in layers of silica and a more open structure in the ODA-BT. As a result, further exfoliation during composite fabrication is expected.

SEM analysis of BT-TGLP composites in **Figure 9c** exhibited the lack of compatibility between the unmodified bentonite and matrix resin, which could lead to the formation of tactoids. During the modification of organic bentonite using appropriate modifiers, the interaction between the matrix resin and the organo-bentonite would be sufficient for a certain degree of exfoliation and/or intercalation even when forming the tactoid. SEM micrograph of ODA-BT containing the composite resin is given in **Figure 5d**. As shown in **Figure 9d**, ODA-BT particles were dispersed in the TGLP matrix, and the resulting composite structure (TGLP-ODA-BT) demonstrated a highly homogenous distribution.

The elemental analysis by EDX of the BT, ODA-BT, and composites is shown in **Table 3**. The energy spectra indicate that the elements present are carbon (C), silicon (Si), aluminum (Al), and oxygen (O). From **Table 3** the BT sample has the highest content of silicon (Si) and aluminum (Al). It is clear that the bentonite is a class of aluminum silicate minerals. For ODA-BT, it was observed that the amount of carbon (C) element (21.12 w%) has significantly increased compared with BT sample (12.79 w%), indicating the presence of alkylammonium cations as intercalant group in the bentonite gallery that additionally supports the modification that occurred. It is noteworthy to point out that the percentage of all the other elements such as Si and Al decreased significantly and this can be due to the presence of carbon (C).

The average tensile strength of unfilled TGLP resin and composite with corresponding bentonite and organo-bentonite loadings was determined from the tests conducted on at least five plywood specimens under dry conditions as shown in **Figure 6**. The tensile strength of TGLP composite has been considerably improved by incorporating both BT and ODA-BT.

The tensile strength of TGLP composite increases nonlinearly with BT and ODA-BT content. From **Figure 10**, the dry tensile strength was more affected by ODA-BT than BT. The reason in the strengthening of tensile properties is probably due to intercalation/exfoliation of the bentonite structure in the phenolic matrix of adhesives. As the silicate layer in bentonite structure has excellent mechanical characteristics compared with TGLP, the enhanced mechanical properties of resin may be linked to the dispersion level of the silicate layers into the matrix of resin. It is believed that the dispersion process of clay in polymer chain provides a large interfacial interaction that may cause a restriction on the mobility.

There are multiple factors that affect the mechanical properties including the ratio of filler, dispersion of the filler, and the adhesion at the filler matrix interface
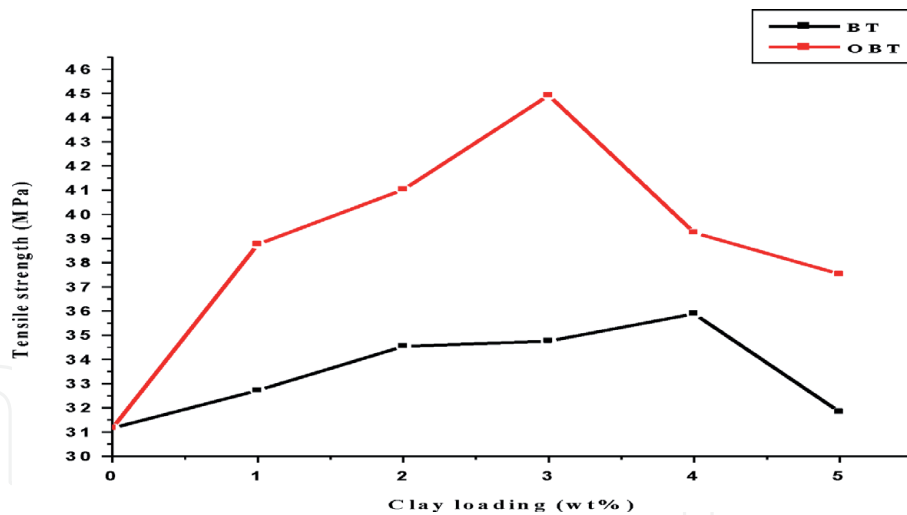
Figure 10.
Effect of the clay loading of TGLP adhesives on tensile strength.

[46]. In addition, the exfoliation degree of the silicate layer in the polymer affects the modulus of composites. This reveals that the significant increase of the tensile strength modulus through the incorporation of low contents of ODA-BT (1, 2, and 3 wt%) can be due to the uniform dispersion of nanoparticles at such a low content. High content of particles (4 and 5 wt%) reduced the dispersion and thus restricts the improvement of tensile strength (**Figure 10**). The elastic modulus has the same sensitivity toward dispersion. Dispersion of filler particles has less effect when BT is used; the limitations of tensile strengths show at a loading of 5% (**Figure 10**).

The decrease of the tensile strength at high content of BT and ODA-BT can be attributed to the agglomeration of particles. An agglomeration of particles could also serve as crack initiation sites, as well as the nonuniform distribution. Through the results, it could be concluded that the use of ODA-BT is better than BT to improve the mechanical properties, particularly tensile strength when used in low concentrations. This can possibly be due to lower silicate layers in the ODA-BT than BT because of the organic modification of bentonite that has a positive effect on ODA-BT, thus increasing the cross-linking density.

With the modification of bentonite, the ODA-BT became more compatible with the TGLP resin chains, due to the decrease of surface energy of bentonite layers; thus the surface polarity of ODA-BT is compatible with the resin polarity. The ODA-BT with lowered surface energy has more ability to interact and intercalate within the interlayer space of resin than BT and thus improves the various properties of the resin.

5. Conclusions

Composite materials have a pivotal role in industries that are now considered the most progressive worldwide. Polymer composites are a mixture of polymers with inorganic or organic fillers that have certain geometric forms. Wood adhesives now represent a vital aspect of the wood-based panel industry, and synthetic condensation resins have become widely used. At present, synthetic adhesives based on formaldehyde such as PF, UF, and MF are predominantly used for wood composite production. A variety of methods have been used to improve the performance of wood adhesives. These methods are widely used in the industry; they include the simple addition of fillers. In this chapter, it was demonstrated that a combination of lignin polyol-tannin (TGLP) and polyethylenimine (PEI) was an excellent

alternative for marine adhesive protein (MAP). The results revealed that the increase in PEI ratio led to an increase of the solid content of TGLP-PEI adhesives. The TGLP adhesives had poor water resistance compared with TGLP-PEI adhesive despite the high tensile strength (31.1 MPa). This is clearly shown when soaking the plywood specimens in the tap water and boiling water, where delamination occurred. However, at 10% of PEI with TGLP resin, the delamination of plywood specimens did not occur.

There are not a lot of studies conducted on the influence of clays on wood adhesives prepared from biomass. The mechanical and thermal characteristics of TGLP system were studied. The modification of bentonite clay was implemented using octadecylamine (ODA) salt. The mechanical properties (tensile strengths) of TGLP composites have been considerably improved by incorporating both BT and ODA-BT. The tensile strengths revealed that the use of low contents of clay is better than using high clay content that could be due to the decrease in dispersion at high contents of clay. These results are particularly clear when using modified bentonite with ODA. This is probably due to the decrease of some silicate layers in the ODA-BT compared with BT.

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