STUDY ON SYNTHETIC AND BIO-BASED PHENOL- FORMALDEHYDE ADHESIVES FOR THE WOOD-BASED INDUSTRY

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Wood-based panels, like plywood (PW), particleboard (PB), oriented strand board (OSB), medium-density fiberboard (MDF), etc., are traditionally manufactured with formaldehyde-based adhesives like urea-formaldehyde (UF), melamine-formaldehyde (MF) and phenol-formaldehyde (PF). These adhesives not only are synthesized by raw materials derived from petroleum, that is a finite recourse, but also give rise to the public concern about the free formaldehyde emissions of the panels produced with them.

This study investigates the performance of phenol-formaldehyde adhesives where 15% of the phenol has been replaced by any of the natural derived materials: soy protein isolate (SPI), tannin, lignin, cashews nut shell liquid (CNSL) and pyrolysis oil of forestry residues. The experimental adhesives were produced on laboratory scale under the same specifications while their physical characteristics were determined using standard laboratory analysis and thermal analysis techniques like Thermogravimetric/Differential Thermogravimetric Analysis (TGA/DTG) and Differential Scanning Calorimetry (DSC). Their adhesion property was investigated through the fabrication of 3-layer plywood panels which were subjected to testing for their shear strength, wood failure and free formaldehyde emissions performance. These tests were conducted according to the procedures determined by the standards used in the industrial practice and in particular: the European standards EN 314.1 & 314.2, the British standard BS6566 and the Japanese standard JIS A1460.

An overall comparative evaluation of the adhesives was carried out using the performance of a conventional phenol-formaldehyde adhesive as a standard. Last, a linear regression statistical analysis was implemented for the location of the most significant physical characteristic of the adhesives relative to their performance in plywood panel application. The experimental adhesives were found to be able to replace successfully a conventional phenol-formaldehyde adhesive on plywood panel application showing also promising flame retardation. The pH of the adhesives was found to be the property with the highest correlation to wood failure performance of the plywood panels.

Key words: plywood, natural adhesives, thermosetting adhesives, fire retardants, formaldehyde free.

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1. INTRODUCTION

1.1 General

For centuries, before coal and hydrocarbons became part of everyday use, mankind has used renewable resources as the only source for energy, textiles, building materials, medicines and personal care products. However, the use of these renewable products declined gradually from the second decade of the 20th century, when petrochemical materials entered the market, offering cheaper and more effective alternatives.

Modern life depends on the petrochemical industry as most drugs, paints and plastics are derived from fossil fuels even though the processes for the production of these products are not sustainable in terms of resources and environmental impact. Moreover, in recent decades, petrochemical products are considered to have serious hazardous effects on human health and the environment.

Nowadays, as our society is becoming more and more aware of these hazards, scientists and industry have turned again to natural resources seeking alternative products and processes, while the policy makers have instituted more environmentally friendly legislation. It is widely accepted by society worldwide that by using "green: materials, we moderate the intense exploitation of fossil resources, reduce the amount of carbon dioxide that enters the atmosphere and take upon ourselves the responsibility for using the earth's resources in a sustainable manner. This will improve resource management, indoor air quality (IAQ), and generally the overall performance and influence of human kind on earth.

Among the various natural resources, biomass is considered to be the most beneficial, because its exploitation provides not only an alternative renewable solution toward fossil fuels and energy, but it can also be converted effectively to various chemicals and bio-based products. The biorefinery concept is important when some of these products, while possibly small in volume, could be high in value. The United States of America resolved that by 2012 almost 8 billions gallons of fuels should be derived from biomass while the cost of bio-ethanol should be reduced to 1.07$/g. Likewise, the European Union, through the "Biomass Action Plan" [1] communicated its decision to increase biomass use to around 150 million tons by 2010. Moreover, transition to a more sustainable bio-based economy, as a political consequence of the Kyoto protocol [2] on global climate change includes a shift of feedstock for energy and chemical industries from petrochemical to renewable resources.

In the sector of polymer production, the idea of using natural derived raw materials for their synthesis is not new. The first man-made polymers were derived from biomass resources (animal bones, horns and hooves, often modified; celluloid; casein plastics, shellac) [3]. However, they were more and more displaced by petrochemical polymers in parallel with the growth of the petrochemical industry since the 1930's. While the oil price shocks of the 1970's led to renewed interest in the possibilities offered by non-petrochemical feedstock, this did little more than temporarily slow the pace of growth in petrochemical polymers. Since the 1980's and especially in the 1990's, however, a comeback of bio-based polymers (polymers that are fully or partially produced from renewable raw materials), has taken place in certain application areas. One of the main drivers for this development in the last two decades has been the goal to provide the market with polymers that are biodegradable. In principle, biodegradable polymers can also be manufactured entirely from petrochemical raw materials, but bio-based polymers have so far played the main role in the domain of biodegradable polymers.

In Europe, biodegradable polymers were originally developed and introduced to the market for two main reasons. Firstly, the limited volume of landfill capacity became more and more a threat and secondly, the bad general public image of plastics called for more environmentally friendly products. While the first issue has largely disappeared from the top of the public agenda because of the introduction of plastics recycling schemes and newly built incineration plants, the environmental performance is an important argument for bio-based polymers, including their biodegradable representatives. Apart from consumer demand for environmentally friendly polymers ("market-pull"), technological progress ("technology push") represents a more and more important driver. Biomass includes a wide range of lignocelluloses including crops, plants, agricultural residues and forestry wastes. These feedstocks have been used for the development of either thermoplastic or thermosetting bio-polymers.

In the wood-based panel industrial sector, various panels like particleboard (PB), medium density fibreboard (MDF), plywood (PW), oriented strand board (OSB) etc, are traditionally produced from by-products of wood processing, like chips, fibres and veneers, stuck together with a thermosetting adhesive. Such adhesives are mostly formaldehyde based. The most common types are urea-formaldehyde, phenol-formaldehyde and melamine-formaldehyde adhesives, which are conventionally synthesized from petrochemical raw materials.

Among the adhesives used for the production of these panels, phenol-formaldehyde (PF) is the preferred adhesive for panels of exterior grade. This adhesive is the second most important wood adhesive after amino adhesives in terms of volume consumption. Nevertheless, the cost of phenol-formaldehyde adhesives is high and follows the fluctuations of petroleum prices while the components of the adhesive are considered to be a significant indoor pollutant and harmful to human health. Thus, it is not coincidental that commercial attempts to replace petrochemical raw materials in adhesives for wood-based panels by other derived from renewable or recyclable resources started with this type of adhesives.

1.2 Subject of the study

In this study, lignin, tannin, cashews nut shell liquid, soy protein and forestry residue pyrolysis liquid have been used as phenol substitutes up to a level of 15% in the synthesis of resol phenol-formaldehyde adhesives. The properties of the five experimental adhesives were determined using standard lab analysis procedures and thermal analysis techniques like Thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG) and differential scanning calorimetry (DSC). The properties of the experimental adhesives will be evaluated and compared with a conventional phenol formaldehyde adhesive synthesised using only petrochemical raw materials. The adhesion property of the adhesives will be surveyed along with their application in the production of lab-scale plywood panels. The panels were evaluated for their mechanical strength and wood failure according to the standards used in industrial practice and in particular: the European standards EN 314.1: "Plywood bonding quality-test methods" and EN 314.2: "Plywood bonding quality – requirements" as well as the British standard BS6566: "Plywood-specifications for bond performance of veneer plywood". The formaldehyde emission of the panels was determined according to the Japanese standard JIS A 1460. The microstructure of wood as a substrate for adhesive, in particular, pine wood used in the plywood production was examined using a scanning electron microscope (SEM). The same wood was also subjected to thermal analysis to determine the highest possible temperature that can be safely survive during the production of plywood panels without decomposing it. Finally, a linear regression statistical analysis was implemented to determine the physical characteristic of the adhesives and the most significant correlation to the performance of plywood panels.

2. WOOD

2.1 General

The term “wood” refers to the secondary xylem formed by cell division in the vascular cambium of both gymnosperms (trees that produce "naked seeds” and are called softwoods) and angiosperms (hardwoods) [4]. Similar secondary xylem can be produced by plants of a different form and structure such as vines and shrubs, the xylem of which may be an important resource of pulping material.

Wood is an organic matter consisting of various chemicals where 90-99% of them are macromolecular compounds (polymers) while the rest 1-10% are compounds of low molecular weight either in simple or oligomer form [5]. The majority of the macromolecular compounds are cellulose, hemicelluloses and lignin. These chemicals constitute the main structural components of wood [4, 5].

In particular, cellulose comprises 40-50% of wood. It is found in the wood cell walls in crystalline and paracrystalline form shaped in thin threads that are called cellulose microfibrils and have indefinite length [5]. Their lengths vary in different cellulose materials and they are of critical importance for the chemical, physical and mechanical properties of wood.

Hemicelluloses are a mixture of polysaccharides. They comprise 15-42% of the wood mass and make up the matrix between the cellulose microfibrils [4, 5].

Last, lignin is a three-dimensional polymer formed by the enzymatic degradation of phenypropanes and their following radical coupling [4]. Lignin comprises about 15-38% of wood and it is conjugated to cellulose with natural bonds and to hemicelluloses with both natural and chemical bonds [5].

The microscope reveals that wood is composed of minute units called cells. According to estimates, 1 cubic meter of spruce wood contains 350–500 billion cells. The basic cell types are called tracheids, vessel members, fibres, and parenchyma [6]. The cells of wood are arranged like a honeycomb (porous and varying in structure) [7]. The cells are divided and spawn in the cambium layer inside the bark.

The xylem of the softwoods consists mainly of tracheids (approximately 90% of wood) which are tapered in shape while in the hardwoods these cells are tubular-shaped and are known as xylem vessels (figures 1, 2, 3, 4).

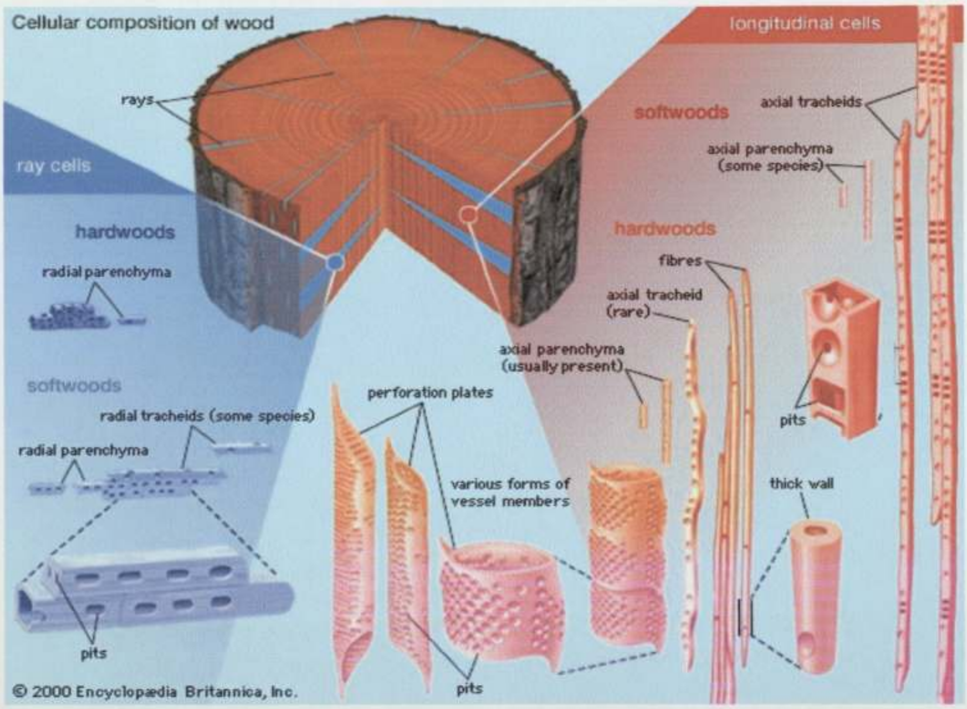


Figure 1: Cells in softwoods and hardwoods
[6]

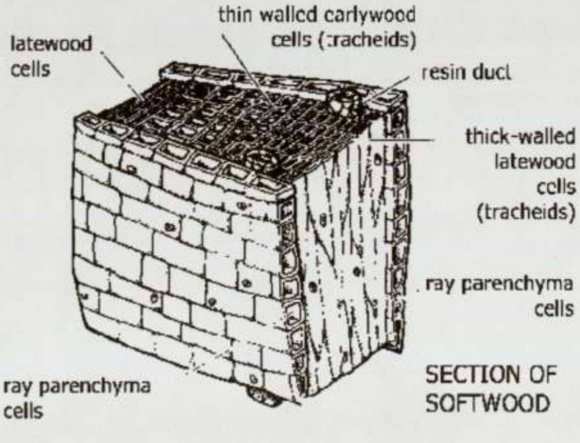


Figure 2: A section of softwood
[8]

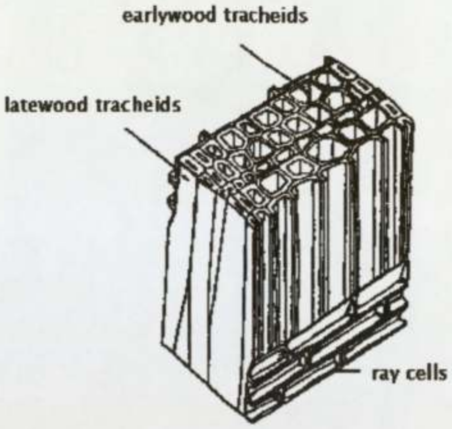


Figure 3: A close up section of softwood
[8]

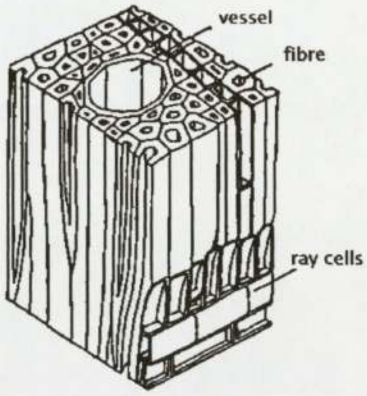


Figure 4: A close up section of hardwood
[8]

Since softwood is the type of wood that is mainly used by the wood-based industry a more detailed description of its cells will be cited.

In softwoods tracheids are not homogeneous. They are composed of several layers due to the differences in the orientation of cellulose microfibrills [4]. In particular there is a primary wall (P) and a secondary wall (S) which consists of three layers: the outer layer S_1 that is relatively thin, the thick middle layer S_2 and the inner layer S_3 [5]. The following figure 5 presents a clear view of these layers [5]. The thin primary wall consists of loose aggregations of microfibres oriented axially to the cell axis while the three layers (S_1, S_2 and S_3) of the secondary wall are organized in a plywood type construction. The microfibrils on the S_1 and S_3 layers are at a large angle to the cell axis instead of the microfibrils on the S_2 layer whose orientation makes a small angle with the cell axis. The middle layer (S_2) is the one that contributes mostly to the bulk of the cell since it has thickness of 1-5μm while layers S_1 and S_3 have thickness of 0.1-0.3μm each [5]. Hence, it is justifiable that many of the mechanical and physical properties of wood are correlated mostly with the S_2 layer [7, 9], (figure 5 - [5]).

The gaps in the secondary wall of wood cells are called pits and they are of two types: bordered and simple.

Cells are connected through an amorphous substance that forms a thin film and it is called middle lamella (ML) [4, 5].

The primary wall (P) is formed during the surface growth of the cell wall and the secondary wall (S) is formed during the thickening of the cell wall.

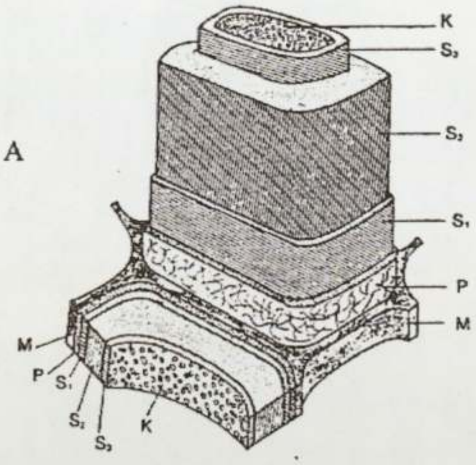


Figure 5: Structure of wood cell wall
[5]

It has been found that lignin exists mostly in the middle lamella and in a lower extent in the layers of the secondary wall. Nevertheless, the S wall makes up a larger proportion of the total tissue volume and thus it is considered that the majority of the lignin exists in the secondary wall [4].

Cellulose is found both in the primary and secondary walls even though the concentration of microfibrils is higher in the layers of the S wall and in fact it is increasing gradually from the S_1 to the S_3 layer [4].

The distribution of hemicelluloses is difficult to detect because the available histochemical techniques are nonspecific and sometimes unreliable. Nevertheless, independent studies agree that the majority of hemicelluloses are located in the secondary wall (S) and the middle lamella (M) [4].

In retrospect, it can be said that the core of wood cells consists of cellulose microfibrils that are surrounded by the para-crystalline cellulose and short-chain hemicelluloses, while lignin covers and binds all of them into a rigid structure.

Cells formed early in the growing season are called early wood cells and are comprised by large cavities (lumens) and thin walls, while the cells formed later in the growing season are named latewood cells and have smaller cavities and thicker walls [7].

2.2 Tree species

The most important group of softwoods is the conifers or cone-bearing trees, which have seeds that are usually visible inside opened cones. Nearly all softwood trees have another common characteristic: their leaves are actually needles or scales and they remain on the tree throughout the winter, which is why they are also called *evergreen trees*. Exceptions are larch (or tamarack) and cypress whose needles drop in the fall, leaving the tree bare during winter.

Hardwoods are trees that produce seeds enclosed in a fruit or nut.

Examples of trees belonging to these two groups are shown in the following table 1.

Table 1: Softwood and hardwood trees

Softwood	Hardwood
	Ash
Cedar	Aspen
Cypress	Beech
Fir	Birch
Hemlock	Elm
Larch	Eucalyptus
Pine	Hickory
Redwood	Maple
Spruce	Oak
Thuja	Poplar
	Walnut

Although there are many more hardwood species than there are softwoods, the softwoods produce a larger share of commercial wood products, particularly those used for structural applications. This is evident by the dominant use of a few softwood species such as the southern yellow pines, Douglas fir, hemlocks, spruces, other pines and true firs, all of which play crucial roles in construction.

2.3 Physical characteristics of wood

One piece of wood may have different chemical and mechanical characteristics from another depending on its origin. These variations are caused by the heterogeneity and complexity of wood in the various tree species.

Wood is highly anisotropic. The three directions are presented in the following figure 6 [9]. The anisotropy arises from the elongation of cells in the longitudinal direction and their growth out from the center of the tree. This makes the radial properties different from the tangential properties.

- Radial direction (R) = normal to the growth rings and perpendicular to the grains.
- Tangential direction (T) = tangential to the growth rings and perpendicular to the grains
- Longitudinal (L) = parallel to the fibre

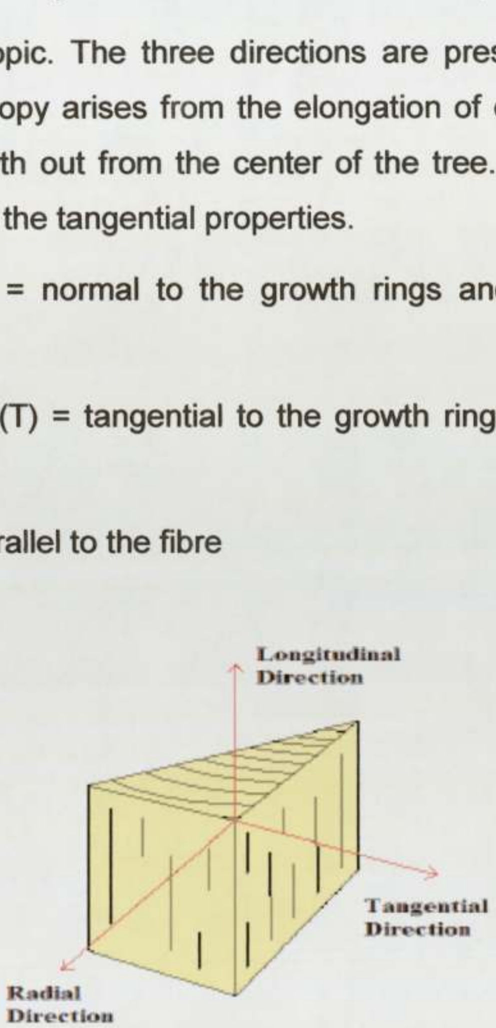


Figure 6: Wood anisotropy
[9]

The mechanical properties of wood are determined by both the angle of the microfibrils (MFA - angle of cellulose microfibrils to the fiber axis in S_2 layer [7, 9] (figure 7) and thw anisotropy of wood.

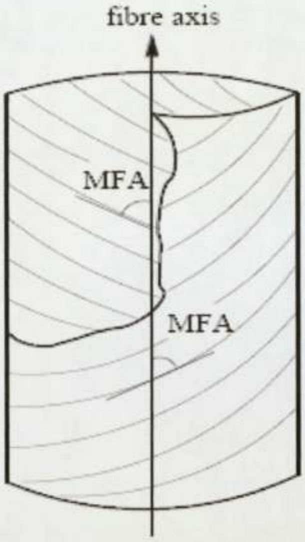


Figure 7: Helical arrangement of microfibrils around the fiber axis [10]

In particular, a parallel orientation of microfibres (angle close to 0°) generally provides the highest mechanical strength. For normal wood the angle of the mcirofibrils is 14-19 degrees. This is the cause for the restricted swelling or shrinkage of wood along the longitudinal direction [11].

Moreover, anisotropy of wood influences properties like tension, compression and shear. The mechanical properties are greater in the direction parallel to the grain. Examples of such variations for spruce are given in the following table 2 [9].

Table 2: Spruce mechanical properties variations due to anisotropy of wood.

Tension parallel to the grain	90 MPa
Tension perpendicular to the grain	3 MPa
Compression parallel to the grain	30 MPa
Compression perpendicular to the grain	6 MPa
Shear parallel to the grain	7 MPa

Other common characteristics are their growth characteristics like growth rings (formed during the annual growth of cells), knots, splits, checks and cracks (separation of wood cells because of growth, drying or mechanical stresses at weak locations). All of them influence the mechanical properties of wood-based products [12].

2.4 Chemical composition of wood

The major chemical components of wood are cellulose, hemicelluloses and lignin while other constituents, present in lesser quantities, are water, different natural adhesives, fats (mono-, di- and tri-glycerides), waxes, tannins and sterols [13]. Softwoods and hardwoods have similar cellulose contents (43±2%) but the amounts of hemicelluloses and lignin vary both in structure and quantity [4]. Figure 8 shows the distribution of components across the cell wall of Scotch pine [11].

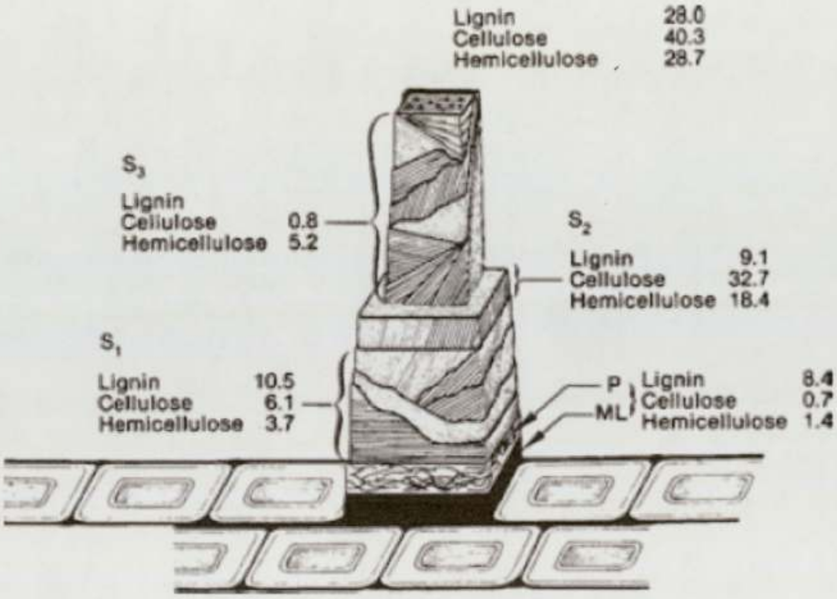


Figure 8: chemical composition of cell wall of Scotch pine [11].

The adhesives found in conifers are called rosins and comprise approximately 90% free rosin acids. The remainder comprises neutral substances like oxidized terpenes and minor quantities of esters and anhydrides [13].

2.5 Uses of wood per part of the tree

Wood is used in many ways (figure 9) [8]:

- Over 60% is cut into planks and panels, used for house framing, flooring, furniture, toys, tools, boxes and many other purposes.

- About 25% is broken down, mechanically or chemically, into small particles which are used for paper production and various types of building panels (for example masonite, caneite, chipboard and fibreboard, etc)
- About 5% is used as it is grown by the tree, for various purposes such as fence posts or to support structures (props).
- About 5% is cut into large timber pieces, such as railway sleepers and bridge girders roofing timbers
- Less than 5% is peeled or sliced into thin veneers, used to make plywood or for decorative purposes.
- In addition to these uses, large volumes of wood are burnt domestically as firewood to provide heat and energy each year.

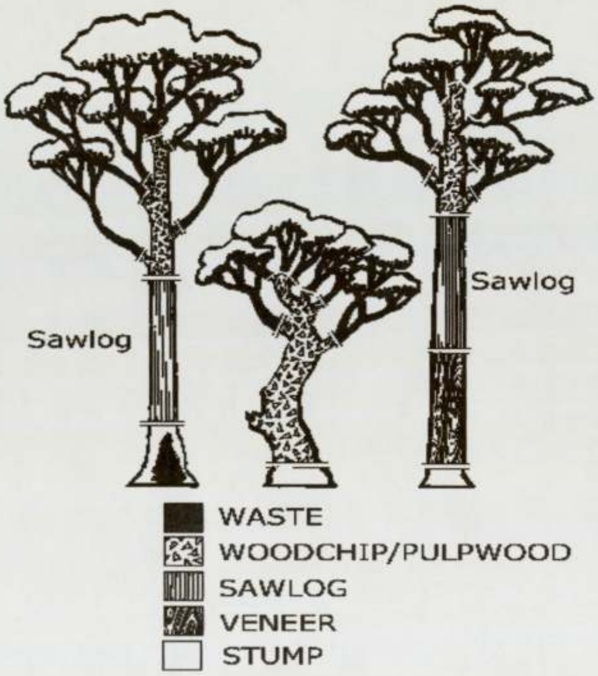


Figure 9: Some of the different ways wood from trees is used [8]

3. COMPOSITE WOOD PRODUCTS

3.1 General

The term "composite wood products" refers to a family of engineered wood panels manufactured from wood pieces of various sizes that are glued together with an adhesive which might also include a number of additives like water repellants, extenders, flame retardant agents and fungicides.

The use of wood composites instead of solid wood both in structural and nonstructural applications has been dictated by performance requirements that the products have to meet as well as from environmental point of view.

The properties of solid wood are determined at the cellular level and can be highly variable for pieces of solid wood both within and between wood species. Products manufactured from solid wood exhibit dimensional instability, surface degradation, biodegradation by fungi and insects and variability in properties (strength, elasticity and hardness). On the contrary, composite wood products are man-made and thus can be manufactured in a way that meets the performance requirements of specific applications.

Moreover, the increasing shortage of timber available for processing and manufacturing makes composite wood materials extremely important from an environmental point of view. The use of composite wood panels allow the utilization of small pieces of timber, which might not be useful as sawn timber, to be utilized to manufacture large dimension composite beams and sheets. This requires less timber overall and products that are lighter and stronger than timber can be made.

Composites are used for a number of structural and nonstructural applications in product lines ranging from panels for interior covering purposes to panels for exterior uses as well as in furniture and architectural trim materials in many different types of buildings.

3.2 Types of wood-based panels

Some of the most popular wood-based panels are the particleboard (PB), fibreboards of various densities like medium density fibreboard (MDF), oriented strand boards (OSB) and plywood boards (PW) [14].

In particular:

Figure 10: Particleboard [15]

Particleboard (PB) is a panel manufactured from particles of wood derived from waste material from the manufacture of dimensional lumber and millwork, like planer shavings, chips, saw-dust and similar, bonded together with an adhesive. Commonly it is produced in three layers where the faces of the panel are of fine wood particles while the core consists of coarser material. Because the wood particles have little or no fiber length, much of the strength of particleboard comes from the adhesive. As such, particleboard is typically not used for making structural applications but it is preferred for kitchen cabinets, shelving, wall paneling and furniture.

Figure 11: MDF and PB [16]

Fibreboards are a group of products that are further classified according to their density. Thus the term fibreboard includes panels of high density (hardboards), medium density (MDF) and low density (insulation boards) [17].

Fibreboards are derived by refining wood chips or chunks into fibres and gluing them together. Wood fibres have a relatively large length-to-cross section ratio, meaning that much of the strength of the product is derived from the fibre. As such, fibreboard products can be made for greater strength applications than particleboard [17]. Especially MDF have excellent surface smoothness and homogeneity of colour that allow its use for high quality furniture, decorative moldings, wall paneling and laminating flooring [18].

Flake board composite panels like oriented strand boards (OSB) are manufactured from flakes (long, narrow strands) of wood bonded together with adhesive. Typically they are produced in three-layer panels where the flakes of each layer are aligned parallel to one another but perpendicular to the strands of the adjacent layer. This gives unique properties to OSB and makes it suitable for many structural and nonstructural applications as well as packaging.

Figure 12: OSB during production stage [19]

Plywood is one of the most widely used wood composites. They are manufactured by an uneven number of veneers (layers or plies) bonded together with an adhesive [18]. A veneer is a thin slice of wood with its thickness determined by the end use. Veneers enable the furniture, cabinet and joinery manufacturers to accomplish designs that would be impossible or very expensive otherwise and difficult to create with solid wood. Plywood is the type of wood composite used in this study and thus it is presented in details in separate chapters.

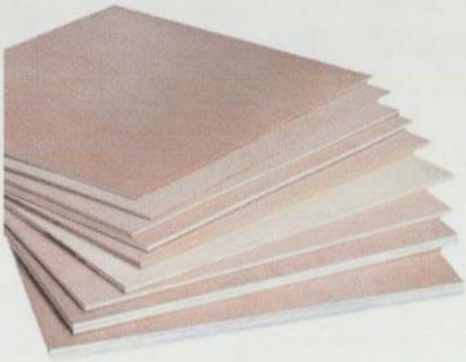


Figure 13: Plywood [20]

The following figure 14 presents a comprehensive scheme of the most common wood composite panels classified according to their particle size, density and manufacturing process [17].

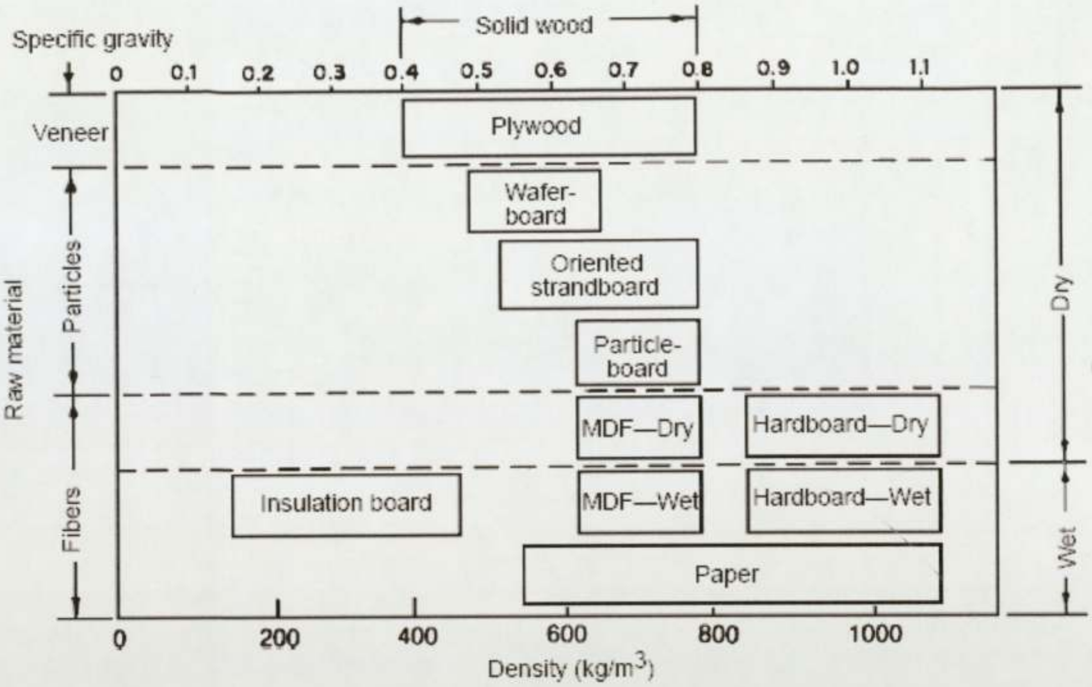


Figure 14: Schematic classification of wood composite panels [17]

In general, wood composites afford durability, quality, versatility, workability and consistency at a lower cost and thus they are preferable to solid wood.

4. WOOD ADHESION THEORIES

4.1 General

Adhesion is the force of attraction between two different substances when they are in contact. The mechanism of adhesion has been investigated for many years. Several theories have been proposed in an attempt to provide an explanation for adhesion phenomena, but no single theory is considered satisfactory to explain adhesion in a general, comprehensive way. In general six main theories of adhesion may be recognized [21, 22]:

1. Mechanical entanglement
2. Adsorption / specific adhesion
3. Diffusion / molecular entanglement
4. Electrostatic / donor-acceptor interactions
5. Direct chemical bonding
6. Weak boundary layer interfaces

The above theories may be grouped according to the adhesion interactions realized [23]. Namely:

a) Interactions that rely on entanglement or interlocking (mechanical and diffusion) and can occur at larger length scales. In particular, mechanical interlocking occurs on the millimeter and micron length scale while diffusion entanglement occurs within the cell wall pores on the nano-scale.

b) Interactions relying on charge and occur on the molecular level or nano-length scale.

c) Electrostatic interactions that may occur over a wide range of length scales, but especially in the case of wood-based industry, where they are used for coating applications, and they may be found on a macro-length scale.

The following table 3 presents a comparison of the length scales of various materials relative to the wood-adhesive interactions [23, 24], that illustrates further the length scale of the adhesion phenomena.

Table 3: Length scales of materials
[23, 24]

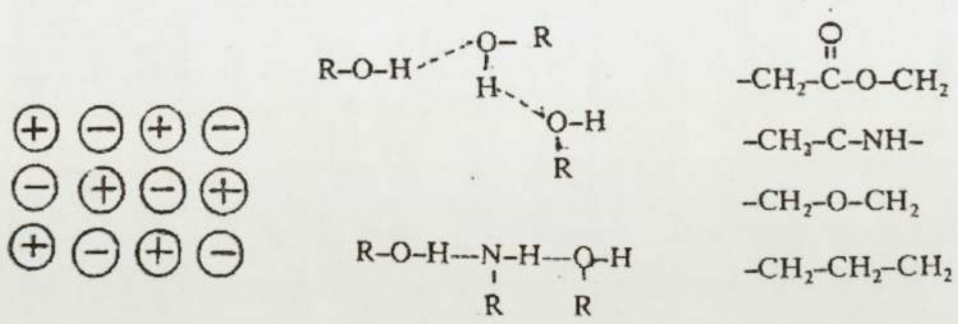
Component	**µm**	**nm**
Adhesive force	0.0002 - 0.0003	0.2 - 0.3
Cell wall pore diameter	0.0017 – 0.002	1.7 – 2.0
PF adhesive molecular length	0.0015 – 0.005	1.5 – 5.0
Diameter of particles that can pass through a pit	0.2	200
Tracheid lumen diameter	4 – 5	
Glue line thickness	50 - 250	

In the case of wood composites manufactured with thermosetting adhesives, the adhesive bond is mostly attributed to mechanical interlocking, the adsorption/specific adhesion and the chemical bonding developed between the adhesive and the wood substrate [13].

According to typical industrial practice, thermosetting adhesive, as pre-polymer in the liquid form, is sprayed or spread onto the wood substrate and then pressure is applied to allow sufficient penetration of the adhesive into the wood pores, allowing a successful implementation of the mechanical interlock. At this stage, a critical parameter for the attainment of a proper wood-adhesive interaction is effective wetting of the wood substrate. Optimum wetting takes place when the contact angle, of adhesive and substrate, is zero [12, 23] even although it is not practically feasible. Generally, the size of the contact angle is determined by the surface tension of the adhesive, as well as the roughness and charge on the surface of the wood substrate. In optimum conditions the contact angle is small but not zero. Nevertheless, it is effective enough to allow the adhesive to flow easily, to wet the wood surface well and penetrate deeply into the lumen in the wood cells.

Owing to their high polarities and in general low viscosities thermosetting adhesives penetrate deeply into the micro-pores of the wood resulting in a robust mechanical interlock [13]. When the adhesive molecules come into intimate contact with the wood molecules then intermolecular forces form between them. At this stage, curing of the adhesive (under the application of heating) results in physical interlocking between the adjacent molecules. The adhesion bonds developed by such molecular and/or atomic interactions are described by the adsorption/specific adhesion theory and the chemical bonding theory.

In particular, the adsorption/specific adhesion theory describes the development of secondary bonds (van der Waals and hydrogen bonds) while chemical bonding refers to the formation of covalent bonding during adhesion [5, 17, 25] (figure 15–[5]).



Ionic interaction Hydrogen bonds Covalent bonds

Figure 15: Secondary and covalent bonds
[5]

Generally, the secondary bonds are weaker than the covalent bonds which developed between the adhesive and the substrate. In particular, the van der Waals bonds, which include dipole-dipole, dipole- induced dipole and dispersion forces, have bond energies about 100 times lower than that of hydrogen bonds, which sequentially have bond energy about 20-50 times lower than that of covalent bonds [5]. The following table 4 shows the bonding strength and the bond energy of the various bond types [25].

Table 4: Bond types and energy
[25]

Type	Bond Energy (kJ/mol)
Primary bonds	
Ionic	600-1100
Covalent	60-700
Metallic	110-350
Donor-acceptor bonds	
Brønsted acid-base interactions (ie, up to a primary ionic bond)	Up to 1000
Lewis acid-base interactions	Up to 80
Secondary bonds	
Hydrogen bonds (excluding fluorines)	1-25
Van der Waals bonds	
Permanent dipole-dipole interactions	4-20
Dipole-induced dipole interactions	Less than 2
Dispersion (London) forces	0.08 - 40

In wood-adhesive interactions, secondary bonds, which develop when a hydrogen atom is shared between two polar groups, prevail since adhesive and adherent have an abundance of polar groups [25, 26]. On the other hand, covalent bonds occur only rarely. If we take into account that the adhesion strength is the strength of each interaction multiplied by the number of its occurrence, then it can be easily inferred that the covalent bonds contribute little to the binding strength [25] while the secondary bonds are the ones that play the most crucial role in strong adhesion.

The following figure 16 illustrates the hydrogen bonding between thermosetting PF adhesive and cellulosic fibres of wood substrate [26].

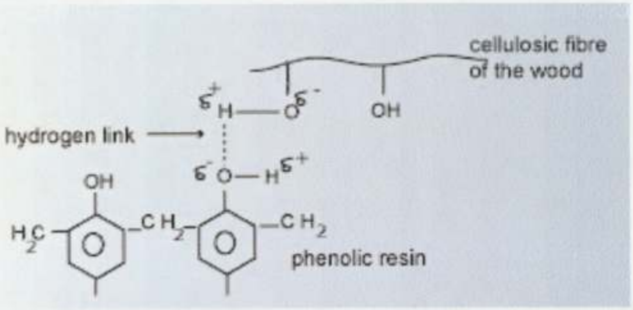


Figure 16: Hydrogen bonding between the -OH groups of the cellulosic fibres and -OH group of a phenolic adhesive [26].

4.2 Strength of adhesion

Adhesives are compounds that adhere or bond two materials together. In order for adhesion to be considered successful, it is necessary that strength (fracture strength) of the bonds inside the hardened adhesive (cohesion) and the ones at the interface wood-adhesive (adhesion) be stronger than that of wood (figure 17) [5]. In the case of wood composites, wood and thermosetting adhesives contain an abundance of polar groups capable of developing both internal (cohesion) and external (adhesion) bonds.

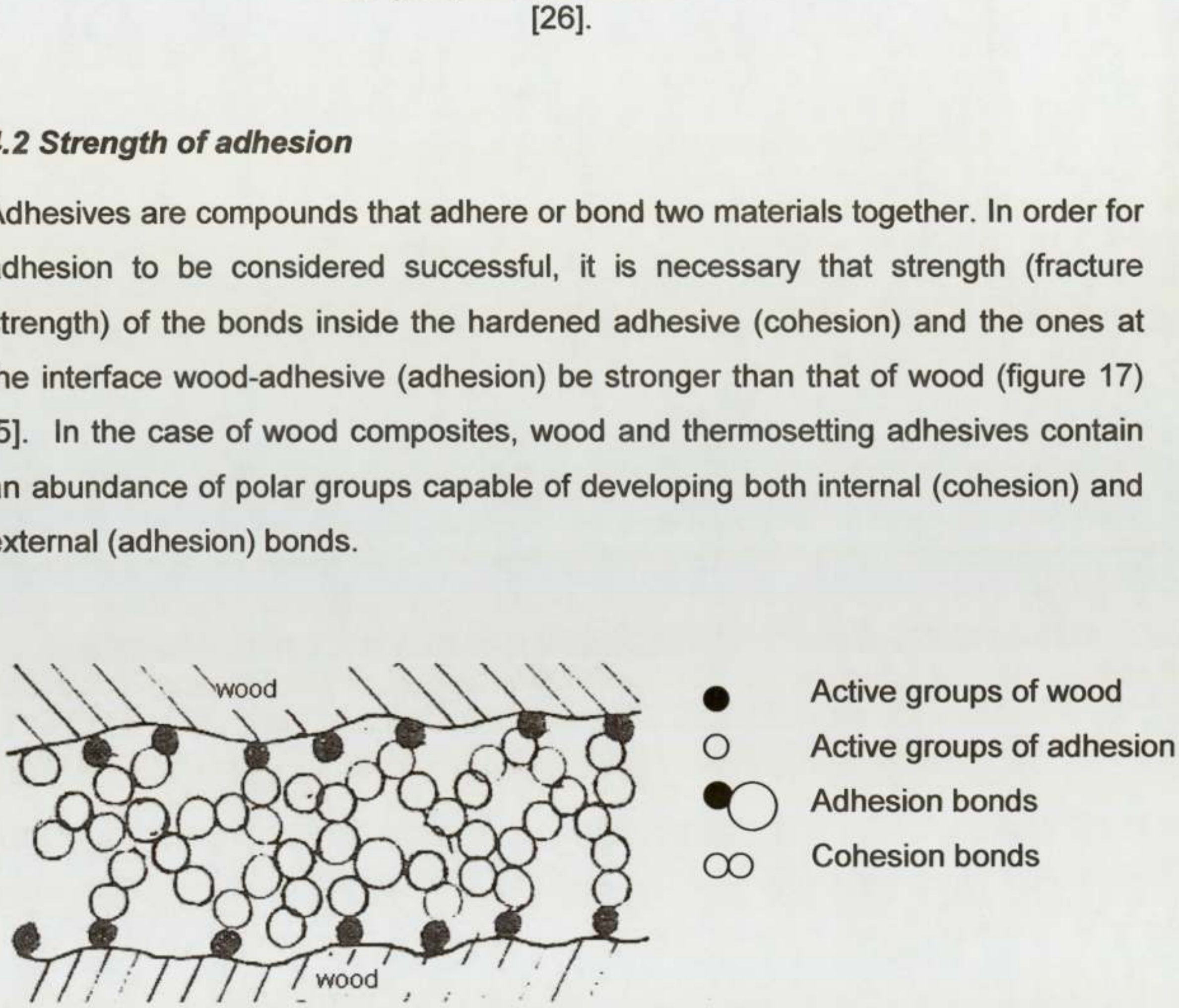


Figure 17: Schematic presentation of bonds developed during adhesion of wood [5]

The strength of the cohesion bonds depends on the type of the adhesive used, as well as the conditions of its polymerization and solidification (curing and hardening).

The strength of the adhesion depends on the number and type of the bonds developed [5] at the wood-adhesive inter-phase. While secondary bonds are sufficient enough to provide stable bonds under dry conditions, they are ineffective when the wood composite is used in humid conditions or if it has to bear heavy loads. In this case, it is the covalent bonds that mostly produce strength to robustness of the adhesion [5]. When the bond is exposed to moisture or humid conditions, free water displaces the adhesive from the adherent and disrupts the secondary bonds but it cannot disrupt covalent bonds.

4.3 Critical parameters for successful adhesion

In order to obtain a strong and durable bonded assembly, further conditions are required such as proper wood surface preparation, satisfactory wetting of wood and optimization of the hardening (curing) of the adhesive during the production of panels [25].

The preparation and cleaning of the wood surface, in order to provide the best interaction with the adhesive, may include either chemical or physical treatment or both. The aim of this preparation is to open as many as possible wood cells and so expand the area available for mechanical interlocking [25].

The satisfactory wetting of wood may be achieved by proper adjustment of the rheological properties of the adhesive to secure optimum contact with the wood surface at the molecular level. The compatibility of the wood-adhesive may be increased by adjusting the polar and non-polar components in the wood and the adhesive. The flow of the adhesive onto the wood substrate also encourages cleavage of the cells. If the cell walls are cleaved in a longitudinal transwall fashion, then the lumen should be the main bonding surface. The composition of the lumen walls varies depending on the S layer that is exposed. The S_3 layer has a high cellulosic content while the S_2 layer has a high lignin content. The middle lamella is also rich in lignin. Even though, it has not been clarified yet if the cleavage of cell is between its three main fractions or between lignin and hemicellulose boundary, it has been suggested that the hemicellulose is the main site on the surface of wood substrate that interacts with water for hydrogen bonding [25]. Microtomic section of cells allowed their clean splitting (figure 18) [25]; the figure illustrates a lot of debris on the surface of the cell walls. Their smearing, which is more intense in hardwoods, may be the cause of slow penetration of adhesives into the lumens.

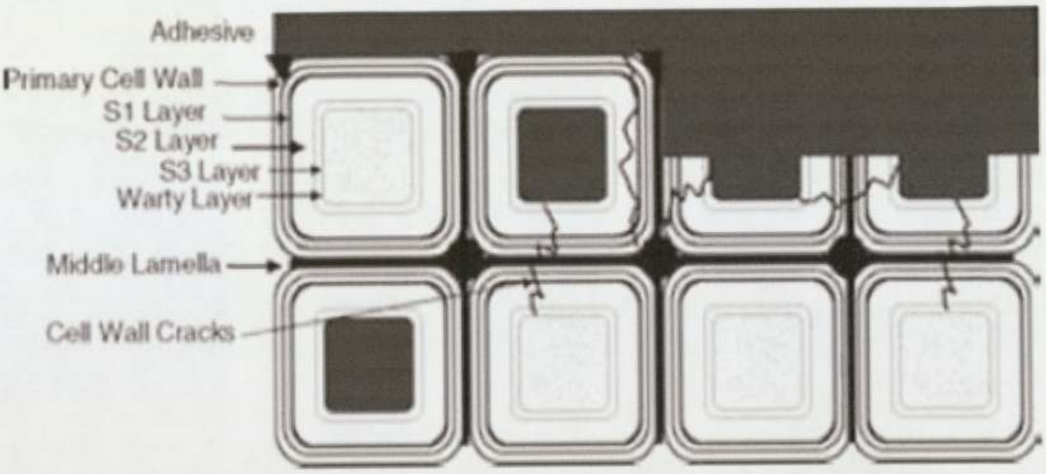


Figure 18: Illustration of a transverse section of wood showing fracture points of the wood cellular structure and surfaces available with which adhesives can interact, assuming clean fractures have occurred [25].

Finally, as the thermosetting wood adhesives are water-born polymers, the selection of the proper temperature and speed of setting (hardening) during the pressing process of the panels is a crucial parameter for the performance of the wood composite. During the setting process the adhesive shrinks while the adherent expands which causes internal stress in the adhesive. Thus, the specifications for the pressing of wood composites (pressing time and temperature) have to be cautious selected to provide not only fast adhesive set rates, which allows higher production speed, but also enough time for the development of a well cross-linked network of the polymer which determines the strength of the adhesion bond.

5. PLYWOOD

5.1 General

Plywood was the first type of engineered wood to be invented [27]. The large-scale industrial production of glued wood products started with the plywood industry in the late 19th century. Nowadays, conventional plywood continues to be the mainstay of the structural panel market. Plywood panels are made from an odd number of constructional veneers, called plies or veneers, bonded face to face with the grain running in alternate directions (cross bonding). The centre ply is known as the 'core', the outer plies as the 'faces' (or the 'face' and 'back') and the intermediate plies are the 'cross bands' (figure 19).

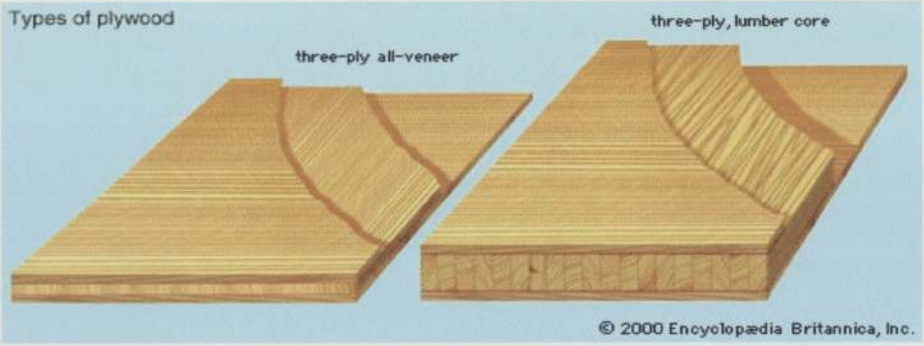


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Figure 19: Types of plywood

The plies are bonded with strong adhesives like the formaldehyde based thermosetting adhesives under heat and pressure.

There are many types of plywood that fit the needs of their multipurpose applications. Each type has specific features, which are obtained from both the wood and the type of adhesive used for its production. Any of the thermosetting adhesives (Urea-formaldehyde, Melamine-Urea-Formaldehyde and Phenol-Formaldehyde) is suitable for bonding plywood while the choice of the adhesive depends on the end use of the panel. Plywood panels intended for outdoor use are manufactured primarily with phenol-based adhesives, which show good resistance to water and weather.

The reason for using an odd number of veneers is that the sheet of plywood must be balanced as near as possible to be stable. Plywood can still twist even when it is balanced because no two veneers are completely identical and the tensions are never perfectly balanced. Another factor that can cause warping is the wetting or heating of one face of the ply; this will cause the veneer to expand or contract, and pull the panel out of true. Three-ply bends easier along the grain direction of the surface plies because only the core ply will have crosswise grain. To ensure the strength and stiffness characteristics of three-plies panels, in the face grain direction, it is required that the thickness of each surface veneer be between 25% and 33% of the total sheet thickness, i.e. the two surface sheets comprise 50% to 66% of the total sheet thickness.

The advantages of using veneered panels in wood products may be summarized as follows [28]:

- Plywood shrinks, warps, twists and swells less than ordinary wood and has great resistance to splitting at the ends, permitting carpenters to fasten plywood sheets with nails or screws close to the edges.
- A more economical use of wood is obtained by using plywood because the maximum surface area from the suitable materials is used.
- They enable the utilization of highly decorated timber showing unusual and beautiful effects from the grain irregularities. In many cases, such timber cannot be seasoned economically in the form of panels.
- Less expensive timbers can be used in the cores of plywood panels making it more profitable and easier to exploit.
- Veneers can generate effects impossible to obtain with solid construction.
- Bent and curved panels are readily fabricated by gluing veneers between shaped forms in a vacuum press.

5.2 Plywood production process

Plywood is commonly produced as follows [27]:

The log is stripped of its bark and subjected to steaming that facilitates the peeling process. A sharp blade cuts the log into veneers that subsequently are dried in ovens. An adhesive mixture is prepared which is comprised of the pre-polymer of the adhesive and an extender to increase the viscosity. The extender usually is rye or wheat flour. This practice has the advantage of lower the price of the adhesive while the use of low viscosity adhesives increases their storage life [12]. A certain quantity of the mixture it is spread over the veneers by roller or extrusion coaters.

The mixture is applied to one veneer while the other is applied cross grained. The time since the spreading of the adhesive to the finishing of plywood construction is called the assembly time. The ply panels are subjected initially to cold and then to hot pressing until the adhesive is cured (set). After pressing, the plywood panels are trimmed, squared and graded.

The most significant factors in the process of plywood production are:

Adhesive application

The quantity of the adhesion mixture applied to the veneer depends on the thickness and properties of the species of the tree from which they are derived. Generally the thicker veneers require higher amount of adhesive. The adhesive have to be applied uniformly and usually it is applied at 150-250 g/m^2[29].

Assembling

Assembling is the method of producing plywood by mounting veneers cross grained, alternating sheets of veneers with and without adhesive. The manufacturing of a plywood starts from the core veneer that it is covered with adhesion on both sides and another sheet of veneer is placed on it with its grains at right angles to the core veneer. According to the usual practice, after the plywood is assembled it stays at room temperature for a certain period of time before cold pressing. This period of time is an important step in the whole process and its duration depends on the species of veneers (hardwood or softwood). Typically it is from 15min to 1h. During this time the liquid adhesive looses water gradually, becomes tacky and produces high solid films. This produces good wetting of the veneers and provides full adhesion during the hot pressing stage [29]. The common terminology used by the manufactures at this production stage is:

a. Pot life: It is the usable life of the adhesive from the time that the adhesive mixture is prepared until it is spread onto the wood surface. Once pot life has expired, the remaining mixture must be discarded.

b. Open assembly time: It is the period from the moment the adhesive is spread until the veneers are clamped together.

c. Closed assembly time: It is the period from the moment that the veneers are placed together until pressure is applied.

Pre-pressing

During this stage plywood is pressed for about 10 minutes without heating but under pressure of about 5-7kg/cm^2. This stage is actually called "cold pre-pressing" and the reason for its occurrence is to expedite the formation of temporary bonds between the wood veneers that usually hold for about 1h. It is not a mandatory step as most phenolic adhesives develop satisfactory pre-press bonds although slowly but it has been adopted by the industry as it provides saving in the production time.

Production temperature

The phenolic adhesives require a certain minimum energy input in order to cure (harden). This energy depends on the type of the veneers being bonded. For example when they are applied to veneers of softwood 1min at 100°C is required, while for hardwood plywood a minimum of about 3min at 100°C is necessary for satisfactory cure [29]. The selection of the right temperature is a critical point to the production process as some water must be present in the glue to permit liquefaction, flow and transfer of the glue before curing. While on the other hand, loss of too much water leads to the formation of "dried out" glue films which subsequently results in inferior and water-sensitive bonds. The optimum temperature for the curing of a phenolic adhesive is above 125°C [29].

Platen pressure

The pressure used during hot pressing should be properly adjusted to avoid precuring on the outer glue lines. Typically a pressure of about 12-14kg/cm^2 is satisfactory for proper bonding within veneers of dense hardwoods or medium-density softwoods. Attention should be paid to the moisture content of the veneers as high moisture levels lead to a rapid increase in press densification and permanent loss of panel thickness [29]

Thickness of veneers

Practically phenolic adhesives can bond veneers of any thickness with proper adjustment of the glue spread. Nevertheless, the preferred thickness for easy drying, minimum handling losses and maximum mechanical strength is estimated to be between 2-4mm [29]. Thicker veneers become rough and deeply cracked after prolonged drying times. On the other hand, thinner veneers have high handling losses unless they have been tapped green. According to the thickness of veneers temperature adjustments are necessary to ensure that the heat in the centre glue lines is enough to cure the adhesive properly and not dry out. Generally, thicker veneers require higher temperatures [29].

The following figure 20, presents schematically the steps in the production of a three-ply panel.

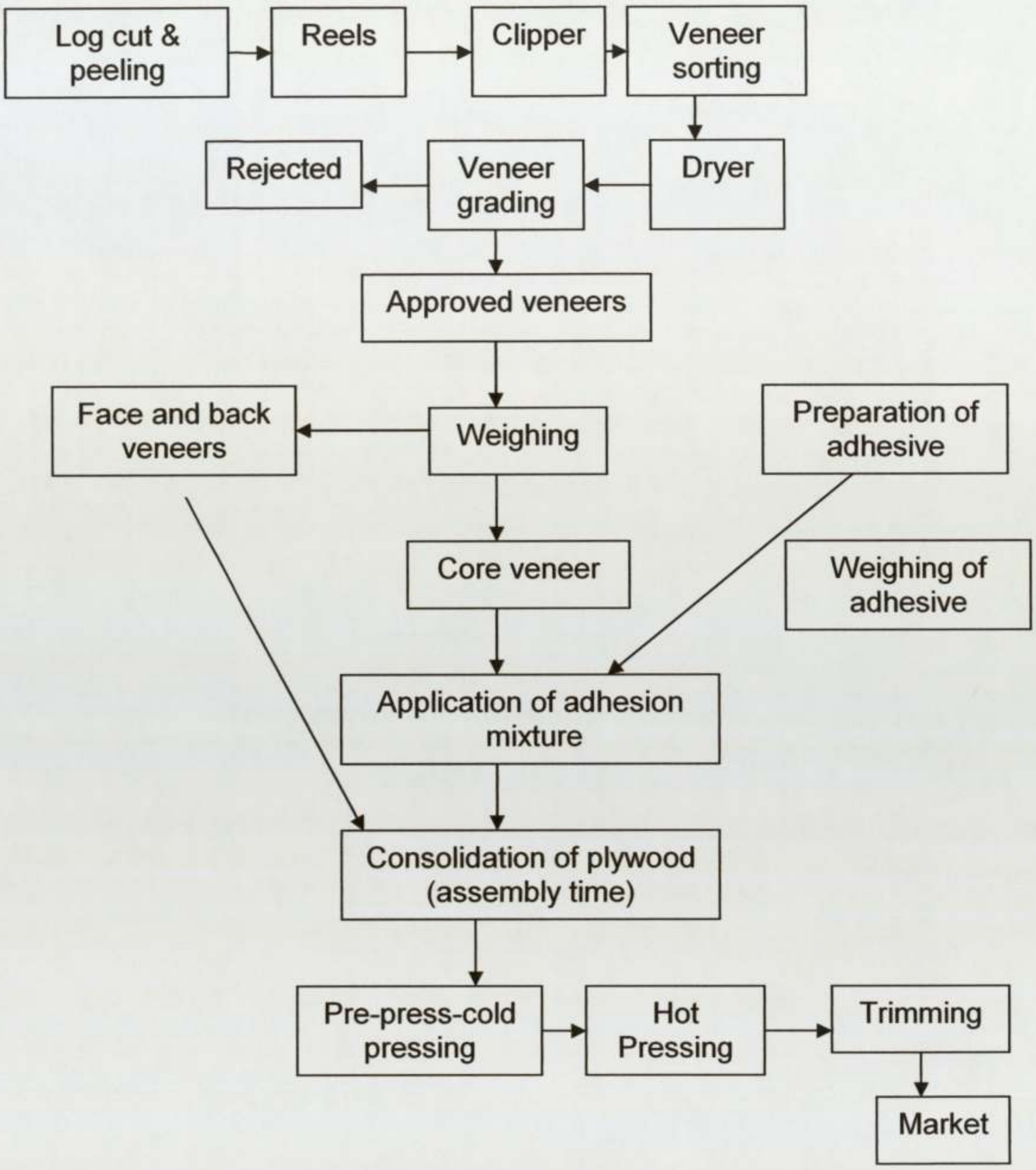


Figure 20: Production steps in a three-ply plywood panel.

5.3 Applications

Plywoods have many applications [30] (figure 21). When they are intended for interior use, urea formaldehyde adhesive is used to bond the veneers, while for marine and exterior grade panels a water resistant phenol-formaldehyde adhesive is used to prevent delamination and retain strength at high humidity [30].

Figure 21: Plywood applications
[30]

6. PHENOL – FORMALDEHYDE (PF) ADHESIVES

6.1 General

Phenol-formaldehyde adhesives are the first synthetic adhesives produced industrially worldwide. In 1872, A. von Baeyer developed an adhesive product from phenol and formaldehyde but it was Dr. Leo H. Baekeland, in 1907-1909, who controlled and modified their reaction, applying heat and pressure, providing an efficient and economic method for the production of phenol-formaldehyde adhesives in large scale. Today, some popular types of these adhesives bear the trade name "bakelite", after the name company that first produced them industrially, the "Bakelite GmbH" [13].

Phenol-formaldehyde adhesives have some outstanding properties like temperature resistance, infusibility, flame retardancy and waterproofing that make them suitable for a wide range of applications [13], especially in the industrial sector of the wood-based panel production. They are the adhesives of choice, when the panels are going to be used in exterior applications.

There are various processes for the formulation of a phenol-formaldehyde adhesive. In all cases, phenol reacts with formaldehyde under the conditions adopted by the synthesis procedure followed. In eacg case a pre-polymer is formed that is further polymerized during the setting process.

The phenol-formaldehyde adhesives available to the market today are of two types. They are either thermoplastics that are known as "Novolak" adhesives or thermosettings which are commonly known as "resol" adhesives [13]. Even though these two kinds of adhesives are synthesized following different reaction mechanisms, they both lead to cross-linked products. In each case the synthesis process is arranged to occur in three distinct stages which are [31]:

A-Stage (fusible): initial addition reactions take place between phenol and formaldehyde to form oligomers of small molecular weight.

B-Stage (plastic): further condensation develops increasing the viscosity as a result of the increased molecular weight of the oligomers. At this stage, the reaction pre-polymer is a rubbery type of material. It has a limited ability to fuse and swell while it does not dissolve in a variety of solvents.

C-Stage (hardened, not fusible): on further heating the pre-polymer hardens and turns into a highly cross-linked material which is rigid, insoluble and does not fuse or swell.

When the adhesive is prepared from resols, the product of B-stage is called *resitol* and of C-stage is known as *resit* [32].

In the wood-based panels industry the adhesives are supplied to the market at B-stage, either in solid or liquid form, while C-stage is implemented during the manufacturing of panels under the application of heat and pressure. The following figure 22 presents schematically the stages described above. In short, the reaction between phenol and formaldehyde occurs to form initially a phenol-formaldehyde adduct which under the application of heating, forms oligomers (adhesive material). The polymerization is completed with the formation of a cross-linked polymer network under the ction of heat and pressure (figure 22) [25].

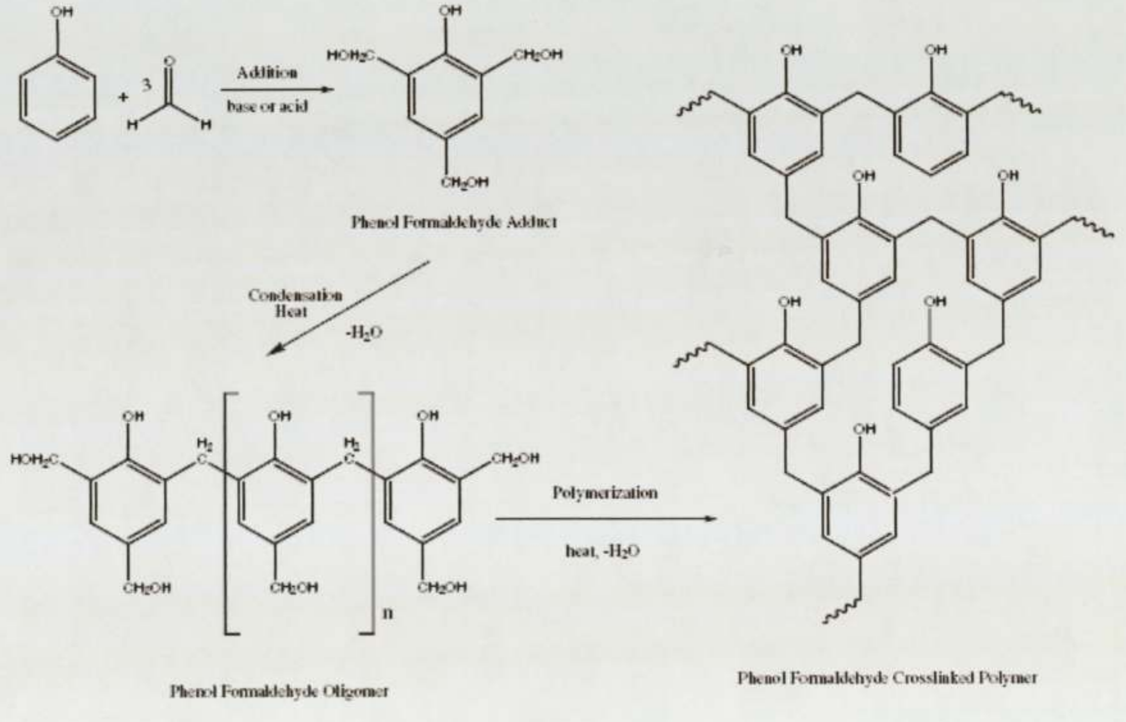


Figure 22: Illustration of the various stages during the synthesis of a phenol-formaldehyde adhesive
[25].

6.2 Novolak adhesives

"Novolak" prepolymers are produced by acidic catalysis at pH values ranging from 4 to 7 and in excess phenol [25], such that the formaldehyde to phenol (F:Ph) mole ratio is less than 1.0 (typically 0.75-0.85) [13]. Under such an acidic environment formaldehyde is protonated [29] (figure 23) becoming a more effective electrophile. It reacts with phenol via nucleophilic reaction forming hydroxymethylphenols at the ortho and meta positions of the phenolic ring (addition stage) (figure 23).

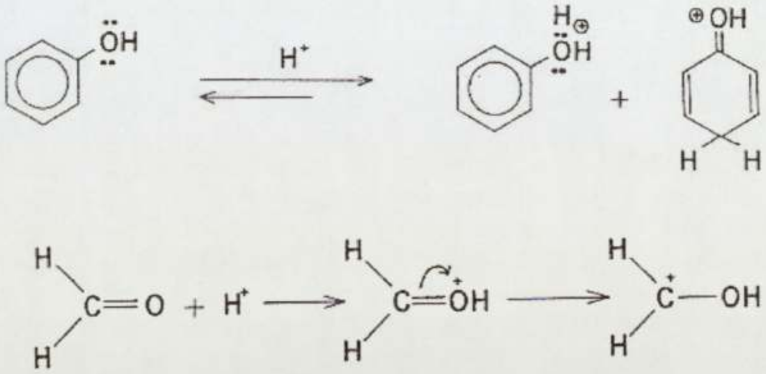


Figure 23: Protonation of formaldehyde
[29]

The hydroxymethylphenol then loses a water molecule, in acidic conditions, forming a benzylcarbonium ion that acts as a nucleophile to a new phenol molecule (linking stage). Thus, a methylene bridged dimer, the dihydroxydiphenylmethane, is formed (figure 24) [29].

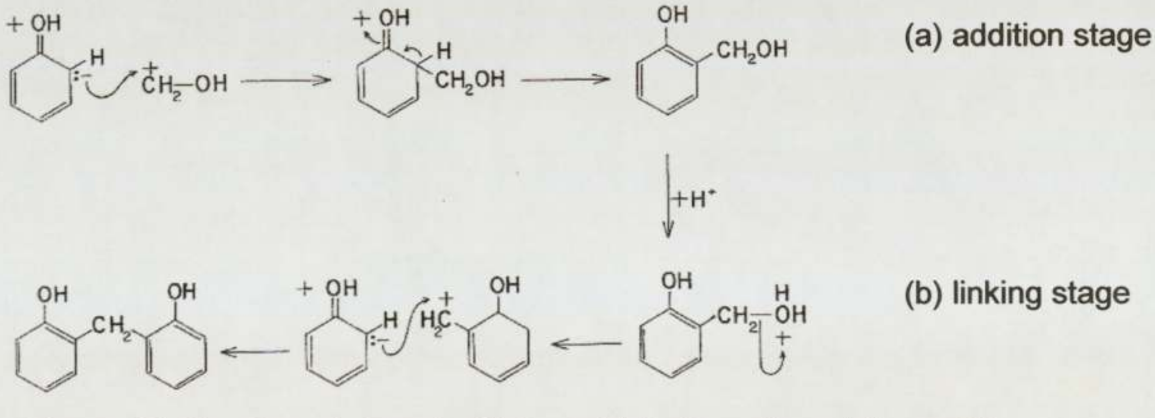


Figure 24: Reaction of phenol with formaldehyde under acidic conditions
[29]

The addition stage (a) is slow, while the linking stage (b) is fast [25]. The linking process is continued until all formaldehyde is consumed. This leads to the formation of colourless linear oligomers with molar mass varying from 500 to 5000 g/mol [33]. These oligomers do not have reactive methylol groups and therefore the addition of a hardening agent that provides formaldehyde (i.e. additional formaldehyde or hexamethylenetetramine) is a prerequisite for the formation of the methylene bridges between the chains of the macromolecules during the C-stage of the polymerization process [29].

In the acid-catalyzed process the initial attack of formaldehyde on phenol proceeds at a relative slow rate [29] while the reaction between benzyl alcohol and phenol proceeds at a fast rate yielding dihydroxydiphenylmethane. Hence, in Novolak adhesives the addition step of slow rate is the one that determines the total reaction while phenol alcohols cannot be isolated as intermediates [29].

6.3 Resol adhesives

The resol adhesives are synthesized under basic pH conditions. The reaction between formaldehyde and phenol in the alkaline pH range was first observed in 1894 by L.Ledere and O. Manasse [13] and is usually referred to as the Ledere-Manasse reaction. Resols have excess formaldehyde and the theoretical formaldehyde to phenol (F:Ph) mole ratio ranges between 1.0 to 3.0 while in practice, it usually varies between 1.6 and 2.6.

The polycondensation process of resol PF adhesives proceeds according to the following three steps:

A-Stage: Addition

During this stage, an aqueous solution of formaldehyde (formol) reacts with phenol in the presence of a base to produce a hydroxymethylated phenol (HMP).

Formaldehyde in an aqueous medium is subjected to a very fast hydration reaction which results in its conversion to methylene glycol [34]. Methylene glycol is also obtained by dissolving paraformaldehyde (solid formaldehyde) in water. In the presence of a base, which is usually sodium hydroxide, phenol undergoes deprotonation of the phenolic hydroxyl group. The phenoxide ion is resonance stabilized. (Figure 25)

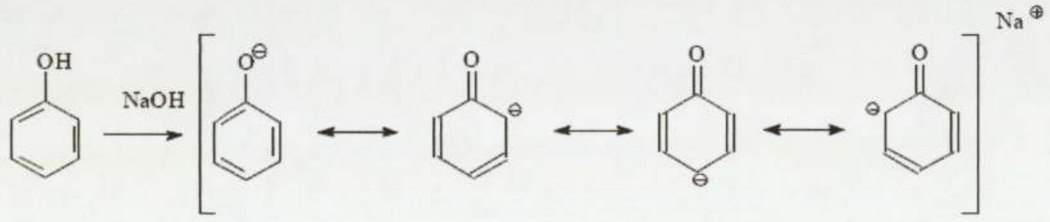


Figure 25: Reactive phenoxide ion under basic conditions

The ionization strengthens the function of phenol as a nucleophile and formaldehyde is attached to the phenolic ring at the ortho and para positions via electrophilic substitution reaction forming a methylolphenol (Figure 26).

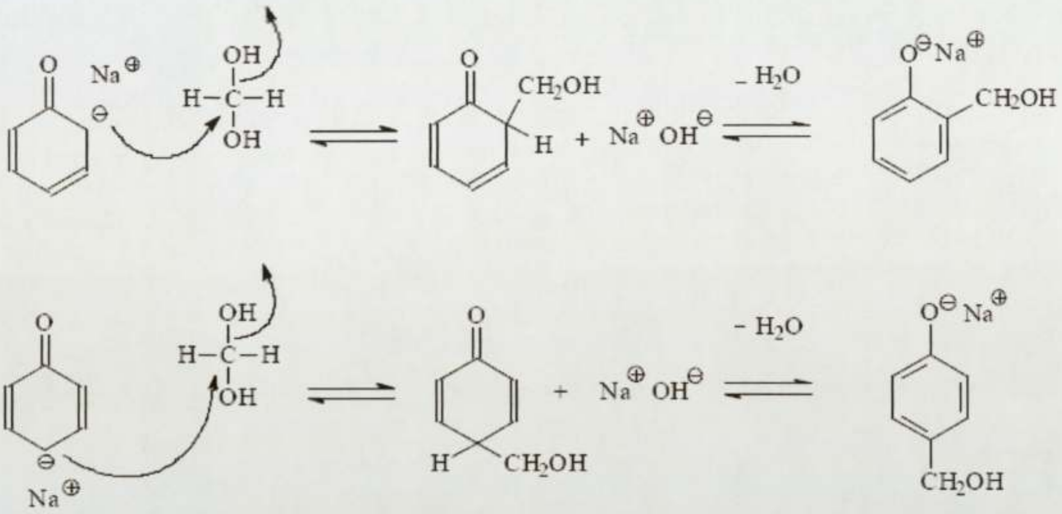


Figure 26: Electrophilic aromatic substitution of methylene glycol on phenol ortho and para positions

The methylolation reaction proceeds with no special preference for the ortho or para substitution. However this can be achieved using special catalysts [35]. The methylolation is strongly exothermic and can involve the risk of an uncontrolled reaction [36]. A typical product mixture comprises mono-, di- and tri-substituted hydroxymethylated phenols (HMPs). In fact, aromatic substitutions of formaldehyde on mono-and di-substituted HMPs proceed at a faster rate than the initial hydroxymethylation thereby yielding high proportions of difunctional and trifunctional derivatives [10]. This is a result of the activating effect of the hydroxymethyl group on the aromatic ring. Excess formaldehyde may also react with phenolic hydroxymethyl groups to produce substituted hemiformal moieties (figure 27).

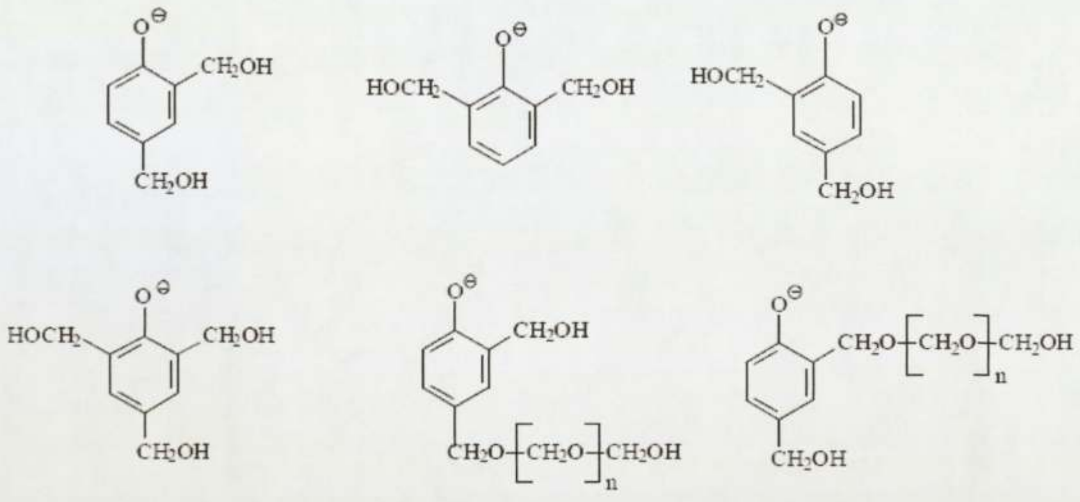


Figure 27: HMP derivatives

At this stage, HMPs are prone to condensation reactions.

B-Stage : Condensation of HMPs

HMPs undergo a step growth condensation reaction which results in the formation of macromolecules of various molecular weights (polymer chain). This reaction normally occurs in a temperature range of 60°C to 100°C. The condensation reactions of methylol phenols have been investigated in particular by three research groups led by Zinke [38], von Euler [39] and Hultzsch [40]. Even though there is not total agreement over the reaction mechanisms proposed by these groups, there is agreement on the two reactions for the formation of the pre-polymer. These involve the linking of methylene phenols through methylene and methylene-ether bridges (figure 28)

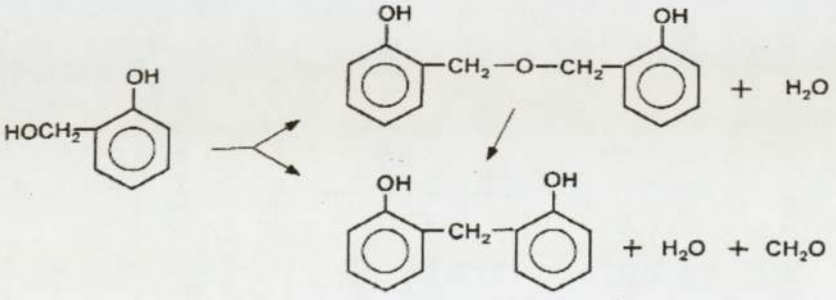


Figure 28: Formation of methylene and methylene-ether bridges in PF adhesive

The formation of dibenzyl ether bridges is very unlikely under strong alkaline conditions and requires temperatures as high as 130°C [37]. In addition, methylene ether bridges tend to convert to the more stable methylene bridges upon additional heating [41].

Von Euler [39] and Hultzsch [40] proposed quinone methides (QM) as intermediates both for the pre-polymer formation (stage 2) and the heat curing of resols (stage 3). (figure 29).

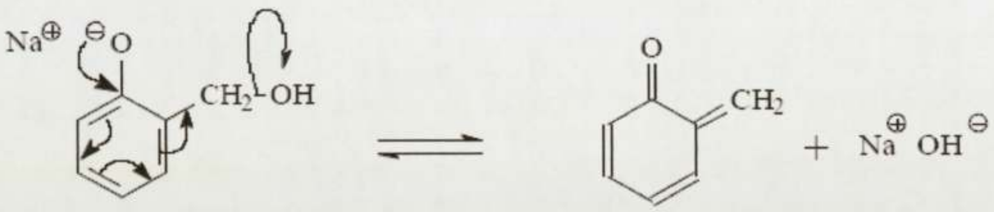


Figure 29: Quinone methide formation from HMPs

Quinone methides are very reactive and react with nucleophilic sites from other phenol or substituted phenol. At this stage, methylene and methylene-ether bridges are generated between HMPs (figure 30).

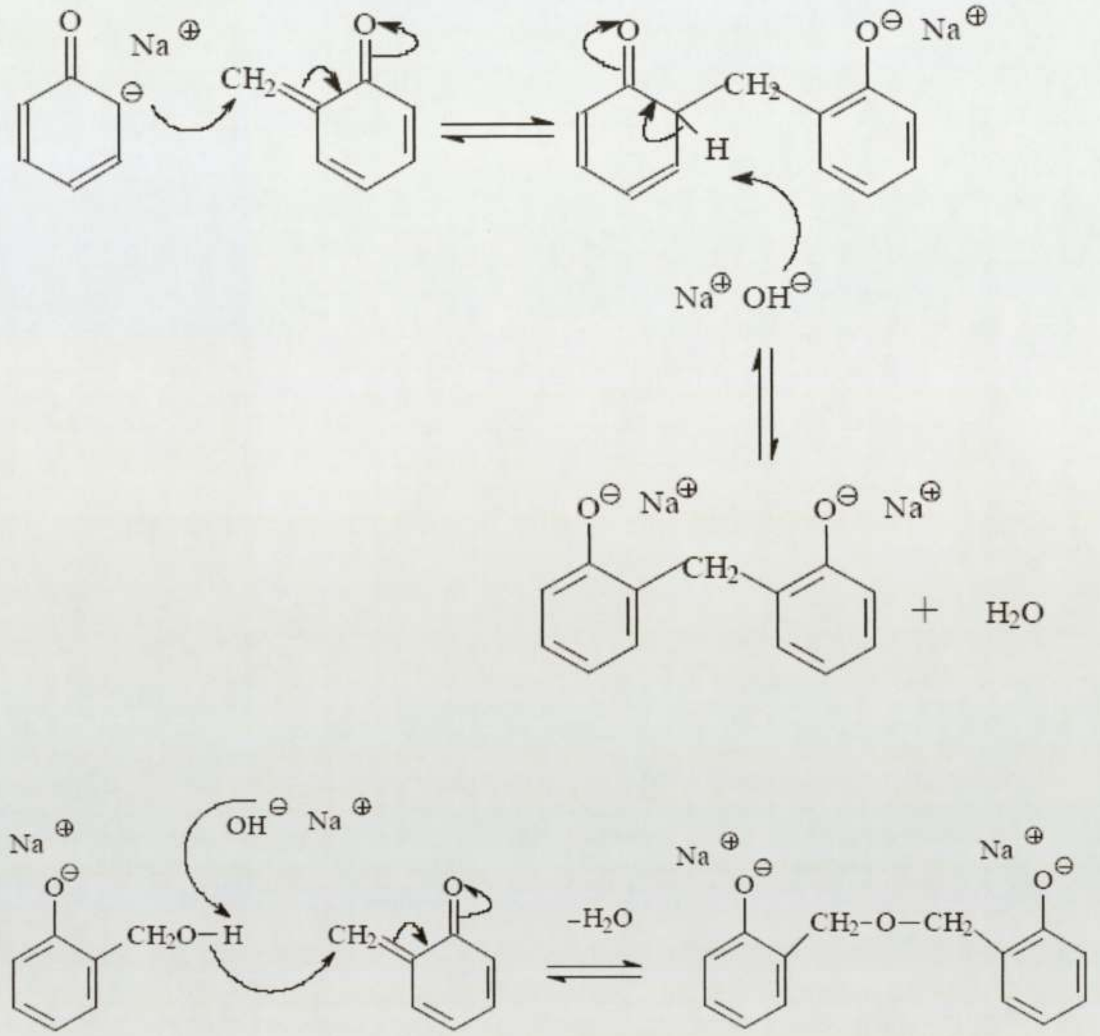


Figure 30: Mechanisms for the formation of methylene and methylene ether bridges

As the polycondensation reaction progresses, the molecular weight of oligomers increases. Usually the condensation reaction is stopped, as soon as the desired molecular weight, which is indicated by measurement of the relative viscosity, is reached.

The resulted prepolymer that is commonly known as resol consists of macromolecules (chains) with various molecular weights and is partially cross-linked [42] (figure 31).

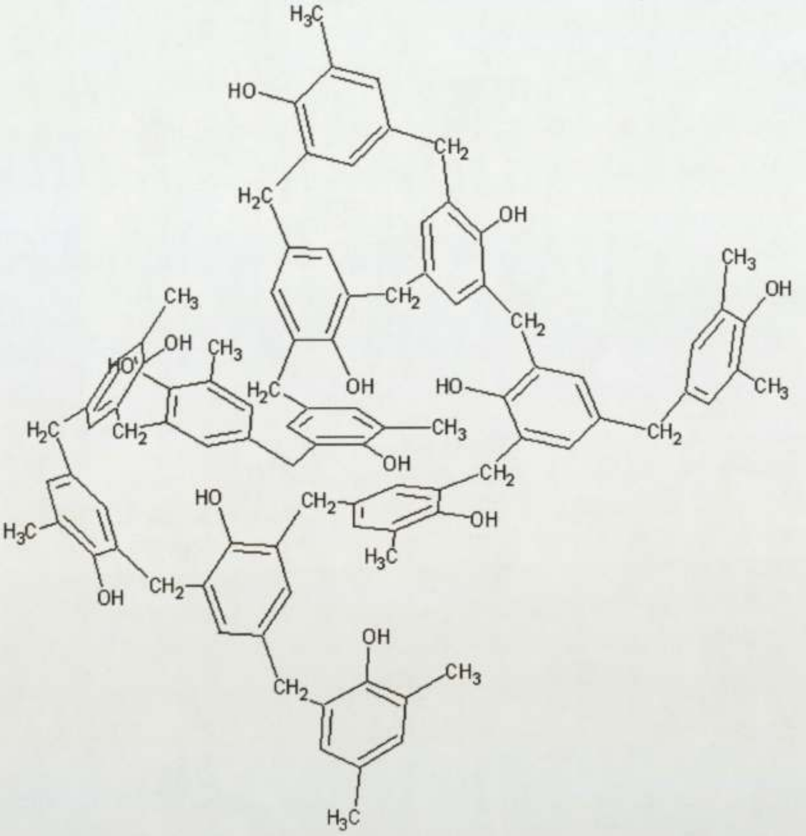


Figure 31: Example of a possible structure for resol phenol-formaldehyde adhesive [31]

In the alkaline catalysed process, formaldehyde addition to phenol is faster than the subsequent step of oligomers formation. Thus the latter step is the one which determines the rate of the total reaction while, the predominant intermediate compounds are the phenol alcohols. Hence, high formaldehyde levels can be used without endangering the formation of the final polymer until sufficient heating is applied. Of course, in any case the formaldehyde to phenol (F:Ph) mole ratio is kept lower than 3, which allows the generation of oligomers with a sufficiently cross-linked backbone and some available reactive sites that may be further cross-linked under proper heating [25].

C-Stage: Curing of PF pre-polymers

The final curing (hardening) of PF pre-polymers is conducted at temperatures between 130°C and 200°C. This is implemented during the wood panel manufacturing process, whereby links develop thermally among the macromolecules (curing process). No catalyst is necessary for curing but when it is used, it is with the view of accelerating the curing of the adhesive.

Using solid state ^{13}C-NMR study of resol adhesives Marciel [43] has suggested the following reaction schemes for the thermal curing of resols:

a) direct involvement of the hydroxyl group of phenol (figure 32)

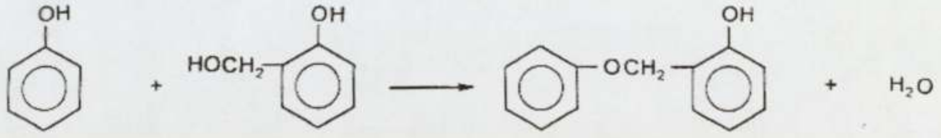


Figure 32: Cross - linking of phenols with ether bridge

b) condensation of methylene bridge with hydroxymethyl group (figure 33)

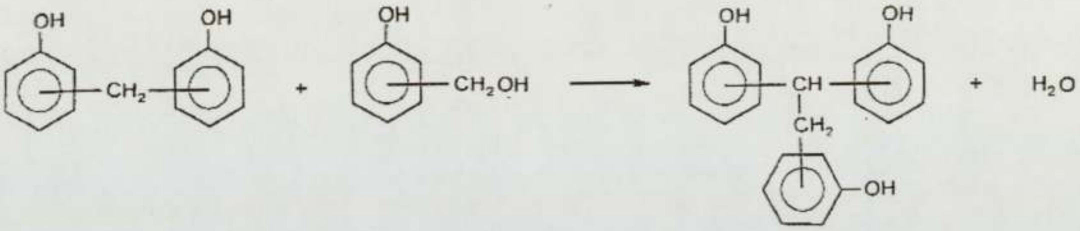


Figure 33: Formation of oligomers

c) cross - linking of methylene bridges with formaldehyde liberated during cure, as proposed by Zinke [38] (figure 34).

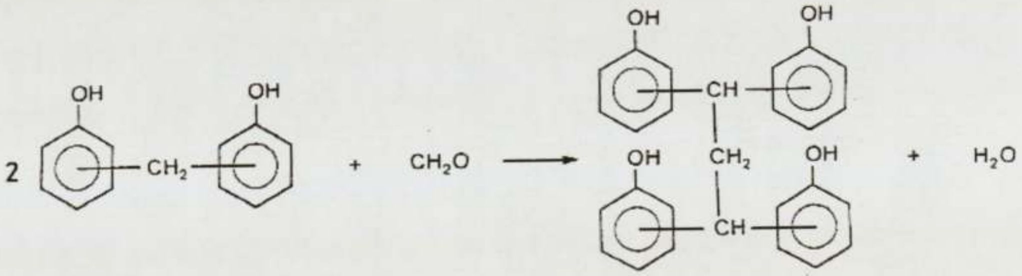


Figure 34: Formation of polymer network

Once formed, the phenol-formaldehyde polymers are extremely stable and do not break down into phenol and formaldehyde molecules.

Even though both types of phenolic adhesives may provide bonding with wood substrate, only the resol adhesives are used in the wood-based panels industry probably because Novolak oligomers have low water solubility while the acids used in the synthesis not only degrades wood but also are corrosive to the processing equipments used in the wood-based panels production [25].

6.4 Parameters that affect the performance of resol PF adhesives

The parameters that define the performance of a PF adhesive are related to variables used in their synthesis and application.

Namely:

6.4.1. Variables during the synthesis of the adhesive

1. Formaldehyde/phenol molar ratio
2. Type of catalyst
3. Non volatile content
4. Raw material quality
5. Additives (i.e. substituted phenols)
6. Order of addition
7. Temperature profile
8. pH profile
9. Molecular weight
10. Molecular weight distribution
11. Degree of molecular branching
12. Miscellaneous colligative properties (i.e. final viscosity, % non-volatiles, gel time)

Studies have been carried out for each of the above-mentioned variables and it is well established that the interactions of all the above-mentioned parameters determine the characteristics of the final product (wood panel). In particular, the effect of some of the most significant variables mentioned above is:

Formaldehyde/phenol molar ratio

In general, high F:Ph mole ratios produce highly branched adhesives while low F:Ph ratios favour more linear structures. As expected, higher F:Ph ratios were found to enhance hydroxymethylation and increase the degree of polymerization

[44]. Moreover, the reactivity, the storage stability are increased proportional to the increase of the F: Ph mole ratio even though it is at the expense of the plasticity of the adhesive since high degree cross-linking increases the brittleness of the adhesive.

Type of Catalyst during adhesive synthesis

Commonly NaOH is used as a catalyst for the synthesis of a PF adhesive in amounts up to one mole per mole of phenol which corresponds to a level of alkali in the liquid adhesive of approx. 10%. The pH of the phenolic adhesive is in the range 10-13. The largest part of the alkaline is free NaOH, while a smaller part is present as sodium phenolate. The alkaline is necessary to keep the adhesive water-soluble via phenolate formation, in order to achieve a degree of condensation as high as possible at a viscosity which still can be used in practice. The addition of alkali drops the viscosity of the reaction mix [12]. This happens because of the ability of sodium hydroxide (NaOH) to disrupt inter-molecular hydrogen bonding in phenolic polymer chains and thus reduce the viscosity. By reducing molecular interactions, sodium hydroxide reduces the resistance to shear and thins the adhesive [29]. The higher the alkaline content, the higher is the possible degree of condensation of the adhesive at a constant and technically usable viscosity; hence the higher is the hardening reactivity of the adhesive.

Hse [45] studied the influence of varying F:Ph and NaOH:Ph molar ratios on the bond strength of experimental panels of Southern pine plywood. Adhesive shrinkage during cure correlated inversely with bond quality; namely the poorer bonds were associated with greater adhesive shrinkage. Cure shrinkage was generally found to increase as the NaOH:Ph molar ratio increased.

Basic catalysts other than NaOH may also be used like $Ba(OH)_2$, LiOH, Na_2CO_3, hexamethylenetetriamine etc. The type of catalyst significantly determines the properties of the adhesive [46]. Replacing the alkali in PF-bonded panels gave some advantages. In particular, Wagner and Greff [47] used ^1H NMR spectroscopy to study the effects of catalyst and F/P molar ratio on liquid resol adhesive structure. They concluded that barium hydroxide was more ortho directing than either sodium hydroxide or hexamethylenetetriamine. Barium hydroxide would be expected to produce more linear polymer than the other catalysts because of its ortho directing mechanism.

Referring to metal hydroxides, It has been recognized that the ortho substitution is considerably enhanced in metal hydroxides catalysts in the following sequence: K<Na<Li<Ba<Sr<Ca<Mg [13].

Additives-Modification of phenolic adhesives

Urea and resorcinol are believed to increase the curing time of PF resol adhesives.

A kinetic study by Guangho and Bernard [48] indicated that the activation energy of PUF adhesives are generally higher than those of phenol-formaldehyde (PF) adhesives during curing processes, but the curing rates of PUF adhesives are faster than those of PF adhesives.

A co-condensation between phenol and urea can be performed in two ways:

a) reaction of methylolphenols with urea [49, 50, 51, 52]. The kinetics of this co-condensation reaction is reported by Yoshida et al. [53] and Pizzi et al. [54].

b) acidic reaction of UFC (urea-formaldehyde concentrate) with phenol followed by an alkaline promoted reaction [55].

Resorcinol has two meta-hydroxyl groups which accelerated and improved the cross-linking of the phenol-formaldehyde adhesives [29].

Final Viscosity-Degree of condensation

As for all condensation adhesives, the viscosity increases as the condensation degree is increased. The contact angles of phenolic adhesives on wood increase strongly with a higher viscosity of the adhesives, according to higher molar masses [56]. An acceleration of the hardening reaction is possible by using as high a degree of condensation as possible. Thicker glue gave superior bonds.

6.4.2. Variables related to the application of the adhesive

1. Hardeners/cure accelerators
2. Extenders and fillers
3. Properties of wood

Even although all of the above-mentioned variables have significant role in the quality of the final product (panel), the one that is most crucial for industry is the utilisation of hardeners or cure accelerators because it reduces production times. The use of propylene carbonate as an accelerator to hardening a PF adhesive has been reported by Pizzi et al. [54, 57, and 58], Riedl and Park [59], Steiner et al. [60], Tohmura [61] and Naruyuki et.al [62]. The mechanism of this acceleration however is not yet clear. It might be due to the formation of hydrogen carbonate ion after hydrolysis of the propylene carbonate or due to the formation of hydroxybenzyl alcohol and aromatic carbonyl groups in the reaction of the propylene carbonate with the aromatic ring of the phenol [32]. Naruyuki et.al [62] claims that propylene carbonate increases the reactivity of the ortho hydroxymethyl group, presumably through the transesterification proposed by Miller and Detlefsen [63]. The higher the addition of propylene carbonate, the lower is the gel time of the PF adhesive [54].

Other accelerators for PF adhesives are potassium and sodium carbonate [60] or sodium and potassium hydrogen carbonate.

6.5 Properties of resol phenol-formaldehyde adhesives

The colour of resol phenol-formaldehyde adhesives varies from dark yellow to brown.

Resols are known to be thermally stable at temperatures up to 240°C, but above this temperature their molecular bonds degrade gradually. At about 400-600°C, random chain scission mostly takes place rather than depolymerisation [13] but above this temperature the polymer decomposes rapidly yielding a large amount of phenols, aldehydes and char [13, 29].

The PF resol adhesives in their A-stage are soluble in water, alcohol, esters, ketones, phenols and some ethers but insoluble in hydrocarbons and oils [29].

Early in the B-stage they are still soluble in water because of the presence of methylolphenols but they have limited solubility in other solvents [29]. At this stage the adhesives react at alkaline pH that varies from 7 to 13.

When prepared from pure phenol and formaldehyde their stability is about 9 months at 5-10°C.

Usually they are available in the market with viscosities above 100 cP at 20ºC and solid content ranging from 40-45% providing that no other additives have been used.

In the C-stage where the adhesive hardens, they are stable to water and resistant to the most ordinary acids except sulphuric acid (when the concentration is more than 50%), formic acid and oxidizing acids such as nitric and chromic acids. They also dissolve in boiling phenols and hot, strong alkali solutions [29].

Phenol-formaldehyde adhesives are more expensive than other common formaldehyde adhesives (urea-formaldehyde and melamine-formaldehyde) but they are more heat and water resistant since the C-C bonds produced are stronger than the C-N bonding present in urea or in melamine. Their higher thermal stability is the reason for them being called thermosets. Their strong C-C bonding is also the reason for the very low formaldehyde emissions.

The major disadvantage of phenol-formaldehyde adhesives is the toxicity of the raw materials and the risk of handling them during the manufacture of PF polymer. Phenol is a highly toxic compound causing protein denaturing and tissue erosion while aqueous formaldehyde is a protoplasmatic poison and it is suspect for carcinogenesis. Both aqueous and gaseous formaldehyde are very irritating in contact with skin, eyes, nose, throat and lungs. Nevertheless, the polymerized product does not have the same toxicity as its raw materials, the free phenol and formaldehyde content in a cured PF adhesive is extremely low and practically non detectable [13].

6.6 Applications

Nowadays PF resol adhesives are used in the production of wood-based panels, of all kinds, but their main application is in plywood (PW) and oriented strand boards (OSB) production.

There is a large literature on phenol-formaldehyde adhesives depending on their applications including wood-based panels, molding compounds, coatings, foundry adhesives, abrasive materials, friction materials etc [13].

7. FAST PYROLYSIS Liquid (BIO-OIL)

7.1.General

Bio-oil is a biomass-derived renewable liquid that can be used for fuel and production of chemicals. In literature references, bio-oil may also be found under other synonyms, including pyrolysis liquid, pyrolysis oil, crude bio-oil, wood oil, bio fuel-oil and liquid wood [64]. The term biomass is used to characterize any living and recently dead biological material, including plant matter, such as wood, agricultural plants and wastes or other living-cell material as well as animal matter that can be used either as a source of energy or for its chemical components [65]. There is a tendency to use the term 'bio energy' for biomass energy systems that produce heat and/or electricity and 'bio fuels' for liquid fuels for transportation. In general, biomass is converted through the following pathways:

1. Physical
2. Biological
3. Thermal
    - Combustion (excess air) for heat production
    - Gasification (partial air) for fuel gas production
    - Pyrolysis (no air) for bio-oil production

The pyrolysis process is available in various modifications (fast, slow, gasification) but the fast pyrolysis of biomass is one of the most recent renewable energy processes to have been introduced.

7.2 Bio-oil from fast pyrolysis method

Fast pyrolysis as a modification of flash pyrolysis is a process in which finely grounded organic material is decomposed, under rapid heating to 450-600°C without oxygen, to yield primarily volatile products and secondary charcoal and gas. The volatile products are very quickly cooled (<2sec) to produce liquids (bio-oil) [64]. A description of the biomass fast pyrolysis process is shown in the following figure 35 [66].

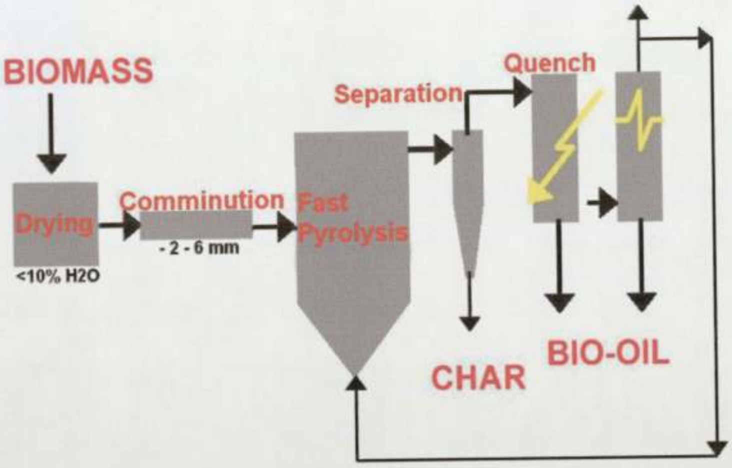


Figure 35: Fast pyrolysis process-general layout [66]

The most common types of reactors used for fast pyrolysis processes are [64, 67]:

- Bubbling fluidized bed
- Circulating fluidized beds/transport reactor
- Rotating cone pyrolyzer
- Ablative pyrolyzer
- Entrained flow pyrolyzer
- Vacuum pyrolysis
- Auger reactor

The type of reactor used is dictated by

i. the biomass material (feedstock) used,
ii. the kind of chemical process applied,
iii. the char removal system,
iv. the condensation system.

A typical composition of pyrolysis oil produced by the fast pyrolysis method is shown in the following table 5.

Table 5: Products of biomass fast pyrolysis

Bio-oil	60-70%,
charcoal	12-15%,
gas (CO, H_2, light hydrocarbons)	13-25%

Generally, wood feedstock (trees and forestry residues) give higher yields of oil than herbaceous biomass [4], while liquid yields decrease at high temperatures and/or long residence times before condensation of the liquid products [69, 70] (figure 36).

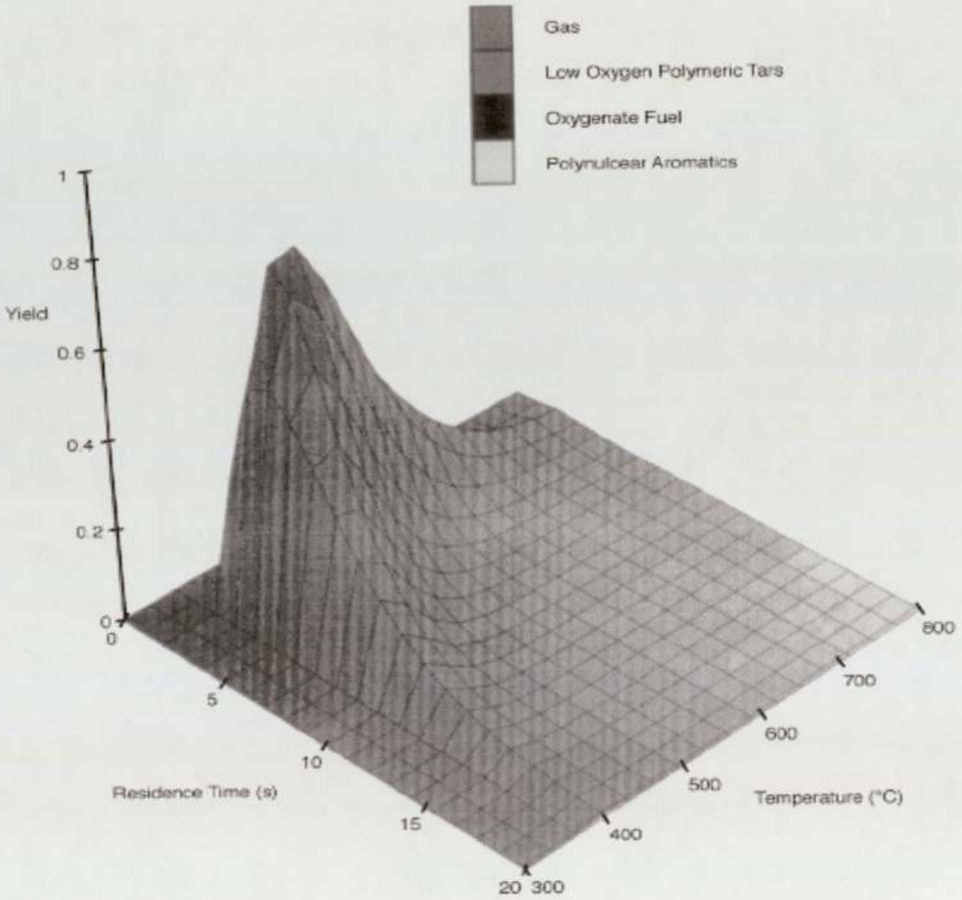


Figure 36: Illustration of fast pyrolysis oil yield and composition depending on the pyrolysis conditions [70]

The pyrolysis liquid (bio-oil) may be upgraded by elimination of oxygen content in order to overcome its inherent deleterious properties like high viscosity, thermal instability and corrosiveness and thus promote its candidacy as a fossil fuel substitute. The upgrading procedure involves various physical and chemical processes. Namely [71, 72]:

- Physical methods: filtration to remove char, steam reforming, emulsification with hydrocarbons, solvent addition.
- Chemical methods: chemicals extracted of the bio-oil, catalytic deoxygenation (hydrotreating, catalytic cracking of pyrolysis vapours).

7.3 Typical composition of pyrolysis liquid (bio-oil)

The chemical composition of the fast pyrolysis liquid is very complex since the degradation of lignin, cellulose and hemicelluloses gives a wide range of chemical compounds. The oil generated after the rapid cooling of vapours may be considered as a micro-emulsion in which the continuous phase is an aqueous solution of cellulose and hemicelluloses decomposition products, while the discontinuous phase consists of pyrolytic lignin macromolecules [69]. The recovery of chemicals requires effective separation schemes. The simplest approach is to separate hydrophilic (water soluble) and hydrophobic (water insoluble) fractions by water addition that induces phase separation.

The water insoluble fraction (precipitated hydrophobic material) consists of high molecular weight material derived mostly but not exclusively from lignin which is called "pyrolytic lignin". It comprises approximately 20% of the total bio-oil and can be used in any known lignin application with advanced performance compared to the lignin derived from the pulping process, since pyrolytic lignin is a degraded product and therefore is of lower molecular weight while it also has a greater ratio of phenolic to methoxy groups [73].

The chemicals in the water soluble fraction (approximately 80% of the total bio-oil) may be further separated into two groups, by extraction with an organic solvent (e.g. diethyl ether, ethyl acetate, etc) [73].

- The organic solvent insoluble fraction includes products of incomplete destruction of the carbohydrate complex of biomass (cellulose & hemicelluloses), hydroxy acids and anhydrosugars (levoglucosane and cellobiosan) [74].
- The organic solvent soluble fraction includes two categories of compounds [74]:

- *Volatile*: small aldehydes (acetaldehyde, 2-furaldehyde and 5-methyl-2-furaldehyde) and ketones (1-hydroxy-2-propanone, 1-hydroxy-2-butanone, etc)
- *Volatile vapour*: straight chain aldehydes with main compound the hydroxyacetaldehyde and furan derivatives, straight chain and ring ketones as well as lignin monomers like guaiacol, phenol and catehol derivatives.

The chemicals present in bio-oil in highest composition are presented in the table 6. Altering the pyrolysis regime (e.g. heating rate and residence time of vapour-gas mixture in the reaction zone) causes substantial variations in the content of the organic substances in the fractions of bio-oil [69, 70]. Alteration to the composition of bio-oil occurs also during storage [68].

Table 6: Main components of Bio-oil

Fraction	**Major components**		**Mass, %**
	Water		20-30
Water insoluble	Lignin fragments	Insoluble pyrolytic lignin	15-30
Water soluble	Aldehydes	Formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal, methylglyoxal	10-20
	Carboxylic acids	Formic, acetic, propionic, butyric, pentanoic, hexanoic, glycolic (hydroxyl acetic)	10-15
	Carbo-hydrates	Cellobiosan, a-D-Levoglucosan, oligosaccharides, 1,6 anhydroglucofuranose	5-10
	Phenols	Phenol, cresols, guaiacols, syringols	2-5
	Furfurals		1-4
	Alcohols	Methanol, ethanol	2-5
	Ketones	Acetol (1-hydroxy-2-propanone), cyclopentanone	1-5

The compounds available from bio-oil are classified into the following categories (table 7) [69].

Table 7: Classification of bio-oil components

C1:	formic acid, methanol, formaldehyde
C2-C4:	Linear hydroxyl and oxo substituted aldehydes and ketones
C5-C6:	Hydroxyl, hydroxymethyl and/or oxo substituted furans, furanones and pyranones
Anydrosugars:	Levoglucosan, anhydro-oligosaccharides
Substituted phenols	Monomeric and dimeric methoxyl substituted phenols
Pyrolytic lignin	
Waxes, fatty acids, adhesives, terpenoid derivatives	

7.4 Physical properties of pyrolysis liquid (bio-oil)

Bio-oil can range in colour from dark green or dark red through to black, depending upon the feedstock and process used to manufacture the product. Its elemental composition is dependent on the feedstock from which it was derived. Some typical properties and characteristics of wood derived bio-oil are cited in the following table 8 [69, 75, and 76].

Table 8: Typical properties and characteristics of bio-oil

Physical property	**Typical values for wood bio-oil**
Moisture content, %	20-30
pH	2.0 – 3.7
Specific gravity	1.1-1.3
Viscosity (at 40°C & 25% water), cp	40-100
Solids (char and sand), wt-%	1%
HHV (depends on moisture), MJ/kg	16-21
LHV, MJ/kg	13-18
Flash point, °C	50-110
Elemental analysis:	
C	55-58%
O	35-40%
H	5.5-7.0%

Some 200 compounds have been identified in the oils [77, 78] but water holds the highest percentage of a single ingredient as it cannot be readily separated because of the hydrophilic nature of aldehydes and ketones which are abundant in the composition of bio-oil [72].

The high oxygen content imparts hydrophilicity to bio-oil, leads to lower energy density than fossil oil (~50%) and immiscibility with the petroleum-derived fuels (hydrocarbon fuels); though it has some potential for blending with petroleum if appropriate technologies are used [72].

Bio-oil has a distinct smell, often described as acrid and smoky. This smell is attributed to the low molecular weight aldehydes and acids [69]. The low pH caused mostly by carboxylic acids makes the oil highly corrosive to some containers. The corrosiveness to carbon steel and aluminium is especially severe at elevated temperatures but bio-oil is non-corrosive to stainless steel and polymeric materials [78].

Bio-oil is combustible and chemically unstable over time or when exposed to high levels of heat because of its high acidity. As bio-oil ages, the viscosity increases, the volatility decreases, and eventually phase separation occurs.

7.5 Chemical reactivity of pyrolysis liquid during storage

The composition of bio-oil includes a wide range of chemical compounds and thus various reactions may occur during storage. The main of these are: [78, 79]:

1. Acids and alcohols react to form esters and water
2. Aldehydes react:
    a. with water to form hydrates (also referred to as glycols), even although hydrates are not stable and the reaction of their formation is reversible. Nevertheless, not all aldehydes have the same equilibrium constant i.e. formaldehyde has a good yield but acetaldehyde not [68]
    b. with alcohols to form hemi-acetals, acetals (ethers) and water
    c. to form oligomers and adhesives
    d. with phenolics in the acidic bio-oil to form novolak adhesives and water
    e. with proteins to form dimers
3. Thiols (mercaptans) react to form dimers
4. Olefins polymerise to form oligomers and polymers
5. Atmospheric oxygen reacts with many of the organics present to form peroxides which catalyse the polymerisation of olefins and the addition of thiols to olefins

Organic acids and the elements commonly found in the char can act as catalysts for many of the above reactions.

As a fuel, bio-oil can be processed to obtain many other useful products (Bio refinery) but it can also be used as a chemical resource without separation. Even although bio-oil consists of a wide range of substances, the most abundant are potential candidates for chemical stocks. Control of conditions can result in an oil that is particularly high in compounds such as phenol, and this can be used directly to make phenolic adhesives for plywood and OSB manufacture.

Because of its high content in carbonyl groups bio-oil can react with ammonia, urea or other compounds with amine groups resulting in a cocktail of non-toxic compounds suitable for use as slow-release fertilisers through the formation of imide and amide bonds [80]. Reaction of the carbonyl and carboxyl groups with ethanol, which itself can be produced from renewable resources, gives a mixture that is more stable than raw bio-oil.

7.6 Prior Art of pyrolysis liquid-based adhesives

The principal intention of biomass fast pyrolysis was the production of combustion and transportation fuel and fuel for electric power. Secondly, the presence of a wide range of chemical substances has motivated its use as a renewable source for the production of chemicals.

Bio-oil is utilized in the industrial production of anhydro-sugars like levoglucosan, while some of its aldehyde components are used as liquids for smoking food. The unrefined bio-oil has been proposed as a wood preservative, that could replace creosote [80].

Fast pyrolysis oil without separation can be used for phenol replacement, up to 50%, in the formulation of PF adhesive for wood-based panel production. Such adhesives were comparable in performance with commercial PF adhesive in 3-ply plywood production [81].

The whole of bio-oil from wood or bark was also used as a phenol substitute up to 50% in resol type PF adhesives. These adhesives when used in preparing OSB or plywood panels they had performances comparable if not superior to a conventional PF adhesive [82].

The enrichment of the unfractionated pyrolysis oil with phenolics from other renewable natural resources like lignin from the pulping industry (alkaline spent liquor) and/or cashews nut shell liquid (CNSL) has proved sufficient to enable phenol replacements up to 80% in resol PF adhesive formulations suitable for most of the wood-based panels types (PB, OSB, MDF, PW, etc). The involvement of tannin adhesive and/or diphenylmethane diisocyanate to this modified PF adhesive is claimed to improve its performance [83].

A process for extracting the phenol/neutral fraction from pyrolysis oil derived from hardwood, softwood and bark residue, using a solvent extraction technique has been developed [84, 85]. The extracted fraction was mixed with pure phenol (50:50) and polymerized with formaldehyde. The adhesives produced compared very well with commercial PF adhesives in plywood applications. However, the lengthy solvent extraction method, associated with a relatively low phenol/neutral fraction yield, makes the process economically inefficient.

Selected bio-oil compounds were recovered and used as a natural adhesive precursor either in liquid or in solid form. This reactive material is claimed to comprise up to 80% phenolic material derived from lignin decomposition and has been found to be suitable for replacement of phenol or both phenol and formaldehyde up to 60% in PF resol adhesive formulations [86, 87].

8. CASHEWS NUT SHELL LIQUID – (CNSL)

8.1 General

The evergreen cashew tree (Anacardium occidentale) is native to north eastern Brazil. Centuries ago it was introduced to the West Indies and Asia. Today it grows worldwide in the tropics and especially in Brazil and India. On the cashew tree there is an oval or pear-shaped "pseudo fruit" called the cashew apple as well as a true fruit which is kidney or boxing- glove shaped stone fruit called a cashew nut. Actually, the stone fruit develops first on the tree, and then the peduncle expands into the pseudo fruit [88]. The nut grows to 2.5-4.0 cm long. Its shell is about of 0.3 cm thick with soft honeycomb structure containing a dark reddish brown viscous liquid called Cashew Nut Shell Liquid (CNSL) [88, 89]. The shell comprises about 50% of the weight of the raw nut, the kernel is about 25% and the CNSL represents the remaining 25% of the weight of the cashew apple [90]. Cashew nut shell liquid (CNSL) is obtained as a by-product of the cashew nut industry.

CNSL is a mixture of *meta*-alkylphenols with variable degrees of unsaturation attached to the benzene ring. Crude cashew nut shell liquid represents one of the major cheapest sources of naturally occurring non-isoprenoid phenolic lipids such as anacardic acids, cardols, cardanols, and methylcardols [91] (figure 37).

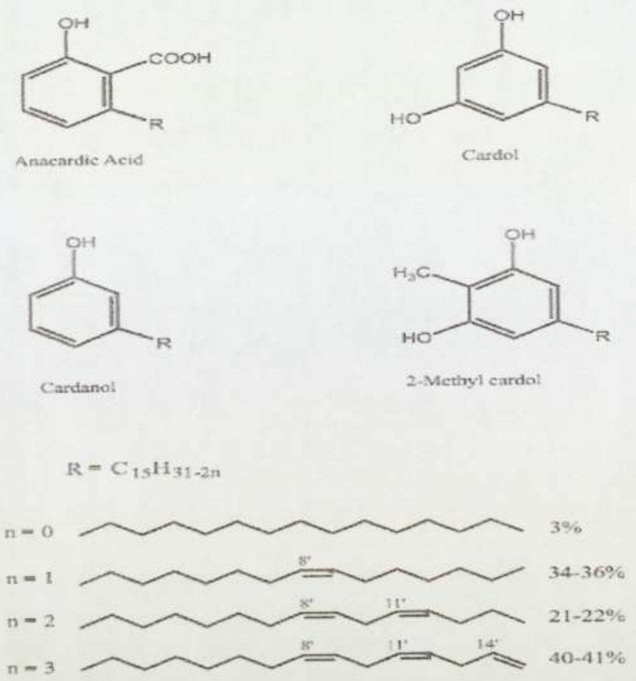


Figure 37: Structures of CNSL constituents

8.2 CNSL separation methods

The processing of cashew nuts involves the conversion of raw in-shell cashew nuts to blanched graded kernels. There are three conversion methods used; drum roasting, oil bath roasting, and steam roasting. Among these, the drum roasting is the oldest and most widely used method since it is cheap and one of the safest from an environmental point of view. According to the description of the Directorate of Cashew nut and Cocoa Development (DCCD), India in the drum roasting method [92], the nuts are fed into a rotating red hot drum which ignites the shell and maintains its temperature because of the burning of the shell liquid. The drum is rotated for 3-4 minutes and the roasted nuts are discharged from the lower end of the drum and immediately covered by ash after sprayed with a little water, so as to absorb the oil on the surface. This facilitates the removal of the remaining oil from the shell.

Raw cashew nut shells contain about 20% oil. When raw cashew nuts are processed by an oil extraction process, about 50% oil is extracted. Balance oil (or liquid as it is known) can be further extracted with the help of expellers. Oil thus obtained, is filtered through a filter press and then weighed and packed in barrels. This is known as untreated CNSL. This oil can be further treated to remove metallic impurities and traces of sulphur compounds.

On the basis of the mode of extraction from cashew nut shell, CNSL is classified into two types: solvent-extracted CNSL and technical CNSL. These two grades have different composition because as the technical CNSL is obtained by roasting the shell at 180-200°C, the anacardic acid, which exists in solvent-extracted CNSL, is easily decarboxylated by heat and transformed into cardanol. The chemical composition of each type of CNSL is cited in the following table 9.

Table 9: Percentage composition of various CNSL types [91]

CNSL type:	Solvent extracted	Technical
anacardic acid	60-65%	-
cardol	15-20%	15-20%
cardanol	10%	60-65%
Polymeric material	-	10%
2-methyl cardanol	Traces	-
2-methyl cardol	-	Traces

The composition of the technical CNSL can change depending on the conditions of the roasting process and reach higher cardanol contents (83-84%), less cardol (8-11%) and maintain the polymeric material at 10% and 2-methyl cardol content at 2% [91].

8.3 Physical properties of CNSL

CNSL is a dark brownish liquid. The treated CNSL (free of metallic impurities and sulphur compounds) has a pH around 5.0, moisture content maximum 0.5%, ash content below 1% and specific gravity (at 25-24°C) 0.955 - 0.975. Its viscosity may vary from 150cP up to 800cP at 25°C [4].

8.4 Chemical reactivity of CNSL

Because of the phenolic nature and unsaturation of the side chain, CNSL offers reaction sites on the aromatic ring and also on the side chain which makes it a suitable raw material for a variety of reactions.

Concisely, CNSL can undergo the following polymerization reactions:

Addition polymerisation through the side chain double bonds using cationic initiators such as sulphuric acid, diethylsulphate etc.

Condensation polymerisation through the phenolic ring with aldehydic compounds like formaldehyde to give phenolic polymers.

Polymerisation after chemical modification to introduce speciality properties.

Oxidative polymerisation

Various combinations of the above.

8.5 Prior art of CNSL-based adhesives

According to literature reviews, CNSL has been used as a phenol substitute up to 95% for the preparation of either Novolac or resol adhesives [94]. Nevertheless, addition of CNSL seems to increase the reaction times and decrease the tensile strength of the products made from this mixture.

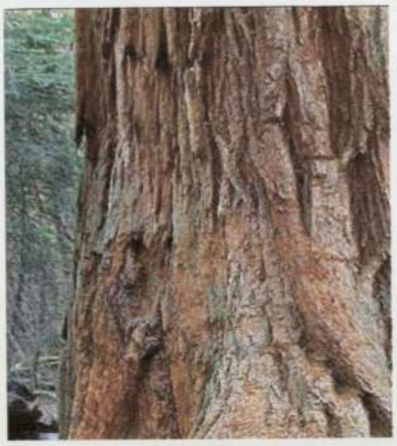
CNSL has also been used in a mixture with biomass pyrolysis oil and alkaline pulping spent liquor, to replace successfully up to 40% of phenol in resol phenol–formaldehyde adhesives suitable for wood-based panel production [83].

Currently, acid catalysed polymers of CNSL are being used as a component in the manufacture of friction dusts [12].

Traditionally, oxidation methods were used for adhesive development, but several synthetic steps were needed making the method economically inefficient. The Bio Composites centre (BC) in turn, utilised successfully the ozonolysis method, where similar reactive monomers were created through the cleavage of the double bonds into aldehydes with the participation of a solvent. The chipboards produced with such an adhesive at 10% addition performed properties comparable to that produced with a phenol-formaldehyde resol adhesive of petrochemical raw materials [95].

9. LIGNIN

9.1 General

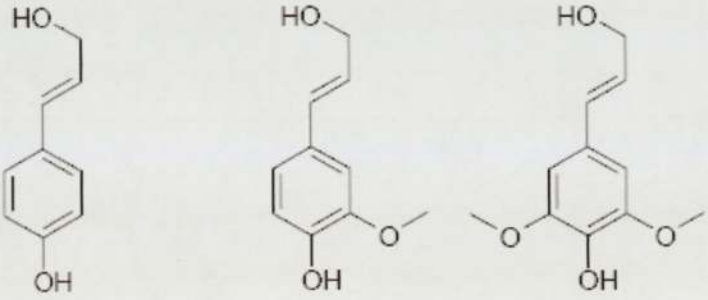


The word lignin is derived from the Latin word "lignum" meaning wood [96]. Lignin is an amorphous, heterogeneous phenolic polymer found in all vascular plants (trees, plants and agricultural crops) mostly between the cells, but also within the cells, and in the cell walls. It is covalently linked to hemicelluloses and thereby cross links different plant polysaccharides. Lignin is essential for the plants because it imparts mechanical support, seals the water conducting system which links the roots to the leaves and provides protection from biological degradation. After polysaccharides, lignin is the most abundant organic polymer in the plant world. The woody substance in softwoods contains 25-35% lignin while in hardwoods it is only 18-25% [96]. Lignin is formed in woody plants by a dehydrogenative polymerization of three phenylpropanoid monomers (figure 38). Namely [97]:

I. 3-(4-Hydroxyphenyl)-2-propen-1ol, (p-coumaryl alcohol) (I)

II. 3-(3-Methoxy–4-hydroxyphenyl)-2-propen-1-ol, (coniferyl alcohol) (II)

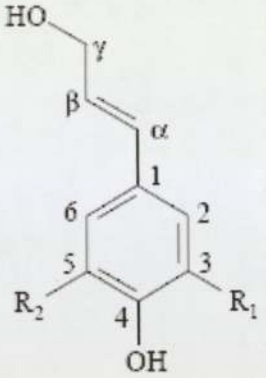
III. 3-(3, 5-Dimethoxy-4-hydroxyphenyl)-2-propen-1-ol, (sinapyl alcohol) (III)



(I) (II) (III)

Figure 38: The three monomeric units of which lignin consists p-coumaryl alcohol (I), coniferyl alcohol (II), sinapyl alcohol (III)

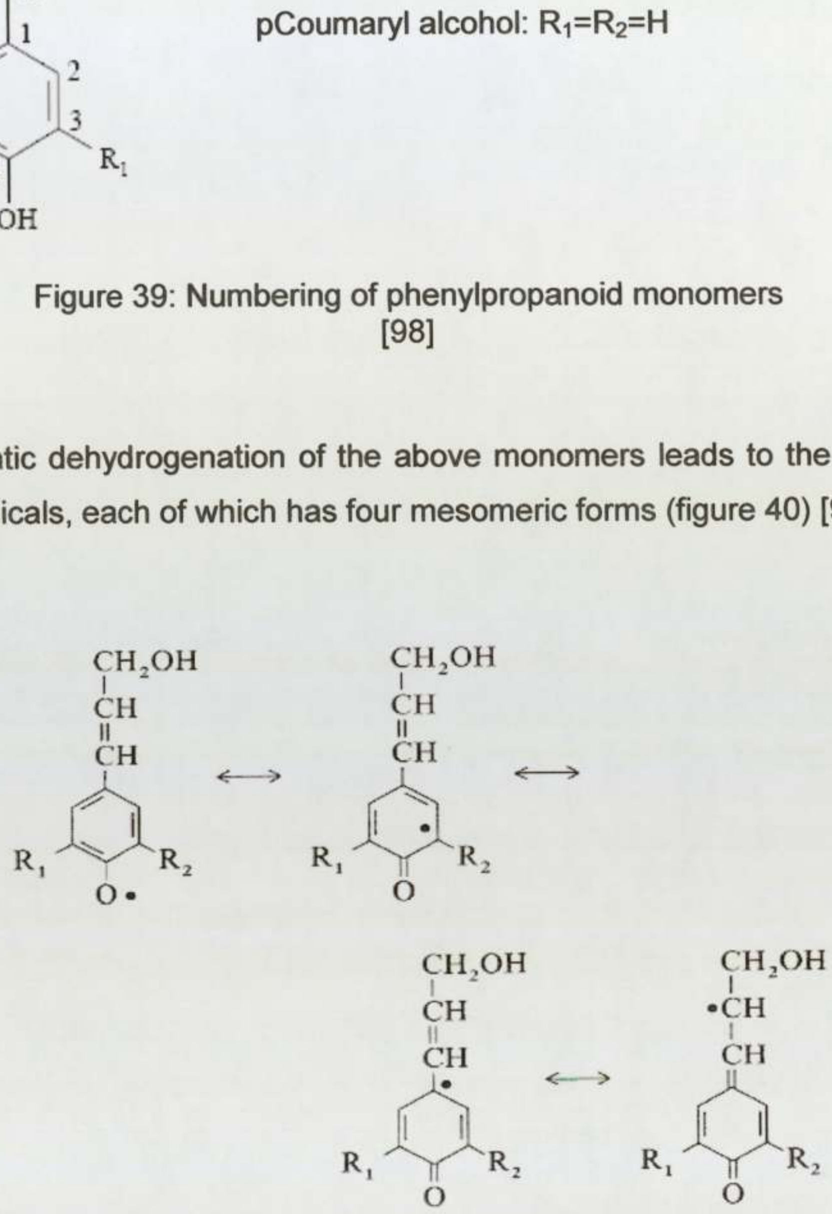
The various reactive positions of phenylpropanoid monomers are numbered as it is depicted in the following figure 39 [98].



Coniferyl acohol/guaiacyl: R_1=OMe, R_2=H
Sinapyl alcohol/syringyl: R_1=R_2=OMe
pCoumaryl alcohol: R_1=R_2=H

Figure 39: Numbering of phenylpropanoid monomers
[98]

The enzymatic dehydrogenation of the above monomers leads to the creation of phenoxy radicals, each of which has four mesomeric forms (figure 40) [97].



R_1, R_2 = H or OCH_3

Figure 40: Mesomeric forms of lignin monomer.

These radicals (monolignols) couple with one another at random via carbon–carbon and ether linkages, to give the three-dimensional network of the lignin polymer. The lignin polymer, unlike cellulose and proteins, lacks regularity in the order of repeating units while the relative amounts of the monolignol units differ considerably between plants. In softwoods the network of lignin is formed primarily by coniferyl moieties (95%), the rest consisting of p-coumaryl alcohol-type units and only trace amounts of sinapyl alcohol moieties, while in hardwoods and dicotyl crops like hemp and flax, a range of ratios of coniferyl/sinapyl have been reported [99]. Lignins derived from monocotyl plants (grasses and cereal straw) also contain significant amounts of p-coumaryl alcohol residues [99]. The structural models of spruce and beech lignins are shown in figures 41 and 42 respectively.

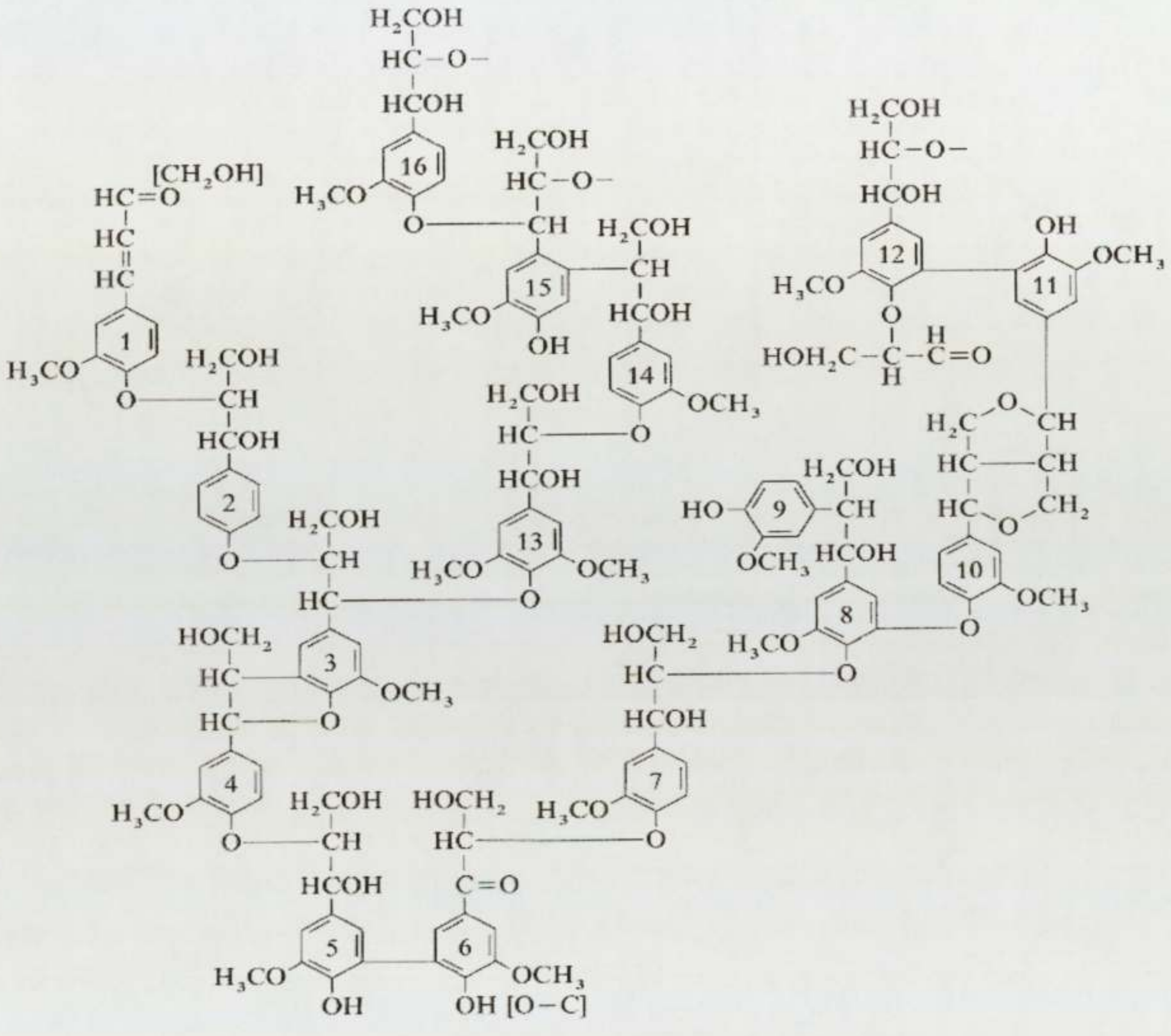


Figure 41: Structural model of spruce lignin

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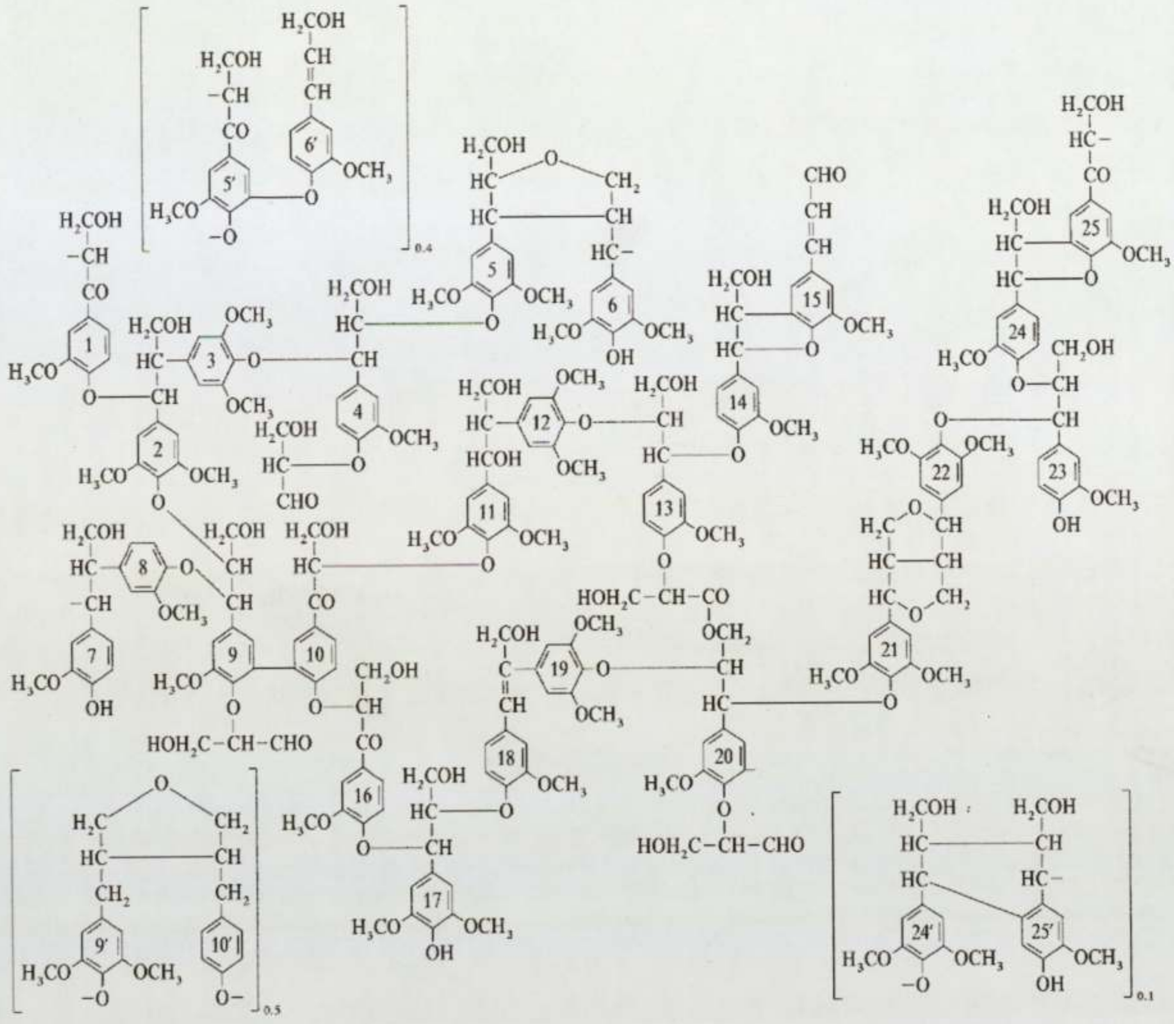


Figure 42: Structural model of beech lignin

Lignin products have become increasingly important in various industrial applications because they are derived from an abundant, renewable forest resource, are non toxic and with various performance. Lignins contain several functional chemical groups, such as hydroxyl (phenolic or alcoholic), methoxyl, carbonyl and carboxyl, in various amounts, depending on the origin of the material and the isolation process applied [100]. Lignin is also an excellent fuel, since it yields more energy than cellulose when burned. It is also a source of raw material for the derivation of phenolic compounds because of its high oxygen content and phenolic nature.

Pyrolysis presents the most likely pathway for the conversion of lignin to low molecular phenols.

9.2. Lignin separation methods

The extraction of lignin from plants in a pure form has proved to be extremely difficult. This is because the true composition of natural "proto" lignin is not known and it is not known because it has never been successfully isolated in the natural form. All methods developed for lignin isolation result in modifications to the physical and chemical structure of the lignin. No one method is ideal for all cases and the limitations of each method have to be borne in mind when results are interpreted. It is difficult even to assess the purity of an extracted sample of lignin because no standards exist with which it may be compared. Many techniques have been suggested for the isolation of lignin from plant materials. Such techniques include alkali, organic acid, enzyme, organosolve and ball-milling treatments and so on. All of these techniques are intended to minimize the alterations to the lignin and provide a true representative sample for fundamental research.

The principal source of technical lignin is a by-product from the pulp and paper industry which alone is capable of supplying unlimited quantities of lignin.

The techniques used for the isolation of lignin from wood may be classified under three categories:

9.2.1 Procedures that remove cellulose to leave lignin

- *Sulphuric acid lignin ("Klason" lignin).* Lignin may be obtained as a residue when cellulose is hydrolysed with sulphuric acid. The lignin product is insoluble in water.
- *Hydrochloric acid lignin ("Willstaetter" lignin).* Lignin is isolated by hydrolysis of pre-extracted wood with 40-42% hydrochloric acid.
- *Periodate Lignin.* The procedure involves the oxidation of wood with 4.5% solution of periodic acid followed by mild hydrolysis of the resultant dialdehydes.
- *Cuprammonium Hydroxide Lignin.* Cellulose in wood may be solubilised in cuprommonium hydroxide, if it is pre-hydrolysed with strong acid.

9.2.2 Procedures that selectively separate lignin from the other wood components.

- *Organosolve lignins.* This process involves treatment of wood with a solvent, usually in the presence of a catalyst. Some of the reagents most frequently used are: methanol, ethanol, phenol, thio-compounds, dioxane organic acid/base and dimethyl sulphoxide.
- *Isolation of lignin by extraction with inorganic reagents:*

  Soda lignin: In this process the wood is treated with sodium hydroxide and sodium sulphide at relative high temperatures and pressure values.

  Kraft lignin (sulphate method): The kraft pulping method, which is also known as kraft pulping or sulphate process is the prevailing industrial process worldwide for the separation of lignin from cellulosic fibres in order to manufacture paper and other related products [98]. The process name is derived from the German word "kraft" meaning strength/power. Both capitalized and lower case names (Kraft process and kraft process) appear in the literature, but "kraft" is the most commonly used in the pulp and paper industry [101].

  Kraft method involves chemical treatment of wood with sodium hydroxide and sodium sulphide (white liquor) at high temperature, pH and pressure value. At the end of the process, there is a brown stock (solid pulp of brown colour) which is collected and washed and a brown liquid (black liquor) containing lignin fragments, carbohydrates from the breakdown of hemicelluloses, sodium carbonate, sodium sulphate and other inorganic salts [101]. The latter is usually concentrated to 60-80% solids and burned for the recovery of the inorganic materials and energy production. During combustion, the sodium sulphate is reduced to sodium sulphite by the carbon available in the mixture (figure 43)

$$Na_2SO_4 + 2\,C \rightarrow Na_2S + 2\,CO_2$$

Figure 43: Reduction of sodium sulphate to sodium sulphite

Kraft lignins are soluble in aqueous alkaline solutions and amines or oxygenated organic compounds requiring different carriers to bring about uniform mixing. One of the main chemical reactions that underpins the kraft process is the scission of ether bonds by the nucleophilic sulphide (S^{2-}) or bisulphide (HS^-) ions (figure 44) [25].

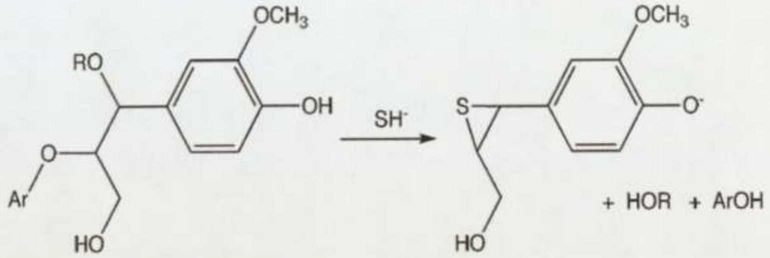


Figure 44: Kraft process - net reaction in depolymerization of lignin by SH^- (Ar = aryl, R = alkyl groups) [25].

Sulphite pulping lignin. The sulphite process employs various salts of sulphurous acid (H_2SO_3) to extract the lignin from wood chips in large pressure vessels called digesters. The salts used in this pulping process are either sulphites (SO_3^{2-}), or bisulphites (HSO_3^-), depending on the pH. The counter ion can be sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) or ammonium (NH_4^+). The sulphite process is acidic pH (~ 1-2) and one of the drawbacks is that the acidic conditions hydrolyze some of the cellulose, which means that sulphite pulp fibres are not as strong as Kraft pulp fibres. Evaporation of water from the spent sulphite pulping liquor (SSL) yields a brown coloured fine solid commonly identified as lignosulphonate. Lignosulphonates are soluble in water and insoluble in mineral oil and hydrocarbons [25]. Most delignification in sulphite pulping involves acidic cleavage of ether bonds, which connect many of the constituents of lignin. The electrophilic carbocations produced during ether cleavage react with bisulphite ions (HSO_3^-) to give sulphonates (figure 45).

$$R\text{-}O\text{-}R' + H^+ \rightarrow R^+ + R'OH$$

$$R^+ + HSO_3^- \rightarrow R\text{-}SO_3H$$

Figure 45: Production of sulphonates

The primary site for ether cleavage is the α-carbon (carbon atom attached to the aromatic ring) of the propyl (linear three carbon) side chain (figure 46) [25].

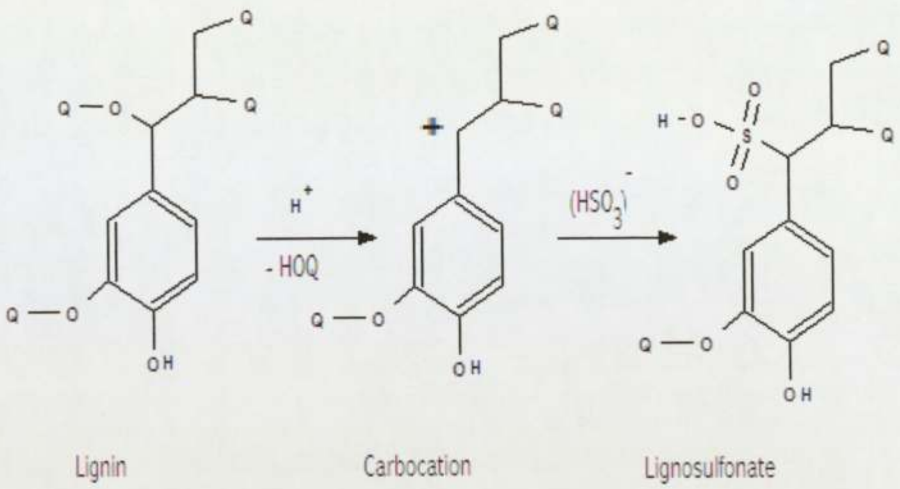


Figure 46: Sulphite process [25]

9.2.3 Miscellaneous Lignin Isolation Procedures

- *Steam explosion.* Steam explosion involves the brief subjection of lignocellulosic material to steam at high temperature and pressure, followed by rapid decompression. The lignins recovered from the process are of low molecular weight compared to lignins derived from chemical pulping and are soluble in alkali and certain organic solvents.
- *Enzymatic liberation.* This process involves the degradation of the cellulose component with enzymes such as cellulases, hemicellulases pectinases and so on. These lignin preparations may more closely resemble "native" lignin due to the very mild processing conditions employed.
- *Milled wood lignin.* The procedure involves grinding wood in the presence of a neutral solvent. As a consequence, milled lignin has been used extensively as a representation of natural lignin in fundamental studies of lignin and lignin pyrolysis.

9.3 Physical properties of lignin

Dark brown mass with a specific smell.

Because it is not possible to isolate native lignin from wood without degradation, the true molecular mass of lignin in wood is unknown. The weight-average molecular mass, $\bar{M}w$, for softwood milled wood lignin is estimated to be 20,000 Daltons, whereas lower values have been reported for hardwood lignin.

Lignin is an amorphous thermoplastic polymer that is somewhat brittle at room temperature and lacks film-forming characteristics when cast from solution. Lignin exhibits a glass transition temperature of ca 160ºC, which is significantly higher than that of most common synthetic thermoplastic polymers. The glass transition temperature of lignin is profoundly affected by moisture and hydrogen bonding.

The calorific value of lignin is higher than that of wood and cellulose. This reflects the greater carbon content of the lignin as a fuel. Owing to the increased contents of carbon (59-67%), and the insignificant carboxyl group content, the calorific value of hydrolytic lignin is much higher, than that of wood.

9.4 Prior art of lignin-based adhesives

Although lignins are available in large quantities at low cost, the applications of lignin are limited because of their highly complex nature. The use of pure lignin adhesives in the wood-based industry is not extensive because of the chemical variation of the lignin feedstock and increased press times required. Lignin, despite being almost completely aromatic, has only a few phenolic rings and no polyhydroxy phenyl rings leading to low reactivity with formaldehyde.

The various processes available for the separation of lignin from cellulose lead to degradation of the natural lignin polymer. For adhesive purposes, these degraded lignins need to be further polymerized to obtain useful adhesion properties [99].

The types of lignin available for industrial usage come predominately from effluents of paper pulping processes - termed black liquors- that contain between 5-50% lignin depending on source [102]. In general lignins may be classified into two categories: those which are sulphur-bearing and those which are sulphur-free. It is the sulphur-bearing lignins which to date have been commercialized. These include lignosulphonates (world annual production of 500,000 tons) and kraft lignins (under 100,000 tons p.a.). Owing to a lack of suitable industrial processes, the sulphur-free lignins are as yet non-commercialized.

Lignin from the kraft pulping process is highly polydisperse and increases in molecular weight as delignification proceeds. Generally, it consists of lignin (ca 45%), hydroxyl acids (ca 28%), inorganics and small quantities of other organics.

The spent sulphite liquor (SSL) from sulphite pulping of wood produces highly solubilised lignin containing essentially monomeric sulphonated aromatics and monosaccharides [102].

In most wood adhesive applications that have been developed, the lignosulphonate replaces only a part of the adhesive adhesive. Exceptions are the cross-linking of lignosulphonate by oxidative coupling reactions or when the curing reaction also results in the loss of the sulphonic acid groups [12]. Three methods of using SSL as the main adhesive with particle board are to use long press times with a post heating step, to heat with sulphuric acid during bonding and to heat with hydrogen peroxide [99]. SSL has also been used as a phenol – formaldehyde extender.

Lignins derived from Soda and the kraft process are called alkali lignin. The chemical modification of lignin includes methylolation, epoxidation, isocyanation and phenolysis reactions. Methylolation of alkali lignin is carried out mainly with formaldehyde that is introduced at the C-5 position of the aromatic ring and to a lesser extent the β-position. Lignin may also be chemically modified to increase its reactivity toward formaldehyde to enhance its incorporation into PF adhesives. This can be achieved by:

- Substitution of the lignin fragments with phenol, introduces more reaction sites. Under acidic condition, phenol reacts with oxysubstituted α-carbons to afford a phenolized lignin adduct [12].
- Activation of the aromatic nuclei of the lignin toward formaldehyde by demethylation, resulting in an increase in the phenolic hydroxyl content of the lignin [12].

The pre-methylolated lignin has been used with PF adhesives in plywood bonding [99].

Apart from the reaction of lignin with formaldehyde, other curing methods that have been investigated include:

- thermal cure with acids
- oxidative coupling using hydrogen peroxide
- use of catalysts

A concentrated table with the modifications, the activation and the respective application on panel production is presented below (table 10).

Table 10: Lignin utilization in wood adhesives

		Activation	Adhesive synthesis methodology	Other components	Adhesive	% natural material	use	Panel
Organosolvent		-	Methylolation or phenolation*		PF	Up to 30%		PB
Alkali lignins	**Soda & Kraft lignins**	Lignin substitution by phenol	Condensing lignin with phenol and formaldehyde		PF		Phenol extender	PW
		Demethylolation	Methylolation with formaldehyde and then addition to PF adhesives		PF		Replace part of PF adhesive	PW
			Glyoxylation with glyoxal and then addition to PF adhesives	Glyoxalated soy flour, tannin and pMDI	PF	70%		
		-	Epoxidation		PF			PW
		-	Isocyanation		PF			PW
		-	phenolysis		PF			PW
		Thermal cure with acids			natural			PW
		Oxidative coupling with hydrogen peroxide			natural			PW
		Use of catalyst		PAE**	natural			PW
				PEI ***				
		-	oxidized by laccase					
Acid lignin	**SSL (low reactivity)**		Methylation with glyoxal	PF/Tannin/ pMDI	natural	55–60%	Replace part of PF adhesive	PB
			Methylolation with formaldehyde	Monosaccharides	natural & PF			PB
			radical condensation.				Phenol extender	PB
			biological transformation				Replace tannin	PB
			Treatment with the enzyme phenoloxidase					PB
		wood activation	furfuryl alcohol	maleic acid anhydride				PB

* phenolation is the process where lignin is treated with phenol under heating. The scope of this treatment is the enhance of lignin with potential reactive sites [103].

** PAE = Polyamino Amide Epichlorohydrin

*** PEI = Polyethylenimine

Other methods are steam explosion, enzymatic liberation and milled wood. The lignin by these methods has been used to replace phenol partially, up to 50%.

10. SOY PROTEIN

10.1 General

Soy is an annual plant native to East Asia. Nowadays soy plant is cultivated in many countries as soy beans and accounts for 56% of the world oilseed production with US soy bean production accounting for 46% of the world production. Other countries with high soy bean production are Brazil, Argentina and China. Its cultivation in Europe is limited owing to the climate and the soil conditions [104]. It may grow prostrate and does not grow higher than 2 meters [105]. The fruit is a hairy pod that grows in clusters of 3–5 with each pod 3–8 cm long and usually containing 2–4 (rarely more) seeds, each 5–11 mm in diameter. Soy beans are a species of legume classed as oilseeds [105]. The shape of soy bean seed varies from almost spherical to elongated and flat. Soy beans are used both as food and industrial raw materials. The industrial varieties are nearly spherical while the elongated varieties are used as a vegetable. The colour of the seed may be yellow, green, brown or black. Industrial varieties are yellow and the presence of seeds of other colours in a lot is considered a defect. Seed size is expressed as the number of seeds per unit volume or weight. Industrial soy beans weigh 18-20 grams per 100 beans. The seeds of "vegetable" varieties are considerably larger.

The seed consists of the seed coat (hull), which accounts for about 8% of the seed weight and provides an effective protective layer to the two cotyledons inside it. The cotyledons represent roughly 90% of the seed weight and contain practically all the oil and protein; the remaining 2% accounts for the hypocotyl axis or germ [105].

In general, dry soy beans consist approximately of 40% protein, 20% oil, 35% carbohydrates and about 5% ash [105]. All of these constituents have found widespread industrial and nutritional use, but especially soy bean protein has been used extensively by the food industry because not only does it contain more protein than other plants, but it is also of higher quality since it provides all the essential amino acids for the body. In addition, the soy bean protein was for many years the product of choice for the synthesis of natural adhesives suitable for the wood-based panels industry. Soy-protein based adhesives were first developed in

1923, when a patent was granted for soy bean meal-based glue [106]. Soy proteins are amide-linked polymers composed of amino acids. They are produced in soy beans as a storage protein to nourish the growth of the germinated seed. The protein molecule is the condensation product (with subsequent release of water) of many individual amino acids joined together by a repeating bond called the peptide linkage. The soy bean protein meal for industrial use may be found in the following three forms:

a) **Flours**. Soy flour is made by grinding soy beans, into a fine powder. It comes in three forms: natural or full-fat (contains natural oils); defatted (oils removed) with 50% protein content and with either high water solubility or low water solubility; and lecithinated (lecithin added).

b) **Concentrated Soy protein** is about 70% soy protein and is basically soy bean without the water-soluble carbohydrates. It is made by removing part of the carbohydrates (sugars) from dehulled and defatted soy beans. Soy protein concentrate retains most of the fibre of the original soy bean.

c) **Isolated Soy protein** is a highly refined or purified form of soy protein with a minimum protein content of 90%, on a moisture-free basis. It is made from defatted soy flour, which has had most of the non-protein components, fats and carbohydrates removed. Because of this, it has a neutral flavor and will cause less gas due to bacterial flatulence.

All of these types find extensive industrial application, but for the production of thermosetting adhesives the isolated soy protein (SPI) is preferred because despite its higher cost compared to the other types, it is the more concentrated and pure source of protein providing maximum formulation flexibility.

10.2 Soy Isolated Protein (SPI) separation methods

Soy protein isolates are highly pure products since the oligosaccharides (low molecular "sugars") as well as the polysaccharides (cell wall material) are selectively removed from the meal (slurry) during the extraction process.

The conventional process for the extraction of soy protein isolates includes the following steps [107]:

1st step - Starting material: soy beans are dehulled, flaked, and defatted to make "white flakes". Then, a slurry is prepared comprising one part of soy flakes and 10-20 parts of water.

2nd step- Protein extraction: An alkali such as sodium hydroxide, lime, ammonia or tri-basic sodium phosphate is added to the slurry, so as to bring the pH from neutral to slightly alkaline, in order to increase the solubility of the protein. In this way protein and oligosaccharides solubilise while the insoluble polysaccharide may be removed by centrifugation. The aqueous extraction is carried out at a pH below 9.

3rd step- Protein precipitation: the supernatant liquid of the previous stage, containing the protein and the "sugars" in solution, is acidified to the isoelectric region) of the protein (pH 4.5). This results in the precipitation of the protein, which can be separated from the oligosaccharide containing supernatant by centrifuge. It is then dehydrated and dried. Thus, an unmodified protein is obtained, which is preferred for the preparation of protein fibres and tacky adhesives but not for paper coating adhesives and similar applications [108]. The proteins of unmodified grade maintain their globular structure with relatively reactive equal number of cationic and anionic sites [109].

4th stage-Solubility restoration: The solubility of unmodified protein may be restored by neutralizing the protein curd with an alkali to generate the proteinate salt.The solution is filtered and the clarified liquor is again acidified to precipitate the protein. The final curd is again dehydrated, dried and ground to about 40 mesh before sent out packed in multilayer paper bags [108].

A scheme of the SPI extraction process is presented below (figure 47) [110].

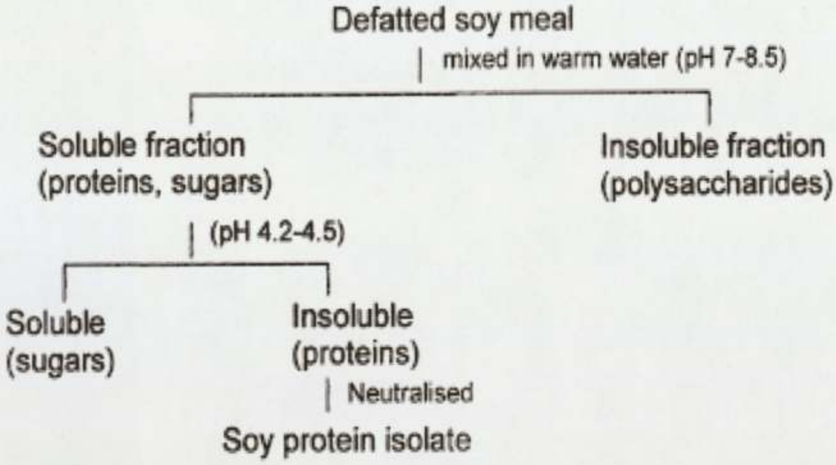


Figure 47: Flow diagram of the extraction process for the soy protein isolate [110]

10.3 Physical properties of isolated soy bean protein

Soy protein isolate has a neutral flavour compared to other soy products. The industrial grade is available as a creamy-coloured powder of neutral pH. In general, soy proteins exhibit heat stability and hydroscopy and their molecular weight ranges from 8,000 to 600,000 Da. In terms of their use as adhesives, certain particle size is usually requested and a specific surface area 3000-6000cm^2/g is considered necessary [110].

The soy protein for industrial use should meet some functional characteristics that include the ability of the protein to thicken (viscosity), solubilize, form gels, foam, emulsify, produce films, absorb water or display surface hydrophobicity. Moreover, the strength of the protein as an adhesive material depends on its ability to disperse water and form interactions between the apolar and polar groups of the protein and the wood substrate. Nevertheless, the globular structure of natural proteins makes the majority of polar and apolar groups unavailable because they are involved in internal bonds and hydrophobic interactions that account for the structure of the protein itself. For this reason, the interaction between molecules is minimal and thus in most cases some treatment is necessary in such a way to allow interactions with other components. This treatment is called "denaturation" and involves the destruction of both the secondary and tertiary structures since the functional properties of proteins are related not only to the amino acid composition and sequence (primary structure) but also to the spatial configuration of the protein molecule and the inter-molecular forces (secondary and tertiary structures) [107].

The "denaturation" process involves uncoiling of the globular-shaped molecular structure of proteins into a random shape as well as hydrolysis or splitting of the molecules to compounds of shorter chain lengths and consequently of lower molecular weight [108, 111, 112].

Proteins can be denatured by heat, changes in pH, organic solvents, detergents, urea, guanidine hydrochloride, proteolytic enzymes or other methods that disrupt to varying extents the hydrogen bonds to amides (secondary structure), salt bridges, disulphide bonds, and non-polar hydrophobic interactions (tertiary structure), or quaternary structure while leaving unaffected the primary structure of the protein.

It has been demonstrated that the degree of dissociation, denaturation and aggregation, mostly of the 7S (β-conglycinin) and 11S (glycinin) globulins, among the various peptides contained in soy protein, play the most significant role in the functionality of soy protein isolates. S stands for Svedberg units; the numerical coefficient is the characteristic sedimentation constant in water at 20°C. The figures are not exact but nominal. Thus, the 11S globulin has a sedimentation constant of 12.3. β-Conglycinin (7S), which accounts for about 34% of soy protein, exists as a trimer and contains three major sub-units: α´, α and β [20], while glycinin (11S), comprising about 42% of soy protein, is composed of an acidic and a basic polypeptide connected by a disulphide bridge; this polypeptide mainly exists as a hexamer [113]. These peptides, which result from SPI, aggregate at pH values higher than the pH at which the non-hydrolysed proteins aggregate (approximately 4.5 at 25°C) [113].

10.3.1. Denaturation process by alkali treatment

Among the various denaturation processes, the application of heating and pH changes are the most common treatments given to SPI intended for use as adhesives. Nevertheless, attention should be paid to the attainment of the optimum pH values during the process since either under-modification or over-modification may lead to undesirable performance of the protein.

The progressive modification of soy bean protein with alkali to give a suitable product can be followed by observing the viscosity changes of the protein solutions as a function of pH. Figure 48 shows the dependence of viscosity on pH undergone by soy bean protein solutions (at 25°C) over an alkaline pH range. The solution was obtained by dissolving the protein in water with sodium hydroxide. The readings were made one hour after the sodium hydroxide was added to the solution since the viscosity of some protein solutions changes rapidly at certain pH values [108]. A curve of 18% casein solution is also presented as a model of the optimum viscosity development.

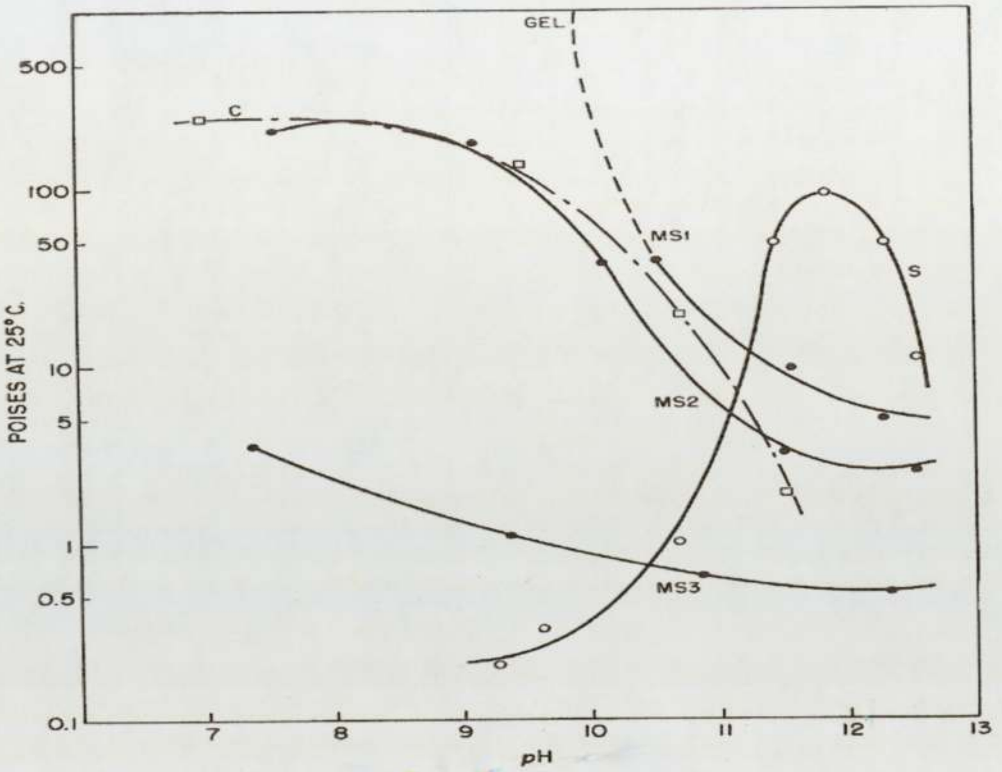


Figure 48: Soy protein viscosity-pH curves.
S = 14% solution of unmodified soy proteinMS1-MS3 = 18% solutions of modified protein, C= 18% solution of casein.

The unmodified protein (curve S) is obtained from the biomass without heating and at a pH close to neutral. This graph was prepared with a 14% solution because higher concentrations underwent rapid viscosity development and gelation. The curves MS1-MS2 are for solutions of 14% alkali modified protein, while curve C is of an 18% casein solution and represents the desirable viscosity development for industrial applications [108]. From the above graph it can be seen that curve MS2 is the closest to the curve of casein while the MS1 curve represents an undertreated sample and MS3 curve an overmodified protein. Both MS1 and MS3 treatments lead to deterioration of the adhesive properties of proteins as adhesive strength and viscosity of protein solutions are closely related [108].

During the denaturation process, foams are formed when globular proteins are opened up and reformed into protein "skins" that hold air bubbles in place. Fats are thought to destroy the foaming properties of the proteins by displacing the proteins that form the air bubble surface, causing the bubble to collapse.

The denaturation process enables the soy protein to spread well on wood surfaces while the exposure of hydrophobic units slow down the water penetration thus improving the water resistance of the adhesive [114]

The extent of protein denaturation, and hence the intensity of heat treatment, is expressed in terms of the soluble protein content that is signified by the Nitrogen Solubility Index (NSI) or Protein Dispersibility Index (PDI). These indices denote the percentage of the total content of nitrogen and protein respectively [110].

10.4 Chemical reactivity of SPI

Generally, the chemical reactivity of proteins depends on side chain, the amino acid composition and the free amino and carboxyl groups [115, 116]. The most reactive protein groups are serine (primary -OH), hydroxyproline (secondary -OH), threonine (secondary -OH), tyrosine (phenolic -OH), aspartic acid (-COOH), glutamic acid (-COOH), lysine (-NH2) and arginine (-C (:NH) NH2) [116,117].

Aldehydes such as formaldehyde, glyoxal and glutaraldehyde react with the amino acid side chain, particularly with the lysine ε-NH_2 group, forming bonds similar to those in the formation of the Schiff base [116, 118].

It is hypothesized that the hydroxymethyl groups (--CH_2OH) of the PF adhesive will react not only with itself but also with various functional groups of the SPI, including tyrosine, serine, threonine, asparagine, glutamine, and arginine to form methylene (--CH_2) or ether(--CH_2O) linkages between the soy protein and the PF adhesive. These condensation reactions between the PF adhesive and soy protein occur particularly during the curing stages of the soy bean-based adhesive at high temperatures while such reactions are greatly influenced by pH values [119, 120].

10.5 Prior Art of soy protein-based adhesives

Soy bean adhesives were used extensively in industry during the 1930's and early 1940's for plywood, construction, and packaging [121]. Neverthless, after World

War II the development of the petrochemical industry provided the adhesive production industry with cheap and more effective raw materials. Today, the progress of biotechnology and the need to replace the petroleum based materials by others from renewable resources as well as the abundance of soy bean grown throughout the world has created a new prospect for the use of soy-based adhesives as adhesives in the wood-based panels industry. Modifications to soy proteins have allowed adhesives to be developed that possess improved shear strength and water resistance.

Soy proteins modified under alkali conditions or with trypsin exhibit greater shear strength and enhanced water resistance [122]. Huang and Sun [123, 124] also obtained superior shear strength and water resistance in adhesives made from soy proteins modified by sodium dodecyl sulphate, sodium dodecylbenzene sulphonate, urea, or guanidine hydrochloride. Crosslinking, acylation, oxidation reaction with alkoxy silane and copolymerisation are also some other methods used for modification of soy protein [28].

Anhydrides, aziridines, epoxides, aldehydes and hexones have been used for soy protein gelatin modification [125], with formaldehyde being one of the most frequently used reagents in gelatin reticulation for non food uses [126]. Dialdehydes, especially glutaraldehyde and glyoxal, are also frequently used for this purpose [116, 117, and 125].

It has also been demonstrated that modification of soy protein with the 3,4 dihydroxyphenyl group and a thiol group that is abundant in marine adhesive protein (MAP), or combining SPI with a polyamidoamine-epichlorohydrin (PAE) adduct improve the strength and the water resistance of panels prepared with such adhesives systems [114, 126, 127].

Soy bean based adhesives have been successfully prepared by copolymerization of soy bean flour or soy protein isolate (SPI) with phenol-formaldehyde (PF) adhesive [119, 120, 128], urea formaldehyde adhesive and polymeric diphenyl methane diisocyanate (pMDI).

Soy protein is also combined with phenol-resorcinol-formaldehyde adhesive (PRF) for the production of an adhesive system suitable for finger joining (wood scraps are bonded together to produce marketable lumber) [129].

It was found that maleic anhydride (MA) may be grafted onto SPI primarily via amide linkages and to a lesser extent via ester linkages (MSPI). Eventhough wood composites bonded with MSPI alone had low dry shear strength and delaminated when they underwent a boiling water test, a combination of MSPI and polyethylenimine (PEI) dramatically increased the strength and water resistance of the resulting wood composites [130].

11. TANNIN

11.1 General

Tannin is a class of polyphenolic substances found in many different plants like grapes, tea leaves, and wood. The word tannin comes from the historical practice of using tannins in tanning animal hides into leather. Examples of plant species used to obtain tannins for tanning purposes are wattle (Acacia sp.), oak (Quercus sp.), eucalyptus (Eucalyptus sp.), birch (Betula sp.), willow (Salix caprea), pine (Pinus sp.), and quebracho (Scinopsis balansae).Today the tanning process is carried out with synthetic materials but tannins are used in other applications like dyeing, photography, wood adhesives, refining beer and wine as well as an astringent in medicines. They are used as supplements in various processed foods, including ice-cream and caramel while they have been included in many pharmacopoeias. Significantly, tannins form a vital element of tea.

Tannins are considered to be residues of plant metabolisms. They are found as shapeless, yellowish or light brown mass-like powders, flakes or sponges. Tannins occur in nearly every plant from all over the world, in all climates. The percentage of tannins present in plants, however, varies. While they are present in significant proportions in some plants, many others have very low concentrations of them. Tannin is found in almost any part of the plant, from root to leaves, bark to unripe fruit but it is mostly concentrated in the bark layer where it forms a barrier against microorganisms such as fungi and bacteria. Speaking about tree species, tannins are common in both Gymnosperms and Angiosperms.

From the chemical point of view they are distinguished into two classes: the hydrolyzable and the condensed types. Because of their low reactivity (nucleophilicity) and lack of macromolecular structure, hydrolysable tannins have limited use in the partial replacement of phenol in commercial PF formulations [131]. In contrast, condensed tannins constituting more than 90% of the total world production of commercial tannins, are both chemically and economically more interesting for the preparation of adhesives [132]. The majority of the condensed tannins available commercially are highly concentrated extracts of *Acacia* (wattle and mimosa), *Scinopsis* (quebracho) and *Tsuga* (hemlock) bark [131]. This study was carried out with condensed tannin and thus it will be presented in more details.

11.2 Types of tannin

11.2.1 Hydrolyzable tannins (gallotannins, ellagitannins)

The basic unit of hydrolysable tannins is gallic acid (3, 4, 5-trihydroxy benzoic acid), (figure 49).

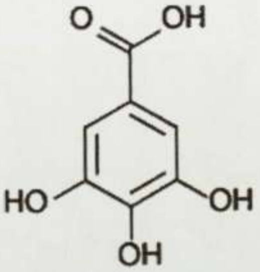


Figure 49:Gallic acid:basic unit of hydrolyzable tannins

The gallic acid is esterified to a core polyol, with glucose mainly, while the galloyl groups can be further esterified or oxidatively cross-linked to form more complex hydrolysable tannins (figure 50).

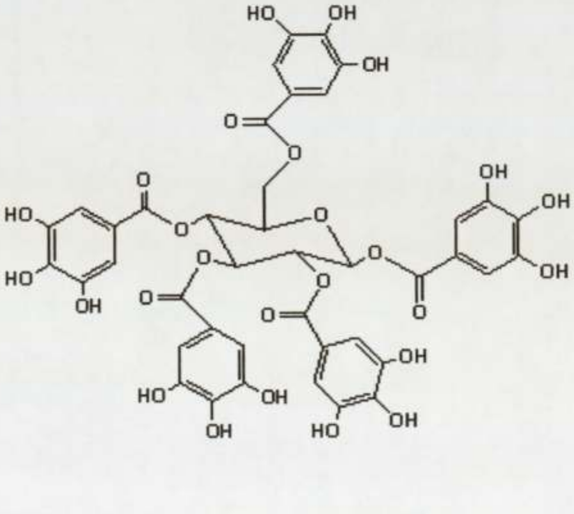


Figure 50: β-1, 2, 3, 4, 6-pentagalloyl-O-D-glucose

Because of their complex structure, gallotannins have many isomers. As their name infers, hydrolyzable tannins are readily degraded under hydrolytic conditions into their fundamental components.

11.2.2 Condensed tannins (protoanthocyanidines)

The precursors of condensed tannins are the flavonoids (flavone-like substances). Flavonoids are characterized as molecules possessing two phenolic groups (A and B) bonded to each other by a "three-carbon" bridge (figure 3-shaded area). This bent bridge, along with an oxygen atom, makes up the "C" ring (pyran ring) [133] (figure 51).

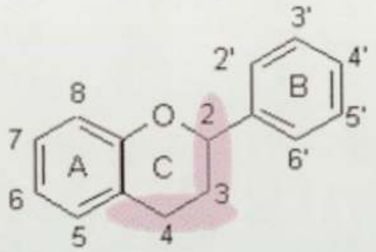


Figure 51: General Structure of Bioflavonoids
[133]

The different classes of flavanoids are distinguished by the molecular groups found at the different numbered positions. The most studied condensed tannins are those based on the flavanoid class of flavanols (flavan-3-ols) [133] even though other flavonoid analogs (like flavan-3, 4-diols, flavonols, flavonones, etc) are also represented in tannin composition but to a lesser extent (figure 52).

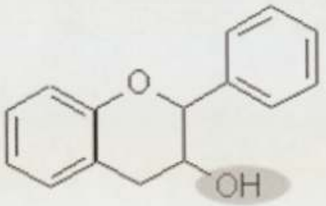


Figure 52: Flavan-3-ol
[133]

Common flavan-3-ols that occur in many plants are catechins. Depending upon the spatial orientation of the "OH" molecule in the 3 position the material is called catechin (C) [(+)-catechin] or epicatechin (E) [(-)-epicatechin] (figure 53).

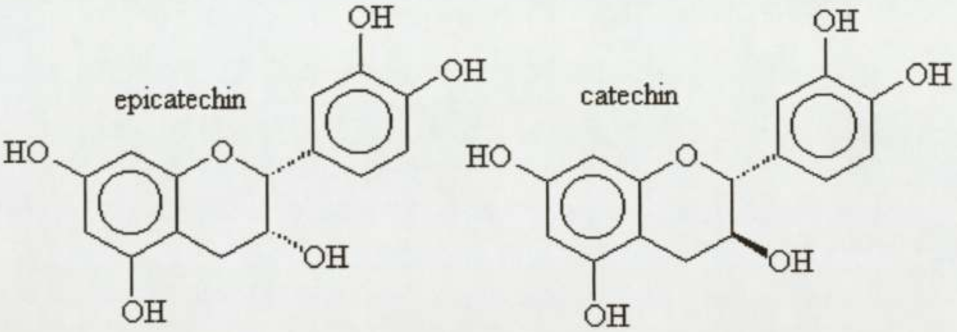
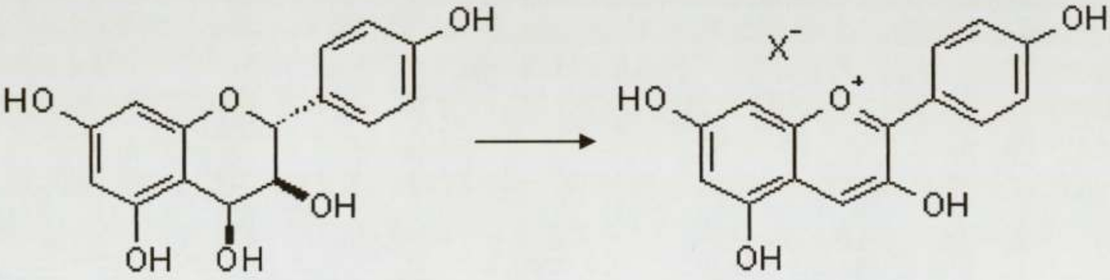


Figure 53: Catechin and epicatechin

Advances in the chemistry of condensed tannins have allowed their "biomimetic synthesis" (in vitro) through the acid catalysed protonation of flavan-3, 4-diols or flav-3-en-3-ols and their subsequent condensation to produce dimers and oligomers [134], while it is considered plausible that *in vivo*, they are synthesized through the formation of a quinone methide intermediate [134] (figure 54).



Flavandiol (Leukoanthocyanidin) Anthocyanidin

Figure 54: Quinone methide intermediate of tannin

Catechins form dimers, trimers and various higher oligomers through interflavan (C4-C6/C4-C8) linkages. When the number of connected catechins is 10 or less they are called oligomers and thus the term used is "oligomeric proanthocyanidins". When the number of connected catechins is more than 10, then the term condensed tannins is generally used. A model structure for condensed tannin is shown on figure 55.

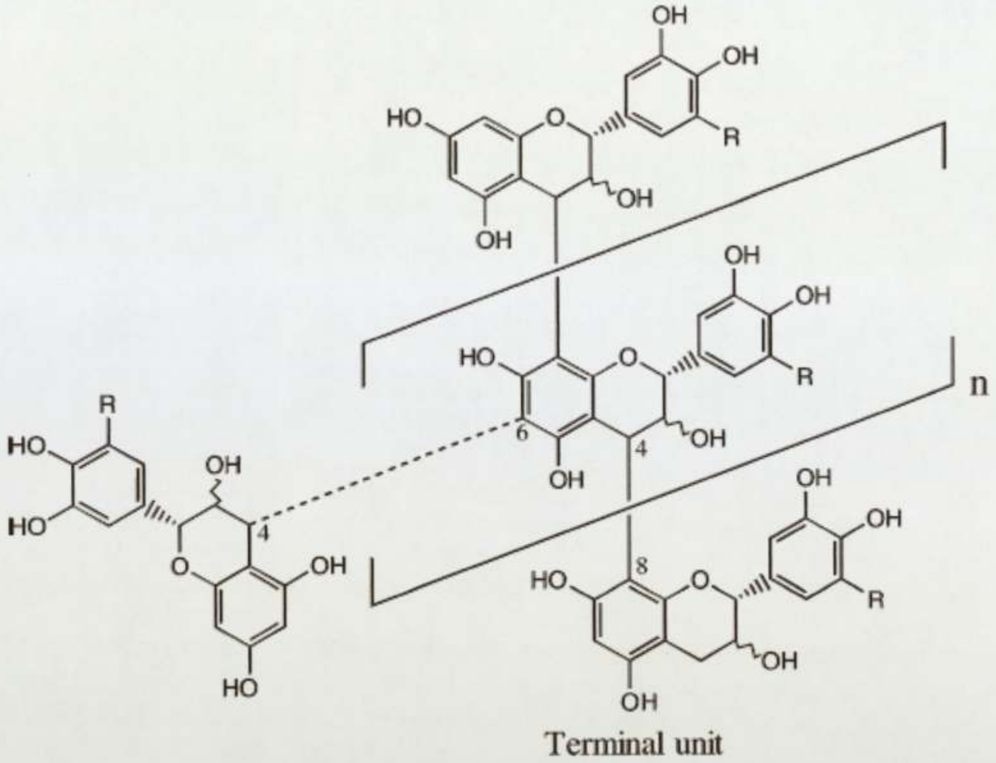


Figure 55: Model structure for a condensed tannin.
If R=H or OH then the structure represents a procyanidin or prodelphinin. The 4→6 linkage (dotted line) is an alternative interflavan bond. The terminal unit is at the bottom of such a multi unit structure [135].

The term proanthocyanidins comes about because when these materials are subjected to 10% hydrochloric acid and heated to boiling they yield an anthocyanidin, (with its intense red colouration), and a catechin [136]. This is termed the Bate-Smith test [137]. In figure 56 there is a schematic presentation of the decomposition of proanthocyanidins.

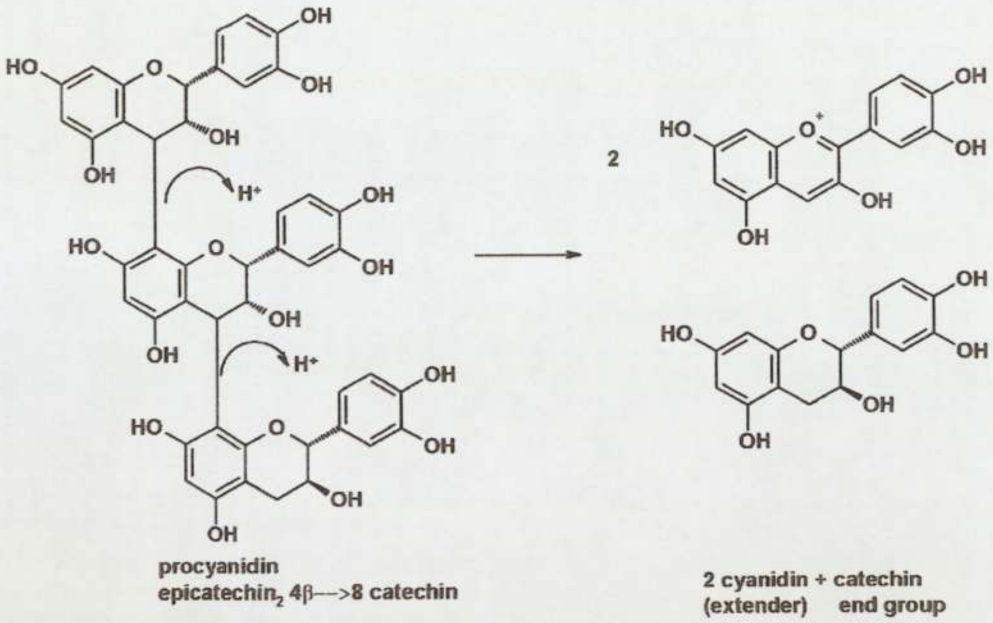
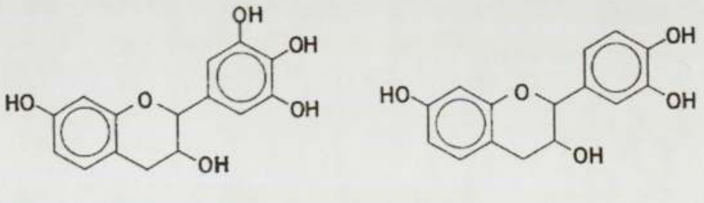


Figure 56: Decomposition of proanthocyanidins
[138]

The flavonoid pattern that constitutes about 70% of tannins is based on resorcinol (A) rings and pyrogallol (B) rings. Another flavonoid analog existed at minor extend is based on resorcinol (A) rings and catehol (B) rings (figure 57) [137].



(a) (b)

Figure 57: a) Resorcinol (A) ring – pyrogallol (B) ring. b) resorcinol (A) ring – catehol (B) ring

11.3 Tannin separation methods

The best age for de-barking trees is between 15 and 30 years old as the older tree has more tannin than a younger one. Tannins exist in the bark of the tree where their concentration is higher in the inner part of the bark (cambium layer) and the lower parts of a tree [139]. The concentration of tannin is a maximum in the bark during spring time.

The samples are collected fresh. After cutting the sample is subjected to freeze-drying as it is the gentlest method of preservation and is recommended instead of freezing, air or oven-drying. The sample may then be stored. According to the most used extraction methods, the material is soaked in hot water solutions of some organic solvents such as acetone, methanol, butanol-HCl or sodium sulphite/sodium carbonate [140, 141, and 142]. The temperature and the contact time as well as the ratio of liquid:solid have been found to affect the efficiency of the extraction. According to Jerez et al. [140] high yields are obtained at temperature 50°C with contact time of about 60-90 min and a liquid:solid ratio of approximately 5:1. The extracts are filtered and concentrated under pressure to the desired solids content [142]. During extraction there is some tendency for tannin self condensation [143].

11.4 Physical properties of condensed tannins

Condensed tannins have complex structures because the flavonoid units differ in some substituents and these are because of the variable sites for interflavan bond formation. They can contain from 2 to 50 or greater flavonoid units. In general, their molecular weight ranges from 500 to 3000 Daltons [144].

In their pure form tannins are colourless, but they colour very rapidly after they are exposed to air due to the oxidation of the phenolic sub-units to quinones [131].

With the exception of some high molecular weight structures, tannins are soluble in water. Depending on their chemical structure and degree of polymerization, condensed tannins may or may not be soluble in aqueous-based solutions of organic solvents. They have the ability to bind proteins and form insoluble or soluble tannin-protein complexes.

Condensed tannins are hydrolysed by mild acids or mild bases [134]. Hot water or enzymes do not hydrolyse condensed tannins [145] as they do hydrolyzable tannins (yielding carbohydrate and phenolic acids) because they are polymers of flavonoid units (i.e. flavan-3-ol) linked by carbon-carbon bonds which are not susceptible to cleavage by hydrolysis. When the condensed tannins (non-hydrolysable) are heated in acids they react to yield a red insoluble substance known as tannin reds or phlebaphenes [146].

11.5 Chemical reactivity of condensed tannins

Tannins exhibit unique reactions as well as reactions normally expected from flavan-3-ols [132].

A) Reactions of A and B rings with aldehydes.

The most common reaction of the A ring is the acid or base catalysed electrophilic aromatic substitution where an electrophile displaces the hydrogen atom at C6 and/or C8 (figure 58).

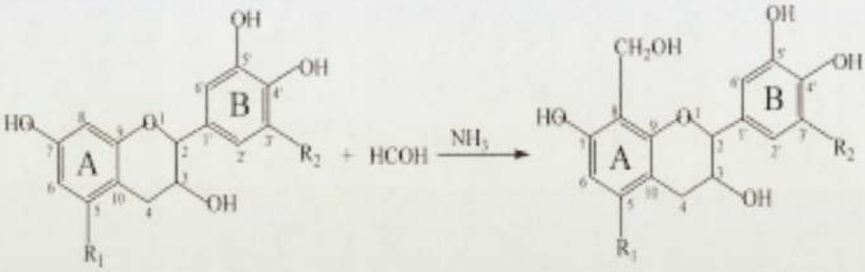


Figure 58: Electrophilic aromatic substitution of H at C8 by formaldehyde [146]

For resorcinolic derivatives, the favoured site is the C6. Increasing the alkalinity of the system leads to an increase in the reactivity of the phenol as a nucleophile. The ring B is relatively unreactive due to the vicinal hydroxyl substituents that cause general activation contrary to the stabilized carbocation intermediates of ring A resulted from the nucleophilic attack. Hence, ring B participates in such reactions only when the pH is higher than 10 [132]. Condensed tannins react readily with formaldehyde forming initially methylol tannin through an electrophilic aromatic substitution (methylolation step - figure 58) and next methylene bridges by the condensation reaction between a methylol group of one molecule and a second tannin while water is released (figure 59).

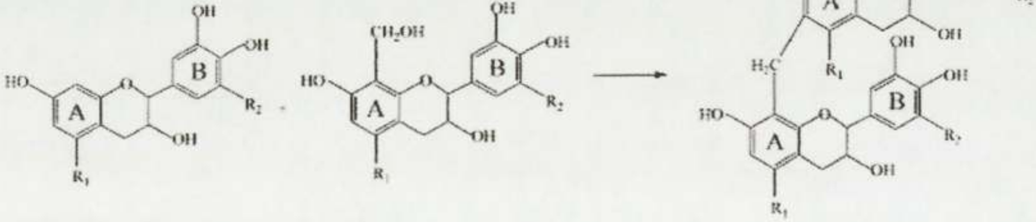


Figure 59: Condensation reaction between tannin molecules through formation of methylene bridges

Nevertheless, due to the size and shape of tannin molecules, they readily become immobile resulting in a polymer with insufficient cross-linking [137]. The tannin – formaldehyde polymer has a short pot life, while the adhesive shows weakness and brittleness. To date, apart from formaldehyde, other aldehyde donors commonly used for the synthesis of tannin adhesives through the mechanism of polymerization are: paraformaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, furfuraldehyde, hexamine, glyoxal and urea-formaldehyde pre-condensates [131, 132].

B) Metal Ion catalysis

Studies have proved that in the presence of a bivalent metal ion the cross-linking of condensed tannins with formaldehyde occurs also through the B ring forming a more dense network [132].

C) Hydrolysis and auto-condensation

Under strong mineral acids condensed tannins go through two competitive reactions: hydrolysis and auto-condensation [132]. Hydrolysis leads to formation of anthocyanidin and catechin, while condensation occurs between the p-hydroxybenzylcarbonium ions, formed from the hydrolysis, with nucleophilic centers of other tannin units [132]. In atmospheric conditions other types of condensation may also be considered possible [132].

D) Sulphonation

This process consists of the introduction of sodium sulphonate groups in the pyran ring (ring C). The heterocyclic ring opens imparting increased solubility and decreased viscosity, rigidity and intermolecular bonding to the tannin molecule [132].

11.6 Prior art of tannin-based adhesives

Tannin-based adhesives have been used in combination with a wide variety of petrochemical adhesives for the production of various types of panels like plywood, particleboards, MDF, OSB and chipboards [131, 148]. Tannin has also been used for the partial replacement of phenol in phenol-formaldehyde adhesives suitable mostly for plywood production [131].

Honey-Moon end joining adhesive formulations, comprised of a synthetic phenol-resorcinol component, a formaldehyde donor and a tannin sulphonate solution with an alkali catalyst have been reported to show good adhesive properties and may be considered suitable for structural exterior use products [131].

A variety of "hardeners" have also been tested successfully for the cross-linking of tannin in order to develop an adhesive suitable for particleboard (PB), plywood (PW) or oriented strand board (OSB) application. Such hardeners are various aldehydes of low molecular weight like formaldehyde, paraformaldehyde, [131, 132, 149], acetaldehyde [150], furfural [150], and glyoxal [151] but also hexamethylenetetramine [152]. These adhesives are considered suitable mainly for particleboard and MDF application.

Studies have also been reported on tannin-based adhesives combined with di-isocyanates such as methyl di-isocyanate (MDI) [153] and polyethylenimine (PEI) [154]. Such adhesives are suitable mostly for plywood application.

The autocondensation of tannins induced by weak Lewis acids [155, 156] results also in adhesives suitable for the production of various wood-based panels.

12. TESTING PROCEDURES AND EVALUATION METHODS FOR WOOD, ADHESIVES AND PANELS

12.1 General

In this study, the raw materials needed for the production of plywood (wood, veneers and adhesives) were inspected for their suitability and effectiveness while the panels produced were evaluated for their properties according to the relative standards used in the industrial practice. In particular:

The quality of veneers used for plywood production was inspected by visual screening and any pieces with holes, knots or cracks were discarded.

The type of wood the veneers were made of, was inspected using scanning electron microscopy (SEM) for the better understanding of its morphology and adhesion mechanism phenomena. Further it was subjected to thermal analysis tests to determine for the location of its decomposition temperature that is crucial parameter for determining the highest pressing temperature which could be applied during the production of plywoods without the wood degradating phenomena.

Certain physical characteristics of the pre-polymers of the adhesives (B-stage) were determined according to standard analytical procedures and compared with the properties of a conventional PF adhesive used in industry. These characteristics were: non-volatile content, viscosity, gelation time, pH, conductivity and alkalinity. These characteristics are considered significant for the safe delivery of the product and partly because the customer requires these values to guarantee manufacture of the wood-based product. Moreover, the thermal behaviour of the adhesives was tested with two thermal analysis techniques:

a) Thermogravimetric/Differential thermal analysis (TGA/DTA) were used to compare the decomposition performance of the experimental adhesives with that of a standard phenol-formaldehyde adhesive. Also, this measurement allowed us to determine the highest temperature that may be safely applied during the pressing of panels without any decomposition of the adhesives and gave an indication of their flame retardant performance.

b) Differential Scanning Calorimetry (DSC) was used to determine the optimum hardening (curing) temperature. Such measurements were carried out on the prepolymer of the adhesives as well as on the wood impregnated with the adhesive in order to inspect the contribution of wood in changing the curing temperature of the adhesive. This allowed proper choice of production conditions during the manufacturing of panels.

Finally, the testing of plywoods was carried out using standard procedures adopted by the industry in Europe. These are the European standard EN 314.1, the British standard BS6566 and the Japanese standard JIS A1460. The plywood panels produced with the experimental adhesives were compared with with a standard phenol-formaldehyde adhesive. All panels were classified according to the European standard EN 314.2 and their free formaldehyde emissions.

Detailed information on the above-mentioned measurement and test procedures are given below.

12.2 Testing and evaluation of wood

As well as visual inspection of the veneers for defects, the pine wood, that was the material of the veneers used, was examined using a Scanning Electron Microscopy (SEM).

Scanning Electron Microscopy (SEM) is a method used in material examination at an appropriate magnification, 500 to 10,000x and provided information about:

- Topography: The surface features and texture
- Morphology: The shape and size of cells
- Composition: The elements and compounds it is composed of.
- Crystallography: The arrangement of atoms in the material.

The scanning electron microscope is similar to a light microscope but it uses a focused beam of electrons instead of light to image the specimen. Due to the energy and wavelength of the electrons that create the image, greater dept of field and higher resolution are achieved compared to conventional light microscopy. For example a light microscope allows magnification of 500x or 1000x and a resolution of 0.2 μm while an electron microscope provides magnification up to 10,000x. Another difference is that a light microscope image shows the entire specimen while the electron beam of electron microscopes scans back and forth over the specimen imaging only one point at a time.

During the SEM inspection, a stream of electrons is accelerated onto the sample which is held at a positive electrical potential. The stream is confined by magnetic lenses into a thin, focused and monochromatic beam, which is guided along a specific path onto the sample by electromagnets (magnetic lens).

The sample is bombarded with electrons (primary electrons), dislodging electrons from the specimen (elastic and inelastic scattering electrons). The elastic scattered (backscattered or reflected) electrons are primary electrons that re-emerge from the sample after collision with the nuclei of the bombarded sample. Back scattered electrons posses more energy than secondary electrons and have a defined direction, and they can only be collected by a secondary electron detector, if this detector is in their path of travel. All emissions above 50eV are considered to be back scattered electrons. These electrons are also collected by a positive biased grid or detector and converrted into an image of the specimen.

The inelastic scattered electrons which are also known as secondary electrons are attracted and collected by a positive biased grid or detector and then translated into a signal. The energy of the primary electrons determines the quantity of secondary electrons collected during the inspection. Primary electrons with increased energy result in increased emission of secondary electrons. Besides, when the energy of primary electrons is high, some electrons with sufficient kinetic energy will penetrate the sample and recombine before reaching the surface for emission. This results in a reduction of the collected secondary electrons, while the images received, even though of high resolution, provide an unclear illustration of the surface and the structure of the sample.

The signals resulted from interactions of the electron beam with atoms at or near the surface of the sample are received from a SEM inspection detector, amplified, analyzed and translated into an image. A SEM image is produced by detecting either back-scattered or secondary electrons. The images created by SEM are three-dimensional and have large depth of field providing a comprehensive understanding of the surface structure. The images obtained from the secondary electrons afford a good mapping of fine surface topographical features while the back-scattered electron imaging is especially useful in distinguishing one material from another because this signal is strongly related to the atomic number (Z) of the specimen. Thus information about the distribution of the various elements in the sample may be obtained [157, 158].

In the case of wood, SEM was used for observations of the wood cell walls. The cellulose in the inner part of the cell is crystalline in nature and form threads which are called microfibrils. They appear to be almost square in cross section images, while in lattice images a single microfibril is considered as an individual crystal. Examples of wood cell images from a Scanning Electron Microscope in the three directions of its anisotropy are shown below.

1. Transverse (cross) section: the softwood is normally simple and homogenous (figure 60) (700x) [159].

Figure 60: cross section of southern yellow pine
[159]

2. Radial section: the most obvious change in the structure of wood refers to the interruption of tracheids by radical pits (figure 61, 62 & 63) (400x) [160].

Figure 61 Figure 62 Figure 63

Radial sections of yellow pine

2. **Tangential section**: Bordered pits are rarely found in tangential surfaces while diagonal microchecks passing through bordered pits in tracheid cell walls are the most visible structural change observed. The microchecks occur at the S_2 cell wall (figure 64, 65, 66 & 67) (400x) [160].


Figure 64


Figure 66


Figure 65

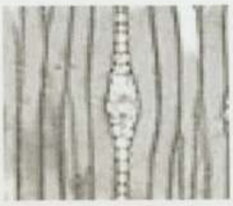


Figure 67

Tangential sections of yellow pine

12.2 Testing and evaluation of adhesives

The measurements carried out for the determination of the physical characeristics of the adhesives are the following :

12.2.1 Oven dry solid content (non-volatiles)

The solid content of formaldehyde-based adhesives was determined by various drying methods. In this study, an aluminium container of 68mm in diameter was weighed, and 2.0±0.1 g of the liquid adhesive was transferred into the container. The container was placed in an oven and the contents were dried at a temperature of 120 ± 1ºC for three hours (3h). The container was removed to a desiccator for 30 minutes and weighed to the nearest 0.1mg. This procedure was carried out in duplicate. The difference in the weight of the adhesive sample is the solid content of the adhesive which is quoted as a percentage by weight.

12.2.2 Viscosity

Thermosetting adhesives are non - Newtonian fluids (their viscosity changes as the shear rate increases) and their viscosity was measured by rheometers. There are various types of rheometers, each of which use a different property to measure the viscisities of fluids. The most common among these are the rotational rheometry, capillary rheometry and falling ball. In the current study, all viscosity measurements, both during the synthesis of the adhesives and analysis were carried out with a Brookfield rheometer RVF. That employs the principle of rotational rheometry; the rheometer measures the viscosity by sensing the torque required to rotate a spindle at a constant speed while immersed in the sample fluid. The torque is proportional to the viscous drag on the immersed spindle, and to the viscosity of the fluid. The readings from the rheometer dial are converted directly into centipoise (cP) and no other calculations are required. In particular, the Brookfield rheometer used (figure 68 – [161]) was equipped with a small sample (less than 18ml) adapter consisting of a cylindrical sample chamber and spindle (figure 69 – [161]).

Figure 68: Brookfield rheometer

Figure 69: Brookfield small sample adapter

The use of the small size adapter allowed rapid temperature control and accurate viscosity measurements at specific shear rates

The measurements were carried out with a spindle No 18.

For the implementation of the measurements, the sample was poured into the chamber and the spindle was immersed in it. The spindle was attached to the viscometer and turned in a clockwise direction. The operating conditions of the viscometer were set while any viscosity value was recorded only after the digital reading had stabilized. For all measurements the temperature of the sample was adjusted to 25°C. Between repeated measurements the adapter was cleaned and dried well with a tissue, because remaining water affects the accuracy of the measurements. As the synthesis process evolved the pre-polymer increased in viscosity and each time the measured torque reached 90% of the full scale range (FSR) the speed was decreased by a factor of 10. The measurements were completed when the viscosity was reached a set value. In all the following experiments the viscosity values are expressed in centipoise (cP) or mPa.s at 25°C.

The following figure 70 shows the viscosity increment over time during the preparation of a standard phenol-formaldehyde resol adhesive.

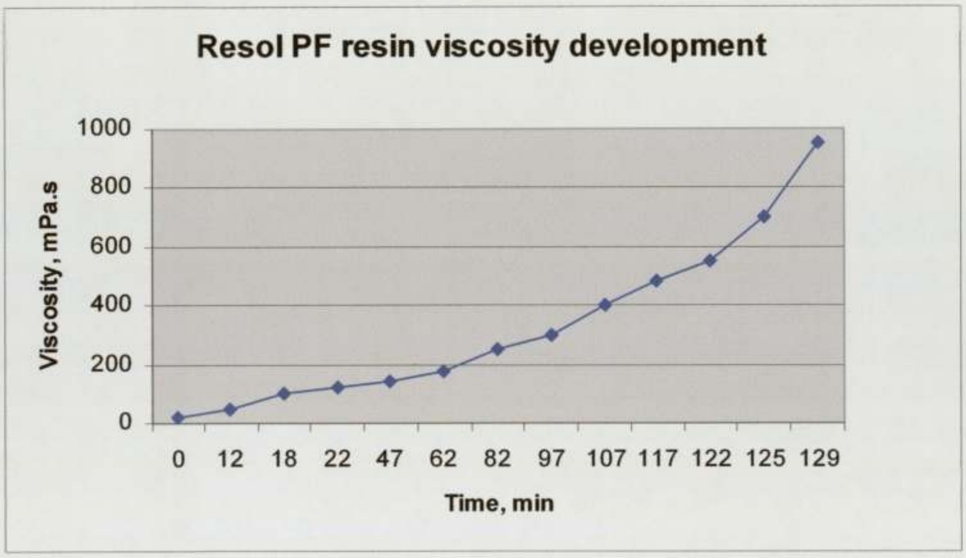


Figure 70: Viscosity development of a standard phenol-formaldehyde resol adhesive

12.2.3 Gelation time

The curing time and behaviour of an adhesive is important in processing panels and provided information on whether the adhesive cures rapidly or according to a slower curing mechanism. Generally, the gelation (gel) time was taken to be the length of the time between adding the hardener and the gelation of the adhesive or the time taken to gel once the adhesive had reached the curing temperature. PF adhesive pre-polymers can gel on heating alone although the addition of a hardener accelerates their cure. The gelation time, the beginning and the end of the gelation process, the length of the gelation period and appearance and strength of the hardened adhesives provides significant information about the system.

In the present work, a quantity of 4 grams of the pre-polymer in liquid form was introduced into a 14mm diameter testtube. The testtube was immersed in glycerin thermostatically controlled at 110ºC. The fluid was stirred continuously with a wooden stirring rod to secure a uniform temperature throughout the mass. A timer was started when the test tube was initially placed in the bath and stopped upon the setting of the adhesive. The recorded time was taken as the “gel time” of the sample measured in minutes.

12.2.4 pH (calibration and measurements)

An electrode generates an electrical voltage according to the Nernst's equation when part of a circuit is immersed in a solution. The potential is dependent on the pH of the solution and measurement of the voltage enables the pH of the solution to be measured. pH 7.0±0.01 is considerd to be the zero point and represents a potential of 0 mV. Nevertheless, due to the potential asymmetry, when the electrode is immersed in a standard buffer solution of pH 7.01 the potential is around ±20 mV but the electrode response is expressed in mV/pH unit. The theoretical slope of an electrode at 20ºC is 595.16mV/pH unit. By dividing the real value of the slope by the theoretical, the sensitivity of the electrode may be found. Both asymmetry potential and sensitivity shift from the standard values with use and aging of the electrode and thus calibration is required to compensate for these variations over a period of time.

In the present studies, a “Crison” pH meter was used equipped with a “Mettler Toledo” electrode. A three point calibration was carried out before measuring the pH of adhesive solutions.

The calibration process involved adjusting the pH reading produced by the electrode (pH sensor) to match the pH values of the buffer solutions (standards). The electrodes were rinsed with deionized water and blotted dry using a piece of tissue, before being immersed initially in the neutral buffer solution (pH 7.0±0.01), acid (pH 4.0) and finally alkaline (pH 9.0) buffers under continuous stirring of the buffer solutions with a magnetic stirrer. The electrode remained in each buffer until the display was constant.

In the current work the pH measurements were made at 25ºC.

12.2.5 Conductivity

Conductivity measurements of solutions enable the determination of the ionic concentration of the solution to be made. The conductivity is determined by measuring electric resistance of the solution, which is dependent on the level of the salt, alkali, or acid in the solution. In particular, the greater concentration of these substances in the solution, the greater the conductivity. As an example drinking water has a conductivity of about 100-1000µS/cm.

The cells used for measuring the electrical conductivity are comprised of two electrodes. An alternating voltage is applied to the electrodes and causes the ions in the solution to migrate towards the electrodes. The instrument measures the current and uses Ohm's law to calculate first the conductance of the solution and then the conductivity by taken the cell data into account.

In thermosetting adhesive the conductivity measurements provide an indication of the ease of heat and steam transfer in the adhesive.

The current measurements of conductivity were carried out using a WTW Cond 330i conduct meter at 25ºC.

12.2.6 Alkalinity

Alkalinity is defined as the acid neutralizing capability of a system. Thus, it is a measure of the ability of a solution to resist a decrease in pH when acids are added. The alkalinity is equal to the stoichiometric sum of the concentrations of bases in solution. Particularly in water, the common natural components that can contribute to alkalinity include [162]: carbonate or bicarbonate, borate, hydroxide, phosphate, silicate, nitrate, dissolved ammonia, the conjugate bases of some organic acids and sulphide. Nevertheless, usually total alkalinity is referred to three components namely hydroxide (OH^-), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). The existence of these ions in solution is pH dependent. At pH values of 4.3 to 8.3, the alkalinity is thought principally due to the HCO_3^- ion. At pH values greater than 8.3 concentration of the CO_3^{2-} ion begins to be important while at pH approximately 10 the OH^- will start to exist [12].

Alkalinity can be measured by titrating a sample with a strong acid until all the buffering capacity of the ions that cause the alkalinity are consumed.

Hence, when alkalinity measurements are carried out on an adhesive the concentrations of the hydroxide (OH^-), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions present in the mass of the sample are measured. These ions have been introduced either directly or through the addition of water required by the recipe in the synthesis of the adhesive.

In the present study the alkalinity of the adhesives was determined as follows: About 0.5g of the adhesive was diluted in 100 g deionized water in a 250 cm^3 beaker. Four drops of bromocresol green-methyl red indicator solution were added and the beaker swirled to mix. Titration was carried out with 0.05M sulphuric acid (H_2SO_4) until the colour of the mixture turned yellow.

12.2.7 Thermal Analysis (TGA/DTG, DSC)

Thermal analysis techniques have the advantage than only a small amount of the sample is required for the measurements ensuring uniform temperature distribution. Such methods are:

- *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis is an analytical method that allows the determination of the thermal stability of a adhesive and the fraction of volatile components by monitoring the changes in weight that occur during the heating of the specimen [12]. Usually analysis is carried out in air or in an inert atmosphere (helium, argon) and the weight is recorded as a function of increasing temperature.

- *Differential Thermogravimetric Analysis (DTG)*

Differential Thermogravimetric Analysis provides a derivative weight loss curve that can be used to determine the point at which the weight loss is most apparent [12].

- *Differential Scanning Calorimetry (DSC)*

This method allows the measurement of the energy required to maintain a zero temperature difference between a sample and a reference material [163]. During the measurement both the sample and the reference material are maintained at the same temperature. The reference material, must have a measurable heat capacity over the range of the temperatures that the measurement is carried out. When the sample is subjected to physical transformations (i.e. phase transition), heat will additionally need to flow into the sample in order for the two materials to be kept at the same temperature. How much more or less heat transferred to the sample depends on the exothermic or enthothermic nature of the transition [164].

DSC measurements provide information about the reaction kinetics, the polymerisation of resols, their degree of cure, cure rate and activation energy [12] to be determined.

In the current study the thermogravimetric measurements were carried out using a SETSYS SETARAM TG-DSC 16/18 equipment while the DSC measurements were conducted on a SETARAM DSC141. All measurements were carried out with a heating rate of 5°C/min.

12.3 Testing and evaluation of plywood

12.3.1 General

According to industrial practice in Europe, plywood panels have to pass certain quality control tests before they can enter the market. These tests refer to mechanical strength, wood failure performance, waterproofing and free formaldehyde emissions. In this study the testing of plywoods were carried out according to the following worldwide accepted standards; namely:

1. EN 314.1: Plywood - Bonding quality - Part 1: Test methods (June 1993). Revision published in 2004.
2. BS6566: Part 8: Specification for bond performance of veneer plywood (1985). The principle of this method is technically equivalent to that of EN 314.1 and this standard is the prevailing one in industrial practice ("knife test").
3. JIS A 1469: Building boards determination of formaldehyde emission – Desiccator method (2000).

Plywood panels are classified according to their end use, grading being conducted according to the specifications determined by the European standard:

EN 314.2: Plywood - Bonding quality - Part 2: Requirements (June 1993). Further classification was carried according to the level of their free formaldehyde emissions.

12.3.2 Testing methods-Description of procedures

12.3.2.1 European Standard EN 314.1

The standard, EN 314.1, specifies a shear test method for determining the bond quality of veneer plywood. Initially sufficient numbers of test pieces were cut to the following dimensions: l_1=25±0.5mm, b_1= 25±0.5mm, b_2=2.5-4.0mm thickness, l_2=50mm (figure 71).

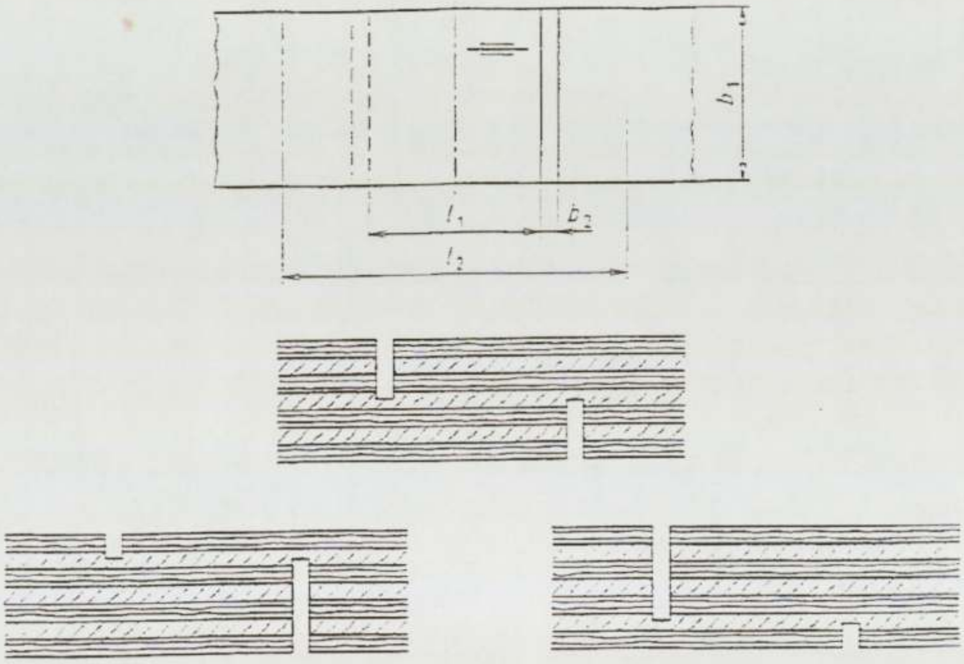


Figure 71: Test piece example with 7 plies (EN 314.1)

Each testpiece was cut with the grain direction of the layers perpendicular to the length of the testpiece and the saw cuts were extended into the layers (figure 71).

In this study the plywood panels were tested under the more severe conditions described in the EN 314.1 standard, as follows:

Before starting each shear test, the plywood samples were subjected to a sequence of pre-treatments depending on the specifications of their intended use. The testpieces, well separated and free to move, were placed in a wire basket which was immersed for 72 (±1) hours in boiling water followed by cooling in water at 20 (±3)°C for at least 1 hour to decrease the temperature of the test pieces to 20°C.

They were then immersed for 4 hours in boiling water, dried in a ventilated oven for 16 to 20 hours at (60±3)°C and immersed again in boiling water for another 4 hours. Finally the test pieces were left to cool in a water bath at 20±3°C for at least 1 hour to decrease their temperature to 20°C.

The specimens were subjected to shear and wood failure tests after excess surface moisture had been removed.

The test pieces were arranged in the centre of a clamping device in such a way that the load could be transmitted from the testing machine, via the ends of the test pieces to the shear area without any transverse loads. The load was applied at a constant rate of separation of the jaws of the tensometer so that rupture occurred within (30±10) *s*. After the shear test was completed, the specimens were subjected to another test to determine apparent cohesive wood failure; the failure should normally be in the wood or in the glue-line between the saw cuts (within the shear test area). The test pieces were allowed to dry before the determination of apparent cohesive wood failure. The apparent cohesive wood failure percentage was determined by comparison of the state of the failure with standards shown in annex A of the EN 314.1. The specimens were graded on a scale from 0 to 100 where the higher score was given to the test piece with the higher apparent cohesive wood failure.

12.3.2.2. British standard BS6566

For the implementation of this test a knife is required of no specific type provided that it has a sharp curved cutting edge and is cranked to allow vacillator actions. The size of the specimens may vary (150-200mm x100mm).

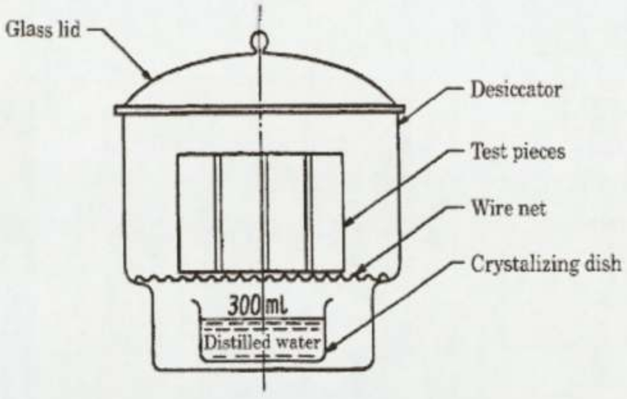
Specimens were immersed in boiling water for 4h ± 15min and subsequently dried at 60±3°C for 20±1h in a ventilated oven. The specimens were then immersed in boiling water for a further 4h ± 15min and finally placed in water at 15±5°C until cooled. If needed, they could be stored in this water bath for a maximum of 3 days before testing.

The knife test was implemented when specimens were still in a wet condition. The knife edge was applied parallel to the grain of the veneer under test. The knife was pushed initially downward and then forward through the veneer under test, making effort to keep the knife in the glue-line. When the knife had penetrated a convenient distance, e.g. 25mm to 50mm, the knife was prised upwards to remove the top veneer. This process could be repeated until a sufficient area of the joint had been exposed. Then the test piece was compared with the master scale rated from 10 (the highest) to 0. The highest bond quality (rate 10) was granted to a test piece when the separation was occurred only through the breaking of the wood itself and the glue line was entirely covered by adhering fibre. The lowest score (zero) was granted to a specimen when the separation was implemented along the glue line and few or no wood fibres had been left adhering to the veneer.

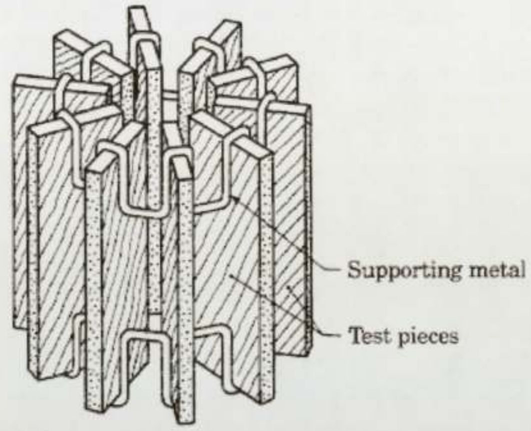
12.3.2.3. Japanese standard JIS A 1469

Formaldehyde emissions of plywood panels are determined according to the Japanese Industrial Standard JIS A 1460(2006): Building boards determination of formaldehyde emission-Desiccator method.

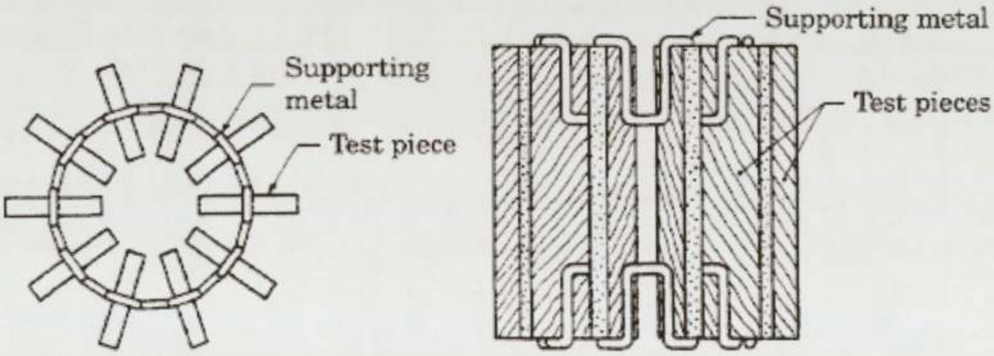
This test refers to the determination of the emitted quantity of formaldehyde. According to this method, test pieces of 150mm±1mm length and 50mm±1mm width were cut from the plywood to provide a minimum surface area of 1800cm^2. The pieces were positioned in stainless steel wire nets that were placed in a glass desiccator equipped with a glass crystallizing dish containing 300±1ml distilled or deionized water (figure 72).



a) Desiccator



b) sketch



c) plan

d) side view

Figure 72: Schematic diagram of desiccator method
a) Desiccator, b) sketch, c) plan, d) side view [165]

The specimens were allowed to condition at 20°C and 65±5% relative humidity until they reached constant mass (by definition the sample should not change in weight during a 24 h interval).

In this test any formaldehyde emitted was absorbed by the water and determined by acetylacetone molecular absorption spectroscopy according to the Hantzsch reaction in which formaldehyde reacts with ammonium ions and acetylacetone to yield diacetylduhydrolutidine (DDL) [162]. This reaction is specific to formaldehyde. The absorption wavelength of DDL is 410-415nm.

A desiccator containing no test pieces was subjected to the same testing conditions. The distilled or deionized water in the glass dish was used for the measurement of background formaldehyde.

For the requirements of the measurement the formaldehyde content was determined using a calibration curve correlating the quantity of formaldehyde (of known formaldehyde water-based solutions) to absorbance. The slope F (mg/l) was obtained graphically or by calculation.

The concentration of formaldehyde in the water, derived from the test pieces in a desicator, was calculated by the following equation:

$$G = \frac{F * (A_d - A_b) * 1800}{S}$$

Where G: concentration of formaldehyde

A_d: absorbance of solution inside desiccator containing test pieces.

A_b: back ground absorbance of formaldehyde

F: slope of calibration curve on the standard solution of formaldehyde

1800: requested total surface area (cm^2)

S: real surface area of test pieces (cm^2)

12.3.3 Evaluation methods and classification of plywoods

Relative to industrial practice in EU, plywood panels are evaluated for mechanical and waterproofing properties according to the methods outlined in the European standard EN 314.2, while their classification with reference to their free formaldehyde emissions is carried out according to their ability to meet certain free formaldehyde limits.

The standard EN 314.2 specifies three classes of panels, namely:

Class 1-Dry Conditions: interior applications with no risk of wetting (moisture content ≤ 12% at 20°C and 65% relative humidity).

Class 2-Humid Conditions: protected exterior conditions (moisture content ≤ 20%, at 20°C and 85% relative humidity).

Class 3-Exterior Conditions: unprotected exterior conditions (moisture content ≥ 20%).

The testing conditions vary for each of these classes while for a successful plywood panel each adhesive has to satisfy two criteria. In particular, the values of the mean shear strength (fv) and the mean apparent cohesive wood failure tests must have values that comply with the limits presented in the following table 11.

Table 11: EN314.2 standard bonding performance requirements

Mean shear strength (fv), MPa	Mean apparent cohesive wood failure w, %
0.2 ≤ fv < 0.4	≥ 80
0.4 ≤ fv < 0.6	≥ 60
0.6 ≤ fv < 1.0	≥ 40
1.0 ≤ fv	No requirement

The plywood panels in this study were subjected to test conditions of class 3 and that refers to extrerior grade panels

Of course there are fyrther standards for evaluation of plywood panels but the prevailing ones in the international trade market are the standards of Europe, Japan and North America. Their test methods are comparable and are presented in a comprehensive table below (table 12).

Table 12: Comparison of plywood test procedures according to various standards

Standard Class	EU	Japan	North America
Dry Type III	24h in water at 20°C	2h in water at 35°C Drying 3h at 60°C	-
Humid Type II Exposure 2	6h in boiling water*	2h in water at 70°C Drying 3h at 60°C	8h in water at 66°C Drying at 82°C to initial weight
Exterior Type I Exposure 1	72h in boiling water*	4h in boiling water Drying 20h at 60°C 4h in boiling water Drying 3h at 60°C	30m in water at 66°C & 50.6kPa V 30m in water at 66°C ATP 6h drying at 82°C 30m in water at 66°C & 50.6kPa V 30m in water at 66°C ATP 15h drying at 82°C **
Additional for exterior	4h in boiling water Oven 16/20h at 60°C 4h in boiling water*	4h in boiling water Drying 20h at 60°C 4h in boiling water*	-

* Followed by 1h immersion in water at 20°C
** 3 cycles

The correspondence of the plywood panel classes according to the above-mentioned standards is presented in the following table 13.

Table 13: Correlation of various standards

Domination	**Europe**	**North America**	**Japan**
Standard	**EN636**	**PS 2-92**	**JAS**
Categories	Class 1: Dry conditions	-	Type III
	Class 2: Humid conditions	Exposure 2	Type II
	Class 3: Exterior conditions	Exposure 1	Type I

The panels may be further classified according to their free formaldehyde emissions values. While each continent has their own standard the prevailing ones in the international market are those of Europe, Japan, and North America. In Europe the testing of wood-based panels may be conducted according to three methods: Perforator method (EN120), Gas analysis (EN 717.2) and Flask method 717.3). While in Japan the testing of panels is carried out according to the dessicator method (JIS A1460). The formaldehyde emissions limits for each class of wood-based panels as they are described by the relative standards are cited in the following table 14. In this study the dessicator method was applied to the determination of free formaldehyde emissions from the plywood panels.

Table 14: Comparative plywood classification according to formaldehyde release

EU		**JP**	
E1	$\leq$ 0.1ppm or $\leq$ 3.5mg/h*m^2	F1	$\leq$0.5mg/L
E2	> 0.1ppm or > 3.5 ÷$\leq$ 8.0mg/h*m^2	F2	$\leq$5.0mg/L
-	-	F3	$\leq$10.0mg/L

13 SYNTHESIS OF ADHESIVES

13.1 Raw materials

The raw materials used were:

- Phenol as 90% water based solution
- Formaldehyde as 37% water based solution
- NaOH as 30% water based solution
- Tannin "Bondtite 345" from "Bondtite" company, South Africa. It is condensed tannin from acacia.
- Lignin organosolve type form from "ALM", India
- Cashew nut shell liquid (CNSL) from the company "Resibras" Brazil
- Soy Isolated Protein from "Du Pont" company
- Forestry residue pyrolysis bio-oil from VTT Technical Research Centre of Finland

13.2 General preparation

A glass reaction vessel was equipped with a Teflon paddle stirrer, a thermometer, a reflux condenser, and a heating mantle. The reaction mass was cooled, if necessary, during the synthesis by immersing the vessel in a cool water bath. A quantity of 1491g of the standard PF adhesive and 1458g of each of the experimental adhesives were prepared. In all cases, the reaction conditions were kept the same for comparative evaluation of the adhesives.

In particular:

All adhesives had mole ratio of formaldehyde to phenol (F:Ph) of 2:1, and NaOH:phenol 0.6:1, and the experimental adhesives prepared having a 15% phenol substitution by any of the above-mentioned natural derived materials.

13.3 Synthesis process of PF control adhesive

The reactor was charged with 669g of formaldehyde, 429g phenol and 330g NaOH. All materials were kept at room temperature during charging into the vessel which lasted about 20 minutes. An exothermic reaction occurred and after about

15 minutes when the exothermic process had come to an end, the reaction mixture was heated up to 88°C allowing the condensation reaction to commence. vessel was immersed in an ice bath in order to give a sharp end to any chemical reactions. When the temperature reached about 40°C, 63g of deionized water were added to the mixture in order to adjust the final viscosity to 400-500cP. The phenol-formaldehyde adhesive thus produced was kept at 4°C until use.

13.4 The synthesis of PF-modified adhesives

The reactor was charged with 665g formaldehyde, 420g phenol and 320g NaOH.

All materials were kept at room temperature during charging into the vessel which lasted about 20 minutes. An exothermic reaction occurred and after about 15 minutes when the exothermic process had come to an end, the reaction mixture was heated to 88°C allowing the condensation reaction to commence. The polymerization reaction was allowed to proceed for 3 hours. Then, 63g of the natural derived material was added to the vessel and the reaction mixture was allowed to proceed for one more hour. The polymerization reaction ceased on quick cooling and when the temperature reached about 40°C. The reaction mixture was then cooled further to room temperature and stored at 4°C until use.

For the needs of his study, one phenol-formaldehyde (PF) standard adhesive was synthesized and used as a control adhesive for the evaluation of the five experimental PF adhesives produced with 15% phenol substitution by each of: forestry residue bio-oil, lignin, tannin, cashew nut shell liquid (CNSL) and soy protein isolate (SPI).

14. PLYWOOD PRODUCTION

In all cases three-ply panels were produced on a laboratory scale using veneers from pine. The veneers had moisture contents of about 5-6% and dimensions 50.5x50.5x0.2 cm^3.

A mixture of pre-polymer and filler/exender was prepared as cited in table 15; water was added when necessary in order to adjust the viscosity of the glue mixture to 3,000-4,000mPa.s [13]. The quantities of the adhesive pre-polymer and the filler/extended are cited in the following table 15.

Table 15: Glue mix formulation for the production of plywood

Material	Quantity in parts by weight (pbw)
Adhesive	100
Wheat flour	18

The glue mixture was spread on both sides of the core veneer at a thickness of 150g/m^2 [29]. Only the core veneer was spread with adhesive while the face veneers were stacked on it without glueing and in a perpendicular order so that the grain of each ply was at right angles to its neighbour (cross-bonding). After 40 min assembly time, the panels were subjected to cold pre-pressing for 15min followed by hot pressing at 130°C for 6 minutes. The pressing pressure was 1.5 MPa.

Duplicate panels were prepared for each of the adhesives prepared.

15. RESULTS

This section of the study includes results of adhesives and plywood test and evaluation as well as results of the inspection of wood by Scanning Electron Microscopy (SEM) and thermal analyse.

15.1 Results from phenol – formaldehyde (PF) standard adhesive and plywood produced with it

15.1.1. Testing results of PF adhesive

The Physical properties of the standard PF adhesive were determined after laboratory analysis and are presented in table 16.

Table 16: Physical properties of the PF adhesive

Adhesive: PF

Property	Unit	Value
Viscosity	mPa.s	420
Solids	%	42.9
Alkalinity	%	6.2
GT	min	10
pH	-	11.1
Conductivity	µS/cm	17.68

Thermogravimetric / Differential Thermogravimetric Analysis (TGA / DTG), and Differential Scanning Calorimetry (DSC) analysis of the adhesive yielded the information shown in the following figures 73 and 74

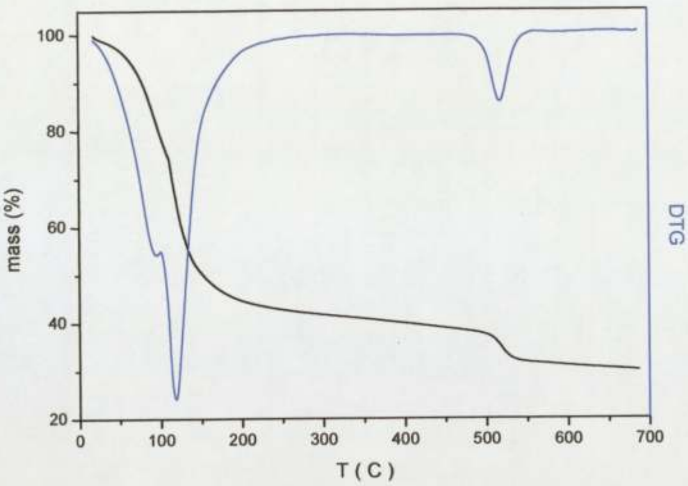


Figure 73: TGA of PF standard adhesive

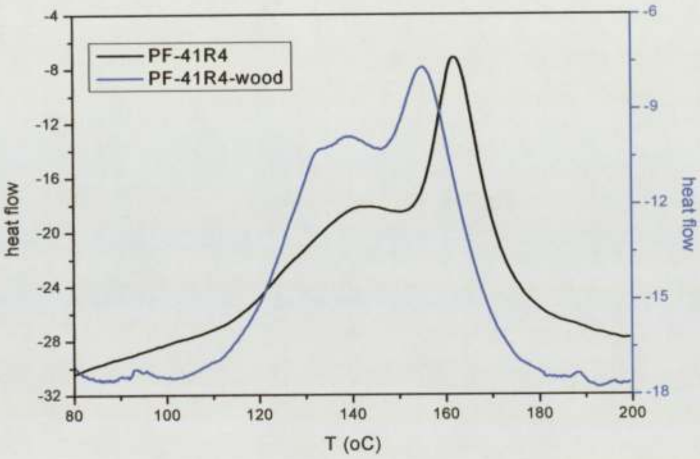


Figure 74: DSC thermogram of liquid PF std. adhesive & wood impregnated with it.

15.1.2 Discussion on PF adhesive testing results

- Thermogravimetric / Differential Thermogravimetric (TGA/DTG) results

In the TGA graph, we observe an initial mass loss up to the temperature of about 150°C that is attributed to the loss of water from the adhesive. In the DTG, this loss is expressed by a curve with a peak temperature at about 118°C.

From the TGA plot it is also observed that the PF adhesive starts to degrade at about 200°C at a very slow rate, while, when the temperature is raised to 490°C, a rapid mass loss is observed. In the temperature range of 490-557°C there is a mass loss of about 6.3% from the adhesive that is attributed to the breakdown of methylene linkages [166] to yield aldehydes and phenols. Finally, about 31% of the mass remains as a coke-like solid mass residue.

- Differential Scanning Calorimetry (DSC) results

Figure 3.2 shows the DSC thermograph of both the liquid adhesive (pre-polymer) and a piece of wood impregnated with this adhesive. The pre-polymer exhibits two endothermic peaks one between 120°C and 150°C with peak temperature (Tp) at 142°C and the other within the range of 150-180°C with a peak temperature (Tp) at 162°C. According to the literature [166, 167] both curves relate to chain building condensations and in particular: the first curve (Tp 142°C) is due of chain building condensation reactions involving both hydroxymethyl groups attached to various phenolic species and self-condensation reactions of 4-hydroxybenzyl alcohol. The second peak (Tp 162°C) is attributed to self-condensation reactions of 2-hydroxybenzylalcohol.

The specimen of impregnated wood shows a similar curve shifted to lower temperatures indicating the ability of wood to accelerate the curing of the adhesive during pressing.

15.1.3 Plywood test results

The above adhesive was used for the fabrication of 3-ply panels that were subjected to tests for the evaluation of their shear strength, wood failure and free formaldehyde emissions. These tests were conducted according to the relevant standards and the results are presented in the following table 17.

Table 17: Test results from plywood produced with PF standard adhesive

Test / property	Unit	Value
BS6566- Knife test, (x10)	%	80
EN 314.1		
Shear strength	MPa	1.04
Wood failure	%	74
JIS A1460- desiccator method Free formaldehyde emissions	mg/l	0.52

15.2. Forestry residue Pyrolysis oil – PF adhesive (PFB) and plywood produced

A forestry residue pyrolysis liquid was provided by VTT Technical Research Centre of Finland within the framework of BIOCOUP EU project (Contract Number: 518312)*.

The sample had the following properties (table 18) [168].

Table 18: Physical properties of bio-oil [168]

Physical Properties	VTT forestry residue pyrolysis oil (bio-oil)**
Water, wt%	24.1
pH	2.9
Density (at 15°C), kg/dm^3	1.22
Elements (dry), wt%	
-C	56.6
-H	6.2
-O (by diff.)	36.9
-N	0.1
-S	0.03
-Ash	0.08
HHV (dry), MJ/Kg	23

** Bottom phase (90 wt% of total liquid)

15.2.1. Test results of PFB adhesive

The PFB adhesive with 15% phenol replaced by forestry residue oil gave the following characteristics (table 19):

Table 19: Physical properties of PFB adhesive

Adhesive: PFB

Property	**Unit**	**value**
Viscosity	mPa.s	440
Solids	%	42.5
Alkalinity	%	6.5
GT	min	12
pH	-	10.8
Conductivity	µS/cm	22.2

The TGA and DSC thermal analysis of the adhesive are shown in the following figures 75 & 76

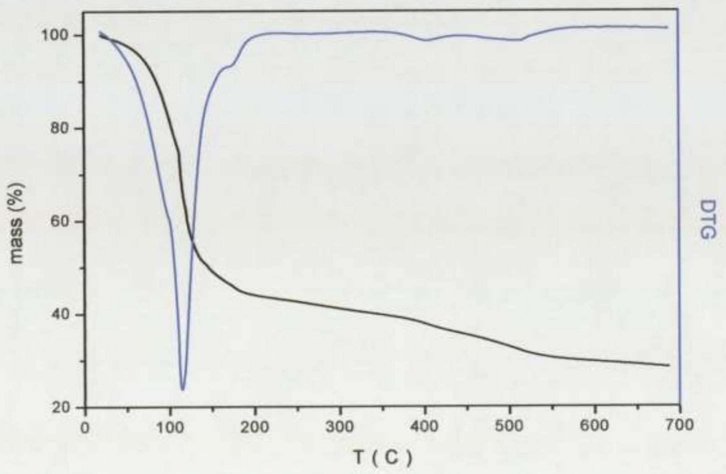


Figure 75: TGA graph of liquid PFB adhesive

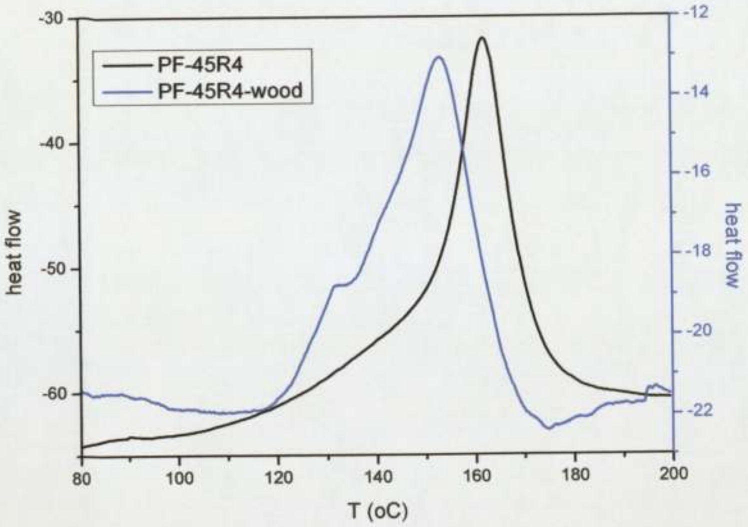


Figure 76: DSC thermogram of liquid PFB adhesive & impregnated wood.

15.2.2 Discussion on PFB adhesive testing results

- Thermogravimetric / Differential Thermogravimetric Analysis (TGA-DTG)

In the TGA graph, we observe a mass loss up to a temperature of about 200°C that is related to the water content of the sample. From the DTG the note of loss reached a maximum at 115°C.

Above 200°C, the TGA graph showed a progressive mass loss up to 550°C; at this temperature about 70% of the total mass of the sample seems to have been lost and thereafter practically no mass loss was observed.

In the DTG graph over the same range of temperatures three smooth curves with peak temperatures at about 190°C, 410°C and 520°C were observed.

According to the literature on PF adhesives [166], the mass loss at 120-240°C is attributed to post curing reactions of phenolic adhesives while a weight loss in the range of 450-550°C is attributed to breakdown of methylene linkages.

Nevertheless, a study by M. Garcia et al. [166] on bio-oil from bark residue in comparison to bio-oil from hardwood shows that the mass loss between 180°C and 232°C is attributed to extractives present in the bio-oil, while the solid residue obtained at 550°C is attributed to the lignin and mineral content of bio-oil.

In our case, the mass loss between 180°C and 230°C may be due to both the extractives present in the portion of bio-oil in PF adhesive as well as some formaldehyde release due to post curing reactions of the phenolic adhesive since the major mass of the adhesives follows the curing conditions of a conventional PF adhesive.

- Differential Scanning Calorimetry (DSC)

The graph presents the DSC thermograph of both the liquid adhesive and a piece of wood impregnated with adhesive.

The liquid adhesive exhibits transition between 140°C and 180°C with peak temperature at about 165°C. This range refers to condensation reactions of the adhesive.

The specimen of the impregnated wood shows a related curve shifted to lower temperatures. In this case the peak temperature seems to be at 155°C that is 10°C lower that the peak curing temperature of the liquid adhesive which suggests that wood accelerates the curing of the adhesive.

15.2.3 Plywood test results

The above adhesive was used for the fabrication of 3-ply panels which were subjected to tests for the evaluation of their shear strength, wood failure and free formaldehyde emissions. These tests were conducted according to the processes described in the relevant standards and the results are presented in the following table 20.

Table 20: Test results from plywood produced with PFB adhesive

Test / property	Unit	Value
BS6566 Knife test	%	50
EN 314.1		
Shear strength	MPa	1.20
Wood failure	%	40
JIS A1460- desiccator method Free formaldehyde emissions	mg/l	0.53

*Part of this research with forestry residue pyrolysis oil VTT Technical Research Centre of Finland was co-funded by the European Commission specific RTD programme "Integrating and strengthening the European Research Area" within the framework of the Integrated Project "Co-processing of upgraded bio-liquids in standard refinery units", acronym BIOCOUP, contract No SES6-518312.

15.3 Results of CNSL-PF adhesive (PFC) and plywood produced

The Cashew nut shell liquid (CNSL) raw materials was provided by the Brazilian company "Resibras"

15.3.1. Testing results of PFC adhesive

The experimental adhesive produced with 15% phenol replacement by CNSL showed the following characteristics (table 21):

Table 21: Physical properties of PFC adhesive

Adhesive: PFC

Property	Unit	Value
Viscosity	mPa.s	448
Solids	%	42.3
Alkalinity	%	6.4
GT	min	11
pH	-	11.7
Conductivity	µS/cm	20.0

The TGA and DSC graphs of the adhesive are presented below in figures 77 & 78

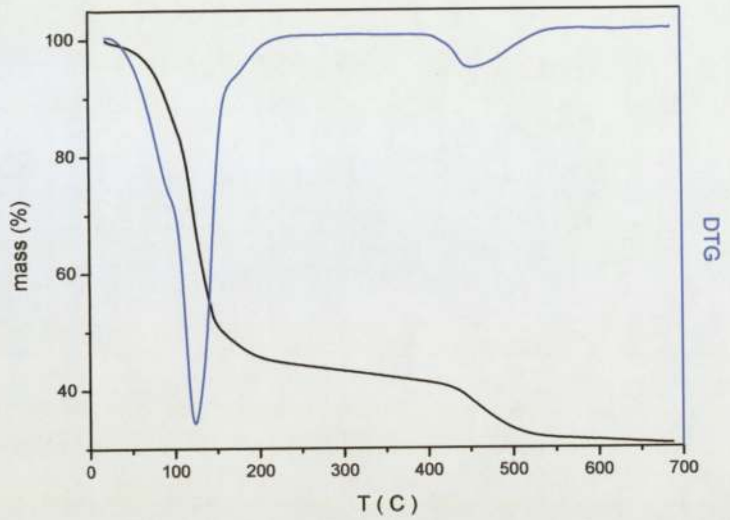


Figure 77: TGA graph of liquid PFC adhesive

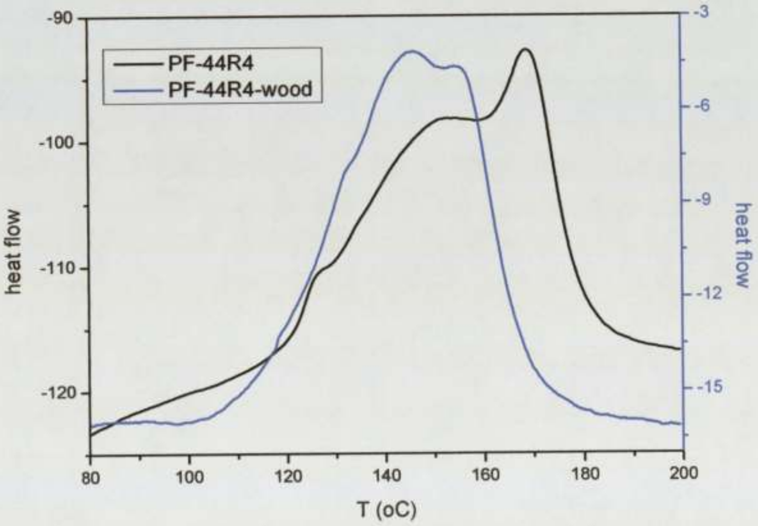


Figure 78: DSC thermogram of liquid PFC adhesive & impregnated wood.

15.3.2 Discussion on PFC adhesive testing results

- Thermogravimetric / Differential Thermogravimetric Analysis (TGA-DTG)

In the TGA graph, we observe a mass loss up to the temperature of about 110°C due to the loss of the water content of the sample. The relative phenomenon in the DTG graph shows an endotherm peak at about 123°C.

In the DTG graph it is also obvious that there is a small mass loss at the temperature range from 164–210°C. This is attributed to the transformation of ether bridges to methylene bridges with simultaneous release of formaldehyde [166]. This range constitutes a mass loss of 3.7% of the total mass.

Above 200°C the mass of the sample slowly reduced until the temperature is about 401°C. Within the temperature range of 401-553°C a massive mass loss of about 20.7% is observed due to the breakdown of methylene linkages [166].

Finally about 21% remains as solid residue.

- Differential Scanning Calorimetry (DSC)

The graph presents the DSC thermograph of both the liquid adhesive and a piece of wood impregnated with adhesive.

The liquid adhesive exhibit an endothermic process made up of two curves in conjunction, between 120°C and 185°C, which are attributed to condensation reactions of the adhesive.

The specimen of the impregnated wood presents a similar curve shifted to lower temperatures, indicating the adhesive is cured faster in presence of wood.

15.3.3 Plywood test results

The PFC adhesive was used in the fabrication of 3-ply panels and there were subjected to tests for the evaluation of their shear strength, wood failure and free formaldehyde emissions. The processes followed tests described by the relative standards. The results are presented in the following table 22.

Table 22: Test results of plywood produced with PFC adhesive

Test / property	Unit	Value
BS6566, Knife test (x10)	%	79
EN 314.1		
Shear strength	Mpa	1.08
Wood failure	%	86
JIS A1460- desiccator method Free formaldehyde emissions	mg/l	0.56

15.4 Results of Lignin-PF adhesive (PFL) and plywood produced

The lignin raw material used was an organosolve type with trade name "ECOBIND". It was provided by the "Asian Lingin Manufacturing" company in India.

15.4.1 Testing results of PFL adhesive

The adhesive modified PF adhesives prepared with 15% of phenol replaced by lignin had the following characteristics (table 23):

Table 23: Physical properties of PFL adhesive

Adhesive: PFL

Property	**Unit**	**Value**
Viscosity	mPa.s	410
Solids	%	42.5
Alkalinity	%	6.1
GT	min	11
pH	-	10.9
Conductivity	μS/cm	20.5

The TGA and DSC graphs of the adhesive are presented below in figures 79 & 80.

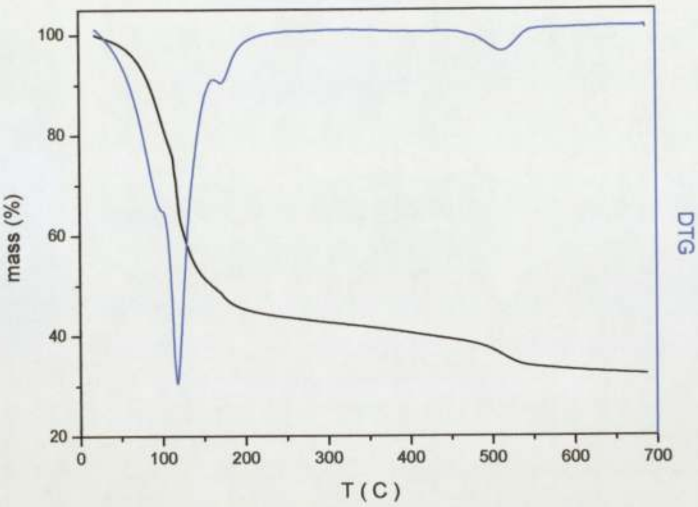


Figure 79: TGA graph of liquid PFL adhesive

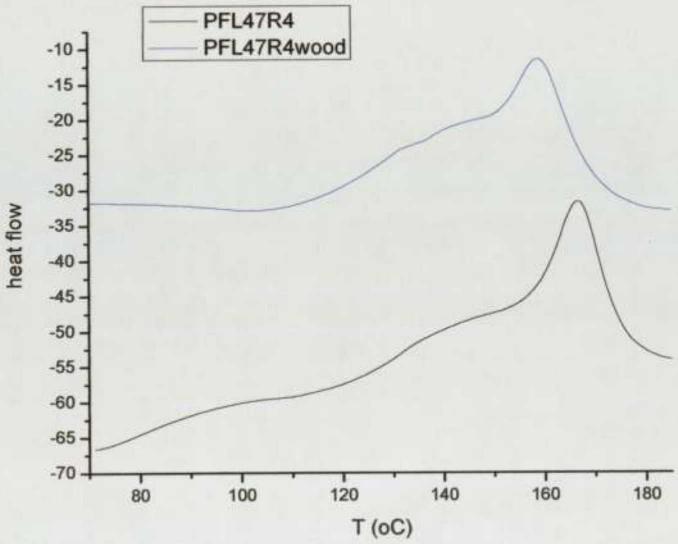


Figure 80: DSC graphs a) liquid PFL adhesive, b) wood impregnated with PFL adhesive

15.4.2 Discussion on PFL adhesive test results

- Thermogravimetric / Differential Thermogravimetric Analysis (TGA-DTG)

Initially we observe a mass loss up to the temperature of about 150°C due to the loss of water from the sample. The related phenomenon in the DTG graph exhibited a peak with note at a temperature at about 119°C.

In the DTG graph it is also obvious that there is a small mass loss in the temperature range 160–201°C (4.8%). Literature attributes this to the transformation of ether bridges to methylene bridges with simultaneous release of formaldehyde [166].

Above 200°C a progressive mass loss takes place while from 463°C to 553°C a fast mass of about 5% of the total mass is observed. This is due to the breakdown of methylene linkages [1]. Finally, about 33.8% weight remains as solid residue.

- Differential Scanning Calorimetry (DSC)

The plot shows the DSC thermograph of both the liquid adhesive and a piece of wood impregnated with it. Both the liquid adhesive and the impregnated wood show similar endothermic transition with Tp for the liquid adhesive at 166.74°C and Tp for the impregnated wood at 158.97°C. This implies that wood accelerates the curing of the adhesive.

15.4.3 Plywood test results

The PFL adhesive was used to fabricate plywood panels with three layers which were subjected to tests to evaluate their shear strength, wood failure and free formaldehyde emissions. These tests were conducted according to the relevant standards recognized by the industry. The results are presented in the following table 24.

Table 24: Test results of plywood with PFL adhesive

Test / property	Unit	value
BS6566, Knife test (x10)	%	75
EN 314.1		
Shear strength	MPa	1.09
Wood failure	%	42
JIS A1460- desiccator method Free formaldehyde emissions	mg/l	0.55

15.5 Results of Soy Protein Isolate-PF (PFS) adhesive and plywood produced

The isolated soy protein (SPI) sample was provided by DuPont Company. The sample had the trade name PC4200 and its physical properties, as provided by the manufacturer, were as follows:

Dry color: white

Molecular weight approx. 175,000Da

Net negative charge: yes

Moisture content: 5-10%

Specific gravity (10% water-based solution): 1.022

Viscosity (9% water-based solution):10-15 mPa.s @ 25°C

pH of 9% solution: 8-11

15.5.1 Testing results of PFS adhesive

The experimental PFS adhesive produced with 15% phenol replacement by soy protein isolate and its pre-polymer were subjected to the standard analysis for the determination of their physical characteristics. The results are shown in the following table 25:

Table 25: Physical properties of PFS adhesive

Adhesive: PFS

Property	**Unit**	**Value**
Viscosity	mPa.s	430
Solids	%	42.7
Alkalinity	%	6.3
GT	min	14
pH	-	11.2
Conductivity	μS/cm	16.81

The TGA and DSC data for the adhesive and impregnated wood sample are presented below in figures 81 and 82. Figure 81 also shows the DTG data for the adhesive.

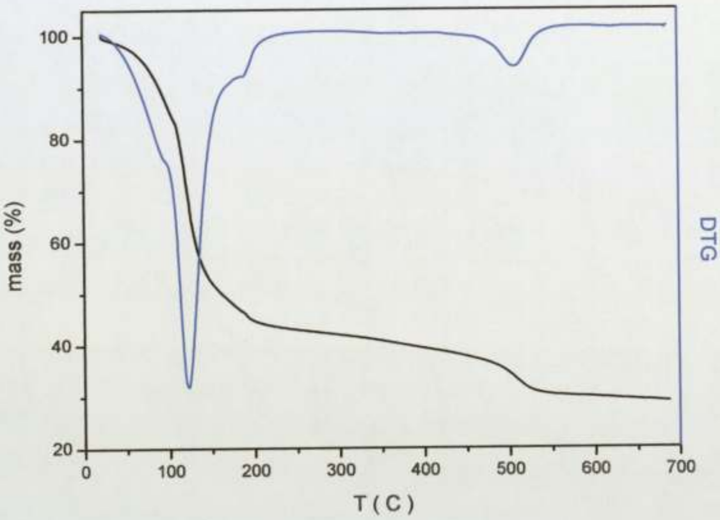


Figure 81: TGA graph of liquid PFS adhesive

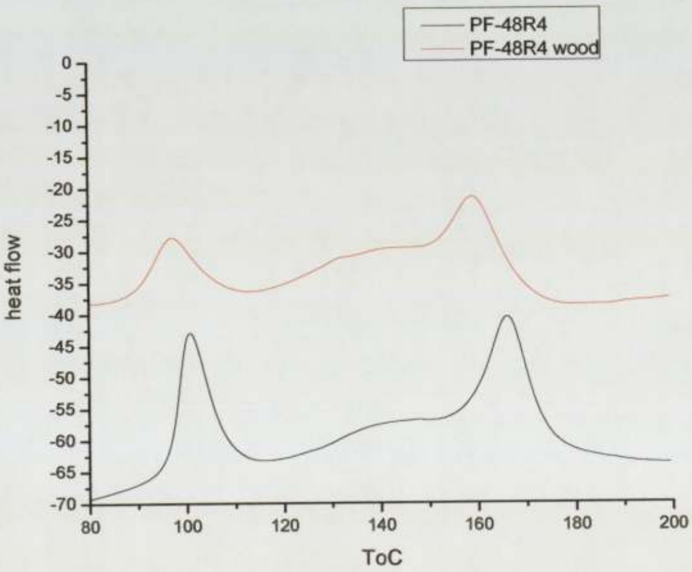


Figure 82: DSC thermogram of liquid PFS adhesive and impregnated wood

15.5.2 Discussion on PFS adhesive test results

- Thermogravimetric / Differential Thermogravimetric Analysis (TGA-DTG)

A mass loss up to the temperature of about 150°C is observed due to the loss of the water from the sample. The DTG data gave a peak temperature at about 120°C.

In the DTG graph it is also obvious that there is a small mass loss in the temperature range of 176–201°C (about 3.5% of the total mass), that according to the literature is attributed to the transformation of ether bridges to methylene bridges with simultaneous release of formaldehyde [166].

Above about 200°C, the mass of the sample gradually reduces while within the temperature range of 453 -551°C a substantial mass loss of 7.3 % takes place. This mass loss is attributed to the breakdown of methylene linkages [166].

About 30% remains as solid residue.

- Differential Scanning Calorimetry (DSC)

The DSC thermograph of both the liquid adhesive and a piece of wood impregnated with it Exhibit similar endothermics but that of the impregnated wood is somewhat shifted to lower temperatures in comparison with the liquid adhesive.

The liquid adhesive (that actually is the pre-polymer of it) presents two endothermic curves. One is within the temperature range of 95-105°C which could be attributed to addition reactions of unreacted methylol groups that remained unreacted under 100°C and another, split into almost two peaks, in the range of 130°C-185°C. The latter refers to self-condensation reactions of the PFS adhesive.

15.5.3 Plywood evaluation results

Plywood panels of three layers were produced from this PFS adhesive and evaluated for shear strength and wood failure as well as their free formaldehyde emissions according to the procedure required by the relevant standards. The results of these measurements are cited in the following table 26.

Table 26: Results from plywood evaluation produced with PFS adhesive

Test / property	Unit	value
BS6566, Knife test (x10)	%	75
EN 314.1		
Shear strength	MPa	1.40
Wood failure	%	84
JIS A1460- desiccator method Free formaldehyde emissions	mg/l	0.56

15.6 Results of Tannin-PF (PFT) adhesive and plywood produced

The tannin used was provided by Bondtide Company of S. Africa. The tannin sample provided had the trade name "Bondtite 345".

15.6.1 Testing results of PFT adhesive

The PFT adhesive produced with 15% phenol replaced by the 15% tannin "Bondtite 345" had the characteristics shown in table 27.

Table 27: Physical properties of PFT adhesive

Adhesive: PFT

Property	**Unit**	**Value**
Viscosity	mPa.s	450
Solids	%	42.8
Alkalinity	%	6.7
GT	min	9
pH	-	11.5
Conductivity	µS/cm	16.9

TGA and DSC analysis of the adhesive are presented below in the figures 83 & 84

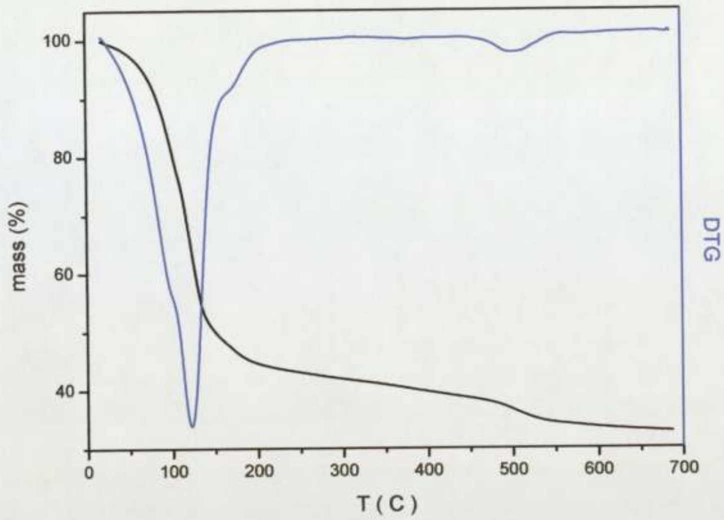


Figure 83: TGA of the liquid PFT adhesive

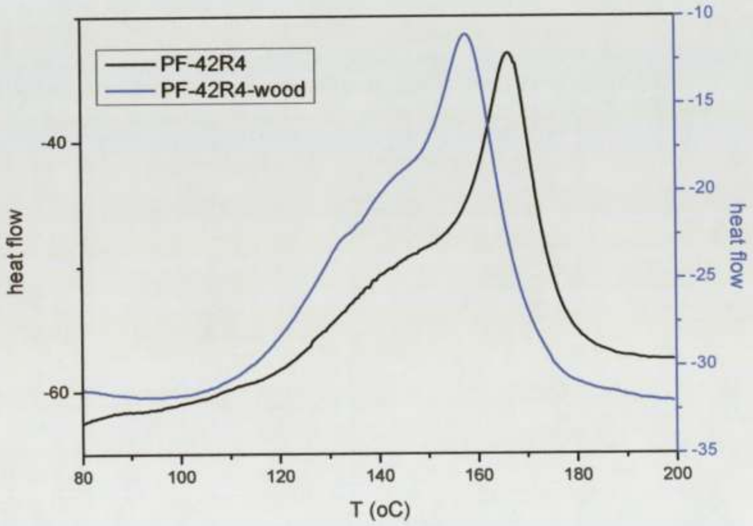


Figure 84: DSC thermogram of liquid PFT adhesive and impregnated wood sample

15.6.2 Discussion on PTF adhesive test results

- Thermogravimetric / Differential Thermogravimetric Analysis (TGA-DTG)

It can be deduced from the TGA figure that there is a mass loss up 150°C due to the loss of water content of the sample. The associated phenomenon in the DTG graph is an endotherm with peak at about 122°C.

DTG of this sample shows a clear an obvious small mass loss of 4.15% in the temperature range of 160–203°C. This is attributed to the transformation of ether bridges to methylene bridges with the simultaneous release of formaldehyde [166] (figure 85).

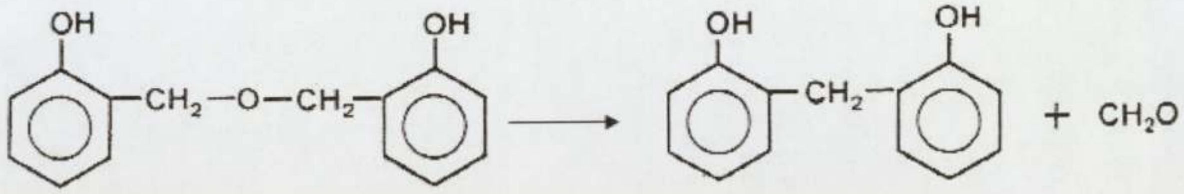


Figure 85: Transformation of dibenzyl ether bridges to dibenzyl methylene bridges

Above 200°C the sample progressively loses weight while within the temperature range of about 459-552°C there is a significant mass loss of about 4%. This is due to the breakdown of methylene linkages [166].

About 34% remains as solid residue.

- Differential Scanning Calorimetry (DSC)

Figure 84 shows the DSC thermographs of both the liquid adhesive and a piece of wood impregnated with adhesive.

The liquid adhesive shows an endothermic curve between 130°C and 185°C with a peak temperature at about 166°C. This is due to condensation reactions of the adhesive. The specimen of impregnated wood shows a similar curve shifted to lower temperatures. In this case the peak temperature seems to be at 158°C. It is possible to conclude that wood promotes the curing of the adhesive.

15.6.3 Plywood test results

The PFT adhesive was used for the fabrication of 3-ply panels and these were subjected to tests to evaluate their shear strength, wood failure and free formaldehyde emissions. These tests were carried out as described before and the results are presented in the following table 28.

Table 28: Test results from plywood produced with PFT adhesive

Test / property	Unit	Value
BS6566, Knife test (x10)	%	78
EN 314.1		
Shear strength	MPa	1.42
Wood failure	%	84
JIS A1460- desiccator method Free formaldehyde emissions	mg/l	0.54

15.7 Results of wood analysis

In the present study veneers from pine wood were used for plywood preparation. This type of wood was subjected to thermal (TGA, DTG and DSC) analysis and Scanning Electron Microscopy (SEM). The relevant graphs and images are presented below.

15.7.1. Thermal study of pine wood

A sample of pine wood was subjected to thermal analysis (TGA/DTG) at a heating rate of 5°C/min to determine its decomposition temperature and also locate the highest temperature that could be applied during pressing of the panels (figures 86 & 87), without decomposition occurs.

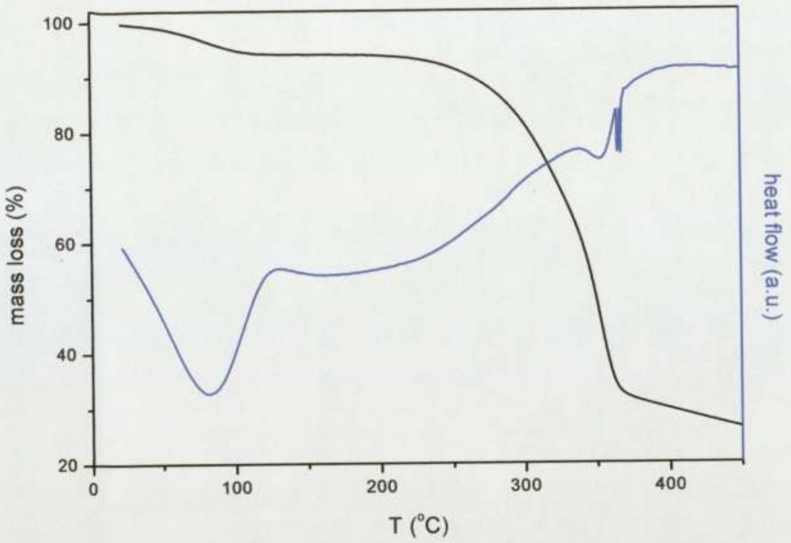


Figure 86: Dependence of mass loss and heat flow of wood on temperature for pine wood.

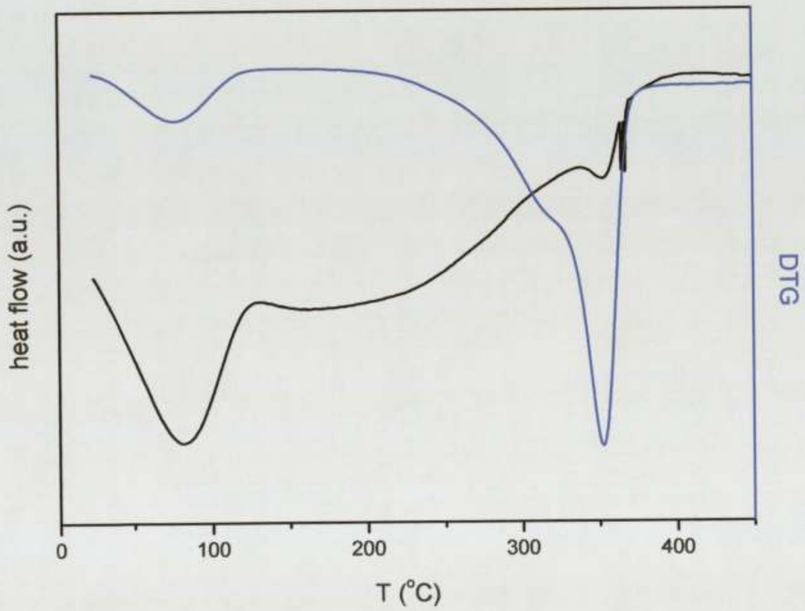


Figure 87: Differential heat flow and mass loss of wood dependence on temperature for pine wood.

The above plots show the dependence of heat flow and mass loss on temperature for the thermal decomposition of wood. The TGA plot shows three temperature ranges of mass loss while the same phenomena on DTG are shown as endothermic peaks.

The first region of decomposition is completed by 140°C and is due to the loss of the water contained within the wood. A second thermal decomposition starts around 210°C and is completed by about 370°C but without stabilization of the wood mass till the end of the measurement at 450°C

Based on the above results we can infer that wood should not be exposed to temperatures over 210°C because it will start to decompose. Nevertheless, when selecting pressing conditions we should also take into account that during panel hot-pressing at constant plate temperatures of 210°C, the temperature in the center of the panel (core) only reaches 100–105°C as the times for curing are very short.

15.7.2 SEM of pine wood

In this study the wood inspection was carried out using JEOL JSM 840A stereo electron scanning microscope adapted with EDS ISIS 300 software for the analysis of the images. The sample was prepared by vaporization of carbon under vacuum using two devices: AGAR and JEOL JEE4X. These were equipped with the necessary computers and software. All specimens were dried before any measurements were carried out at 100°C for 15h in order to ensure that any moisture was removed. For the needs of this test small wood blocks were separated from the veneers and sections were cut at random with a microtome knife. These SEM images of the pine wood (figures 88-95) are in agreement with those provided by the literature (figures 60-67).

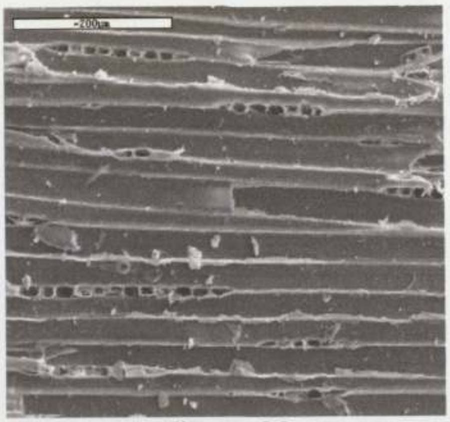


Figure 88

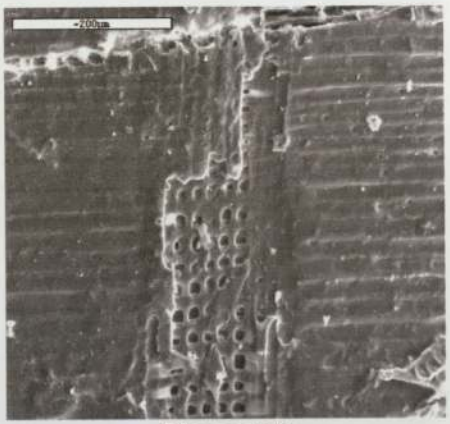


Figure 89

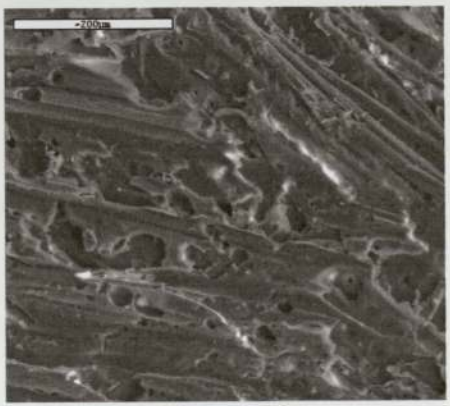


Figure 90

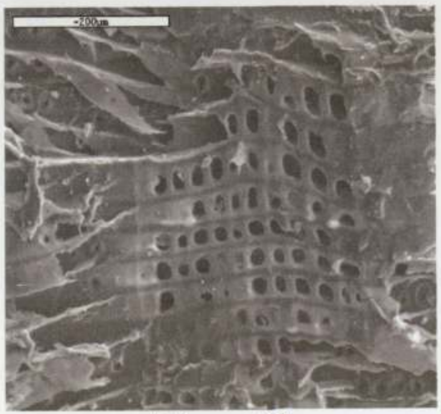


Figure 91

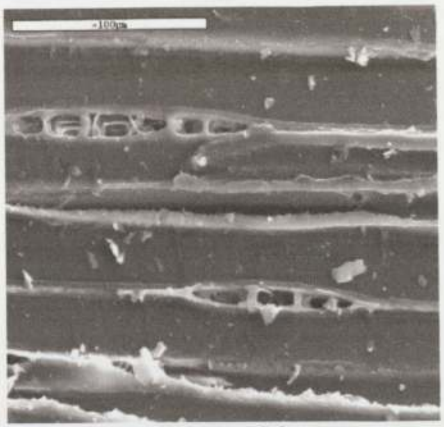


Figure 92

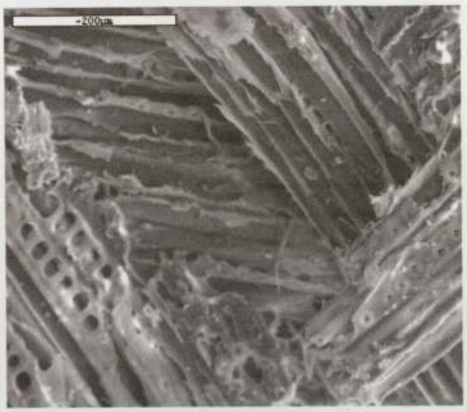


Figure 93

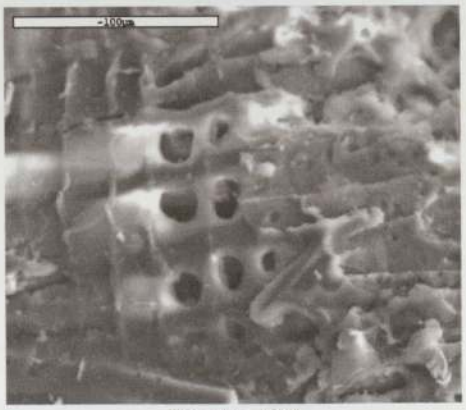


Figure 94

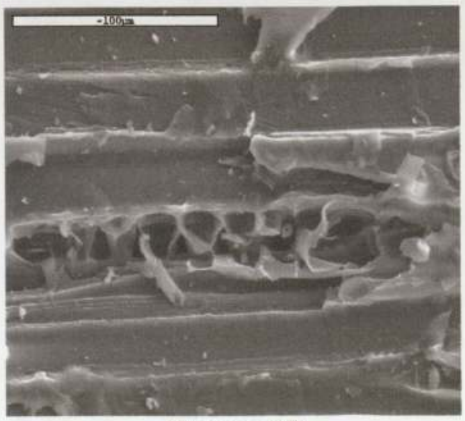


Figure 95

Figures: 88 & 89 are tangential sections, 90 shows half-bordered pits on a radial section, 91 & 92 are microchecks of cell wall on a tangential section, 93 is half-bordered pits on a radial section, 94 is radial section and 95 is tangential section of wood.

The images 88-95 are of different specimens and are illustrative of the uniform type of cells (tracheids) present in pine wood.

15.8 Overall results of adhesives and plywood evaluation

15.8.1 Overall results of the standard lab analysis of the adhesives

In order to be able to evaluate the contribution of each phenol substitute without the interference of other variables, all adhesives were prepared under the same reaction conditions, and the values of the physical properties of the pre-polymers, presented in table 29, show little variation.

Table 29: Overall review of pre-polymers' physical properties.

Adhesive:	**PF std**	**PFB**	**PFC**	**PFL**	**PFS**	**PFT**
Ph Sub. 15%	-	Bio oil	CNSL	Lignin	Soy Protein	Tannin
Property	**Value**					
Viscosity, cP	420	440	448	410	430	450
Solids, %	42.9	42.5	42.3	42.5	42.7	42.8
Alkalinity, %	6.2	6.5	6.4	6.1	6.3	6.7
pH	11.1	10.8	11.7	10.9	11.2	11.5

Because the physical properties of macromolecules are strongly related to the distribution of the various molecular weights and the average weights of the pre-polymers [169], it could be inferred that a similar backbone structure of the pre-polymers has been achieved in this group of products. Of course, in the case of the modified pre-polymers, the range of materials used for the replacement of phenol has resulted in some active chemical moieties other than that available in the standard PF adhesive. These moieties provide reactive sites capable of further cross-linking during the curing process. This fact is illustrated and verified mainly from the diversity of the gel time values of the pre-polymers and to a lesser extent from their conductivity values which are an indication of the ionic concentration and acidity of the pre-polymers (table 30).

Table 30: Overall review of pre-polymers' lab evaluation.

Adhesive:	**PF std**	**PFB**	**PFC**	**PFL**	**PFS**	**PFT**
Ph Sub. 15%	-	Bio oil	CNSL	Lignin	Soy Protein	Tannin
Property	**Value**					
Gel Time, min	10	12	11	11	14	9
Conductivity, μS cm^{-1}	17.68	22.2	20	20.5	16.81	16.91

The lower gel time value refers to the shorter time needed for the hardening (cure) of the pre-polymers which of course depends on the number of the reactive sites available on the macromolecules.

15.8.2 Overall results of the thermal analysis of the adhesives

- Thermogravimetric analysis (TGA)

The overall results of the thermogravimetric analysis (TGA) of the adhesives are presented in the following figure 96.

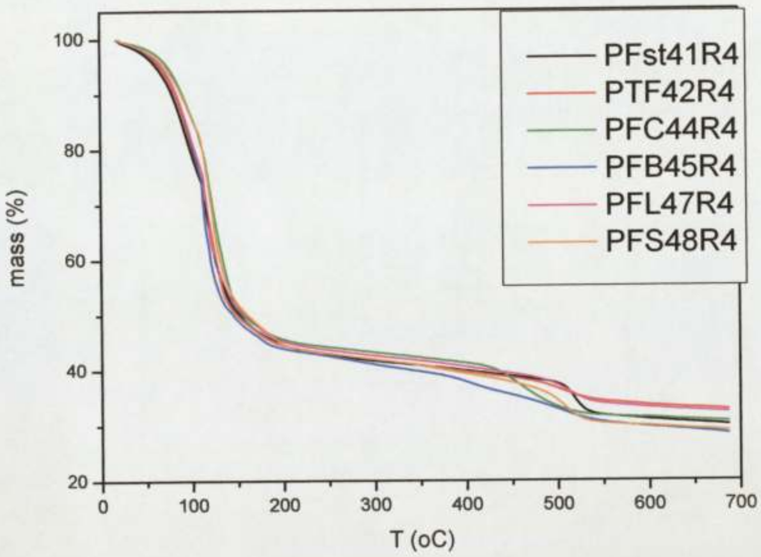


Figure 96: TGA of total liquid adhesives

The TGA of these adhesives provides information about their stepwise thermal degradation occurring at different temperature intervals and hence provides information about the flame retardant characteristics of the polymers under fire conditions. Moreover, it has been proved [170] that there is a linear correlation between the flammability of a polymer and the limiting oxygen index (LOI – provides a numerical flammability scale [171]), while correlations have also been established between the structure of polymers and their char formation [13]. Therefore not only the temperatures at which the macromolecules break down and liberate a range of chemical moieties but also the quantities of the char formed are important parameters for a flammability survey. The following table 31 includes an overall presentation of the decomposition temperatures, the percentage mass loss during the various stages of the heating process as well as the percentage of the remained solid mass (char) for each of the adhesives.

Table 31: Overview of mass losses and decomposition temperature

	Temperature where decomposition starts (To), °C	Mass loss , %		solid mass residue (char), %
		during additional condensation	During sharp decomposition	
PF std	490.8	-	6.3	31.5
PFB	415.6	3.8	7.3	30.2
PFC	401.3	3.7	20.7	21.2
PFL	463.5	4.8	5.1	33.8
PFS	452.8	3.55	7.3	30.2
PFT	459.0	4.1	4.0	34.2

In general, resol phenol-formaldehyde adhesives exhibit flame retardation because of the stable three-dimensional network formed resists thermal stress without melting or softening which favours detachment and vaporization of the easily flammable low molecular weight species. The phenol-formaldehyde polymers when heated to their ignition temperature are converted into a char forming material that functions as an insulator [13].

- Differential Scanning Calorimetry (DSC)

DSC measurements were carried out both for the pre-polymers and the wood impregnated with the adhesives. This illustrated a clear contribution of the wood to the reduction of the curing temperatures. The overall results of the measurements are cited in the following figures 97 and 98.

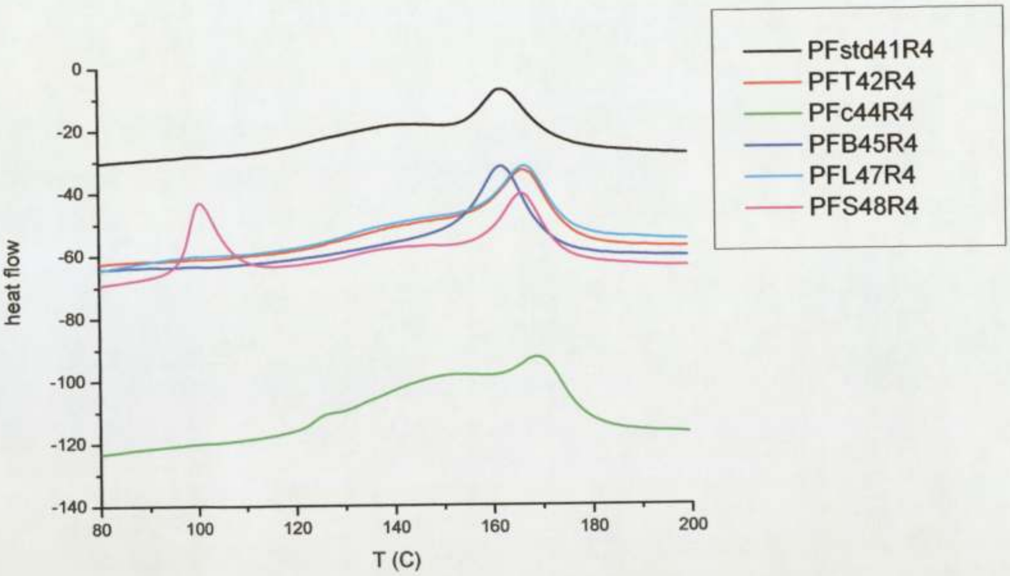


Figure 97: DSC of liquid adhesives

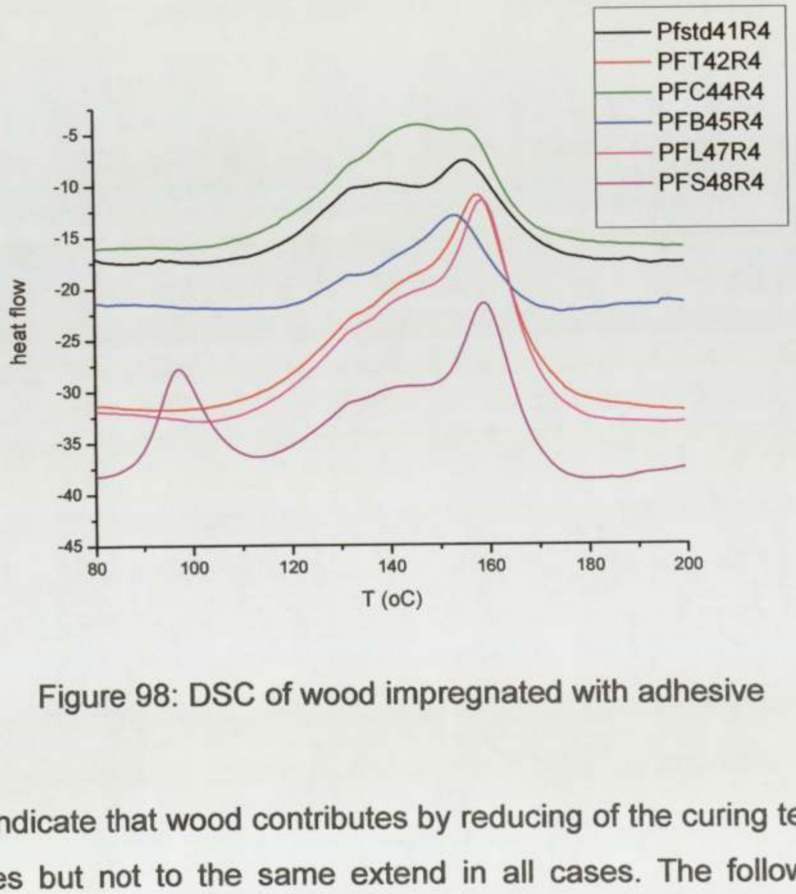


Figure 98: DSC of wood impregnated with adhesive

The results indicate that wood contributes by reducing of the curing temperature of the adhesives but not to the same extend in all cases. The following table 32 shows the curing peak temperatures of the pure adhesives, along with the reduction when wood is present during the measurement.

Table 32: Peak curing temperatures of pure adhesives and impregnated wood.

	Peak curing temperature, °C		Change of curing temperatures
	Pure adhesive	Wood and adhesive	
PF std	162.42	155.81	6.61
PFB	162.67	153.84	8.83
PFS	166.20	159.57	6.63
PFT	166.91	158.41	8.50
PFL	167.43	159.57	7.86
PFC	169.76	155.65	14.11

From these results it is obvious that the standard phenol–formaldehyde adhesive cures at the lowest temperature (approx. 162°C) while the PFB adhesive, where part of the phenol has been replaced by wood pyrolysis oil (bio-oil) has a similar reaction. The other modified adhesives cure (harden) at higher temperatures.

Nevertheless, when the DSC evaluation is carried out with wood impregnated with each of these adhesives, the peak curing temperature is reduced by about 6 to 8°C. The higher reduction occurs with the PFC adhesive (where phenol has been partially substituted by CNSL) and the least at the PF standard adhesive.

15.8.3 Overall evaluation of the plywoods

The plywood prepared with the experimental adhesives were tested to determine their shear strength and wood failure according to the European standard EN 314.1 as well as the British standard BS 6566 since they are mostly used by industry. The formaldehyde emissions of the panels were determined using the desiccator method as described in the Japanese standard JIS A1460. A summary of the results is presented in the following table 33.

Table 33: Collection of results from plywood evaluation

Adhesive:	**PF std**	**PFB**	**PFC**	**PFL**	**PFS**	**PFT**
Ph Sub. 15% by:	-	Bio oil	CNSL	Lignin	Soy Protein	Tannin
BS6566 Knife test (x10), %	80	50	79	75	75	78
EN 314.1						
Shear strength, MPa	1.04	1.20	1.08	1.09	1.40	1.42
Wood failure, %	74	40	86	42	84	84
JIS A1460 FF – desiccator, mg/l	0.52	0.53	0.56	0.55	0.56	0.54

These results allow the adhesives to be classified according to the European standard EN 314.2. Table 34 shows the requirements to pass EN 314.2 standard while the associated figure 99, which was composed according to the description of that standard, combine shear strength performance of plywood panels and wood failure results, designating a pass grade by values in the white area and a fail grade by the values in the blue area.

Table 34: European standard EN 314.2 requirements

Mean shear strength fv, MPa	Mean apparent cohesive wood failure w, %
$0.2 \leq fv < 0.4$	≥ 80
$0.4 \leq fv < 0.6$	≥ 60
$0.6 \leq fv < 1.0$	≥ 40
$1.0 \leq fv$	No requirement

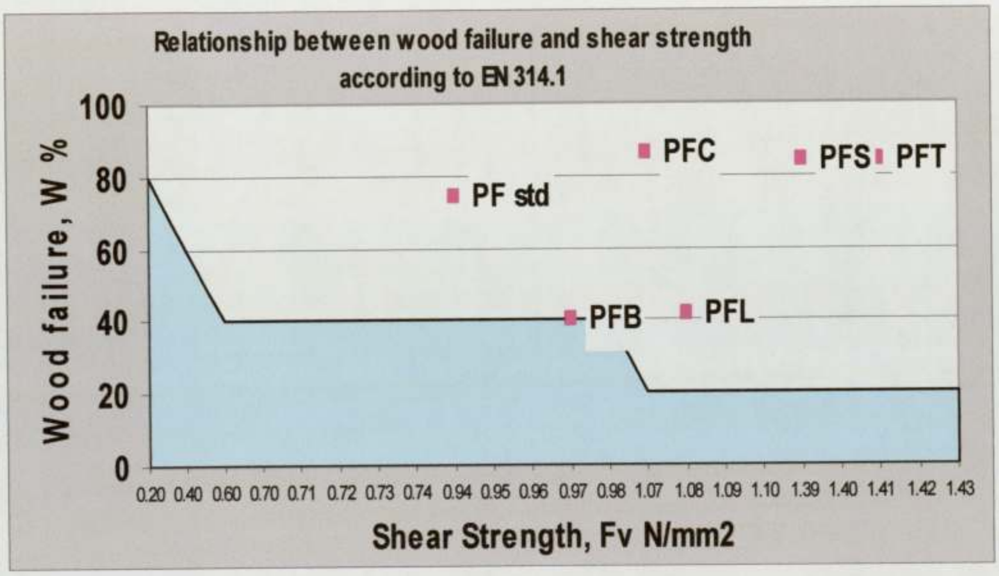


Figure 99: Classification of adhesives according to EN 314.2 standard.

The following figure 100 presents a histogram of the levels of the free formaldehyde emissions for the panels.

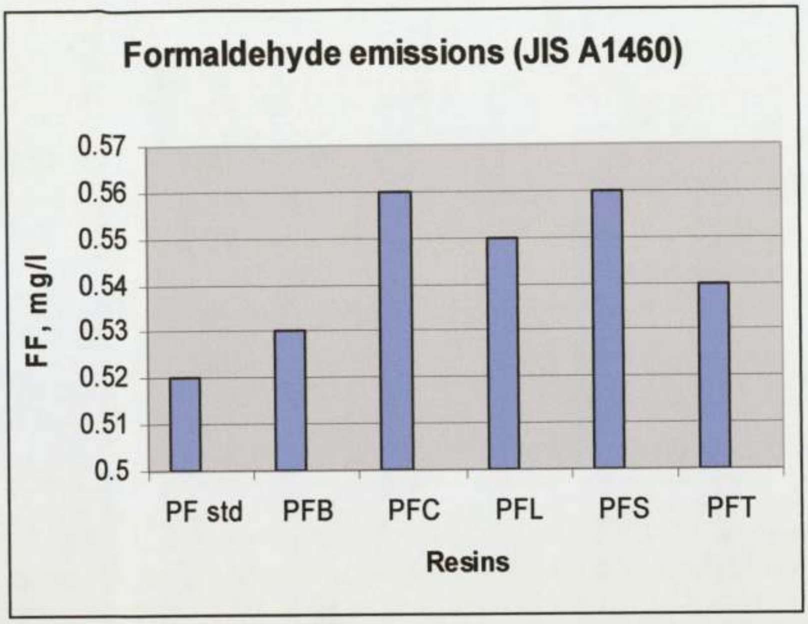


Figure 100: Free formaldehyde emissions of plywood panels-Desiccator method

A schematic survey of the properties of the plywood prepared by the different adhesives is presented in the following figure 101.

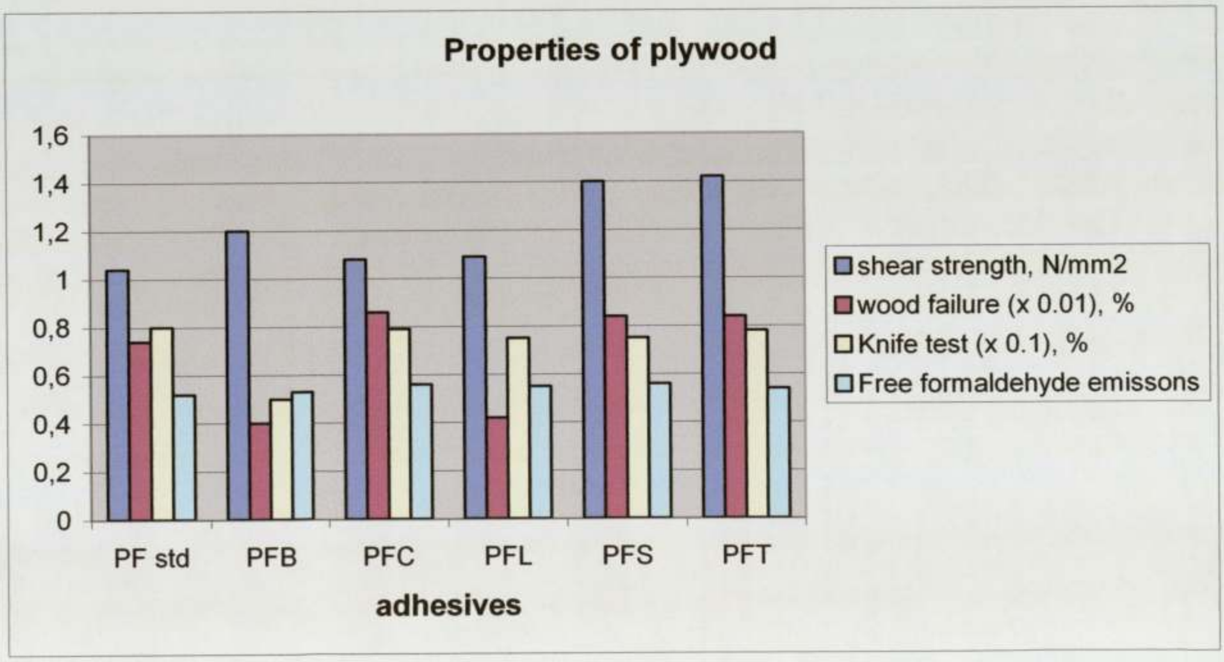


Figure 101: Overall evaluation of plywood panels

16. STATISTICAL ANALYSIS OF RESULTS

A linear regression statistical analysis was examined out on the physical characteristics of the pre-polymers to determine which was the most significant in determining the properties of the plywood panels.

It is known that the physical properties of the pre-polymers have a strong effect on the adhesion performance and the free formaldehyde emissions of the panels manufactured from them. The following table 35 gives an overview of the physical characteristics of the pre-polymers and the subsequent properties of the plywood panels produced.

Table 35: An overview of the physical characteristics of the adhesives and the properties of plywood produced.

EN 314.1		Free formaldehyde	Viscosity	Solids	Alkalinity	pH	Gel time	Conductivity	Adhesive
Shear strengh	Wood failure								
MPa	%	mg/l	cP	%	%	-	m	µS/cm	-
1.04	74	0.52	420	42.9	6.2	11.1	10	17.68	PF std
1.20	40	0.53	440	42.5	6.5	10.8	12	22.20	PFB
1.08	86	0.56	448	42.3	6.4	11.7	11	20.00	PFC
1.09	42	0.55	410	42.5	6.1	10.9	11	20.50	PFL
1.40	84	0.56	430	42.7	6.3	11.2	14	16.81	PFS
1.42	84	0.54	450	42.8	6.7	11.5	9	16.91	PFT

The linear regression statistical analysis of the above data provided the following correlation (table 36):

Table 36: Results from linear regression statistical analysis

Property of plywood (Y)	Statistical parameters	Physical characteristics of pre-polymers (X)					
		viscosity	solids	alkalinity	pH	gel time	conductivity
Shear strength	Multiple R	0.4456	0.3347	0.6189	0.1895	0.2183	0.5253
	R^2	0.198	0.112	0.383	0.035	0.047	0.276
	Coefficients						
	c	-0.823	-9.520	-1.851	0.178	0.967	1.962
	m	0.00468	0.21567	0.48	0.09166	0.021	-0.0398
	p-value	0.375	0.516	0.190	0.719	0.677	0.284
Wood failure	Multiple R	0.4753	0.2729	0.3029	**0.8609**	0.0985	**0.7842**
	R^2	0.225	0.0744	0.0918	**0.7412**	0.0097	**0.6150**
	Coefficients						
	c	-210.55	-1058.57	-124.48	**-532.73**	82.134	**214.132**
	m	0.644	26.44	30.28	**53.66**	-1.23	**-7.666**
	p-value	0.340	0.6007	0.559	**0.0027**	0.8525	**0.06478**
Free formaldehyde emissions	Multiple R	0.1536	0.5678	0.0755	0.459	0.474	0.0816
	R^2	0.0236	0.3224	0.0057	0.211	0.224	0.0066
	Coefficients						
	c	0.475	2.316	0.5797	0.300	0.4931	0.5448
	m	0.00015	-0.0416	-0.0057	0.0216	0.0044	-0.0006
	p-value	0.771	0.239	0.886	0.359	0.342	0.877

The physical meaning of the above statistical parameters is:

Multiple R: Indicates the linear correlation between X an Y. The closer the value is to ±1, the higher is the correlation (positive or negative).

R^2: shows the percentage of the total variation of the dependent variable which is due to the independent variable. A value of 1 is the optimum value and indicates full dependency.

Coefficients m, c: The m is the slope and the c is the Y-intercept of the straight line (Y=mX+c) that best fits the data.

The value of c has no practical meaning in our case, as it shows the value of the property (Y) when X=0 which is not a realistic value of X. However, the value of m (slope) is important because it shows the rate at which Y (property of plywood) changes with respect to X (physical characteristic of pre-polymer) i.e. change of 1 unit to X, results in a change (increase or decrease) of 1 unit to Y.

Value-p: It reveals the validity of the ANOVA method and relilability of conclusions. The closer to zero its value, the safer are the conclusions drawn.

Reviewing the above statistical analysis correlation, it can be seen that the only conclusion that can be safely inferred is the marked dependence of wood failure on the pH of the adhesive and to a lesser (but signficant) extent on the conductivity of the pre-polymers. In particular, as the pH values increase wood failure also increases, while the opposite trend is followed in the case of conductivity. The shear strength performance of the plywood panels seems to have a low dependence on the measured physical characteristics though alkalinity could be chosen as the most significant one (though not very significant as the p value in this case is 0.19). Lastly, no correlation was obtained between free formaldehyde emissions and any of the physical characteristics measured within the framework of this study. However, if one had to be chosen as most relevant it would be the solids of the adhesives because it had the lowest p-value. For a more in-depth statistical analysis of the correlation between the physical characteristics of the pre-polymers and the properties of plywood panels a future study specialized exclusively on this subject and provision of greater amount of data are required.

17. DISCUSSION ON THE RESULTS

The specifications of the experimental adhesives resulting from the laboratory analysis show a physicochemical similarity to the standard PF one. Nevertheless, the gel times indicate that the tannin modified adhesive (PFT) needed a shorter time to cure (harden) at 110ºC while the soy protein modified (PFS) needed the longest one.

Taking into account the thermal decomposition of the adhesives by studying their total TGA plot, it could be inferred that all of them have satisfactory thermal stability and may be safely used in the production of wood-based panels. Of course, the most stable one is the standard PF adhesive while the least stable one is the one modified with CNSL (PFC) because it degraded at the lowest (shorter) decomposition temperature (To). The classification of the adhesives according to their thermal stability follows the order: PFstd>PFL>PFT>PFS>PFB>PFC. Nevertheless, for the evaluation of their fire resistance performance, not only their decomposition temperature but also the quantity of the char formed has to be taken into account. Hence from this point of view the order of the adhesives according to the percentage of the residual mass of char would be: PFT>PFL>PF std>PFB=PFS>PFC.

The standard PF adhesive may be considered to be the most stable but the tannin modified adhesive (PFT) produces the most percentage of char residue, which as already mentioned, functions as insulator in a fire.

Form the DSC graphs it is obvious that the PFS adhesive (soy protein modified) underwent an endothermic process within the range of 98-110°C. This could be theoretically attributed to a condensation reaction of methylol groups to form methylene and ether methylene linkages that, due to the large size of the initial protein molecule, are stereochemically hindered. But when the temperature was raised to 100°C they acquired the necessary mobility to form linkages. Of course further tests are needed for the validation of these results but it is outside of the scope of this study. The comprehensive table 4 shows that all the adhesives exhibited peak curing temperatures from 162°C to about 170°C where the lower temperature belongs to the standard PF adhesive and the higher one to the CNSL modified one (PFC). Nevertheless, when wood participates in the measurements the latter adhesive performs the highest temperature reduction of all the others. Nevertheless, the DSC measurements of the wood impregnated with adhesive, show that the pyrolysis oil modified adhesive (PFB) would be the one of the lower curing peak temperature during the plywood production process; something that might mean financial profits for the plywood manufacturer since time saving of the duration of the production process may arise.

According to the results of the plywood evaluation, it seems that all the experimental adhesives have quite strong adhesion properties while the free formaldehyde emissions of the panels have comparable values. In particular, all the adhesives seem to have good shear strength and high apparent cohesive wood failure while the free formaldehyde emissions of the plywood produced with them are very low and quite close to F2 class (≤0.5mg/l) of the Japanese standard JIS A 1460.

The figure 101 presents a comprehensive illustration of all the properties of the plywood panels while figure 99 illustrates the ranking of the adhesives according to the European standard EN314.2. Thus, the CNSL modified adhesive (PFC) which appears in the top of white area of this graph, is the best performing adhesive although it has the highest free formaldehyde emissions (figure 100) to the plywood panel produced with it. Nevertheless, this value is still acceptable and has little difference from that of the other adhesives. In contrary, the PFB adhesive has the lowest performance of all modified adhesives and it lies closest to the fail/pass line. .

From a consideration of the linear regression statistical analysis of the physical properties of plywood panels in correlation with the physical characteristics of the adhesives it can be concluded that the wood failure performance of the plywood panels is closely dependent primarily on the pH of the adhesive and secondarily on its conductivity. Of course these results need to be further elucidated and verified with studies focused on this subject.

18. CONCLUSIONS

In summary it can be said that resol phenol-formaldehyde adhesives in which phenol has been replaced up to 15% by any of the naturally derived materials: lignin, tannin, soy protein, cashews nut liquid (CNSL) and forestry residue pyrolysis oil (bio-oil) may be prepared successfully with no change in experimental procedures.

Plywood panels produced from any of these modified adhesives can be considered to be formaldehyde free, and show flame retardation. Plywood panels produced with PF adhesive modified with any of cashews nut shell liquid (CNSL), soy protein isolate (SPI) or tannin have better shear strength and waterproofing properties than the conventional phenol-formaldehyde adhesive.

Also it has been statistically proved that the most significant physical characteristic of the adhesives which determine wood failure property of the panels is firstly pH and secondarily the conductivity of the adhesive.

In conclusion; any of the modified PF adhesives tested in this study exhibited promising performance in the production of plywood panels with improved properties. Trials with higher substitution levels of phenol are worthwhile and should be conducted in future studies.

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20. APPENDIX

Photos of annex A of the European standard EN 314.1 for the determination of the percentage of the apparent cohesive wood failure by comparison (figure 102, 103, 104).

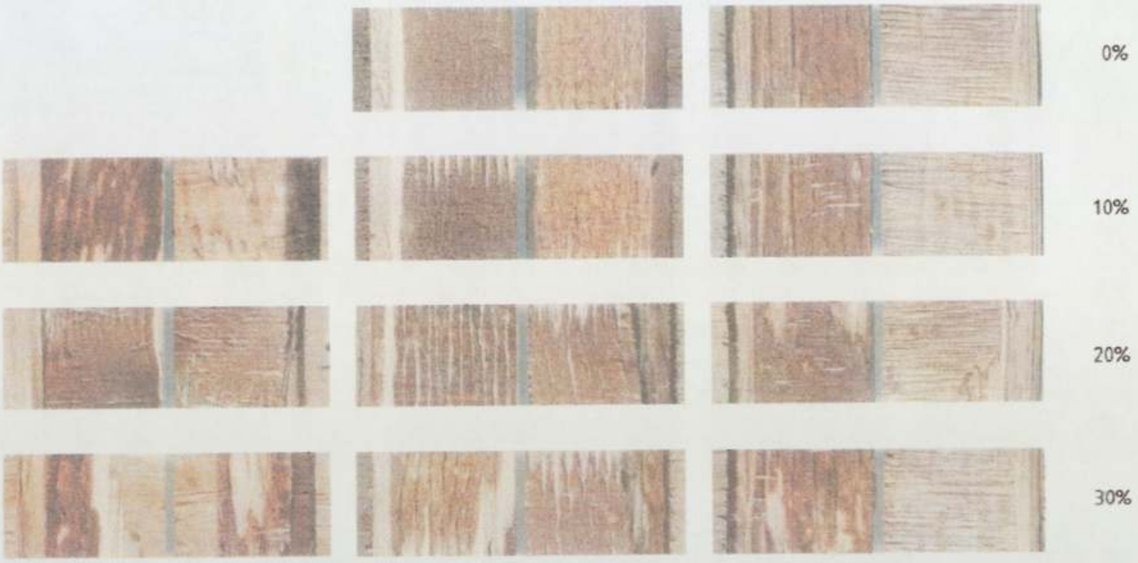

Figure 102: Wood fibre failure 0-30% reference illustrations by EN 413.1 standard

Figure 103: Wood fibre failure 40-60% reference illustrations by EN 413.1 standard

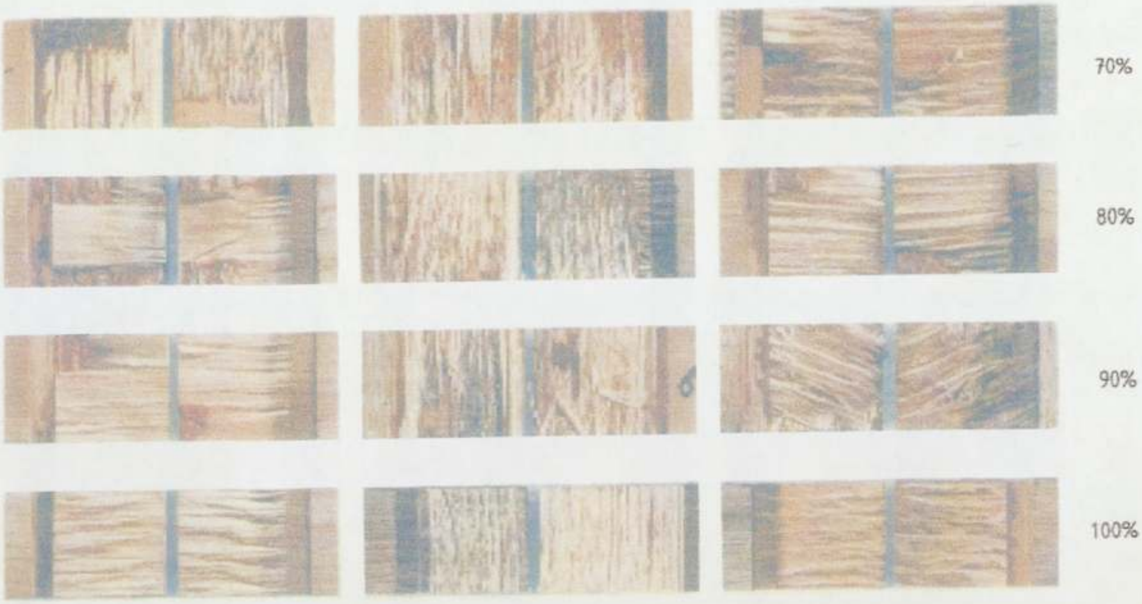

Figure 104: Wood fibre failure 70-100% reference illustrations by EN 413.1 standard