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Factors affecting the enhancement of Acacia hybrid particleboard

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FACTORS AFFECTING THE ENHANCEMENT OF *ACACIA* HYBRID PARTICLEBOARD

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ABSTRACT

Acacia hybrid has been planted in Malaysia's forest plantation for wood resources. Evaluation of the wood showed that the wood has density 446 kg m^{-3}, good dimensional stability and low acid buffering capacity (0.10 mmol l^{-1}). The amount of reactive polyphenols from 80 °C water extraction was 45.5% which is considered high for wood. The polyphenols tremendously decreased at extraction temperatures of 120 °C and over. Particleboards of *Acacia* hybrid bonded with urea formaldehyde (UF) resin consistently showed better physical and mechanical properties than recycled wood. Thickness swelling of the boards was 15%, water absorption 30%, modulus of elasticity 26.25 MPa and modulus of rupture 3811 MPa. The boards quality continued to be high when bonded with melamine urea formaldehyde (MUF) and phenol formaldehyde (PF) resins when compared to spruce particleboards. Internal bond strength of the boards was ranged from 0.9 to 1.3 MPa. The work showed that the *Acacia* hybrid is potential for high quality particleboards.

Decay of *Acacia* hybrid boards due *to Pleurotus ostreatus*, *Trametes versicolor*, *Pycnoporus sanguineus* and *Coniophora puteana* was investigated. Internal bond strength of boards bonded with UF and MUF resins strongly deteriorated (86 to 100% loss) due to decay fungi. *T. versicolor* and *C. puteana* caused severe loss in weight (14.9% to 37.3%) of the boards. Improved decay resistance of the boards was achieved when bonded with PF resin. The board was dimensionally stable and has high degree of internal bond strength even after decay fungi exposures. Maximum weight loss was 8.3% due to *P. ostreatus*. Internal bond strength of the boards after decay test was between 0.5 and 1.1 MPa. Investigation on the effect of *Acacia* hybrid extractives (hot water extraction at 80, 100, 120 and 160 °C) to wood gluing was carried out using automatic bonding evaluation system (ABES). Significant increment in shear strength (5.2 MPa) of wood veneers was obtained when the UF resin was mixed with extractives from 80 °C extraction with 8% solids content. The effect of extractives on the UF resin was likely to be influenced by the amount of reactive polyphenols. Subtle changes occurred in the thermal behaviour of UF resin mixed with extractives at temperatures between 240 and 340 °C probably caused by the decomposition of UF polymer. The FTIR analysis showed that the resin and extractive mixtures have similar structural peaks to those of a typical UF resin.

The extractives were characterised using MALDI-TOF mass spectrometer. Extractives from 80, 100 and 120 °C extraction contained compounds with molecular weight between 332 and 647 Da probably of simple polyphenols. Four major compounds were considered with molecular weights of 544, 560, 566, and 582 Da. Extractives from 80 and 100 °C extraction contained polymers with repetitive unit of 74 or 148 Da which could be of lignans. Extractives of high temperature extraction (160 °C) had two different compounds, hexose polymers with 162 fragment unit and acetylxylose with 174 Da fragment.

Better performance of *Acacia* hybrid particleboards could be related to reaction of simple polyphenols (galloyl glycosides, lignin glycosides and flavonoids) in the extractives with formaldehyde of the resins which involved methylolation and condensation processes. This is supported by the significant weight loss of UF and extractives mixtures from thermal analysis.

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ABBREVIATIONS

MALDI-TOF	Matrix-assisted laser desorption/ionization- time-of-flight mass spectroscopy
IUCN	International Union for Conservation of Nature
MTIB	Malaysian Timber Industry Board
DNA	Deoxyribonucleic acid
AWPA	Australian Wood Panels Association
RH	Relative humidity
FTIR	Fourier transform infra red
UF	Urea formaldehyde
MUF	Melamine urea formaldehyde
PF	Phenol formaldehyde
EPF	European Panel Federation
ASTM	American Society for Testing and Materials
MOE	Modulus of elasticity
MOR	Modulus of rupture
IB	Internal bond
TS	Thickness swelling
WA	Water absorption
MC	Moisture content
NMR	Nuclear magnetic resonance
ABES	Automatic Bonding Evaluation System
TMA	Thermal mechanical analysis
DSC	Differential scanning calorimetry
XO	Xylo-oligosaccharides

CHAPTER 1

INTRODUCTION

Particleboard is a composite panel product manufactured from lignocellulosic particles which are pressed and bonded together with a thermosetting resin or other suitable binder. Particleboard is usually used as a substitute for wood and plywood for indoor panel applications because it is cheaper, denser, more uniform and available in as large sizes and volumes. The disadvantages of anisotropy of solid timber can be reduced. Particleboards have been widely available since the 1950s (Maloney 1993).

Today particleboard production still focuses on general application boards with some emphasis on higher end products. With the increase of material and manufacturing costs, the challenge today is toward the production of particleboards at an economic scale that meets the market expectations (Dory [undated]). This can be achieved by the incorporation of advanced manufacturing technologies. The use of wider types of cellulosic materials other than wood has been explored which includes the use of recycled wood and non-wood materials including kenaf, hazel nut husk and wheat straw (Acker 2007; Copur et al. 2007; Kalaycioglu and Nemli 2006; Boguillon et al. 2004). The possibility of using alternative or modified adhesives which are cost effective have lower or zero formaldehyde emission, and give good mechanical and physical properties has been investigated (Papadopoulos et al. 2002; Bisanda et al. 2003; Moubarik et al. 2010; Cetin and Ozmen 2002; Gao et al. 2011).

In Malaysia, the lignocellulose feedstock availability has always been an important challenge in particleboard production. In the past the industry enjoyed a consistent and uniform supply of rubberwood obtained from rubber trees (*Hevea brasiliensis*) which were initially planted for latex production (Hong 1996). Nowadays the availability of rubberwood is insufficient due to increasing demand by the wood industries and the depletion of rubberwood supply itself (EAS 2010). The planted area of rubber trees declined from 1.8 million ha in 1990 to 1.4 million ha in 2000 to 1.2 million ha in 2008. Alternative raw materials from other wood species and other resources have been considered. Properties of particleboards from plantation species

such as *Acacia mangium, Paraserianthes falcataria*, and *Gmelina arboea* have been determined and compared to rubberwood (Chew et al. 1991). Kenaf (*Hibiscus cannabinus*) has been suggested as a non-wood alternative for particleboard. Paridah et al. (2009) evaluated the properties of board made from base fibre and core material of kenaf, whereas Izran et al. (2010) optimised a treatment system to improve the fire performance of kenaf board. Oil palm (*Elaeis guineensis*) biomass is considered as the most available non-wood resource (Wan Asma et al. 2010). The annual capacity is about 15 million tonne in the form of empty fruit bunch, shell, mill effluent, and tree trunk. Researches on oil palm particleboards have been extensively conducted (Chew et al. 1991; Hashim et al. 2010; Ratnasingam and Wagner 2009).

The main objectives of this study are to evaluate on the potential of *Acacia* hybrid - a fast growing species planted in Malaysia's forest plantation, as raw material for particleboard, and to investigate the contribution of extractives from *Acacia* hybrid to wood bonding.

This thesis has been divided into eight chapters. Chapter one is this introduction to the study. Chapter two is literature review on topics related to the study. Chapter three is about properties of the *Acacia* hybrid either from solid wood, processed particles or extractives. Chapter four examines the properties of particleboards from *Acacia* hybrid bonded with three types of thermosetting resins and compared this with two different types of wood. Chapter five evaluates the decay resistance of the particleboards. Chapter six discusses therole of *Acacia* hybrid extractives in wood gluing with urea formaldehyde resin as in chapter three an enhanced bonding was noted. Chapter seven is on mass spectrometry analysis of the extractives by MALDI-TOF (Matrix-assisted laser desorption/ionization- time-of-flight mass spectroscopy. Lastly chapter eight discusses the main findings of the study before a series of conclusions and recommendations for further study.

CHAPTER 2

LITERATURE REVIEW

2.1 *Acacia* hybrid

2.1.1 Introduction

Acacia hybrid is a tree species which originated from the natural crossing between *Acacia mangium* and *Acacia auriculiformis*. *A. mangium* is native to northern Queensland in Australia, Papua New Guinea, Irian Jaya, and the Moluccas Islands in Indonesia, whereas the *A. auriculiformis* is from savannas of Papua New Guinea and Irian Jaya, the islands of the Torres Strait, and northern Australia (Turnbull 1986). Like other Acacia species, both are fast growing trees that can adapt to a wide range of soils and have been planted in the tropics and subtropical areas. The hybrid of *A. mangium* and *A. auriculiformis* occurs naturally in plantations where both trees are available. In Malaysia, *Acacia* hybrid was first reported at Ulu Kukut, Sabah in 1971 (Rufelds 1987).

Generally, the morphological traits of *Acacia* hybrid i.e. flower colour, pod aspect, leaf shape and size, bark aspect and colour, wood density, are intermediate between the *A. mangium* and *A. auriculiformis* (Galiana et al. 2003). The flowers are creamy to whitish and arranged in a straight or slightly bent, 8 to 10 cm long spike (Kijkar 2003). The seed pod is very curly and twists like pods of other *Acacia* species. Five to nine seeds, about 0.3 x 0.4 cm each, are available in a pod. The bark of mature tree is greenish brown or brown and smooth as the bark of *A. auriculiformis*, with slightly scalely and shallow furrows at the foot of the tree. The stem, though not as straight as that of *A. mangium*, is much straighter than *A. auriculiformis* and has no angles or ribs (Darus and Ghani 1989).

2.1.2 Growth of *Acacia* hybrid

Acacia hybrid grows in Malaysia, Indonesia, Thailand, Vietnam and China (Kijkar 2003). It is the most planted *Acacia* species after *A. mangium* and *A. auriculiformis* (Patzek

and Pimentel 2005), and became a vigorous potential species for plantation in Southeast Asia (Galiana et al. 2003; Sornsathapornkul and Owens 1999). It is estimated that about 46,000 hectares of *Acacia* hybrid plantations were planted in Vietnam in 2003 (Bueren 2004). Worldwide, there are 83 million hectares of *Acacia* species plantations with 95% situated in Asia (IUCN 2001).

In Malaysia, the exact volume of the planted trees has not been reported. In West Malaysia (Peninsular Malaysia), a small area, 16 hectares, has been planted with *Acacia* hybrid which was scattered in small plantations in 2002 (Krishnapillay and Ong 2003). In East Malaysia (Sabah and Sarawak), a vast plantation area has been established. More than 3700 hectares of *Acacia* species including *A. mangium*, *A. auriculiformis* and *Acacia* hybrid were planted in Sarawak in 2000 (Forest 2008). In Sabah, besides *A. mangium*, about 5355 hectares of other *Acacia* species were planted in 2006 (History 2008). Realising its potential, the species became part of eight selected species for the forest plantation programme (MTIB 2007).

Acacia hybrid has superior tree characteristics and resistance to pests and diseases over the parental species (Pinso and Nasi 1992; Chia 1993). The tree usually has fine branching and apical dominance which eventually produces a single-stemmed tree with good length of clear bole (Pinyopusarerk 1990, cited in Lee 2002). The tree can adapt to wide range of soils. Besides sandy loam or sandy clay loam soils, it can grow on lateritic crude soils. With adequate technique, it could be grown on coastal sand dune soils (Mohd Ghazali et al. 2007). It can tolerate temperatures from 12 to 35 °C, annual precipitation of 1200 to 1850 mm, and elevation of 50 to 350 m. The tree can reach 8 to 10 m height and 7.5 to 9.0 cm diameter at breast height within 2 years (Kijkar 2003). The trees planted in Vietnam have a growth rate that almost double of their parent species, enabling harvest some 2-3 years earlier than non-hybrids (Bueren 2004).

The tree has a higher wood density and cellulose content compared to *A. mangium* and is less prone to heartrot disease (Wong 1993). A survey by Ito and Nanis (1997) of five-year-old plantations of *A. auriculiformis*, *A. mangium* and *Acacia* hybrid found that heartrot occurred in *A. mangium* while no incidence was observed on either *Acacia* hybrid or *A. auriculiformis*.

Vegetative propagation can produce higher yield of planting materials with uniform characteristics in a minimum time period compared to propagation by seeds. Tissue culture technologies could be more cost-effective than conventional methods for large scale cloning. *Acacia* species are generally propagated by seeds for large scale plantation programmes but for *Acacia* hybrid vegetative propagation is preferred because of limited capacity for producing interspecific hybrid seeds (Galiana et al. 2003). The acclimation potential of *Acacia* hybrid vegetative propagules to soil water stress had been investigated by (Kabir et al. 2006).

The clones of *Acacia* hybrid were varying in growth and some wood properties (Kim et al. 2008). The pattern of distribution of specific gravity showed that there were low and high specific gravity zones in the stem. Clones with high specific gravity can be predicted at a young age and there was no significant correlation between diameter growth and specific gravity.

Identification of *Acacia* hybrid, *A. mangium* and *A. auriculiformis* for breeding programme is possible using Random Amplified Polymorphic DNAs markers (Widyatmoko and Shiraishi 2003). The mating system and seed variation of *Acacia* hybrid (*A. mangium* × *A. auriculiformis*) were studied using allozymes and random amplified polymorphic DNA markers, respectively (Ng et al. 2009). The results suggest that a maximum of four seeds per pod could be sampled for the establishment of a mapping population for use for genetic linkage studies. Fifteen polymorphic microsatellite loci had been isolated in *Acacia* hybrid (Ng et al. 2005). The loci were also characterised in both parental species.

Investigation of the extent and pattern of genetic variation for isozyme analysis of *Acacia* hybrid and four other *Acacia* species were carried out using horizontal starch gel electrophoresis (Nor Aini et al. 2006). *Acacia* hybrid has high level of genetic variability with *A. aulacocarpa* and most related to *A. mangium*. The species was identified as the most promising species in terms of genetic variability.

2.1.3 Timber properties

The timber properties of *Acacia* hybrid are similar to those of *A. mangium*, although the hybrid has a slightly higher wood green density (455 kg m^{-3}) (Kha 1996). Mohd

Shukari et al. (2002) found that juvenile *Acacia* hybrid has similar wood strength to *A. mangium*. Compared to *A. auriculiformis*, *Acacia* hybrid has lower density and wood strength (Mohd Hamami et al. 1998). Nevertheless *Acacia* hybrid proved to be useful in construction and as raw material for wood composites and paper (Bueren 2004).

Most of the water in wood should be removed to obtain satisfactory performance for most uses. Wood with a high moisture content takes a long time to dry and, if kiln dried, uses a lot of energy. Variations in moisture content of the stems of *Acacia* trees were studied by Yamamoto et al. (2003) using increment core methods. The moisture contents of the stems of *Acacia* hybrid and *A. mangiu*m were generally higher than the *A. auriculiformis*. The two species had 'wet-heartwood' which refers to higher moisture content of the heartwood compared to the surrounding sapwood.

Oil-heat treatment causes some changes in the chemical composition of *Acacia* hybrid wood (Izyan et al. 2010). The yield of chemical components of *Acacia* hybrid wood changed when treated at 180 to 220 °C with organic palm oil. The amount of holocellulose and cellulose decreased, whereas the hemicellulose and lignin increased as the treating temperature increased. Heat treatment of *Acacia* hybrid in nitrogen at 210-230 °C darkened the wood and gave better dimensional stability than untreated wood (Tuong and Li 2010). FTIR analysis showed that hydroxyl group content of the wood decreased due to heat treatment.

Chemical modification enhanced the weathering resistance of *Acacia* hybrid and *A. mangium* to discoloration, brought about weight loss and reduction in mechanical properties (Bhat et al. 2010). Succinic anhydride worked better in protecting the wood than propionic anhydride modification.

2.2 Properties of particleboard

2.2.1 Effect of wood to particleboard properties

The wood itself has a significant influence on the properties of particleboard as explained by Moslemi (1974) and Maloney (1977). Wood furnish varies physically and chemically and thus needs different process parameters during handling and board manufacture.

Medium density board from lower density wood usually has superior strength properties (bending strength, internal bond, modulus of elasticity and tensile strength) than boards made from higher density wood because the boards made from lower density wood have higher inter-particle contact thus have better adhesive bonds between the particles (Moslemi 1974). Even though there is greater amount of adhesive spread per unit surface area in higher density particles, the inter-particle contact between lower density particles has more influence in medium density particleboard.

For high density particleboard, factor of adhesive spread per unit surface area is more important in influencing the board strength. Vital et al. (1974) made high density particleboards from four exotic hardwood species and found that modulus of rupture and modulus of elasticity increased linearly with increase in wood density and board density. The internal bond increased as board and species density increased but these were also affected by the inherent characteristics of the species.

The wood acidity is also an important consideration when acid sensitive resins are used i.e. urea formaldehyde, because the curing of the resin depends on the establishing of chemical fields at a certain range of acidity generated by the wood or catalyst (Moslemi 1974). However the curing of most phenolic resins does not require acid conditions to take place.

The wood acidity can be measured by determining the pH and buffering capacity values. Studies by Xing et al. (2004) and Pedieu et al. (2008) indicate that pH and buffering capacity are variable with the type of raw material. Xing et al. (2004) found a linear relationship between the pH and both absolute and relative buffering capacity. This was confirmed by Pedieu et al. (2008). The extractive contents (i.e. the solvent extractable including hot water comprising non structural components) of wood varies between species and heart- and sapwoods and ranges from very low in some sapwoods and up to 30% in the heartwood of some highly durable, high density hardwoods. Extractive substances include tannins, polyphenols, essential oils, fats, resins, waxes, gums, starch and simple metabolic intermediates. The extractives of some wood species can cause problems in the bonding, i.e. resin usage and curing rate, poor water resistance properties of the board and ‘blow’ during hot pressing.

Positively, the extractives of some species can impart water resistance to the board (Maloney 1977, Alamsyah et al. 2008).

2.2.2 Determination of particleboard properties

Particleboards can be produced for various applications, usually categorised as general purpose, for load bearing or flooring, and moisture resistant (JIS 2003; AWPA 2008; BSI 2003). Some are designed to have special properties such as fire resistance, low acoustic transmission and resistance to wood destroying agents (fungi, insects). Properties that are usually determined to correlate with boards' applications are modulus of rupture (bending strength), modulus of elasticity (stiffness), internal bond strength (resistance to being pulled apart), thickness swelling (after various periods of water exposure), surface soundness, screw holding strength and formaldehyde emission levels. Other properties may also be assessed such as hardness, linear expansion, water absorption, fire hazard assessment and decay resistance in fungi and termite tests. Thus the quality of a board can be quantified by measuring its properties. Standard specifications are established to ensure quality boards are being delivered by manufacturers. The specifications might vary between the authorities or countries due to difference in the conditions of implementation. For example, specification for modulus of rupture of 12 mm thick general purpose particleboards according Australian standard is 18 MPa, which is higher than of European standard (12.5 MPa) (AWPA 2008; BSI 2003).

2.2.3 Influence of moisture on particleboard properties

The relative humidity (RH) of the environment surrounding a board has an influence on properties since the boards are largely made from wood. Hence wood-moisture related factors such as hygroscopicity, bound water, free water, moisture content, fibre saturation point,equilibrium moisture content, adsorption and desorption are correlated (Siau 1995).

Correlation of shrinking and swelling of wood with specific gravity may be shown by following (Stamm et al. 1964):

$$S = fg \quad (2.1)$$

Where **S** is the total volumetric shrinkage from green to the oven-dry condition on a percentage basis, **f** is the fibre saturation point on a percentage volume per unit weight basis, and **g** is the specific gravity of the wood on a swollen volume basis.

Study by Mantanis et al. (1994) on several North American wood species showed that the wood swelling was affected by wood density and extractive contents. Raising the wood temperature above room temperature significantly increased the rate of swelling.

According to Tsoumis (1991) changes of moisture will significantly affect the thickness of particleboard much more so than in the plane of the board direction, i.e. the length and width. The shrinkage and swelling in thickness is larger in boards made from high density wood. Localised density differences in boards will lead to warping. Particle geometry and resin percentage affect absorption of water into the board. The dimension changes are smaller in boards from thinner particles and high resin percentage. Thickness swelling is greatly reduced by applying various treatments to the particles, e.g. wax additions and heat treatments during pressing. Water exposure also reduces other properties such as internal bond, bending strength and elasticity.

2.3 Fungal decay in particleboard

2.3.1 Wood fungal decay

Wood fungal decay is a deterioration of wood structure of standing tree or cut wood by free radical action and the extracellular enzymatic activities of fungi. In standing trees decay can affects the roots, sapwood and heartwood (Reeves 1999). The trees may be seen dying by having weak branches, small leaves or slow growth. Some appear to be healthy, yet structurally weaken by decay within the heartwood. Fungal decay may occur in most wood species exposed to suitable fungal growth factors.

The fungal decay causes changes to the physical, mechanical and chemical properties of wood. It causes weight loss in wood related to fungal activity. Salmiah and Amburgey (1993) found that the decay resistance of *A. mangium* wood to *Trametes*

versicolor and *Gloeophyllum trabeum* are moderately resistant and not resistant depending on the wood sources based on American Standard D2017-81 (ASTM 1989).

A small weight loss can significantly reduce wood strength properties, particularly impact bending strength or toughness (Wilcox 1978) and loss of strength measurements are a sensitive measure of decay. Besides this loss decay can be assessed in term of changes in other mechanical properties such as modulus of rupture, modulus of elasticity, work to maximum load and breaking radius (Sexton et al. 1993). Wood decay also increases permeability, increases electrical conductivity, reduces volume, changes colour and brightness and reduces calorific value. Fungi generally degrade hemicelluloses but the rate of degradation of cellulose and lignin depend on the decay type and conditions (Eaton and Hale 1993; Fackler et al. 2006).

Strength losses of wood also depend upon the fungi and the type of wood undergoing decay (Highley 1999). The losses in toughness can range from 6% to more than 50% by the time a 1% weight loss has occurred in wood. By the time of a 10% mass loss, most strength losses may exceed 50%.

Accelerated wood decay test showed that brown rot fungi cause greater losses of impact bending and breaking radius values than white rot fungi (Pechman and Schaile 1950; Henningsson 1967; Sexton et al. 1993). Brown rots rapidly reduce wood strength early in decay process, while white rots caused slower progressive decrease in wood strength (Zabel and Morrell 1992). Wood strength loss by brown rot fungi is closely related to degradation of hemicellulose components (Winandy and Morrell 1993). Hemicellulose sidechains, such as arabinose and galactose degrad in early stages of decay. Main-chain hemicellulose carbohydrates such as mannose and xylose degraded in later stages. Oriented strand board suffered reduction in specific gravity, wood strength and weight loss due to decay fungi (Ross et al. 2003; Kent 2006).

2.3.2 Growth requirements for wood decay fungi

Wood decay is a result of complex interactions between organisms present in the wood (biotic interactions), and those occuring between organisms and the abiotic environment in and around the wood itself (Rayner and Boddy 1988). Fungal decay of wood is due to the activities of fungal growth in the material. Basic requirements for

fungi to grow are as follows: adequate but not too much water, adequate oxygen and a favourable temperature and a susceptible food source i.e. wood.

Wood becomes susceptible to fungi attack at moisture contents of greater than 20% (dry weight basis) or more than fibre saturation point (Eaton and Hale 1993; Rayner and Boddy 1988). At fibre saturation point, free water is not available in cell lumens and this restricts microbial activity. Certain mould fungi can grow at moisture contents as low as 15% and certain Xerophilic fungi can grow on wood at moisture content of less than 20%. Low moisture content in wood restricts the accessibility of water supplies to fungal hyphae thus placing them under stress and impedes both the movement of degradative agents and the return of wood cell wall breakdown products to the hyphae. At high moisture content, water may fill into void space of wood leading to reduced oxygen supply and ultimately anaerobic conditions, consequently reducing fungal growth, respiration and these may severely restrict decay activities.

Fungal growth requires free oxygen for metabolism (Nofal and Kumaran 1999). Aerobic respiration of fungi needs atmospheric oxygen as reactant. Many fungi have optimal growth at atmospheric oxygen of 19 to 20%. In low oxygen environments, fungal growth will be slower thus wood decay will be slow. Their growth decreases when oxygen concentration drops below 1% to 2%. Decomposition of wood by fungi is reduced by low oxygen level or by high carbon dioxide concentrations (Jensen 1969). Gaseous metabolites including carbon dioxide inhibit the growth of fungi and lignin decomposition of wood (Zadražil et al. 1991). Increasing the oxygen flow over the wood reverses the inhibition. Oxygen stress may not only adversely affect the growth of some fungi but also interfere with the chemistry of the decay process (Nsolomo et al. 2000).

Most fungi can grow at ambient temperatures between 0 °C and 40 °C (Nofal and Kumaran 1999) with wood decay fungal optima between 20 °C and 30 °C (Eaton and Hale 1993) and maxima of 35 °C. A few thermophilic fungi grow at higher temperatures of 35 °C to 50°C. The growth of most wood inhabiting fungi is retarded at temperatures higher than 46 °C and they are inactivated above 60 °C (Nofal and Kumaran 1999). An early study by Montgomery (1936) showed that most wood decay fungi cannot survive high temperature of up to 65 °C. At the other end of the

temperature range fungi become dormant at freeze drying temperatures and with additional cryoprotection procedures can survive in liquid nitrogen storage (Yang and Rossignol 1998).

Wood has organic and inorganic compounds as sources of energy and nutrients for fungi to grow (Eaton and Hale 1993). They are carbohydrates (lignin, cellulose, hemicelluloses and soluble sugars) and minerals. Fungi can also break down fats and proteins. The inorganic compounds include major elements such as nitrogen, phosphorus, potassium, sulphur and magnesium, and micronutrients such as iron, copper, zinc and boron. The micronutrients can become toxic when present at higher concentration.

2.3.3 Types of wood decay fungi

Recent classification of kingdom Fungi was established in 2007 as a result of collaborative research involving mycologists and scientists working on fungal taxonomy (Hibbett et al. 2007). The collaboration accepted 1 kingdom, 1 subkingdom, 7 phyla, 10 subphyla, 35 classes, 12 subclasses, and 129 orders. The phyla have been classified based on their sexual reproductive structures. They are: Microsporidia, Chytridiomycota, Blastocladiomycota, Neocallimastigomycota, Glomeromycota, Ascomycota and Basidiomycota. The Ascomycota and Basidiomycota phyla are contained within a subkingdom called Dikarya. A cladogram of the fungal kingdom is shown in Figure 2.1.

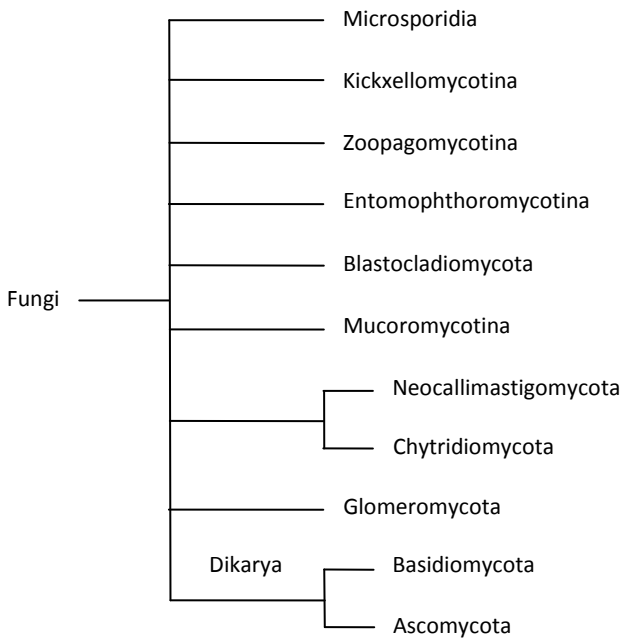


Figure 2.1: Cladogram of kingdom fungi (Hibbett et al. 2007)

Most wood decay fungi are from the sexual phyla Ascomycota and Basidiomycota and related asexual fungi from the Deuteromycota. Members of Ascomycota produce sexual spores in a sac-like ascus (Eaton and Hale 1993). Eight haploid ascopores are usually formed in each ascus. Soft rot fungi and staining fungi are of this phylum. Fungi of Basidiomycota reproduce sexually via basidia that normally hold external meiospores.

Fungi that cause decay in wood can be categorised as brown rot, white rot and under conditions of higher moisture or preservatives, soft rot. Brown and white rot describes the colour of decayed wood as either darkened or bleached in appearance, while soft rot was originally termed to describe the surface softening of wood exposed in industrial water cooling towers.

Brown rot fungi are predominantly of the Basidiomycota. Wood attacked by the fungi becomes reddish brown to dark brown in appearance and softened to some depth when wet (Eaton and Hale 1993). The fungi destroy wood by degrading the hemicellulose and cellulose without extensively depleting the lignin which remains as a brown, chemically modified framework (Cowling 1961, cited in Flournoy et al. 1991). Microscopically the wood may be modified by bore hole formation through the cell

walls and examination by polarised light microscopy at the late stages of decay can reveal a loss in birefringence, caused by loss of the crystallinity of the cellulose during degradation. Examples of brown rot fungi include *Coniophora puteana*, *Serpula lacrymans*, *Antrodia vaillantii* and *Lentinus lepideus*. The brown rot fungi form a relatively small group of the wood decaying Basidiomycota.

White rot fungi are members of the Basidiomycota and Ascomycota (Deacon 1997). Wood attacked by the fungi becomes lighter in colour or ultimately bleached. In early stages of colonisation and decay light coloured woods may be darkened with brown tinges and streaks (Eaton and Hale 1993). White rot fungi produce enzymes which oxidise the wood cell wall phenolics (laccases, manganese peroxidase and in some cases lignin peroxidase) in wood. Thus they are able to degrade lignin extensively and often other major cell wall structural components (hemicellulose and cellulose). White rot may take two main forms, simultaneous decay where lignin, cellulose and hemicelluloses are depleted at similar rates and preferential decay where the cellulose is little attacked, particularly in the early stages of decay. Microscopically simultaneous decay is characterised by cell wall thinning, erosion and enlarging bore hole formation while the preferential lignin degradation activity of selective decay results in cell separation at the middle lamella interface Basidiomycota examples include *Trametes versicolor*, *Pleurotus ostreatus*, *Phanerochaete chrysosporium* and *Schizophyllum commune* although several thousand white rot fungi from the basidiomycota have been reported.

Soft rot is prevalent under conditions which are less favourable for decay by the Basidiomycota and typically this is under lesser aerated conditions achieved in aquatic environments, in water logged soil and in preservative treated wood (creosote, chromated copper arsenate and its replacements) in ground contact. Wood attacked by soft rot fungi is often softened in the outer surface layer and microscopic examination reveals an interesting geometric (biconical) cavity pattern within the cell wall S2 layer (Findlay and Savory 1954; Corbett and Levy 1963; Eriksson 1981). In addition to cavity attack a cell wall erosion analogous to simultaneous white rot decay is reported. Some of the soft rot fungi are reported as having little or no effect on lignin while others have been shown capable of slowly metabolising lignin, but at a much slower rate than with white rot. Soft rot fungi are said to degrade wood more

rapidly under higher levels of soluble nitrogen. Soft rot is typically caused by fungi from the Ascomycota and related asexual species. Common examples include *Chaetomium globosum*, *Lulworthia purpurea*, and *Pleospora herbarum*.

In decay tests brown rot fungi are said to give high weight losses on the sapwood of both softwoods and hardwoods, whereas in many natural environments white rot fungi may also be active in softwoods. Under laboratory decay conditions white rot fungi generally give lower weight losses on softwoods, even in low durability softwoods. This situation is also experienced with soft rot fungi and one of the major factors limiting both white rot and soft rot decay is both the amount and composition of lignin. In softwoods a predominantly monomethoxy, guaiacyl lignin is found, whereas in many hardwoods there may be appreciable numbers of the dimethoxy residues, giving a guaiacyl-syringyl lignin.

2.3.4 Particleboard fungal decay

Particleboards for exterior and humid applications are prone to fungal deterioration. Attack pattern of the fungi is dependent on the characteristics of the wood materials (Chung et al. 1999). The effect of decay fungi on particleboard is usually determined by measuring weight difference of the samples before and after exposure or by changes in mechanical properties. Effects of fungi on board dimensions are less reported. The decay resistance of particleboards has been enhanced by acetylation of the particles, preservative addition, natural extractives content, coating of board surfaces and phenol formaldehyde impregnation.

Weight loss values of particleboards from the decay tests are varied, related to factors such as type of wood and binder, board density, binder percentage, moisture content, sample size, test condition, type of fungi and length of exposure (Table 2.1). Weight loss of low density seraya (*Shorea* spp.) particleboard was 20.8% and 30.6% when exposed to *Fomitopsis palustris* and *Trametes versicolor* respectively (Imamura et al. 1986). Cypress boards had weight loss of 15.22% and 0.03% due to *Gloeophyllum trabeum* and *Trametes versicolor* respectively (Okino et al. 2004). Decay resistance of southern yellow pine board was less than 5% and 11% when exposed to *Postia placenta* and *Gloeophyllum trabeum* for 12 weeks in soil block culture (Clausen et al. 2001). Decay of commercial particleboard due to *Trametes versicolor* and *Fomitopsis*

palustris was 2.28 and 1.29% respectively (Muin and Tsunoda 2004). Weight loss of particleboard from rubberwood was 37.2%, oil palm empty fruit bunches was 29.2% and rubberwood-oil palm mixed was 27.2% due to *Pycnoporous sanguineus* decay (Zaidon et al. 2007).

Table 2.1: Weight loss of particleboards due to decay fungi

Board	Density (kg m^{-3})	Resin	Fungus	Weight loss (%)	Reference
Shorea spp.	500	Isocyanate	*Fomitopsis palustris* *Trametes versicolor*	20.8 30.6	Imamura et al. 1986
Cypress	700	UF	*Gloeophyllum trabeum* *Trametes versicolor*	15.22 0.03	Okino et al. 2004
Southern yellow pine	700	UF	*Postia placenta* *Gloeophyllum trabeum*	5 11	Clausen et al. 2001
Commercial (species not known)	Na	Na	*Trametes versicolor* *Fomitopsis palustris*	2.28 1.29	Muin and Tsunoda 2004
Rubberwood Oil palm Rubberwood-oil palm	650	MUF	*Pycnoporous sanguineus*	37.19 29.16 27.20	Zaidon et al. 2007

Note: test protocols differed from reference to reference

Decay resistance of particleboard can be enhanced by acetylation of the particles (Imamura et al. 1986, 1989; Okino et al. 2004), preservative addition (Clausen et al. 2001; Muin and Tsunoda 2004; Zaidon et al. 2007), natural extractives addition (Dix et al. 1998; Yalinkilic et al. 1998; Nemli et al. 2006; Hashim et al. 2009), coating of board surfaces (Nemli et al. 2005) and phenol formaldehyde impregnation (Kajita and Imamura 1991).

Treatments may have mixed effects on the physical and mechanical properties of particleboard. Acetylated board of *Cupressus* spp. showed better physical but lower mechanical properties than the control panels (Okino et al. 2004) when bonded with a urea formaldehyde (UF) resin. Both the modulus of rupture and stiffness of boards made from rubberwood bonded with UF resin were markedly reduced by boric acid and deltamethrin treatments (Zaidon et al. 2007). Dimensional and bonding properties of particleboard were improved by impregnation with phenol formaldehyde resin

(Kajita and Imamura 1991). Besides decay resistance, acetylated particleboard did not swell appreciably as a result of exposure to decay (Imamura et al. 1986).

2.4 Effects of wood extractives on particleboard

2.4.1 Introduction

Wood extractives are non-structural wood compounds which can be extracted from wood by organic solvents and water. They can be categorised as lipophilic and hydrophilic types based on polarity of the solvents (Sjostrom 1993). Lipophilic compounds dissolve in fats, oils, lipids and non polar solvents such as hexane and toluene. Part of hydrophilic compounds can dissolve in water and other polar solvents such as acetone and methanol.

Extractives may be in higher concentrations in certain parts of the tree such as branch bases, roots, heartwood and bark (Fengel and Wegener 1989). At a cellular level extractives are concentrated in the ducts of resin canals, vessels and parenchyma cells, but may also be found in the middle lamella, intercellular spaces and cell walls of tracheids and fibres. The content and composition of extractives vary between wood species, geographical site and season (Doussot 2002; Canas et al. 2000; Harlow et al. 2006). High amounts of extractives are found in a number of tropical woods.

Wood extractives are known to be responsible for wood property modification, especially decay resistance. Several extractives are toxic to bacteria, fungi and termites (Asha et al. 2003; Matsushita et al. 2006; Sharma et al. 1981; Yamamoto and Hong 1988; Santana et al. 2010; Shibutani et al. 2007). Some effect colour, odour, and enhance strength and hygroscopicity of the wood (Imamura 1989; Koch 2003; Pandey 2005; Nussbaum and Sterley 2007; Chopra et al. 1959; Moredo and Sakuno 1991; Nzokou and Kamden 2004).

2.4.2 Groups of wood extractives

Wood extractives are mostly of terpenes, terpenoids, fats, waxes and phenolic compounds (Sjostrom 1993).

Terpenes and terpenoids are the main constituents of essential oils of the plants (Fengel and Wegener 1989). The substances are used widely as fragrant in perfumery, as flavour additives in food, and in medicines. Derivatives of terpenes and terpenoids expand the variety of usage. An example of a terpene is vitamin A.

Terpenes are derived from the basic unit of isoprene, C_5H_8, into groups of molecules, $(C_5H_8)_n$, which are linked together to form linear chains or rings (Sjostrom 1993). Terpenes can be grouped according to number of isoprene units such as monoterpenes (2 units), sesquiterpenes (3 units), diterpenes (4 units), sesterterpenes (5 units) and polyterpenes (long chains).

Terpenoids are derived from terpenes in which methyl group have been removed or oxygen atoms added. The terpenoids also can be classified, as above, according to the number of isoprene units. Examples are monoterpenoids (2 units), triterpenoids (6 units), tetraterpenoids (8 units) and polyterpenoids (long chains). Steroids and sterols are produced from terpenoids precursors.

Fats are esters of fatty acids with glycerol and mostly occur in wood as triglycerides (Sjostrom 1993). Waxes are esters of fatty acids with higher alcohols, terpene alcohols or sterols. Free fatty acids and alcohols can be derived from fats and waxes.

Free fatty acids are partially liberated from triglycerides and are present in heartwood. The fatty acids can be saturated and unsaturated depending on double bonds. Saturated fatty acids are long-chain carboxylic acids that usually have between 12 and 24 carbon atoms and have no double bonds. Examples are palmitic (C_{16}), stearic (C_{18}), arachidic (C_{20}) and lignoceric (C_{24}). Unsaturated fatty acids are like saturated fatty acids, except that the chain has one or more double bonds. Examples are oleic (C_{18}), linolenic (C_{18}) and eicosatrienoic (C_{20}).

2.4.3 Phenolic extractives

Phenolic compounds consist of basic aromatic hydrocarbon and hydroxyl, C_6H_5OH. In the tree, the compounds are largely occupied in heartwood and bark. Main groups of phenolic compounds are: stilbenes, lignans, hydrolysable tannins, flavonoids and condensed tannins (Sjostrom 1993).

Stilbenes are derivatives of diphenylethylene and possess a conjugated double bond system commonly found in wood, bark and leaves of trees (Figure 2.2) (Hart and Shrimpton 1979). Most stilbenes in wood have a resorcinol-A ring (3,5-dihydroxyl). Stilbenes in heartwood are produced either during the heartwood formation or in sapwood as an active response to infection or injury. The stilbenes have been reported to have significant biocide activity against wood decaying fungi (Schultz et al. 1990; Lindberg et al. 1992). Stilbenes with free phenolic hydroxyl groups are the cause of photo-induced darkening of some wood species such as afrormosia (*Periscopsis elata*) and spruce (Morgan and Orsler 1968; Zhang and Gellerstedt 1994).

Lignans are formed by oxidative coupling of two phenylpropane units. Many derivatives of lignans have been identified and isolated such as matairesinol, isolariciresinol, medioresinol, pinoresinol, secoisolariciresinol and lignin rhamnosides (Eklund 2004; Bonzanini 2009; Shen et al. 1999).

Flavonoids have a tricyclic $C_6C_3C_6$ carbon skeleton (Sjostrom 1993). Examples are isoflavonoid and neoflavonoid (Figure 2.2).

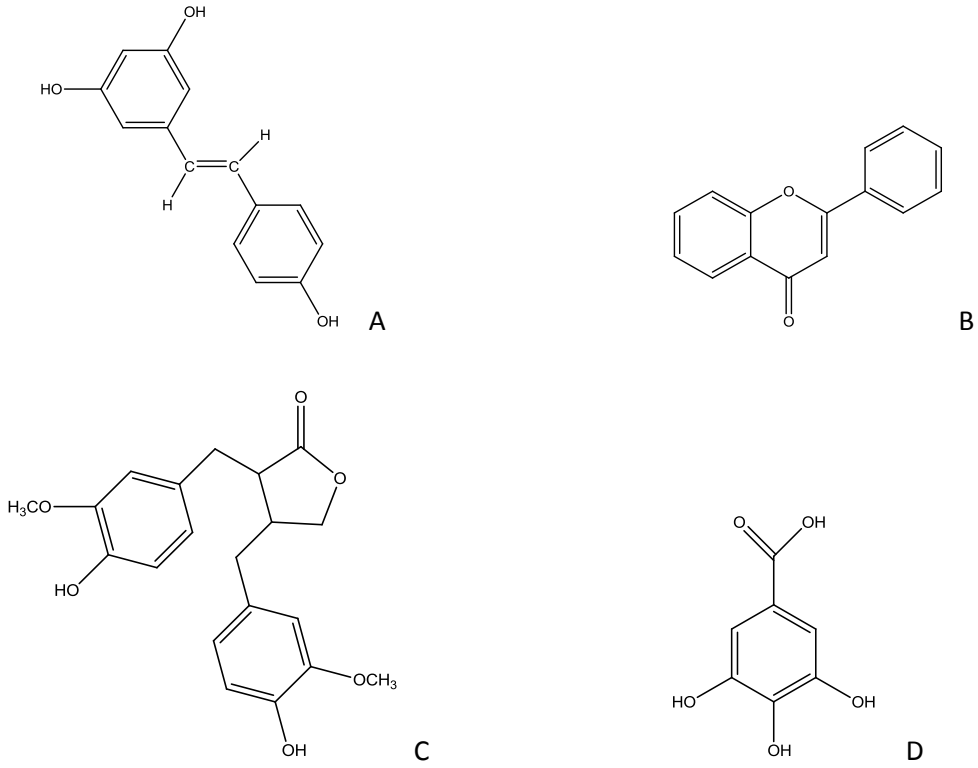


Figure 2.2: Example of stilbene (resveratrol) (A), flavonoid (flavones) (B), lignan (matairesinol) (C), hydrolysable tannin (gallic acid) (D) (Zhang and Gellerstedt 1994; Sjostrom 1993; Eklund 2004; Pizzi 1983b)

The term tannin is originally refers to the use of wood extractives for tanning of animal hide into leather. Tannins are phenolic compounds with hydroxyl and other groups that are able to form complexes with proteins and other compounds. Molecular weights of tannins from *Eucalyptus* spp. range from low to medium (Mw 1800 – 15000) (Cadahía et al. 1996).

There are two main classes of tannins: hydrolysable tannins and condensed tannins. Hydrolysable tannins are simple phenolic compounds such as pyrogallol and ellagic acid, and esters of sugar, mainly glucose, with gallic and digallic acids (Pizzi 1983b), whereas condensed tannins are polyflavonoids and are of importance due to greater availability in wood than the former. Hydrolysable tannins produce gallic and ellagic acids and sugars when hydrolysed (Sjostrom 1993).

Besides leather making, condensed tannins can be used for the preparation of adhesives and resins because of its reactivity with formaldehyde (Kim 2003). There are two types of condensed tannins commercially available for adhesives: wattle tannins and pine tannins. Wattle tannins are extracted from mimosa wattle (*Acacia mearnsii*), quebracho (*Schinopsis* spp.) and mangrove (*Rhizophora* spp.); whereas pine tannins are from radiata pine and pecan nut (*Carya illinoinensis*). Condensed tannin such as wattle and quebracho are composed of approximately 70% polyphenol tannins, 20% to 25% nontannins, mainly simple sugars and polymeric carbohydrates, the latter of which constitute 3% to 6% of the extract and heavily contribute to extract viscosity, while the balance is accounted for by a low percentage of moisture (Scharfetter et al. 1977, cited in Pizzi 1982).

The performance of all particleboards is influenced by physical conditions such as press time and temperature and this is especially true for boards made using tannin adhesives as well as by chemical conditions such as the chemical structure of tannins and hardener (Kim et al. 2003). Wattle tannin-based boards were more influenced by physical conditions while pine tannin-based boards were influenced by the chemical structure of the pine tannin nuclei which included A-ring phloroglucinolic derivatives. The curing behaviour and viscoelastic properties of wattle and pine tannin-based adhesives were studied by dynamic mechanical thermal analysis and FTIR-ATR spectroscopy (Kim and Kim 2003).

Wood-based panels made from urea formaldehyde resin are not weather resistant. Condensation of tannins with small amount of urea formaldehyde resin prevented water deterioration of plywood (Pizzi 1979), while the urea formaldehyde component improved crosslinking and strength of wood tannin-formaldehyde networks. Vetter and Barbosa (1995) studied the tannin extraction method from mangrove bark (*Rhizophora mangle*). Even though yield of extracting with hot water (24.2%) was less than that using 0.5% aqueous sodium hydroxide (57.1%), the former had more polyphenols per oven dried soluble solids (88.7%) than the latter (44.8%). The polyphenol content per oven dried soluble solids of hot water extract was similar to commercial tannin powder of *Acacia mearnsii*.

Steaming of *Acacia mearnsii* bark improved the extractability of condensed tannins from the bark and also their protein adsorbing capacity (Ohara and Ito 1995). A total phenolics content of 25.31% was obtained by steaming the bark at 140 °C for 30 minutes, giving a yield higher than hot water extraction (21.70%) (Duan et al. 2005).

Tannin can be used to substitute some of the phenol in phenol formaldehyde resin for wood-based panels, however a high substitution ratio of tannin to phenol influences the properties of the boards. Tannin from larch (*Larix gmelini*) was used to substitute 60% of the phenol in phenol formaldehyde resin. Particleboards made using the resin meet the standard requirement of exterior grade board (Lu and Shi 1995). Some of the board properties (internal bond, modulus of elasticitiy and modulus of rupture) were nearly similar to particleboard using phenol formaldehyde resin (Lu and Shi 1995).

Instead of using chemically modified tannin adhesives, non-fortified or non-modified tannin extracts can be used as effectively to produce excellent exterior grade particleboard with fast pressing times industrially. This can be achieved by pH-controlled reactivity adjustments of the tannin extract in the glue mix (Pizzi and Stephanou 1994). Besides their use in adhesives, tannins also have potential as inhibitors to corrosion in closed systems (Afidah and Kassim 2008).

2.4.4 Wood extractives of *Acacia* species

The amount of wood extractives in *Acacia* species varies (Barry et al. 2005). Yield of methanol extract of *Acacia mangium* heartwood was 2.9-3.9% which is 2.5 times less

than of *Acacia auriculiformis* heartwood (9.3-9.7%) (Lemmens et al. 1995; Barry et al. 2005). Yield of alkaline extract (13.4%) was 2 times less (24.0%) and yield of hot water extract (3.3%) was 3 times less (10.6%) between *A. mangium* and *A. auriculiformis*. The extractive yields of *Acacia* hybrid (*A. mangium x A.auriculiformis*) are intermediate between those of *A. mangium* (Methanol: 4.6%, 1%NaOH: 11.6% and hot water: 2.9%) (Latifah 2005).

Heartwood has a greater extractives content than sapwood with heartwood-to-sapwood ratio from 1.9 to 2.3 in *Acacia melanoxylon* (Lourenco et al. 2008). The total polyphenols of bark of *A. mangium* and *A. auriculiformis* are 14.2% and 12.9% respectively which is greater than *Rhizophora apiculata* (8.0%) and *Larix leptolepis* (5.3%) (Makino et al. 2009). The amount of phenolic compounds of *A. mangium* bark was similar to wattle tannin (Miyazaki and Hirabayashi 2010). The geographical effect on the concentration of extractives of *Acacia* species is insignificant as shown by Barry et al. (2006) and Lourenco et al. (2008).

The wood extractives of a variety of species of *Acacia* genus have been largely characterised (Seigler 2003). *Acacia* heartwoods extractives contain mostly flavonoids and condensed tannins with similar hydroxylation patterns (Foo 1984). The *Acacia* heartwood flavonoids typically show 7,4'-, 7,3,4'-, 7,8,4'- or 7,8,3',4'-hydroxylation exemplified by the flavan-3,4-diols guibourtacacidin, mollisacacidin, teracacidin and melacacidin (Clark-Lewis and Porter 1972). Two flavonoids have been found in *A. mangium* which are 2,3-*cis*-3,4',7,8-tetrahydroxyflavanone and teracacidin (Tachi et al. 1989; Pietarinen et al. 2004). Eight flavonoids have been identified in *A. auriculiformis* heartwood, all having 4',7,8-hydroxylation pattern, and include isoteracacidin (the 2,3-*cis*-3,4-*trans* isomer) and 4',7,8-trihydroxyflavanone, in addition to the two reported for *A. mangium* (Drewes and Roux 1966).

Certain effects of *Acacia* extracts have been investigated. Extracts of *A. mangium* and *A. crassicarpa* knotwood has strong antioxidant potency (Pietarinen et al. 2006). The extracts contained large amounts of flavonoids (melacacidin and teracacidin) and biflavonoids (proanthocyanidins, promelacacidins and proteracidins) (Pietarinen et al. 2005).

Wood-cement boards made from *A. mangium* have inferior strength due to reduced hardening accelerator efficacy. Teracidin has been isolated from the wood and inhibitory index test confirmed that the compound has high inhibitory effect for cement hardening in the boards (Tachi et al. 1989).

An important relationship between extractives and heart rot has been shown in field studies. *Acacia mangium* is susceptible to heart rot disease - whereas *A. auriculiformis* and hybrids between the two species appear to be resistant (Ito and Nanis 1997; Lee 2002). Differences between the extractives of sound and of heart rot affected heartwood of *A. mangium* can be observed by an increase in yield of the polar extractives and a decrease of ether extractives in affected heartwood (Lange and Hashim 2001). *Acacia auriculiformis* heartwood extracts had higher antifungal activity than *A. mangium* (Mihara et al. 2005). Flavonoids of 3,4',7,8-tetrahydroxyflavanone and teracacidin from both species showed antifungal activity. Higher levels of the flavonoids might contribute to heart rot resistance since *A. auriculiformis* contained higher levels of the flavonoids. The total phenol content in *A. auriculiformis* is about fivefold than of *A. mangium* (Barry et al. 2006).

Alamsyah et al. (2008) studied the wood gluing of tropical tree species by using thermo-mechanical spring method and found that the extractives of *A. mangium* in resorcinol formaldehyde adhesive interfere with the chemical cure of the adhesive. Hoong et al. (2009) studied fortification of sulphited tannin from the bark of *A. mangium* with phenol formaldehyde resin for use as a plywood adhesive. The board had a shear strength that met the requirements of European standards.

In pulp making, extractives in wood lead to higher consumption of bleaching chemicals and lower pulp yield and brightness (Wallis et al. 1996). *Acacia melanoxylon* heartwood had more extractives than sapwood (9.5% and 4.2% respectively) (Lourenco et al. 2008). The high presence of extractives decreased the wood quality for pulping by producing lower pulp yield, higher kappa number and lower brightness.

Removal of extractives improved the thermal stability of wood as shown by Shebani et al. (2008). For un-extracted wood, *Acacia cyclops* has a better thermal stability than pine and eucalyptus.

2.5 Particleboard adhesives

The four major synthetic resin types usually used in the wood-based panel industry are urea formaldehyde, melamine urea formaldehyde, phenol formaldehyde and polyisocyanate (Maloney 1993).

Urea formaldehyde (UF) resin is the reaction product of amino groups with aldehydes of formaldehyde. It is the most used resin for interior grade plywood and particleboard production (Frihart 2005). The resin is inexpensive, non-flammable, fast cure rate, and has a light colour. However the bonds are not water resistant and formaldehyde continues to evolve from the adhesive. UF resin is produced from the reaction between urea and formaldehyde to form combinations of linear and branched polymers, as well as tridimensional networks, in the cured resin (Pizzi 1983a). The reaction is divided into two stages (Figure 2.3). The first is the alkaline condensation to form mono-, di-, and trimethylolureas. The second stage is the acid condensation of the methylolureas to produce soluble and insoluble resins which cross-link by ether bridges. Curing process results in an initial increase in resin viscosity followed by gelation and finally complete cross-linking to produce a rigid thermoset resin. Resins with low formaldehyde-to-urea ratio have longer pot life, lower free formaldehyde, higher viscosity, lower water resistance, lower strength and stiffness, and slower curing rate than resins with high ratio.

The poor water resistant of UF resin has led to the development of melamine urea formaldehyde (MUF) resin (Frihart 2005). The MUF resin has acceptable water resistance with much lighter colour and lower cost than other water resistance resin such as phenol formaldehyde and resorcinol formaldehyde. The resin depends on the melamine-to-urea ratio. Production of the resin is chemically similar to that of UF resin (Maloney 1977). The melamine is added into urea at about 40:60 ratio to fortify the urea (Pizzi 1983a).

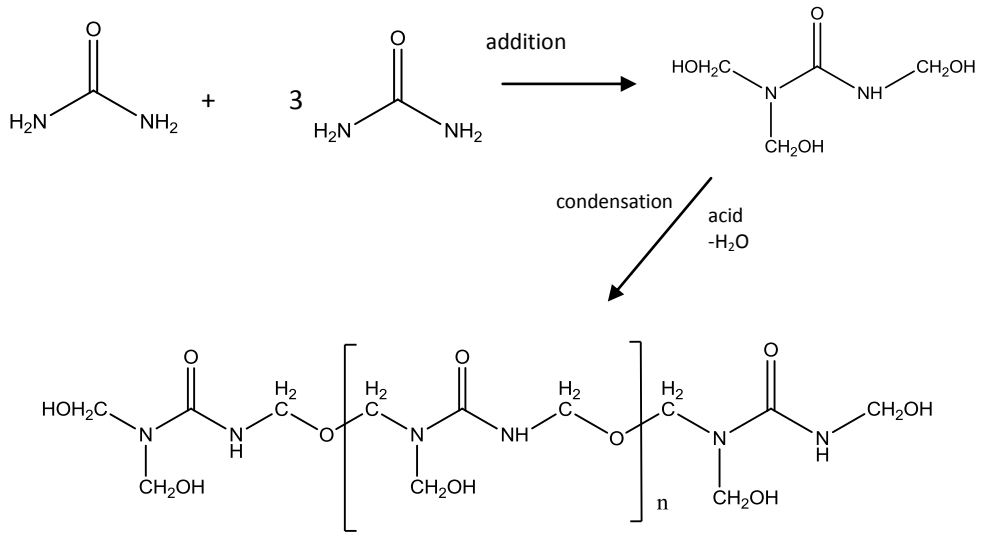


Figure 2.3: Two stages reaction of urea formaldehyde resin production (Frihart 2005)

Phenol formaldehyde resins are widely used in laminations and composites because of their durability which is derived from good adhesion to wood, high strength of the polymer and excellent stability of the adhesive (Frihart 2005). The resin is used where water resistance is required. The resin is produced from the condensation process between phenol and formaldehyde in either acid or alkaline conditions to produce resin that can undergo further polymerisation during the setting process (Pizzi 1983a; Frihart 2005). There are two basic pre-polymers – novolak and resol. Novolak resins are obtained under acidic conditions with a formaldehyde-to-phenol ratio of less than one, whereas resol resins are obtained under alkaline conditions with an excess of formaldehyde (Figure 2.4).

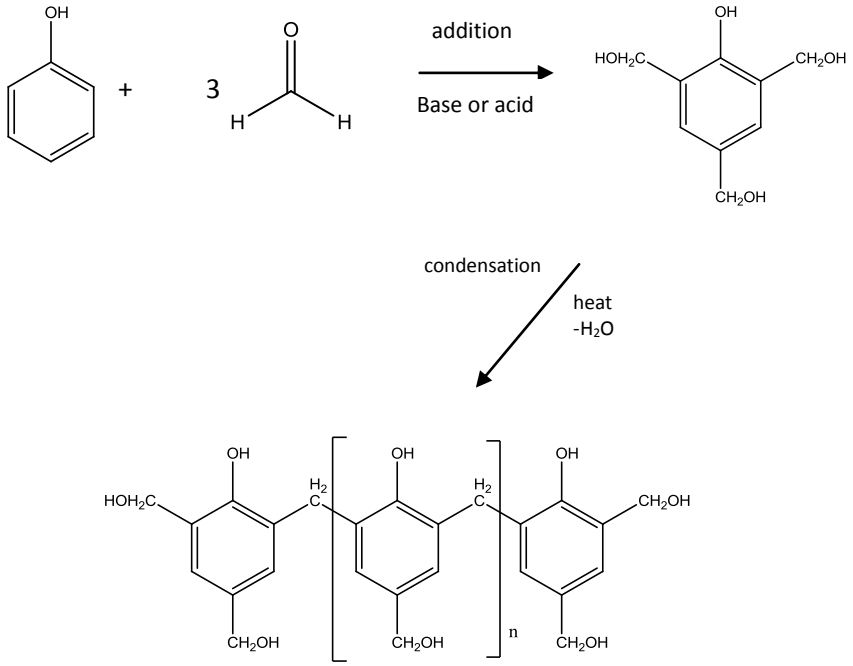


Figure 2.4: Reaction process for phenol formaldehyde production (Frihart 2005)

Polyisocyanates are used because of their reactivity with groups that contain reactive hydrogens, such as amine and alcohol groups at room temperature (Frihart 2005). The high reactivity of isocyanates makes the polymerisation proceed rapidly and usually to high conversion. However it will react with any available water present in wood. This reduces the effective molecular weight by altering the stoichimetry and can compete with desired reactions with the wood. The adhesive properties of isocyanate are based on the reactivity of the NCO groups, and covalent bonds taking the form of urethane bridges are formed with the hydroxyl groups of the wood (Pizzi 1983a).

In this study, the physical, mechanical and decay properties of particleboard from *Acacia* hybrid bonded with synthetic resins will be determined and discussed. The effects of extractives on the board properties will be evaluated.

CHAPTER 3

EVALUATION OF *ACACIA* HYBRID WOOD

3.1. Introduction

Raw material factors affect the manufacture and properties of particleboards. Wood density influences binder consumption and at a given board density, an increase in wood density can decrease particleboard mechanical properties and increase linear expansion and thickness swelling (Vital et al. 1974). Acidity and buffering capacity of raw materials affects the curing rate of acid sensitive resins, particularly urea formaldehyde resins (UF). The curing time of UF resin decreases as the pH value of raw material used decreases (Johns and Niazi 1980; Xing et al. 2004). Wood type, surface texture and geometry have significant impacts on particleboard quality (Maloney 1993).

Wood mass, density, dimensions and mechanical properties are affected by its water content (Skaar 1984). Water in wood exists as liquid and vapour states in cell lumens (free water) and as part of cell wall materials (bound water), bound onto readily available hydroxyl groups, mainly on the hemicelluloses components. During drying wood reaches fibre saturation point when all of the free liquid water is removed from the lumens. By drying further, bound water starts to leave cell wall and the space created collapses or relaxes resulting in wood shrinkage. Conversely it swells when the water is replaced, either by wetting from water vapour or from a liquid source. This hygroscopic characteristic of wood effects particleboard properties as well, and wood movement may reduce the effectiveness of the wood-resin bonds.

The extractives of wood may also influence the particleboard properties either positively or negatively. The extractives may be categorised as lipophilic and hydrophilic, and can be extracted with solvents of specific polarity.

Objectives of this part of the study are as follows:

i) To determine and evaluate the properties of *Acacia* hybrid wood obtained from a plantation.

ii) To evaluate the properties of *Acacia* hybrid particles as compared to recycled wood.

iii) To determine the yield of extractives of *Acacia* hybrid using a hot water extraction method.

3.2 Materials and methods

3.2.1 Acquiring and processing of wood

Eight trees of 10-year-old *Acacia* hybrid, up to 18 cm diameter breast height, were obtained from Golden Hope Plantation experimental plot in Rantau, Negeri Sembilan, Malaysia (Figure 3.1). After felling the trees were cut into usuable logs from basal to top (1 meter length, 6-18 cm diameter each). The logs were debarked, chipped, converted into particles using knife-ring flaker and screened through a 1 mm diameter sieve to exclude the fines.

Recycled wood chips were sourced from Kronospan, UK. The material is used throughout Europe to manufacture particleboard. Although there are issues with suitability, due to preservatives, paints and other treatments, and recycled wood produces slightly inferior board compared with virgin wood of the same species, recycled wood has been adopted as the preferred furnish primarily for economic reasons. Nevertheless, recycled wood has been successfully used by the European particleboard industry consuming in 2003 a total of 2.6 million tonnes of recycled wood annually (EPF 2004). Todays figures are probably higher despite a recession as wood recycling capacity has increased. All particleboard producers within the UK utilise recycled wood in their particleboard manufacture. Besides recycled wood, spruce chips were obtained from Kronospan. Utilisation of the wood is discussed in Chapter 4.

a. Logs were cut 1.5 m length for easy handling

b. Heartwood and sapwood of *Acacia* hybrid

Figure 3.1: *Acacia* hybrid logs

3.2.2 Wood density

Ten blocks of heartwood (dark brown) and sapwood (yellowish, <10% intermediate heartwood) of *Acacia* hybrid were randomly collected from the logs and cut to 20 x 20 x 20 mm respectively. Scots pine sapwood blocks of similar size were obtained from Bangor University and used for comparison.

Density of the woods was determined according to water displacement principle (TAPPI 1976). The blocks were soaked in deionised water at atmospheric pressure for an hour before test. Using a needle, the soaked blocks were weighed by immersion in a beaker, partially filled with water, placed on an electronic balance. Increment of the balance reading was recorded as water weight. The blocks were then dried at 105 °C to constant weight. Basic density of the woods was calculated as follows:

$$\text{Basic density} = \frac{\text{oven dry weight of wood}}{\text{weight of immersed wood}} \qquad (3.1)$$

The basic density value was times 1000 to convert into wood density, kg m^{-3} (1000 kg water = 1 m^3).

3.2.3 Water absorption and volume changes of wood after wet-dry exposure

Acacia hybrid and pine samples were prepared as in 3.2.2 with apparent radial, tangential and longitudinal direction. The samples were dried in oven at 105 °C to constant weight before being submerged in water under vacuum at ambient 20 °C (Figure 3.2). After 48 hours, the samples were taken out, excess water was dabbed off, and the blocks were weighed. They were then oven dried for 24 hours at 105 °C and cooled in a desiccators charged with dry silica gel. The weights and dimensions (longitudinal, L, radial, R, and tangential, T) of the samples were measured at the same point after each process. The submersion-drying process was repeated five times. The water absorption was determined as the weight difference of the sample before and after immersion in percent, whereas the volume changes were percentage difference of the volume (L x R x T) before and after immersion.

Figure 3.2: Water absorption apparatus

3.2.4 Wood pH and buffering capacity

Determination of pH and buffering capacity of *Acacia* hybrid and recycled wood particles were measured according to He and Yan (2005). The aqueous extracts were prepared by refluxing 25 g of dry wood particles in 250 g of distilled water for 20 minutes. The aqueous extract was then cooled and filtered through a Whatman #1 filter paper using a vacuum to obtain an extractive solution. The pH values were determined at room temperature with a pH meter calibrated in the acid pH range (pH values of 4 and 7). The acid buffering capacity was measured through the titration of a 50 ml extractive solution with a 0.025N NaOH to reach the titration end-point at pH 7. The alkaline buffering capacity measured through the titration of same volume of solution with a 0.025N H_2SO_4 to reach the titration terminal at pH 3. The buffering capacities were described as follows:

$$\text{Acid buffering capacity (mequiv / 100g of wood)} = \text{Volume of NaOH tritrant used for 100g of wood} \times \text{Normality of NaOH} \quad (3.2)$$

$$\text{Alkaline buffering capacity (mequiv/100g of wood)} = \text{Volume of } H_2SO_4 \text{ tritrant used for 100g of wood} \times \text{Normality of } H_2SO_4$$

(3.3)

The absolute acid buffering capacity is defined as the difference between the acid buffering capacity and the alkaline buffering capacity, whereas relative buffering capacity is the efficiency of acid buffering capacity compared to alkaline buffering capacity in a solution (Xing et al. 2004; Pedieu et al. 2008). The relative buffering capacity can be described as follows:

$$\text{relative acid buffering capacity} = \frac{\text{acid buffering capacity}}{\text{alkaline buffering capacity}}$$

(3.4)

3.2.5 Particle geometry determination

Air dried particles of *Acacia* hybrid and recycled wood were analysed on an Endecotts sieve shaker for 2 hours using sieves available at the laboratory (Table 3.1). Twenty particles were randomly collected from each sieve to determine their largest length, width and thickness using a micrometer. Slenderness ratio of the particles was calculated by length over thickness (Moslemi 1974).

Table 3.1: Sieves used for particle analysis

No	Sieve size (mm)
1	3.35
2	2.80
3	1.40
4	1.00
5	0.60
6	0.25

3.2.6 Determination of the extractives in the *Acacia* hybrid

Acacia hybrid particles (14% moisture content) of less than 1 mm size from 3.2.1 had been extracted at various stages during the study, some at quite late stages in an attempt to explain board properties (Table 3.2). The particles were soaked in either water or methanol at a wood to solvent ratio 1:10. A higher amount of water used (1:50 ratio) in 100 °C extraction to avoid wood bubbling according to ASTM D1110-84 (ASTM 1993). The mixtures were heated at between 80 and 160 °C temperature for 2-3 hours. In the case of methanol extraction the sample was soaked at ambient temperature for 1 day. After extraction the extracts were filtered through Whatman #1 filter paper. The filtrates were then concentrated under reduced pressure using Buchi rotary evaporator at 60 °C. The methanol filtrate was concentrated at 40 °C.

Table 3.2: Extraction of *Acacia* hybrid particles

	Label	Solvent	Wood to solvent ratio	Temperature/ Pressure	Time	Heating apparatus
1.	A100	Water	1:50	100 °C	3 hour	Heating mantle
2.	A80	Water	1:10	80 °C	2 hour	Water bath
3.	AM	Methanol	1:10	Ambient	1 day	-
4.	AA	Water	1:10	2.4 bar	2 hour	Autoclave
5.	A120	Water	1:10	120 °C	2 hour	Parr reactor
6.	A160	Water	1:10	160 °C	2 hour	Parr reactor

3.2.6.1 Extractive contents

The extractive contents were determined by gravimetric method. First, moisture content of the wood was predetermined in order to calculate the mass of moisture free wood. The moisture content was percentage difference of the wood before and after oven dried. Hot water soluble of the extraction is calculated as follow (ASTM 1993):

$$\text{Hot water solubility, \%} = \frac{(W_1 - W_2)}{W_1} \times 100 \qquad (3.5)$$

Where:

W_1 = weight of moisture free wood

W_2 = weight of oven dried wood after extraction with hot water

3.2.6.2 Determination of extractives reactivity

The reactivity of extractives with formaldehyde was determined by using Stiasny method (Voulgaridis et al. 1985; Hoong et al. 2009). Fifty millilitres of extractive (0.4%, w/w) was pipetted into a reaction flask before adding 5 ml of 37% formaldehyde solution and 5 ml 10 M hydrochloric acid, and heated under reflux for 30 minutes at boiling temperature. The hot mixture was filtered through a weighed sintered glass crucibles (porosity 2). The precipitate was washed and dried at 105 °C and weighed. Reactivity of the extractives was calculated as follow:

$$S, \% = \frac{A}{B} \times 100 \qquad (3.6)$$

Where,

S = reactivity (Stiasny number)

A = dry weight of the precipitate, g

B = dry weight of the extract in the 50 ml aqueous extractives

3.2.7 Statistical analysis

Means, standard deviations, means comparison and error bars of the data were obtained using SPSS software version 16.

3.3 Results and discussion

3.3.1 Physical wood properties of *Acacia* hybrid

Heartwood and sapwood occurrence. Similar to *A. mangium,* the heartwood and sapwood of the *Acacia* hybrid have distinctive colours. The former is darker or brown

in colour than the latter is yellowish and these are considered to be extractive related. The proportion of heart and sapwood also varies (Figures 3.1a, b). In most cases there is a narrow sapwood band but in some samples it is quite large. The difference is probably related to growth performance even though the trees are of same age. In *A. mangium* plantation, nitrogen applications have some effects in improving heartwood to sapwood ratio of the trees (Ani et al. 1990). Young *Acacia* hybrid has higher proportion of distinct colour difference between the heartwood and sapwood (Izyan et al. 2010). This gives uneven appearance of the timber which might hinder it utilisation. The colour variation can be reduced by applying treatment to the timber such as heat treatment.

Perez Cordero and Kanninen (2003) discussed the proportion of heartwood of teak (*Tectona grandis*). Heartwood volume in a tree increases exponentially with increasing DBH. Trees in high density plantations are expected to produce higher heartwood proportions since have smaller crowns and consequently less need for a high proportion of conducting sapwood area would influence greater heartwood formation. However few studies found that trees in wide spacing plantations have a higher heartwood proportion than more dense plantations.

Wood density. The *Acacia* hybrid has density of 446 kg m^{-3} which is comparable to that of the pine samples tested (Table 3.3). The value for *Acacia* hybrid resemblance that reported by Kha (1996) and Rafeadah et al. (2003). However the density is much lower than value (660 kg m^{-3}) reported by Kim et al. (2008) on dry 8-year-old *Acacia* hybrid measured using electronic densitometer. *Acacia* hybrid has slightly higher density than *A. mangium* but in terms of other wood properties they were found similar (Kha 1996, Mohd Shukari et al. 2002).

Table 3.3: Average density of *Acacia* hybrid and pine

Wood	Density (kg m^{-3})	
	value	Standard deviation
Acacia hybrid heartwood	446 b	18
Acacia hybrid sapwood	536 a	34
Pine sapwood	441 b	20

Different letter within the same column indicates a significant difference at 95% confidence level

The density of sapwood was found to be significantly higher than the heartwood and pine. In most tree species, wood density increases gradually from pith to bark (Saranpää 2003) as more mature wood is produced to support a heavier tree. This is in agreement with Kim et al. (2008) in which specific density increased from pith to bark of six clones of *Acacia* hybrid. Similar trend reported by Ani and Lim (1993) on 5-year-old *A. mangium*. Evaluation on black locust wood by Niklas (1997) showed the decrease in density and increase in Young's elastic modulus from sapwood to heartwood. Besides sapwood and heartwood, density of wood is affected by age and height level (Githiomi and Kariuki 2010).

Water sorption and desorption. Water absorption and desorption of *Acacia* hybrid and pine are displayed in Figure 3.3. After 48 hours, the water absorption of *Acacia* hybrid was nearly 100% whereas in pine maximum absorption was achieved at 160%. Throughout the cycles, the *Acacia* hybrid had inconsistent absorption ranging from 72 to 102% with the highest observed in cycle three. The heartwood absorbed slightly more water than sapwood. In pine the absorption was consistent throughout the cycles and significantly higher than the hybrid. The submersion-drying cycle caused slight reduction in dried weight of the wood with largest difference was in pine followed by heartwood and sapwood of the *Acacia* hybrid.

The absorption of water was slightly higher in the heartwood of *Acacia* hybrid rather than the sapwood. Lower density of the heartwood probably provided more lumen volume for liquid uptake thus explained the water absorption. Nevertheless the difference of the hybrids was not significant. Although Bowyer et al. (2003) suggested that extractive effects in heartwood could make it less water permeable, the situation was not applicable for the *Acacia* hybrid.

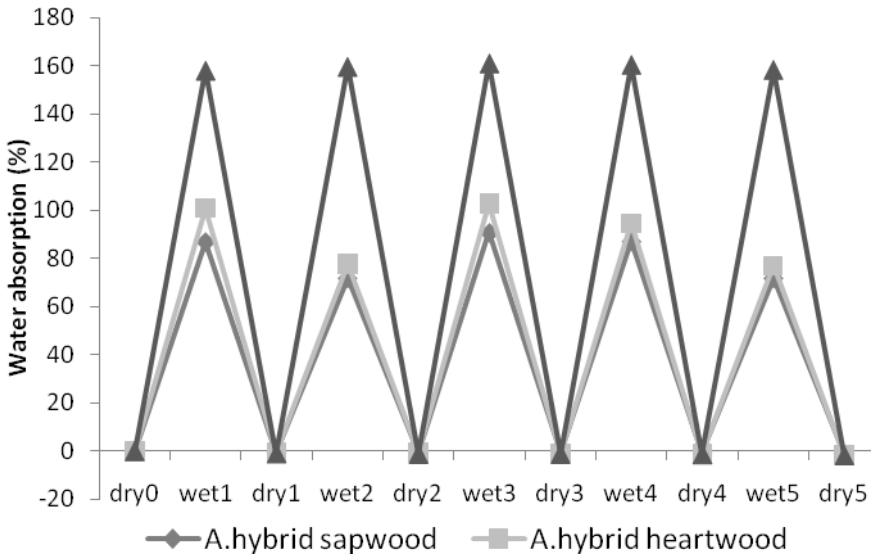


Figure 3.3: Water absorption of *Acacia* hybrid and pine at wet-dry exposure

Volume changes and shrinkage. As with water absorption, the woods had maximum changes in volume after the first wetting cycle (Figure 3.4). Volume changes due to water absorption in *Acacia* hybrid were between 8.1 and 9.6% compare to pine which was much higher, at about nearly 20%. Drying of the woods did not shrink the blocks back to their original volumes. The *Acacia* hybrid remained between 0.1 to 0.8% and pine was much higher at about 6.5%. Contradictory to water absorption findings the sapwood of *Acacia* hybrid had slightly higher volume changes than the heartwood but the difference was not significant.

The volume changes are a product of changes in the three anisotropic dimensions of the longitudinal (l), radial (r) and tangential (t) directions. These expansions were higher in pine followed by *Acacia* hybrid (Table 3.4). Average tangential expansion in pine was 10.9% (t), 6.4% (r) and 2.8% (l). Expansion in *Acacia* hybrid sapwood was 5.1% (t), 3.0% (r) and 1.0% (l), whereas *Acacia* hybrid heartwood was 4.5% (t), 3.2% (r) and 0.8% (l). Tangential shrinkage (expansion) of wood is usually twice that of radial, whereas longitudinal shrinkage (expansion) is very low (0.1-0.2%) (Ashworth 1996; Rogowski 1997).

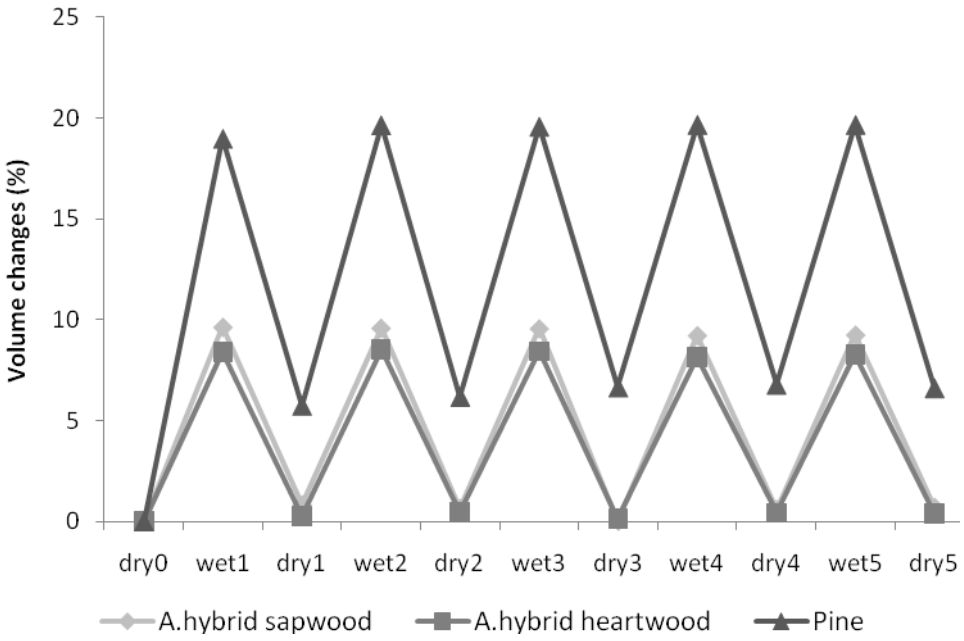


Figure 3.4: Volume changes of *Acacia* hybrid and pine after wet-dry exposure

Table 3.4: Dimension changes of Acacia hybrid and pine after wet-dry exposure

	Average changes (%)		
	Tangential	radial	Longitudinal
Acacia hybrid sapwood	5.1	3.0	1.0
Acacia hybrid heartwood	4.5	3.2	0.8
Pine	10.9	6.4	2.8

Wood with lower density tends to absorb more water. Moisture contents across stem of freshly felled *Acacia* hybrid, *A. mangium* and *A. auriculiformis* were high between 146% and 253% (Yamamoto et al. 2003). *Acacia* hybrid and *A. mangium* found to have higher moisture content in the heartwood, condition related to wetwood. The term wetwood is used to describe tree/wood with heartwood infused with water (Ward and Pong 1980). The heartwood usually has higher moisture content than the surrounding sapwood. Wetwood problem could be related to biological (bacterial), non-biological (injury) and normal age growth formation causes. However the wetwood in *Acacia* hybrid and *A. mangium* found to be free from abnormal and biological causes (Yamamoto et al. 1997, 2003). Relation of wetwood and dimension stability of the *Acacia* species has not been discussed.

3.3.2 Wood acidity

The pH and buffering capacity vary depending on the type of wood (Table 3.5). The particles of *Acacia* hybrid had lower pH and buffering capacities than recycled wood. The relationship between pH and buffering capacity could not be determined due to the limited number of samples. However, the results are in line with Xing et al. (2004) and Pedieu et al. (2008) i.e. pH value correlates to absolute acid buffering capacity and relative acid buffering capacity based on relationship equations in Table 3.6. Xing et al. (2004) found that wood pH has no relationship with acid buffering capacity and alkaline buffering capacity. The pH and absolute acid buffering capacity relationship in Table 3.5 is consistent with the equation produced by Xing et al. (2004) but the relationship with relative acid buffering capacity was slightly outside the equations. Absolute acid buffering capacity or relative acid buffering capacity is related to the final hydrogen ion (H^+) in the solution. The higher the absolute or relative capacity value is, the higher H^+ in the solution. *Acacia* hybrid had a higher H^+ in the solution thus produced a lower pH value. The pH value has linear relationship with the gel time of urea formaldehyde (UF) resin (Xing et al. 2004), however effect of wood acidity on UF resin is insignificant at a high content of catalyst. Particle size does not influence the pH value and quantity of extracted soluble acids, but influences the quantity of the extracted insoluble acids (Medved and Resnik 2004). Therefore finer particles will produce a shorter gel time with UF resin due to the estimated insoluble acids.

Table 3.5: Wood pH and buffering capacity of *Acacia* hybrid and recycled wood

Wood	pH	Acid buffering capacity (mmol l^{-1})	Alkaline buffering capacity (mmol l^{-1})	[1]Absolute acid buffering capacity (mmol l^{-1})	[2]Relative acid buffering capacity
Acacia hybrid	4.88	0.10	0.26	-0.16	0.38
Recycled wood	5.20	0.17	0.50	-0.33	0.34

[1]Absolute acid buffering capacity = acid buffering capacity – alkaline buffering capacity.

[2]Relative acid buffering capacity = acid buffering capacity/alkaline buffering capacity.

Table 3.6: Relationship of pH and both absolute and relative acid buffering capacity according to Xing et al. (2004) and Pedieu et al. (2008)

Relationship	Xing et al. (2004)	Pedieu et al. (2008)
pH – absolute acid buffering capacity	y = -0.11x + 4.88 R^2 = 0.78	y = -0.3247x + 4.6561 R^2 = 0.7578
pH – relative acid buffering capacity	y = 1.36x + 6.32 R^2 = 0.63	Y = -0.5949x + 5.2442 R^2 = 0.8894

3.3.3 Particle dimension of *Acacia* hybrid as compared to recycled wood

The particle size distributions for both woods were different due to differences between the lab scale and commercial processes (Figure 3.5, raw data in appendix Table 1) used for their production. Although the particle size distribution was different for each of the furnishes, it should be noted that the particle size distribution centred around 1.4 mm sieve mesh size with approximately 76% of the *Acacia* hybrid particles being between 0.6 and 2.8 mm in size while recycled wood had a higher volume, 83%, in the same size range. The *Acacia* hybrid had more even size distribution.

Overall analysis of particle sizes showed that the width was not significantly different between the differing furnishes but varied as the particle size became smaller, i.e. < 1.4 mm (Figure 3.6). Recycled wood particles of > 2.8 mm in size were significantly longer and thicker than *Acacia* hybrid (Figure 3.7, 3.8). Differences in the wood type and size have been reported to give a significant effect on properties of particleboard (Maloney 1977). Miyamoto et al. (2002) showed that effects of small particle had a varied effect on properties of boards manufactured from Japanese cypress. Within this study particles of differing surface areas were compared and it was found that although the reduction in particle size had a positive effect on the internal bond strength and thickness swell, it did not have a significant effect on modulus of elasticity (MOE) and modulus of rupture (MOR).

Slenderness ratio increases the propensity of the particles to buckle. The slenderness ratio of *Acacia* hybrid was higher than recycled wood particularly on particles > 1.4 mm (Figure 3.9). With particles < 1.4 mm there was no significant difference between the lengths of the *Acacia* hybrid and that of recycled wood particles. Therefore, there was no significant difference between the slenderness ratios. An increase in slenderness

ratio results in a stiffer and stronger board in bending but a decrease in internal bond strength (Moslemi 1974). In agro-based fibreboard studied by Lee et al. (2006), MOE and MOR increased with increasing of slenderness ratio but internal bond and thickness swelling values decreased.

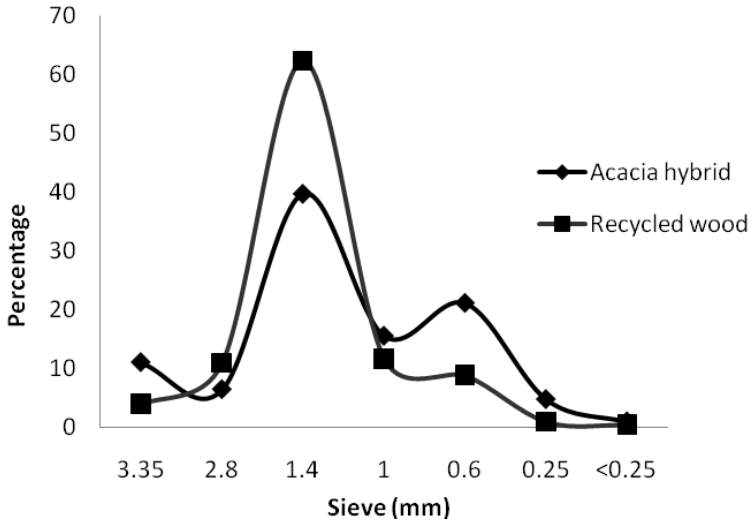


Figure 3.5: Distribution of *Acacia* hybrid and recycled wood particles

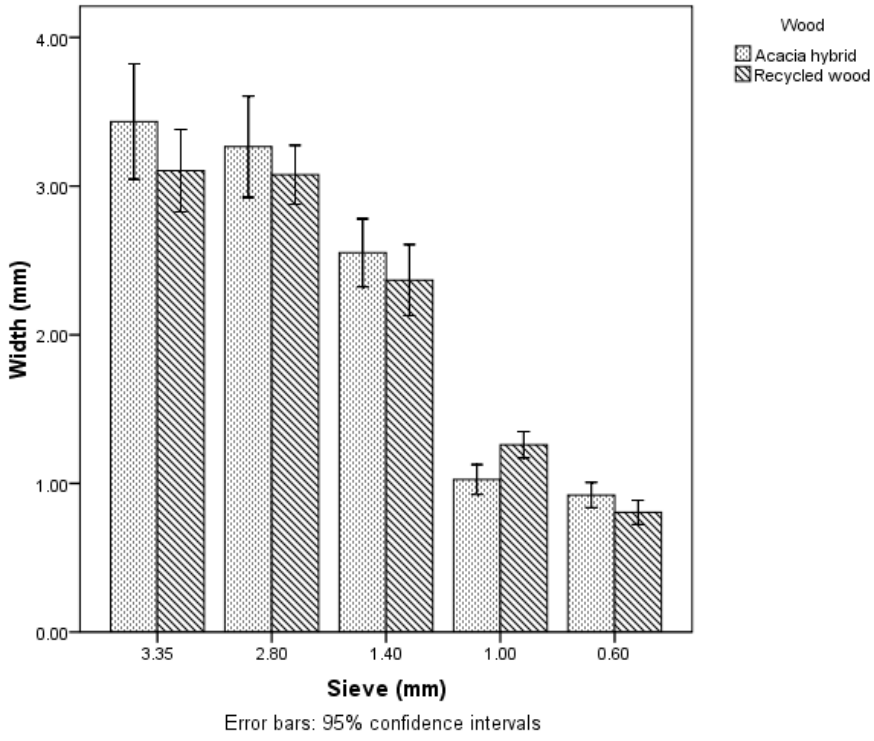


Figure 3.6: Width distribution of *Acacia* hybrid and recycled wood particles

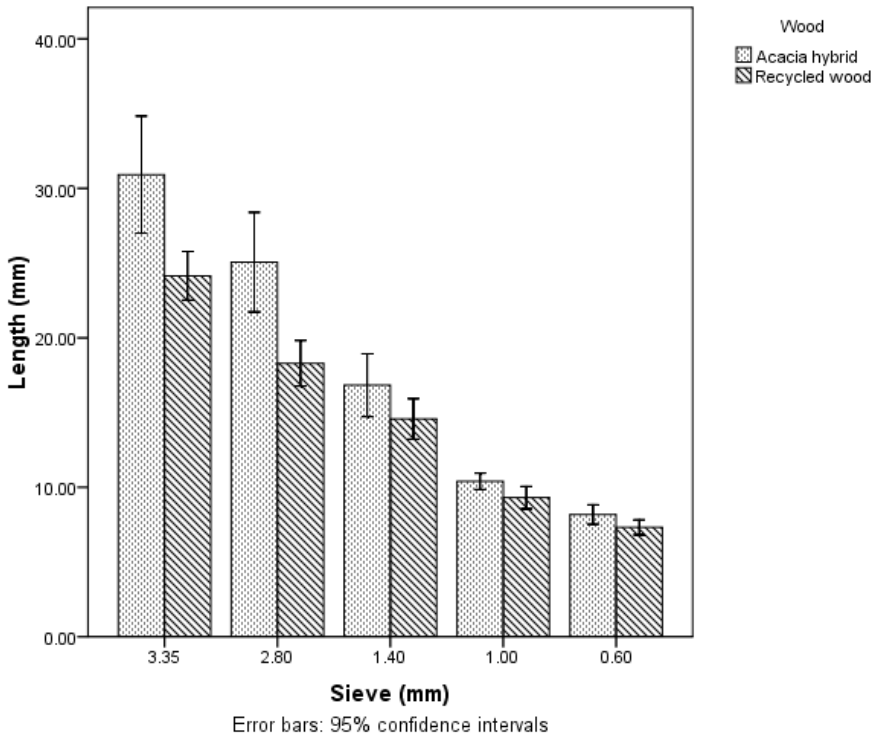


Figure 3.7: Length distribution of *Acacia* hybrid and recycled wood particles

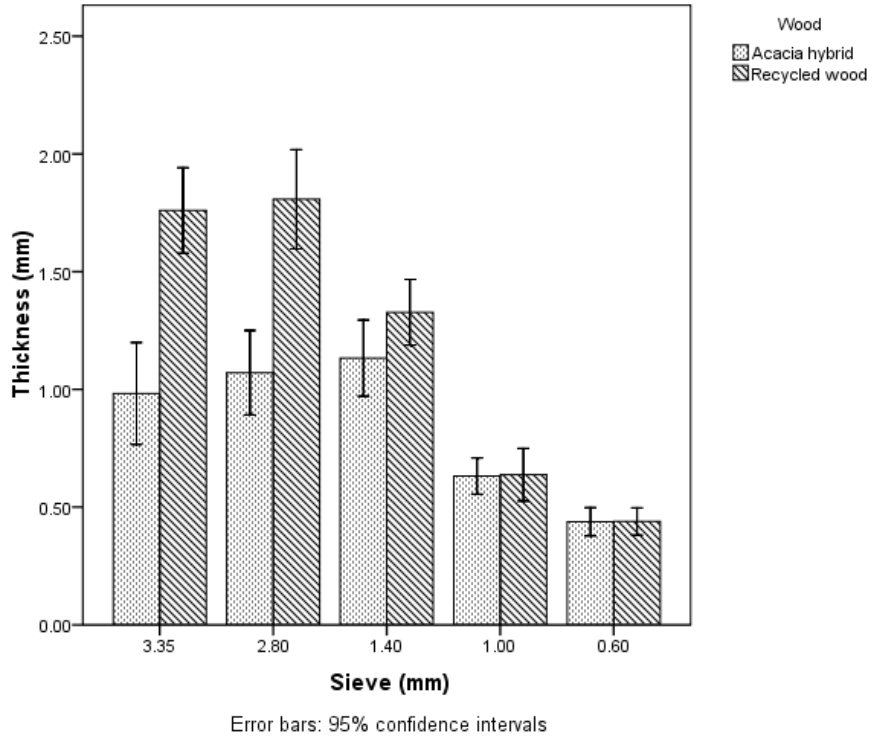


Figure 3.8: Thickness range of *Acacia* hybrid and recycled wood particles

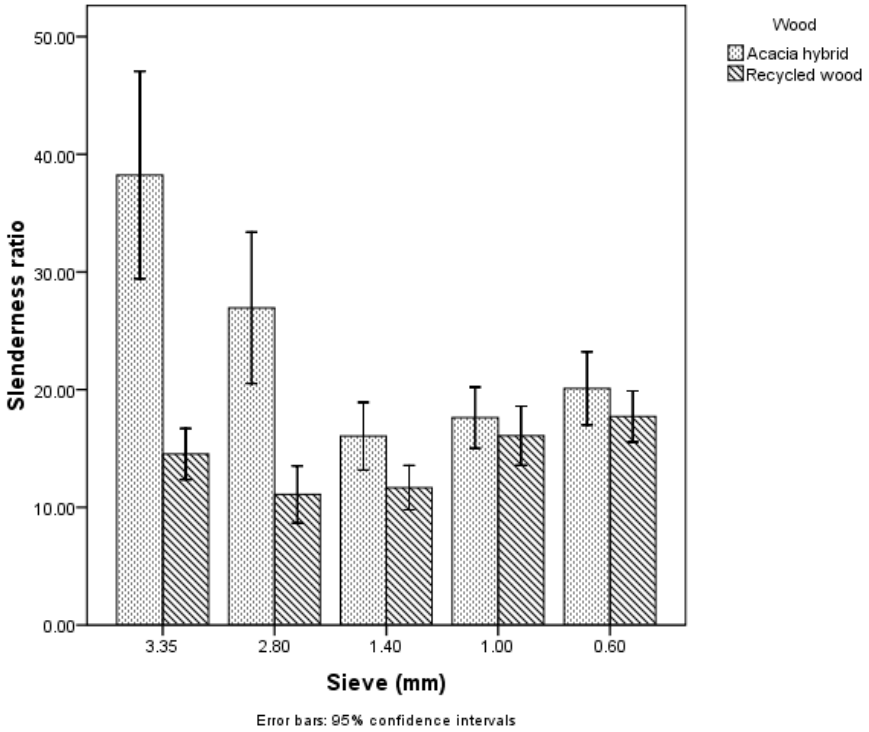


Figure 3.9: Slenderness ratio of *Acacia* hybrid and recycled wood particles

3.3.4 *Acacia* hybrid extractives

Acacia hybrid extractives were obtained from various extraction procedures. Water was used in the extraction since in the board manufacture water is used in resin, i.e. a water based urea formaldehyde resin. The pH and recovery of the extractives is shown in Table 3.7. The values for AA and AM extractives (142 °C water and ambient methanol, Table 3.2) were not recorded since these extractives were produced for a short trial. The hot water extractives have solubility in the range of 0.4 to 17.2% and pH 4.4 to 5.5. The solubility of A100 (6.3%) was higher than A80 (4.25%) due to higher extraction temperatures and amount of water used. The high temperature extraction of A120 and A160 were conducted at pressures of 4 and 6 bar respectively. The recovery of A120 (7.42%) was only slightly higher than A100, whereas extraction A160, at 160 °C, produced a high percentage (17.18%) possibly due to the degradation and extraction of wood cell wall structural components particularly hemicelluloses. The filtrate of A160 was more yellowish in colour than others which were dark green. Changes in the extractives content due to extraction temperature are expected.

Hemicelluloses could be removed from wood by pressurised hot water extraction (Andrusyk et al. 2008). Study by Leppanen et al. (2011) indicates that small amount of

hemicelluloses were removed from Norway spruce at 120 to 160 °C and dissolution was significantly enhanced when higher extraction temperatures were applied. Apparatus set up and variable setting affected the extraction since dissolution of the components in *Acacia* hybrid was only apparent at 160 °C.

The extractives were acidic with pH values within the range of wood acidity stated above. The pH value decreased from 5.5 to 4.4 most probably caused by acetic acid which is liberated via hydrolysis of the acetyl groups of polysaccharides (Tunc and van Heiningen 2008; Leppanen et al. 2011).

Table 3.7: *Acacia* hybrid extractives pH and water solubility

Extractives, temp, time	pH	Solubility (%)
A80, 80 °C, 2 h	5.51	4.25
A100, 100 °C, 3 h	5.06	6.30
A120, 120 °C, 2 h	4.90	7.42
A160, 160 °C, 2 h	4.37	17.18

The yield and quality of the extractives depend on extraction procedure especially the extraction temperature (Makino et al. 2009). Basically the yield increases with increase in temperature. Extraction of heartwood and sapwood can produce between 2 to 16% extractives. Bark usually has abundant amount of extractives at 43 to 60%. Hot water extracts of bark or heartwood (of various species) comprise about 60-80% of polyphenolic tannin polymers (Roffael et al. 2000). The yield of extractives from *Acacia* hybrid heartwood was small compared to the bark of *A. mangium* (15.4%; water-to-bark 6:1, 75 °C, 3 h) and *Acacia auriculiformis* (20.4%; water-to-bark 10:1, digester, 10 min) (Hoong et al. 2009; Devi and Prasad 1991). The yield was within the amount of extractives (4-10%; hot water, details not mentioned) from the wood of *Acacia nilotica* (Khristova and Karar 1999). Similar amount of extractives (0.9-4.4%; hot water, TAPPI T 207 method) obtained by Lange and Hashim (2001) from the wood of *A. mangium*.

The reactivity of extractives can be measured by stiasny number, which is concerned with the reaction of phenolic components to a certain amount of formaldehyde. Phenolic based polymers are usually used as wood binder with the presence of formaldehyde as cross linking agent. The amount of reactive phenol components in A80 extractives is 46% which is about similar to A100 (Table 3.8). High temperature

extraction resulted in only small amounts of reactive phenol with only 14% at 120 °C and down to 3% as the extraction temperature increased to 160 °C.

Table 3.8: Stiasny number of water soluble *Acacia* hybrid extractives

Extractives	Stiasny number (%)
A80	45.50
A100	42.55
A120	13.50
A160	3.00

The stiasny number of hot water extract of *Acacia* hybrid (46%) wood is higher than those reported for fir (*Abies nordmanniana*, 26%) and eucalyptus (*Eucalyptus camaldulensis*, 29%) (Hafizoglu and Holmbom 1995; Çolak et al. 2009). The fir wood has comparable amount of reactive phenols with common spruce and significantly higher than Scots pine (Hafizoglu and Holmbom 1995). The phenol components were definitely lower in wood than bark since the latter usually has high extractives content. The amount of reactive phenols in the fir bark was 36% higher than in the wood (Hafizoglu and Holmbom 1995). Reactive phenols in bark of *Acacia* species had been reported in several studies which depicted similar trend. The bark of *A. mangium* had stiasny number of as low as 80 to 100% (Mohd Nor et al. 1989; Hoong et al. 2009). The stiasny of *Acacia mearnsii* bark (black wattle) was between 76 and 94% (Schimleck and Yazaki 2003) whereas the commercial tannin of *Acacia mearnsii* was 86% (Zhao et al. 1994, 1995).

3.4 Conclusion

The *Acacia* hybrid heartwood and sapwoods are distinguishable by colour. The density of the wood was 446 kg m^{-3}, similar to *Acacia* hybrid reported by other researchers. The density of the heartwood was slightly lower than sapwood. The wood strength characteristics are expected to be similar to *A. mangium*. The wood was more dimensionally stable and absorbed less water than the comparative wood (pine) and showed no difference in term of water resistance between the heartwood and sapwood. The *Acacia* hybrid was acidic at pH 4.9 and only needed small amount of acid to reduce the pH value.

The particles of *Acacia* hybrid were generally smaller in size than the recycled wood. Slenderness ratio of *Acacia* hybrid was about 38 on particles of over 1.4 mm size. The particles dimensions could affect the strength of particleboard produced using *Acacia* hybrid and recycled wood.

Acacia hybrid extractives of aqueous solutions have been produced for to study the effect of extractives to adhesion of wood. It was found that the extractives content increased with increasing of extraction temperature. However, the active polyphenols in the extractives decreased as the temperature increased.

CHAPTER 4

ACACIA HYBRID PARTICLEBOARDS WITH UREA FORMALDEHDYE, MELAMINE UREA FORMALDEHYDE AND PHENOL FORMALDEHYDE RESINS AS BINDER

4.1 Introduction

Objectives of this part of the study are as follows:

i) To determine the properties of particleboards from *Acacia* hybrid and compare them to those of recycled wood particleboard.

ii) To evaluate the properties *Acacia* hybrid particleboards bonded with urea formaldehyde, melamine urea formaldehyde and phenol formaldehyde as compared to recycled wood and spruce boards.

4.2 Materials and methods

4.2.1 Board production

Single-layer homogenised particleboards were produced from *Acacia* hybrid, recycled wood and Sitka spruce (*Picea sitchensis*) to a nominal thickness of 12 mm and target density of 650 kg m^{-3}. The particles were blended with thermosetting resins (10% of wood weight) (Table 4.1) in a rotary blender before being pre-pressed in a 500 x 500 mm pre-press. The resins were urea formaldehyde (66% solids), melamine urea formaldehyde (66% solids) and phenol formaldehyde (56% solids) of commercial resins obtained from Dynea, UK. Properties of the resins are shown in Table 4.2. Wax (1% of resin weight) was added to the urea formaldehyde resin prior to wood blending. The mat then pressed in a Schwabenthan laboratory press controlled with a PressMan control unit. The press was maintained at 200 °C for 3 minutes to ensure full cure of the resins.

Table 4.1: Materials used for particleboard production and replicates

Material	Resin	Board replicates
1. *Acacia* hybrid	Urea formaldehyde	5
	Melamine urea formaldehyde	3
	Phenol formaldehyde	3
2. Recycled wood	Urea formaldehyde	5
3. Spruce	Melamine urea formaldehyde	3

Note: Boards with urea formaldehyde resin were tested for static bending besides thickness swelling and internal bond thus required additional 2 replicates of boards

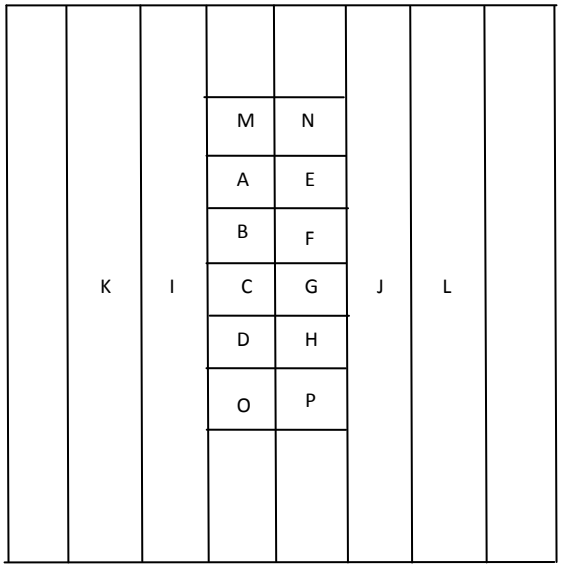
Table 4.2: Properties of thermosetting resins

Resin	Solids content (%)	pH	Gel time, 103 °C (s)	Viscosity, 25 °C (cps)
Urea formaldehyde	66	8.15	38*	340
Melamine urea formaldehyde	66	8.50	60*	360
Phenol formaldehyde	56	11.22	14	210

* 0.5% ammonium chloride hardener added

4.2.2 Sampling of test materials

The pressed particleboards were conditioned at ambient atmosphere for two days before being cut into test sizes. Two replicates of *Acacia* hybrid and recycled wood boards with urea formaldehyde resin were cut according to cutting diagram (Figure 4.1) for comparison of board properties i.e. static bending, thickness swelling, internal bond, density profile, and cyclic test at same board location. Three replicates ofs urea formaldehyde boards, melamine urea formaldehyde and phenol formaldehyde boards were cut to small test pieces of 50 x 50 mm each. The test pieces were randomly selected and tested for thickness swelling and internal bond strength. Others test pieces are used for decay fungi test in Chapter 5.



Static bending = I, J, K, L; Thickness swelling = A, C, F, H

Internal bond and density profile = B, D, E, G; Cyclic test = M, N, O, P

Figure 4.1: Cutting diagram of particleboards with urea formaldehyde resin

4.2.3 Thickness swelling and water absorption

The test was conducted on samples (50 x 50 mm, 8 pieces) according to BS EN 317: 1993 (BSI 1993a). They were conditioned at 65% relative humidity and 20 °C to constant weight prior to thickness determination and weighing. Thickness and weight determinations were also done after immersion in water at 20 °C temperature for 2 and 24 hour periods. Differences between the values, before and after immersion, were expressed as percentages.

The boards were then dried in a forced air oven at 103 °C follow by immersion in water at 20±5 °C for 24 hours. Board thickness and weight were measured after each process. The immersion-drying cycle was repeated for a total of eight cycles.

4.2.4 Water uptake test

Acacia hybrid and recycled wood boards of 50 x 50 mm from 4.2.2 were randomly selected (8 pieces) and cut further to 25 x 25 mm test pieces. The test pieces were conditioned at 65% relative humidity and 20 °C to constant weight. The boards then immersed in water and vacuum impregnated at 20 °C, sucking pressure 1005 mbar, and left to soak for 15 hours. The weight uptake was determined.

4.2.5 Density profile

Density profile through the thickness of the boards of *Acacia* hybrid and recycled wood boards with urea formaldehyde resin (50 x 50 mm, 8 pieces) was determined by means of gamma radiation transmitted using an ATR density profiler (software version 2.09) through the sample across the thickness.

4.2.6 Static bending

Static bending tests were conducted on *Acacia* hybrid and recycled wood boards with urea formaldehyde resin, (290 x 50 mm, 8 pieces) according to BS EN 310: 1993 (BSI 1993b). The boards were conditioned at 65% relative humidity and 20 °C to constant weight. An Instron universal testing machine (model 5500R with 50 kN load cell) was used to determine the strength of the boards. Load was applied to the board at crosshead speed 6.6 mm min^{-1} throughout the test (Figure 4.2). The modulus of elasticity (MOE) of each test piece was calculated by using the slope of the linear region of the load-deflection curve as following:

$$MOE = \frac{L^3\left(F_2 - F_1\right)}{4\,bt^3\left(a_2 - a_1\right)} \qquad (4.1)$$

Where,

L = span = 240 mm

b = width (mm)

t = thickness (mm)

$F_2 - F_1$ = increment of load on the straight line portion of the load-deflection curve

$a_2 - a_1$ = increment of deflection at the mid-length of the test piece (corresponding to $F_2 - F_1$)

The bending strength or modulus of rupture (MOR) was calculated by determining the ratio of the bending moment at the maximum load to the moment of its full cross section.

$$MOR = \frac{3F_{max}L}{2bt^2} \qquad (4.2)$$

Where,

F_{max} = maximum load (N)

L = span = 240 mm

b = width (mm)

t = thickness (mm)

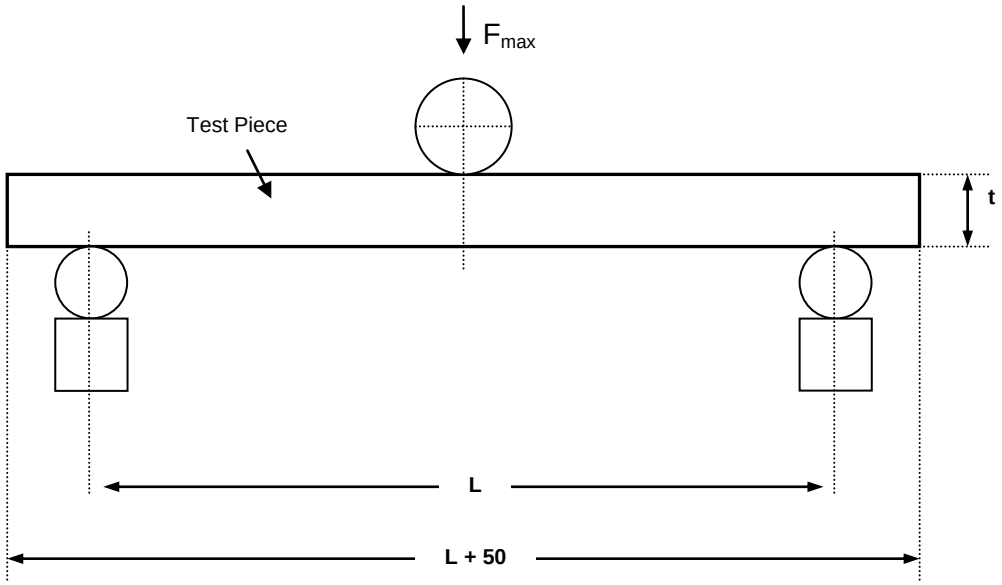


Figure 4.2: Arrangement of the static bending apparatus

4.2.7 Internal bond

Internal bond tests were carried out according to BS EN 319: 1993 (BSI 1993c). Boards (50 x 50 mm, 8 pieces) were attached to wood block with hot-melt glue on both surfaces. The glued assemblies were stored under controlled conditions of 65±5% relative humidity and a temperature of 20±2°C for 24 hours. The internal bond value

was determined using Instron universal testing machine (model 4301, 5 kN load cell) at crosshead speed of 0.8 mm min^{-1}. Internal bond, IB (in N mm^{-2} or MPa to two decimals) of each test piece was calculated according to following formula:

$$IB = \frac{P'}{b \times L} \qquad (4.3)$$

Where

P' = breaking load, N

b = width of test pieces, mm

L = length of test pieces, mm

The IB of the board was the mean value of all results obtained from the test pieces.

4.2.8 Cyclic test

The test was carried out on *Acacia* hybrid and recycled wood boards with urea formaldehyde resin according to BS EN 321: 1993 (BSI 1993d). Board samples (50 x 50 mm, 8 pieces) were exposed to three cycles, each comprising immersion in water, freezing, and drying. The boards were immersed with their faces vertical in water at 20 °C for 72 hours. After immersion period, the boards were removed from the tank, wiped off with a cloth, then placed with their faces vertical in freezer at temperature between -12 and -20 °C for 24 hours. After freezing the boards were transferred to the drying oven at 70 °C for 72 hours where they placed with face vertical and well separated from each other. The complete testing cycle of 168 hours was repeated three times. The thickness swelling and internal bond values of the boards were determined according to the above standards.

4.2.9 Statistical analysis

Data were analysed using computer statistical software SPSS version 16. Analysis was undertaken to establish means, standard deviations and the significance differences between two set of comparable data.

4.3 Results

4.3.1 Comparative properties of UF-bonded *Acacia* hybrid and recycled wood particleboards

Board production. Five replicates of particleboards were successfully produced from *Acacia* hybrid and recycled wood particles with urea formaldehyde resin as binder. The average core temperature development for boards manufactured from both types of furnishes are shown in Figure 4.3. At the end of the test, the core of *Acacia* hybrid reached a slightly higher temperature than the recycled wood even though it showed slower heat transfer. The difference was due to the materials rather than pressing system since the temperature of platens was consistent in the series of trials throughout the boards.

The density profile of a board is dependent on the particle configuration, moisture distribution in the mat, hot press temperature and rate of closing, resin reactivity and the compressive strength of the wood particles (Kelly 1977). Having compared density profiles of boards made from both recycled furnish and *Acacia* hybrid, it was observed that boards in this study had typical 'u-shape' density profiles with the peak densities near the surfaces and the lower in the core region (Figure 4.4). Overall densities of both *Acacia* hybrid and recycled wood boards were statistically similar (Table 4.3). Boards from recycled wood had significantly higher density on the lower surface; however, this was not noted with the *Acacia* boards.

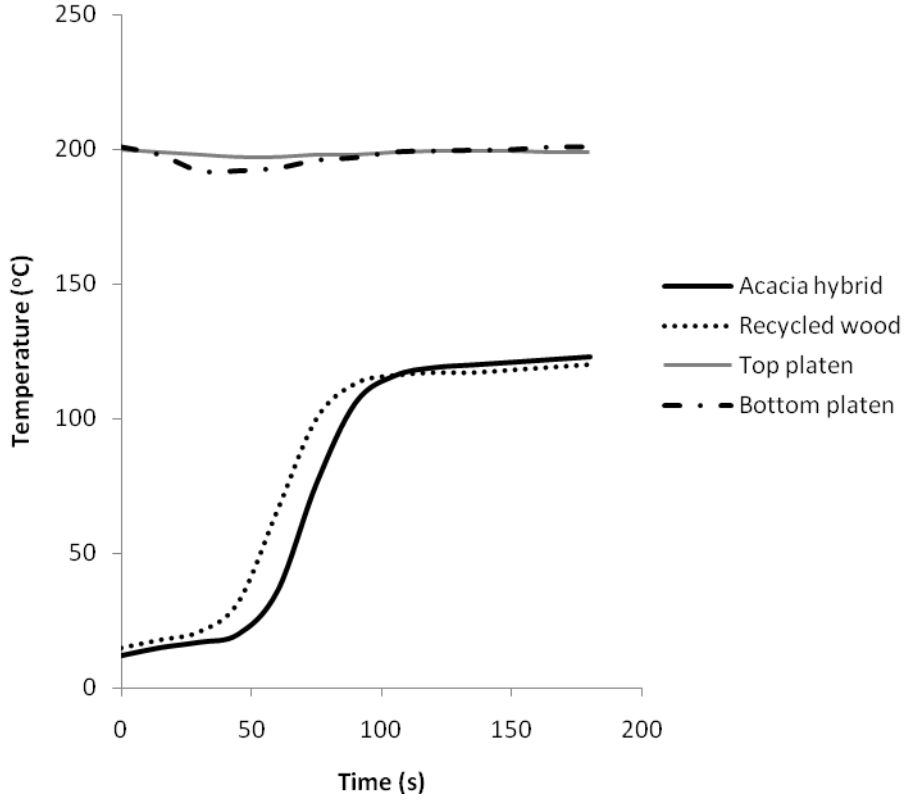


Figure 4.3: Temperature behaviour at the centre of *Acacia* hybrid and recycled wood mat during hot pressing

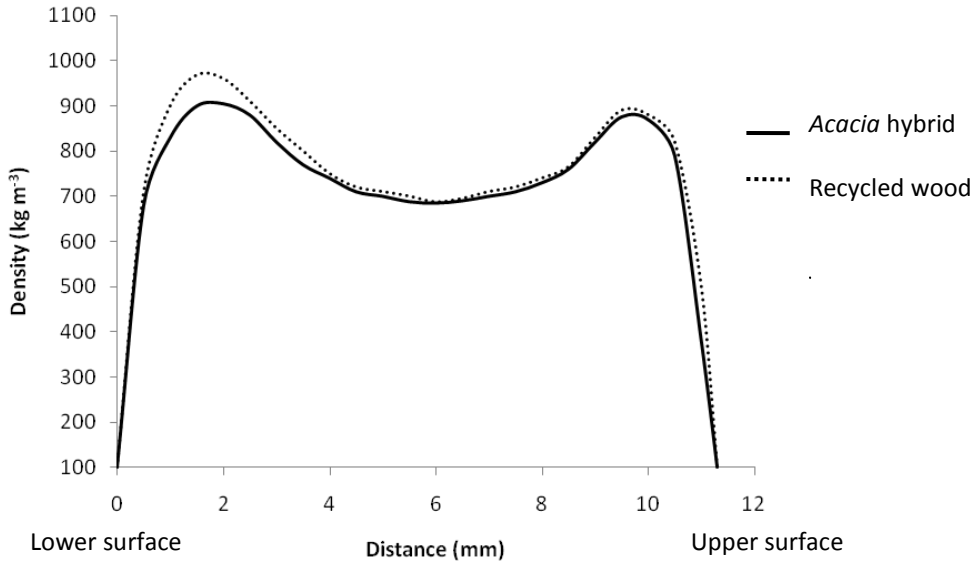


Figure 4.4: Average density profile of particleboard from *Acacia* hybrid and recycled wood

Table 4.3: Vertical density distributions of *Acacia* hybrid and recycled wood boards

	Average density (kg m^{-3})	Face-left/average density ratio	Face-right/average density ratio	Core/average density ratio
Acacia hybrid	747.87 a (18.55)	1.21 b (0.01)	1.17 a (0.01)	0.92 a (0.01)
Recycled wood	758.87 a (24.65)	1.28 a (0.02)	1.18 a (0.03)	0.90 a (0.01)

In parentheses is standard deviation
Different letter within the same column indicates significant difference at 95% confidence level

Board swelling tests and absorption. Boards from *Acacia* hybrid swelled to between 5 and 15% after 2 and 24 hours immersion respectively (Table 4.4). These values were significantly lower than recycled wood which recorded 2.0 and 2.4 times more swelling. In addition the water absorption values of the recycled wood board after 2 and 24 hour immersion were 2.4 and 2.1 times more than the *Acacia* hybrid. The thickness swelling of *Acacia* hybrid was similar to that of *A. mangium* particleboard (Razali and Kuo 1991). However, *A. mangium* particleboard produced by Chew et al. (1991) had a five times higher thickness swelling. The thickness swelling of *Acacia* hybrid met the standard requirement for load-bearing boards in dry conditions.

Table 4.4: Physical properties of particleboard from *Acacia* hybrid and recycled wood bonded with urea formaldehyde resin

Board	Thickness swelling (%)		Water absorption (%)	
	2 hour	24 hour	2 hour	24 hour
Acacia hybrid	5.27 b (0.43)	14.86 b (1.30)	6.11 b (0.50)	30.01 b (1.81)
Recycled wood	10.55 a (1.63)	35.70 a (3.60)	14.91 a (1.20)	63.66 a (3.51)
BSI (2003)[1]	-	Max. 16	-	-

In parentheses is standard deviation (n = 8)
Different letter within the same row indicate significant different at 95% confidence level
[1] BS EN 312-4 2003: Particleboards specifications: requirements for load-bearing boards for use in dry conditions

Cyclic swelling tests. Exposure to wet and dry cycles caused an increase in the thickness of the boards (Figure 4.5). Boards of *Acacia* hybrid and recycled wood had expanded up to 35 and 70% respectively by the last cycle (cycle 8). Drying of boards

resulted in some recovery of thickness but not to their original thickness (about 25 and 52% respectively for *Acacia* hybrid and recycled wood). Overall, the swelling and shrinkage as well as the rates of swelling and shrinkage were smaller in *Acacia* hybrid boards.

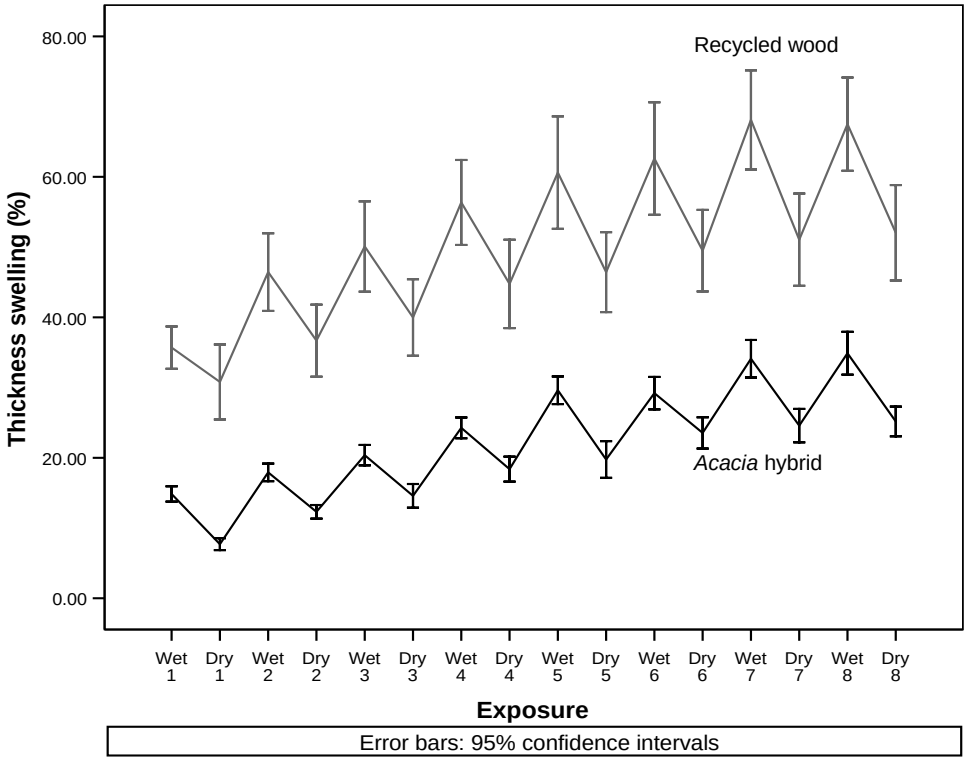


Figure 4.5: Thickness swelling of particleboard from *Acacia* hybrid and recycled wood bonded with urea formaldehyde resin after wet-dry exposure

The boards also had highest water absorption in the first wet exposure, i.e. before the first drying cycle (Figure 4.6). The water absorption values of wet exposure were inconsistent throughout the cycle. Boards of recycled wood took twice the amount of water compared with the *Acacia* hybrid. In the re-dried condition, boards of recycled wood had lower water absorption than *Acacia* hybrid due to mass loss from the wet exposures.

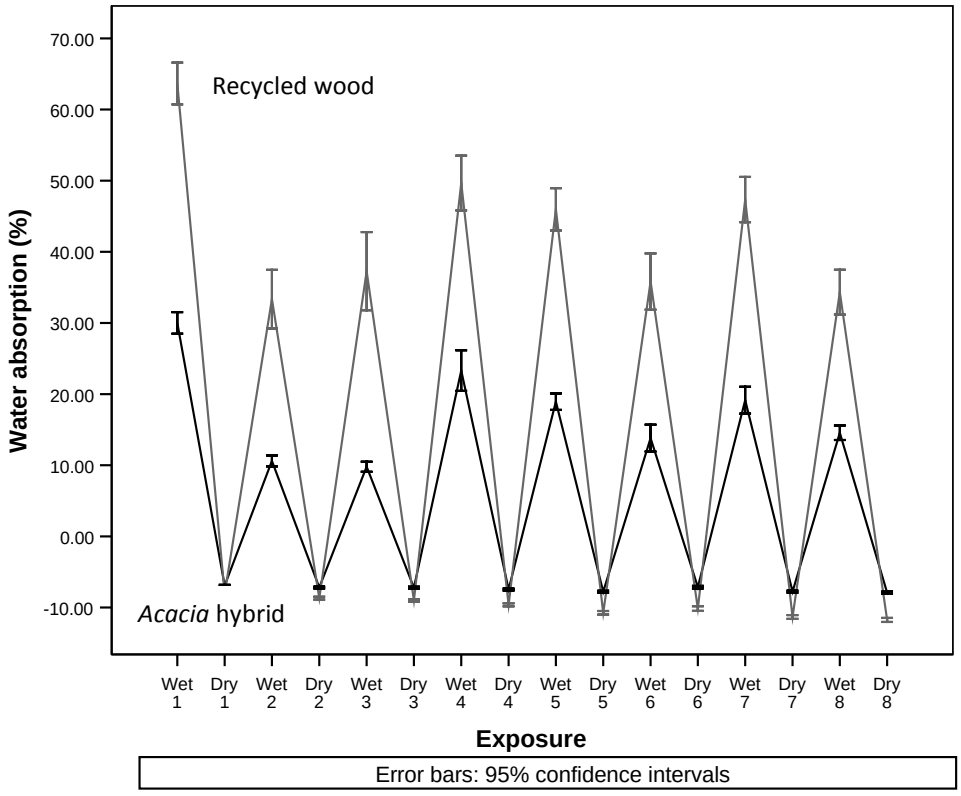


Figure 4.6: Water absorption of particleboard from *Acacia* hybrid and recycled wood bonded with urea formaldehyde resin after 8 cycle wet-dry exposure

The response of thickness swell and the water uptake of samples when immersed in water are shown in Figures 4.7 and 4.8. The rates of thickness swelling values were high in the first 4 hours followed by a slower rate and after 19 hours, maximum swelling and absorption were recorded (Table 4.5). Boards produced from recycled wood swelled nearly twice as much as the *Acacia* hybrid boards. This is in line with results in Table 4.4 and Figure 4.5. The swelling was significantly different throughout the test even though the difference smaller as immersion ended (Table 4.5). The water absorption of the recycled furnish boards showed higher increment for 7 hours of exposure, then decreased and stabilised to nearly the same value as *Acacia* hybrid (Table 4.6).

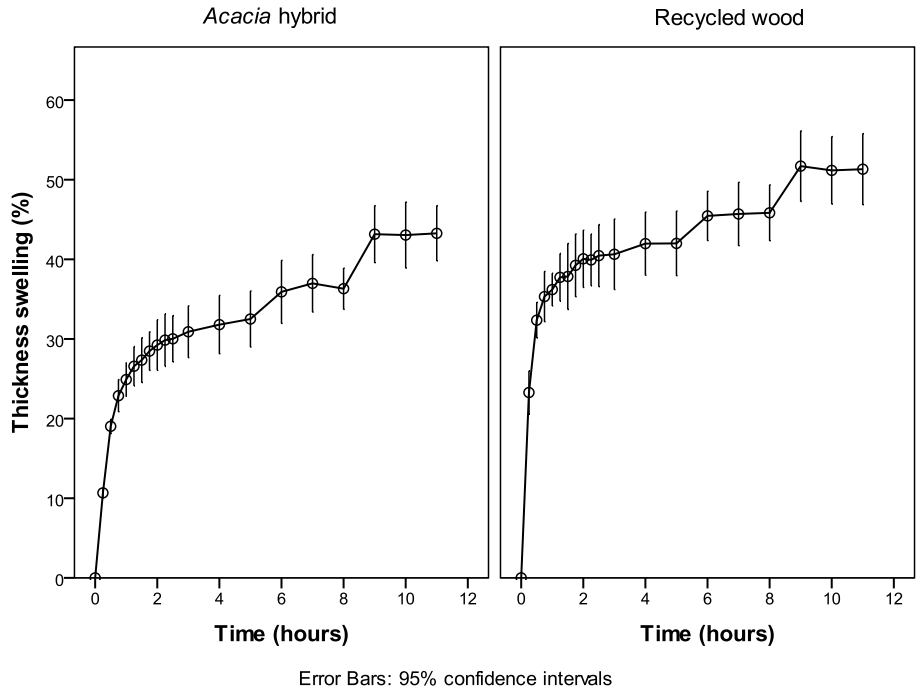


Figure 4.7: Thickness swelling of particleboard from *Acacia* hybrid and recycled wood from the water uptake test after 11 hours exposure

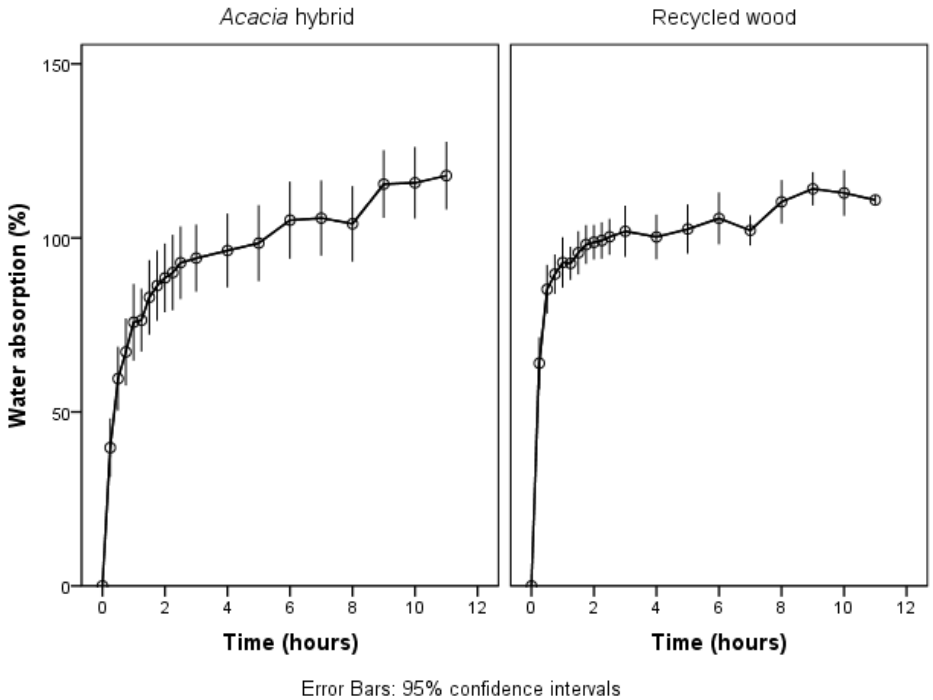


Figure 4.8: Water absorption of particleboard from *Acacia* hybrid and recycled wood from the water uptake test after 11 hours exposure

Table 4.5: Statistical comparison of thickness swelling of particleboard from *Acacia* hybrid and recycled wood from the water uptake test after exposure between 12 and 67 hours

Board	Thickness swelling (%)					
	12 h	13 h	14 h	19 h	43 h	67 h
Acacia hybrid	44.57 b	44.50 b	44.58 b	46.83 b	47.78 b	48.04 b
Recycled wood	51.60 a	51.94 a	52.13 a	53.28 a	54.78 a	54.76 a

Different letter within the same column indicate significant different at 95% confidence intervals

Table 4.6: Statistical comparison of water absorption of particleboard from *Acacia* hybrid and recycled wood from the water uptake test after exposure between 12 and 67 hours

Board	Water absorption (%)					
	12 h	13 h	14 h	19 h	43 h	67 h
Acacia hybrid	119.05 a	119.82 a	115.97 a	125.39 a	121.53 a	122.13 a
Recycled wood	113.15 a	115.57 a	110.50 a	122.74 a	119.95 a	120.84 a

Different letter within the same column indicate significant different at 95% confidence intervals

The extreme exposure in the freezing cyclic test caused high thickness swell values of up to 90% (Table 4.7). Severe bonding loss and leaching are expected since the swelling was not significantly different between the boards.

Table 4.7: Thickness swelling and internal bond after the freezing cyclic test of particleboard from *Acacia* hybrid and recycled wood

Board	Thickness swelling (%)	Internal bond (MPa)
Acacia hybrid	90.24 a (6.59)	0.017 a (0.006)
Recycled wood	83.21 a (5.43)	0.011 b (0.002)

In parentheses is standard deviation (n = 8)

Different letter within the same column indicate significant different at 95% confidence intervals

Mechanical strength properties: IB, MOR and MOE. Boards from *Acacia* hybrid had higher internal bond strength even after the wet–dry exposure and cyclic test (Tables 4.7 and 4.8). With dry boards (BS EN 319), most failure occurred at the middle whereas for exposed boards, failure was near to the surface. The urea formaldehyde resin interacted well with *Acacia* hybrid to give high tensile strength. During exposures, the resin reacted with water, thus, weakening the particle bonding (as is expected with

urea formaldehyde resin). Particles were being lost from boards after the extreme exposures of the cyclic test.

The *Acacia* hybrid board had greater MOR and MOE values (Table 4.8). The MOR was 90% greater (12.43 MPa) and MOE was 49% higher (1256 MPa) than recycled wood. The MOR of *Acacia* hybrid is comparable with *A. mangium* boards as reported by Razali and Kuo (1991), and slightly lower than boards produced by Chew et al. (1991). The internal bond strength is similar to values reported by Razali and Kuo (1991) and Chew et al. (1991).

Both *Acacia* hybrid and recycled wood boards surpassed the mechanical strength requirements for general purpose applications specified by European standard. In fact the strengths of *Acacia* hybrid boards exceeded the requirements for load bearing board for use in dry conditions (BSI 2003).

Table 4.8: Static bending and internal bond of particleboard from *Acacia* hybrid and recycled wood

Board	Static bending (MPa)		Internal bond (MPa)	
	MOR	MOE	BS EN 319	Wet-dry exposure
Acacia hybrid	26.25 a (2.29)	3811 a (173)	0.95 a (0.22)	0.187 a (0.118)
Recycled wood	13.82 b (1.98)	2555 b (268)	0.61 b (0.08)	0.039 b (0.066)
Type P1[1]	Min. 12.5	-	Min. 0.28	-
Type P4[2]	Min.16.0	Min. 2300	Min. 0.40	-

In parentheses is standard deviation

Different letter within the same row indicate significant different at 95% confidence intervals

[1] Particleboards specifications: requirements for general purpose boards for use in dry conditions (BSI 2003)

[2] Particleboards specifications: requirements for load-bearing boards for use in dry conditions (BSI 2003)

4.3.2 Properties of *Acacia* hybrid particleboards bonded with urea formaldehyde, melamine urea formaldehyde and phenol formaldehyde resins as compared to recycled wood and spruce

Board manufacture. Three replicates of particleboards were produced from *Acacia* hybrid bonded with melamine urea formaldehyde (MUF) and phenol formaldehyde (PF) resins. A similar number of boards were produced from spruce with the MUF resin as binder. The spruce boards had rough surfaces since 93% of the particles were over 1.4 mm size (Figure 4.9). The percentage was relatively higher than the *Acacia* hybrid and recycled wood (Figure 3.5) which might have altered the board properties. The boards were used to compare with the *Acacia* hybrid boards alongside the recycled wood. For this purpose all boards were cut to small test pieces (50 x 50 mm).

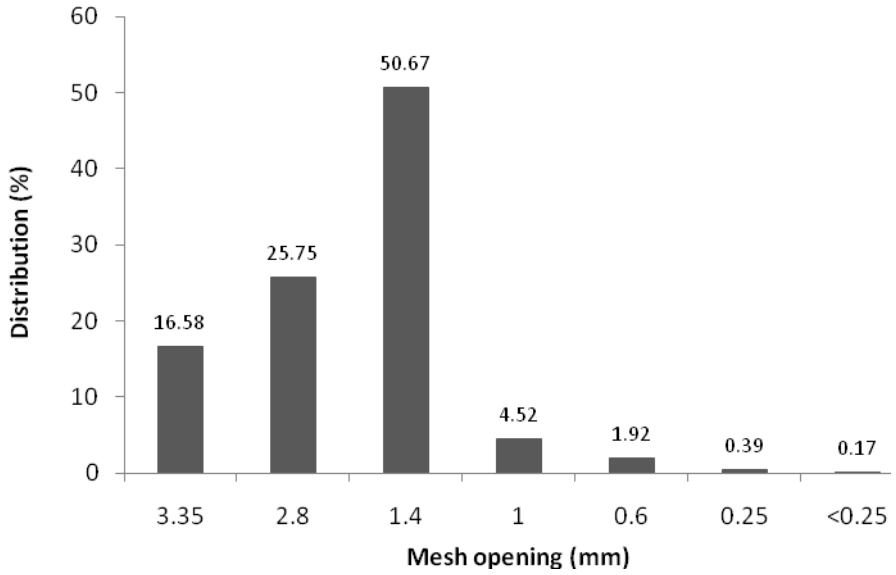


Figure 4.9: Size distribution of spruce particles

Board swelling tests and absorption. The *Acacia* hybrid and spruce boards were tested for water immersion together with the previous UF resin boards (*Acacia* hybrid and recycled wood). Test samples were randomly collected from sets of 50 x 50 mm boards. Between the *Acacia* hybrid, boards bonded with UF resin showed the highest thickness swelling after 2 and 24 h water immersion (Figure 4.10, 2.7% and 11.2%, raw data in appendix Table 2) whilst the lowest values were recorded with the PF resin bonding (0.68% and 5.15%) and intermediate values were noted for the MUF resin

bonding (1.89% and 7.49%). This is despite the PF resin boards absorbing much more water than others (Figure 4.11).

The physical properties of the UF bonded particleboard were similar to those of the PF and MUF boards when subjected to dry testing. Addition of wax into the UF resin improved the water resistance of the board in some extent, however the wet physical properties were lower than those of the PF and MUF bonded boards. The *Acacia* hybrid boards performed better when immersed in water than the recycled wood and spruce boards. The swelling was much lower than the standard limit of 16%. The trend of UF bonded *Acacia* hybrid and recycled wood were in agreement with the previous tested samples even though there were distinctive differences (Table 4.4). The previous samples were obtained at the middle of the boards which is usually dense with particles. The moisture absorbance of spruce was higher than the *Acacia* hybrid and recycled wood after 2 hours immersion. The board absorbed 25% water even though it was MUF resin bonded which normally gives some degree of water resistance (Pizzi 1983a). Nevertheless the spruce boards had comparable dry IB strength with board bonded with UF resin.

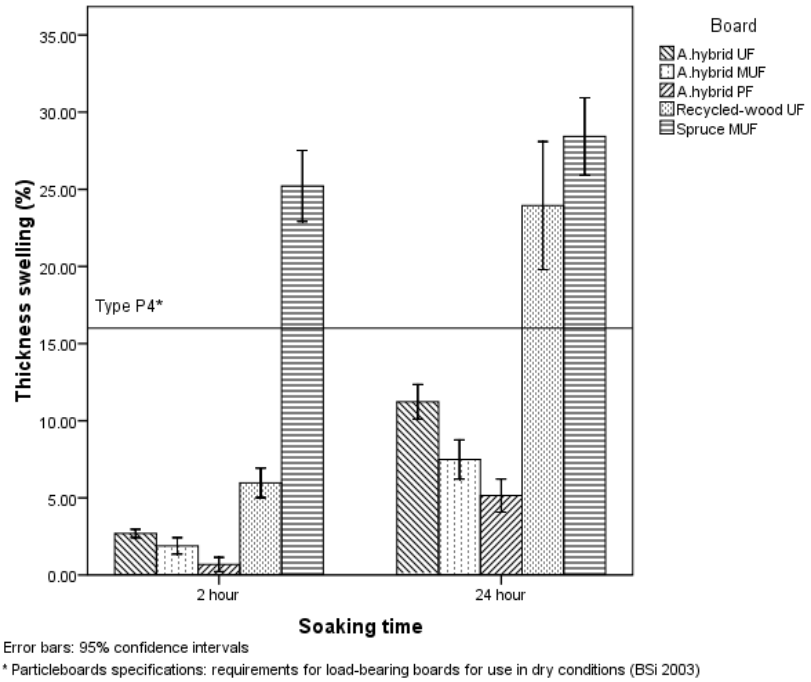


Figure 4.10: Thickness swelling of particleboards from *Acacia* hybrid, recycled wood and spruce

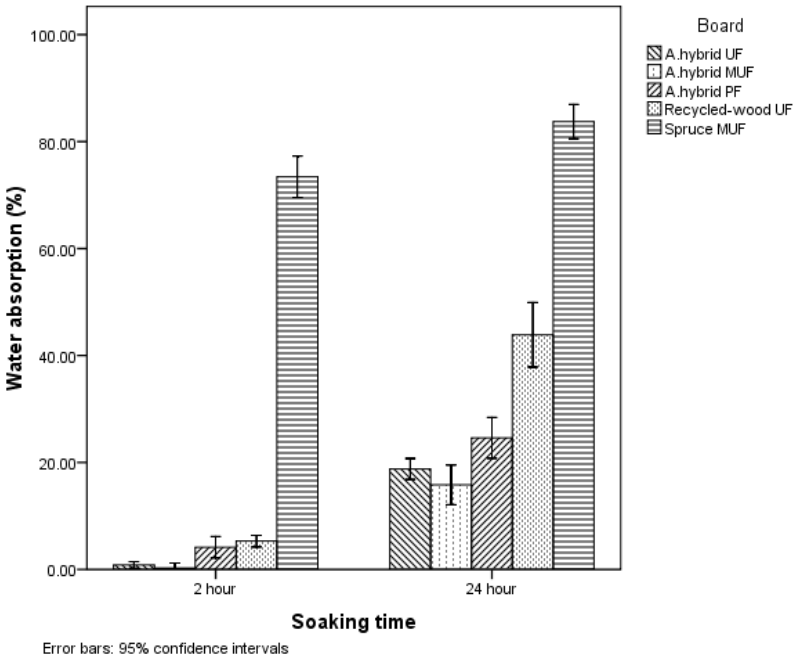


Figure 4.11: Water absorption of particleboards from *Acacia* hybrid, recycled wood and spruce

Immersion-drying test. The swelling of boards increased further as the board immersion repeated (Figure 4.12). Drying of the boards resulted in some recovery in thickness but not to their original dimensions. Some of the values were indistinct at first cycle but apparently different as the cycle continues. Overall, the swelling and shrinkage were highest in recycled wood board followed by spruce and *Acacia* hybrid. The *Acacia* hybrid boards with PF resin had better dimensional stability than those made with the MUF and UF resins. Swelling and shrinkage of the boards were consistent after sixth cycle. In spruce boards and *Acacia* hybrid with PF resin, the changes were consistent as early as third cycle. Nevertheless most thickness increment along the cycle was not statistically different from one cycle to the next.

In *Acacia* hybrid boards, PF resin bonded boards had higher water absorption at early cycle than the UF and MUF boards (Figure 4.13). As the cycles continue the water absorption slightly reduced thus became not different with the UF and MUF boards. Large amount of water contained by wet spruce boards followed by recycled wood and *Acacia* hybrid. The water absorption of wet *Acacia* hybrid boards was consistent as the cycles continue comparing to spruce and recycled wood boards.

In addition to type of resins the wood factor might affect the thickness swelling and water absorption values. The *Acacia* hybrid had lowest thickness swelling and water absorption in all resin types. In Figure 4.12, initially the recycle wood boards had some resistant to swelling comparable to spruce followed by enormous expansion as the cycle continued. The spruce boards had high water absorption capacity without excessive swelling compared with the recycled wood.

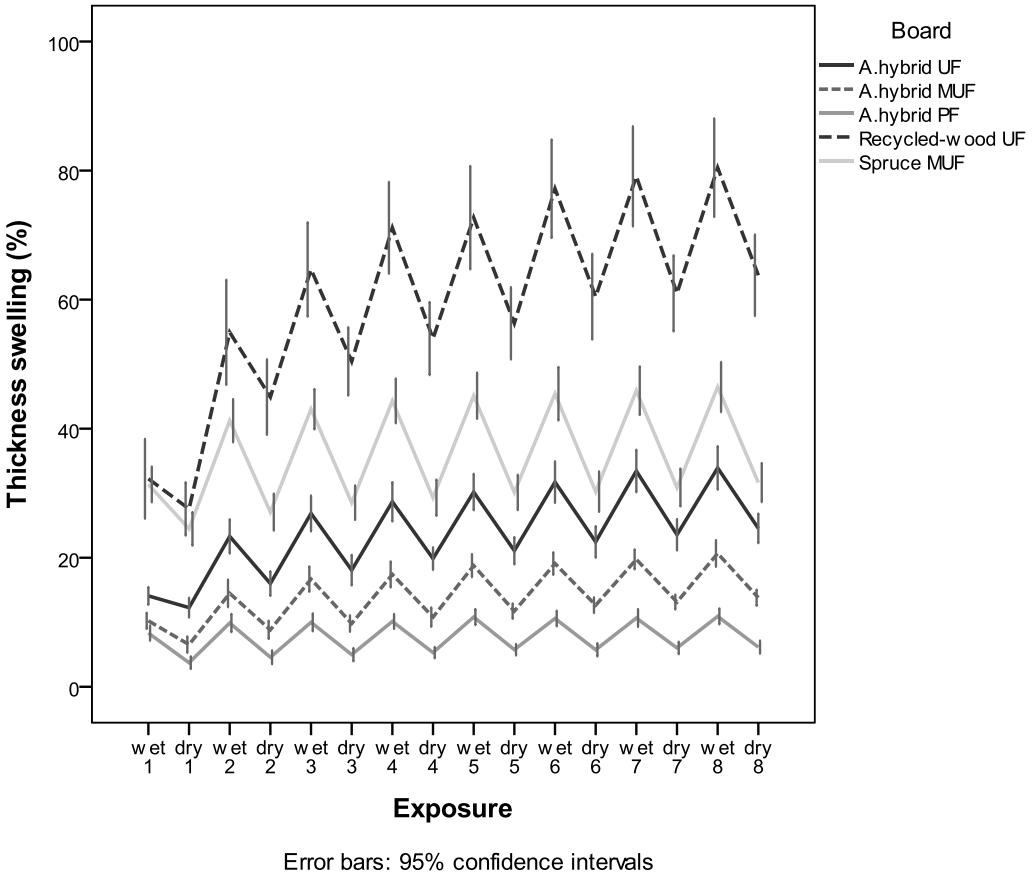


Figure 4.12: Thickness swelling of particleboards with different resins resulting from immersion-drying cycles

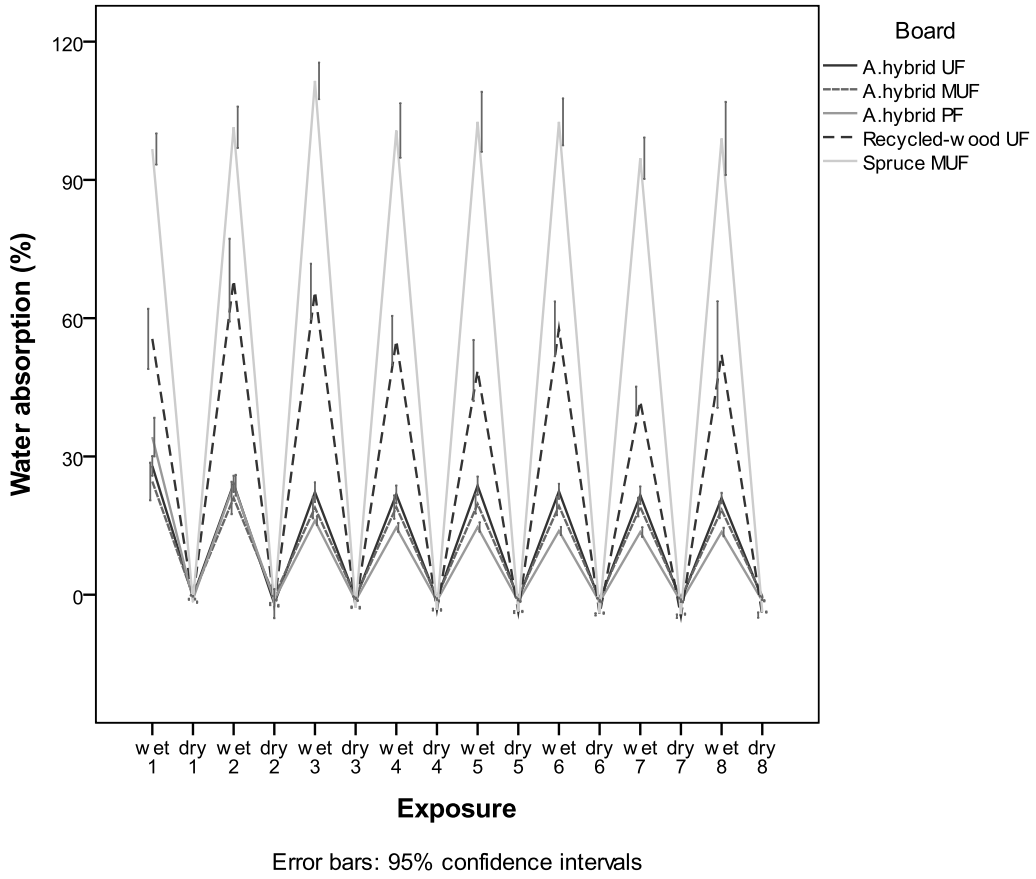


Figure 4.13: Water absorption of particleboards with different resins resulting from immersion-drying cycles

Internal bond test. Tensile strength perpendicular to board surface of *Acacia* hybrid, recycled wood and spruce boards is shown in Table 4.9. The test samples were of randomly cut from the boards. All boards produced good IB strength that exceeded the minimum standard requirements. The *Acacia* hybrid had superior IB especially in boards with MUF resin although acceptable strength parameters were shown by the spruce and recycled wood boards. The use of 10% PF and MUF resin (of dry board weight) gave a statistically significant high IB strength. The test specimens mostly broke at the middle of the board thickness, perpendicular with loading force. High tensile force (over 3500N) was necessary to break some of the *Acacia* hybrid specimens which resulted in failure between the block and glue and these were omitted from the calculation. The MUF resin also gave high IB values (0.7 and 1.3 MPa) in the boards. The spruce boards produced acceptable dry IB strength (over standard specification 0.4 MPa) even though physical properties of the boards deteriorated in

after wetting. The IB values of UF bonded *Acacia* hybrid and recycle wood boards were similar with previous test samples (Table 4.8).

Table 4.9: Internal bond of particleboards

Board	Internal bond (MPa)	Standard deviation
Acacia hybrid UF	0.93 bc	0.15
Acacia hybrid MUF	1.28 a	0.15
Acacia hybrid PF	1.03 b	0.18
Recycled wood UF	0.64 d	0.10
Spruce MUF	0.73 cd	0.07
Type P1[1]	Min. 0.28	
Type P4[2]	Min. 0.40	

[1] Particleboards specifications: requirements for general purpose boards for use in dry conditions (BSI 2003)

[2] Particleboards specifications: requirements for load-bearing boards for use in dry conditions (BSI 2003)

Values with same letter within the same column are not significant different at 95% confidence levels

4.4 Discussion

The vertical density gradient from density profile of particleboards substantially influences the properties of board (Kelly 1977). Bending strength could be enhanced by the presence of density gradient while tensile strength perpendicular to the panel surface and inter-laminar shear are adversely affected (Schulte and Frühwald 1996; Dai et al. 2004). Vertical density distributions of the boards are shown in Table 4.3. Except at the lower surface, the density gradients of *Acacia* hybrid and recycled wood boards were not significantly different. The furnished mats of *Acacia* hybrid and recycled wood had similar moisture contents (9.6% moisture for the recycled wood and 10.2% for the *Acacia* hybrid boards) when entering the hot press so this should not affect the profile (Figure 4.2). It is likely that the variance in peaks in the recycled wood boards is due to the pre-cure of the resinated furnish after contacting the hot press. The recycled wood had faster heat transfer that might have resulted in the pre-cure.

The swelling that occurs after immersion of boards is from the sum of two components, namely, swelling by hygroscopic particles and the release of compression stresses imparted to the board during the pressing of mat in the hot press (Halligan

1970). The release of compression stresses, known as springback, is not recovered when the board is in a redried state. Even though particles of *Acacia* hybrid used to produce a board were bulkier than recycled wood, the board had less springback as shown by the recovered dimensions of dried samples (Figure 4.5). On the other hand, the recycled wood samples absorbed water more rapidly - twice the amount of water compared with *Acacia* boards. The cyclic wet-dry exposure had a considerable effect on board properties and the greatest disruption occurred by the seventh cycle. A further cycle did not significantly change the thickness swell.

Although the particle size distributions were different within the two furnish types, both were centred on the 1.4 mm sieve size, with a large percentage of chips in the 0.6 and 2.8 mm size range. As noted earlier, Moslemi (1974) reported that an increase in slenderness ratio produces a stiffer and stronger board in bending with a decrease in the IB strength; this is in agreement with the work of Miyamoto et al. (2002) which states that as chips get smaller in length their internal bond strengths increase. The slenderness ratio of *Acacia* hybrid particle was relatively higher than recycled wood. However, in this study, all properties of the *Acacia* hybrid were significantly higher than those tested for the recycled furnish. This is contrary to what has been reported in research undertaken on effects of particle size distribution alone (Moslemi 1974; Miyamoto et al. 2002). It can, therefore, be inferred that besides the vertical density difference, the *Acacia* hybrid wood itself is having an effect on the properties of the particleboard.

The use of PF and MUF resins added to the moisture resistance of the boards. The resistance based on resin usage can be arranged as follows PF> MUF> UF. This is supported by the results of TS of the *Acacia* hybrid boards in Figure 4.13. Phenol formaldehyde bonded boards have more resistance to springback caused by water immersion than the MUF and UF boards (Hann et al. 1963). The incorporation of melamine into UF resin improved the low resistance of UF bond to the influence of humidity and water (Dunky 1998). However, the melamine changed the characteristics and reactivity of the resin by increasing buffering capacity of the resin caused by the triazine ring of the melamine (Stefke and Dunky 2006). Besides hardener addition, adjustment to the hot pressing process can be performed in order to cure the MUF board. In this study, the MUF boards of both *Acacia* hybrid and spruce were

sufficiently cured based on high IB values of the boards. Besides moisture resistance, MUF resin could improve the mechanical properties (internal bond, modulus of rupture and modulus of elasticity) of particleboard as compared to UF resin as shown by Colak et al. (2007). The MUF board of *Acacia* hybrid had the significantly highest IB value (Table 4.7). The results can vary in other types of particleboards, for example particleboards from hazelnut husk with UF, MUF and PF resins produced by Copur et al. (2007) were not significantly different in terms of IB and MOR properties but for the physical properties (thickness swelling and water absorption) were improved in the order PF > MUF > UF.

Overall, boards from *Acacia* hybrid had better MOR, MOE, IB and TS properties than the recycled wood and spruce. Internal bond of the boards were significantly high even after exposed to severe conditions. Even though resins have influenced board properties, outstanding properties of *Acacia* hybrid boards were contributed from the wood itself. In this study, possible influence of wood extractives to board properties has been investigated.

4.5 Conclusion

The boards of *Acacia* hybrid with urea formaldehyde resin showed better physical and mechanical properties than recycled wood. In this study, *Acacia* hybrid had consistently performed better than recycled wood. Although the increased slenderness ratio of *Acacia* hybrid particles would have had an effect on the MOE and MOR of the panels, it should be noted that the internal bond strength of the *Acacia* hybrid particleboard was higher than that of the recycled wood. *Acacia* hybrid boards bonded with the UF, MUF and PF resins have better moisture resistance than the boards of recycled wood and spruce. The moisture resistance increased with the use of PF resin followed by the MUF. The *Acacia* hybrid boards have high IB strength from 0.9 to 1.3 MPa from the three resins. This work shows that the *Acacia* hybrid is a potential resource for high quality particleboards for external use, although at present its decay resistance is not proven (see Chapter 5).

CHAPTER 5

EFFECTS OF DECAY FUNGI ON PARTICLEBOARD FROM *ACACIA* HYBRID

5.1 Introduction

Particleboards are prone to fungal deterioration because wood is susceptible to fungal decay under suitable conditions (moisture content above 20%, suitable temperatures and aeration, mineral nutrients). Decay can be reduced using treatments which minimise water uptake into the board (surface coating and resin impregnation) and cell wall (acetylation) and by preservation (Imamura et al. 1986; Kajita and Imamura 1991; Clausen et al. 2001; Nemli et al. 2005). The heartwood of some woods are resistant to decay due to the presence of metabolites laid down during heartwood formation. These may be toxic to fungi (Dix et al. 1998; Hashim et al. 2009) or they may reduce the effectiveness of their decay systems. However fungal exposure can cause other detrimental effects to the physical and mechanical properties of particleboard (Okino et al. 2004; Zaidon et al. 2007). Utilisation of certain resins such as phenol formaldehyde and melamine urea formaldehyde decrease absorption of water into wood. However these boards are still susceptible to decay when exposed to wet conditions. Fungi that attack wood can be categorised as brown rot, white rot and soft rot (Eaton and Hale 1993). The most destructive forms of decay in unpreserved wood are normally regarded as the brown and white rot forms of decay and white rot fungi are generally regarded as important in hardwood decay. The extent of decay by fungi in wood is usually determined by weight loss. Effects of decay on the board dimensions and mechanical properties are less widely used as criteria.

Objectives of this part of the study are as follow:

i. To determine the decay resistance of *Acacia* hybrid particleboard exposed to brown rot and white rot fungi.

ii. To evaluate the physical and mechanical changes of *Acacia* hybrid particleboard due to the above fungal decay types.

iii. To compare with particleboard made from a commercially available furnish.

5.2 Materials and methods

5.2.1 Fungal decay test

Experiments with four decay fungi (1 brown rot, 3 white rot) were conducted (1) to determine the virulence of decay fungi, (2) to evaluate the decay of wood particles, and (3) to evaluate the effect of decay fungi on the particleboards. The tests were based on European pre-standard, DD ENV 12038 (BSI 2002). White rot and brown rot fungi suitable for wood-based panels were used for the study (Table 5.1). Culture stocks of the fungi were prepared on 4% malt extract, 2% agar (40:20 g/l distilled water). All wood blocks and board samples were dried at 103 °C until constant mass. They were then weighed and measured dimensionally and sterilised with gamma radiation. Wood particle dry masses were determined and they were sterilised by autoclaving. Samples were then exposed for up to 16 weeks to actively growing cultures cultivated on 4% malt agar in jars. Before inoculation, a sterile polypropylene mat (thick weed control geotextile) was placed on the malt-agar medium surface to prevent water logging of the specimens.

The virulence of the fungi was determined by exposing twelve replicates of beech (*Fagus sylvatica*) and pine sapwood (*Pinus sylvestris*) blocks (20 x 20 x 20 mm) to fungi at 21 °C and 70% RH for 2, 4, 8 and 12 weeks. Four blocks of same species were arranged in a jar (Figure 5.1). In the absence of whole wood blocks of *Acacia* hybrid, wood particles were used to examine the relative decay resistance of *Acacia* hybrid. To achieve this eight replicates of both *Acacia* hybrid and spruce particles were placed in polypropylene mesh containers (25 x 25 x 25 mm). Beech and pine blocks (20 x 20 x 20 mm) were used for comparison. All four samples were arranged in a jar and exposed to fungi for 16 weeks. The effect of fungi on particleboards was determined by exposing eight replicates of particleboards (50 x 50 mm) from Chapter 4 for 16 weeks. One test specimen per each sample was arranged in a jar.

For *P. ostreatus* exposure samples were covered with sterile wet vermiculite (wetted to the water holding capacity plus 10% as advised in the standard) to ensure sufficient moisture in jars. All three experiments had sterile control samples exposed in un-

inoculated jars over the malt-agar medium. For reference, another set of control samples were stored at 20 °C temperature, 65% relative humidity.

After the fungal exposure, the samples were cleaned of surface mycelium, weighed, dried (103 °C to constant weight) and re-weighed. Dimensions (length, width, thickness) of dried wood and boards were determined after incubation. The mass loss due to decay was calculated as the difference between oven dry mass of each board before and after incubation and expressed as a percentage of dry mass loss. Moisture content of the exposed boards was the percentage of the weight difference before and after oven-drying after decay exposure. Swelling was the percentage of the thickness difference after and before the exposure. The board expansion due to the exposures was calculated as follow:

$$\text{Board expansion (\%)} = \frac{(l_2 \times w_2) - (l_1 \times w_1)}{(l_1 \times w_1)} \times 100 \qquad (5.1)$$

Where,

l_1, w_1 = length and width of board before exposure

l_2, w_2 = length and width of board after exposure

Table 5.1: Fungi used in decay resistance test

	Fungus	Strain	Type
1.	*Pleurotus ostreatus*	40C	White rot
2.	*Trametes versicolor*	863	White rot
3.	*Pycnoporus sanguineus*	-	White rot
4.	*Coniophora puteana*	11E	Brown rot

A

B

C

Figure 5.1: Arrangement of boards for fungi exposure test: (A) virulence of fungi, (B) decay of wood particles, and (C) decay of particleboards

5.2.2 Internal bond after fungi exposure

Five replicates of boards exposed to the fungi above were tested for internal bond strength as in Chapter 4.

5.2.3 Statistical analysis

Statistical analysis of variances, linear relationships, correlations and error bars were determined using SPSS software version 16.

5.3 Results and discussion

5.3.1 Virulence of decay fungi

Beech and pine blocks were used to check decay performance of the fungi. Maximum mass loss of the wood was 35 and 23% respectively (Figure 5.2). The mass loss increased with increasing exposure time. Overall the beech had higher weight loss than pine after the exposure. The moisture contents of the wood were well above the minimum threshold of 20% (Eaton and Hale 1993) in the sterile controls throughout the experiment which should have allowed optimal decay conditions (Figure 5.3). Generally decay caused elevated moisture contents, which increased with decay up to 8 weeks exposure.

In beech, the highest decay rate was caused by *P. sanguineus* (3.62% wk $^{-1}$) followed by *C. puteana* (2.43% wk $^{-1}$), *T. versicolor* (2.05% wk $^{-1}$) and *P. ostreatus* (1.07% wk $^{-1}$). Decay generally increased linearly but had slowed with some fungi by 12 weeks (*T. versicolor*, beech; *C. puteana*, pine)

Pine wood had highest weight loss due to *C. puteana* (2.02% wk $^{-1}$) followed by *T. versicolor* (1.23% wk $^{-1}$), *P. ostreatus* (0.71% wk $^{-1}$) and *P. sanguineus* (0.56% wk $^{-1}$). Figure 5.3 shows that the wood had lower MC after 12 week in *P. sanguineus* (not different to the control) which might have slowed the decay.

Mass loss due to *P. sanguineus* was very high in beech rather than pine besides significant higher activity of *P. ostreatus* and *T. versicolor*. Decay of the wood caused by *C. puteana* was about the same.

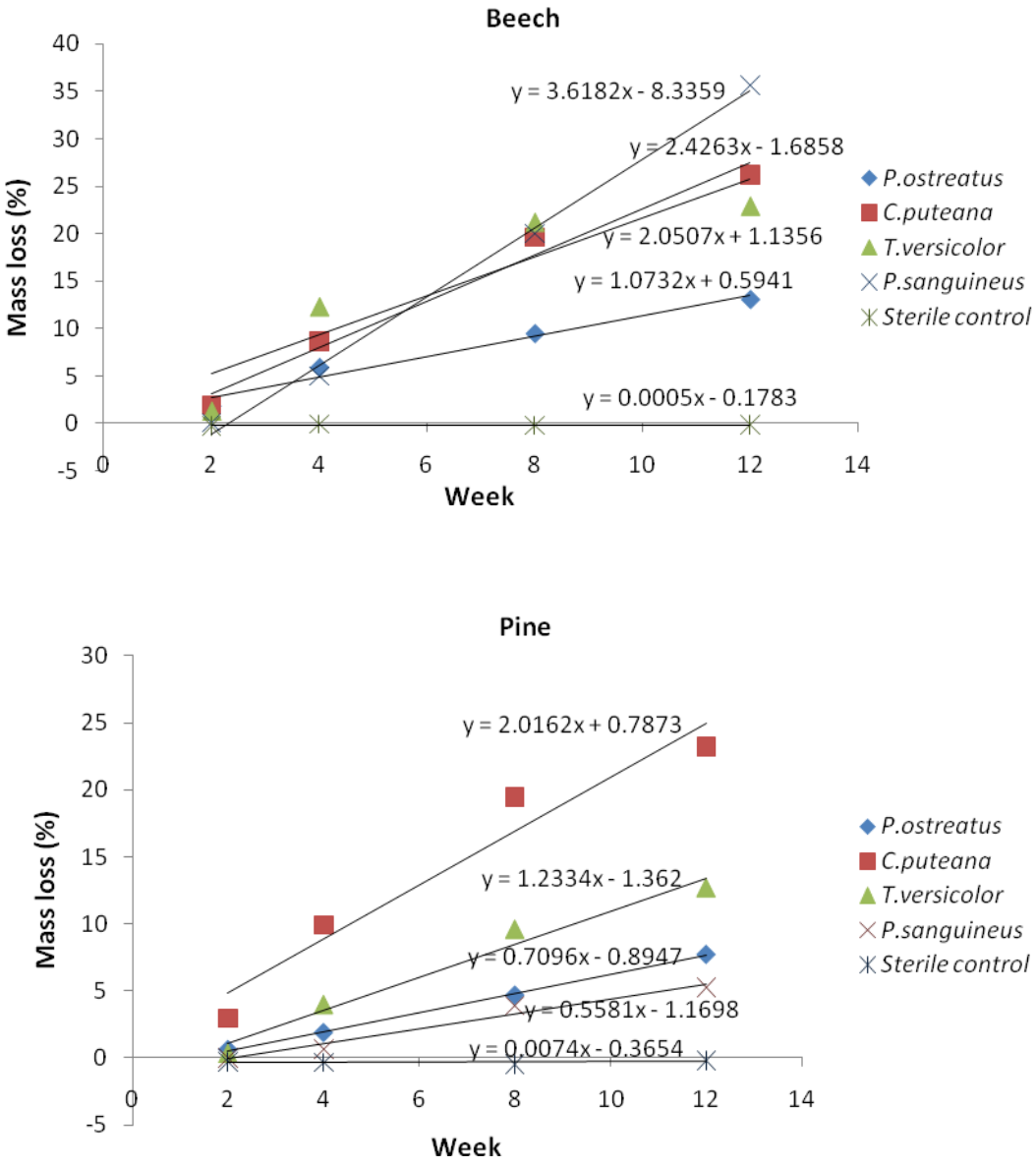


Figure 5.2: Mass loss of beech and pine exposed to decay fungi (n = 12)

Weight loss resulting from decay of beech was more severe than in pine especially after being exposed to *T. versicolor* and *P. sanguineus*. Similar results were shown by Kartal and Green (2003), Pandey and Pitman (2003), and Pointing et al. (2003) after exposing the wood to *T. versicolor* and *P. sanguineus*. Decay of pine (softwood) due to *C. puteana* supposed to be higher than beech (hardwood) since the fungus action is specialised for softwood (Pandey and Pitman 2003; Macchioni et al. 2007). However in Figure 5.2 decay of pine caused by the fungus was about similar to beech.

Coniophora puteana, T. versicolor and *P. sanguineus* were suitable to be used in this study since they were able to cause 20% mass loss. *P. ostreatus* was used too for comparison even though it caused lower mass loss.

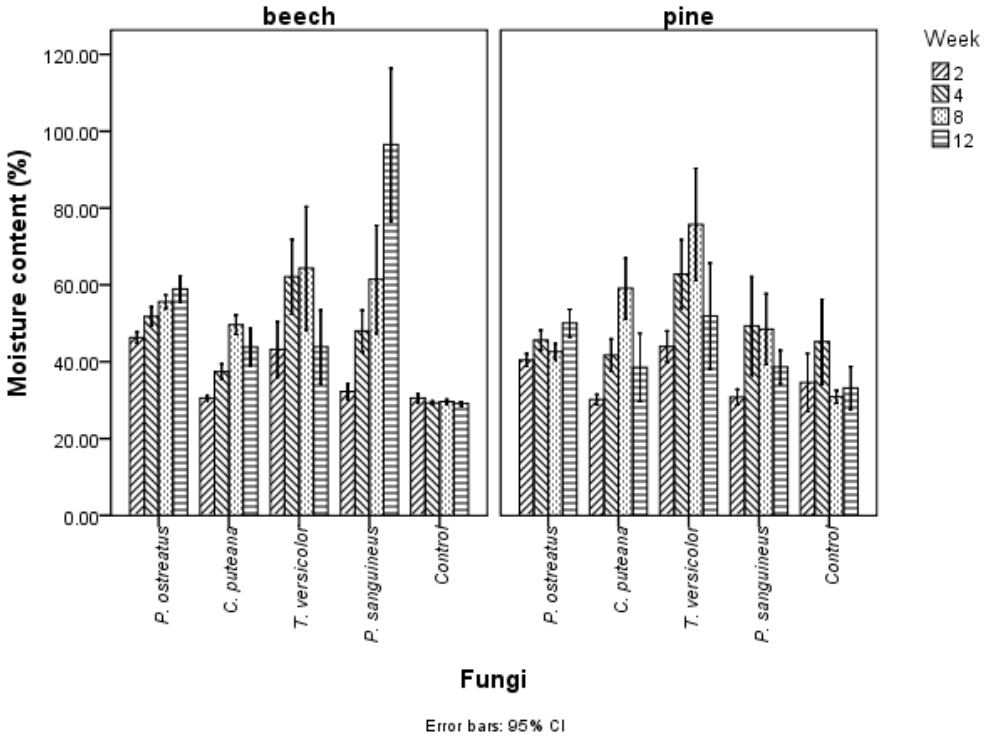


Figure 5.3: Moisture content of beech and pine exposed to decay fungi (n = 12)

5.3.2 Decay of wood particles

The mass loss of wood particles ranged from 3 to 40% depending on fungal type (Figure 5.4, raw data in appendix Table 3). The moisture contents were all suitable for decay and were above threshold values of 20%, but were slightly low and not especially elevated above the control for some of the *P. ostreatus* exposed particles (Figure 5.5, raw data in appendix Table 4). Low weight losses were experienced with all except for the beech where elevated moisture contents were seen.

High decay was expected and seen in the beech with all fungi but given the preference of white rot fungi for hardwoods and the relatively low decay rate of white rot on the spruce and pine sapwood particles are also as expected.

Against the white rot fungi the decay of the *Acacia* hybrid was low as well (2.18 – 3.45%), although slightly higher than the spruce (0.6 – 2.22%). The brown rot fungus, *C. puteana* gave high decay rates causing around 20% mass loss in the most resistant, *Acacia* hybrid, which was around half of that of the least resistant, spruce. Despite the lower weight loss of the *Acacia* hybrid particles a 20% weight loss is an indication of relatively low decay resistance. Even though high mean mass loss occurred with the spruce particles, this was not significantly different to beech and pine.

Comparison between this experiment and the virulence test showed lower mean percentage mass losses with the particles than the wood when exposed to *T. versicolor* and *P. sanguineus*. A possibility of slow decay process in the particles by white rot fungi is low since active mass loss has been shown in wood control especially beech.

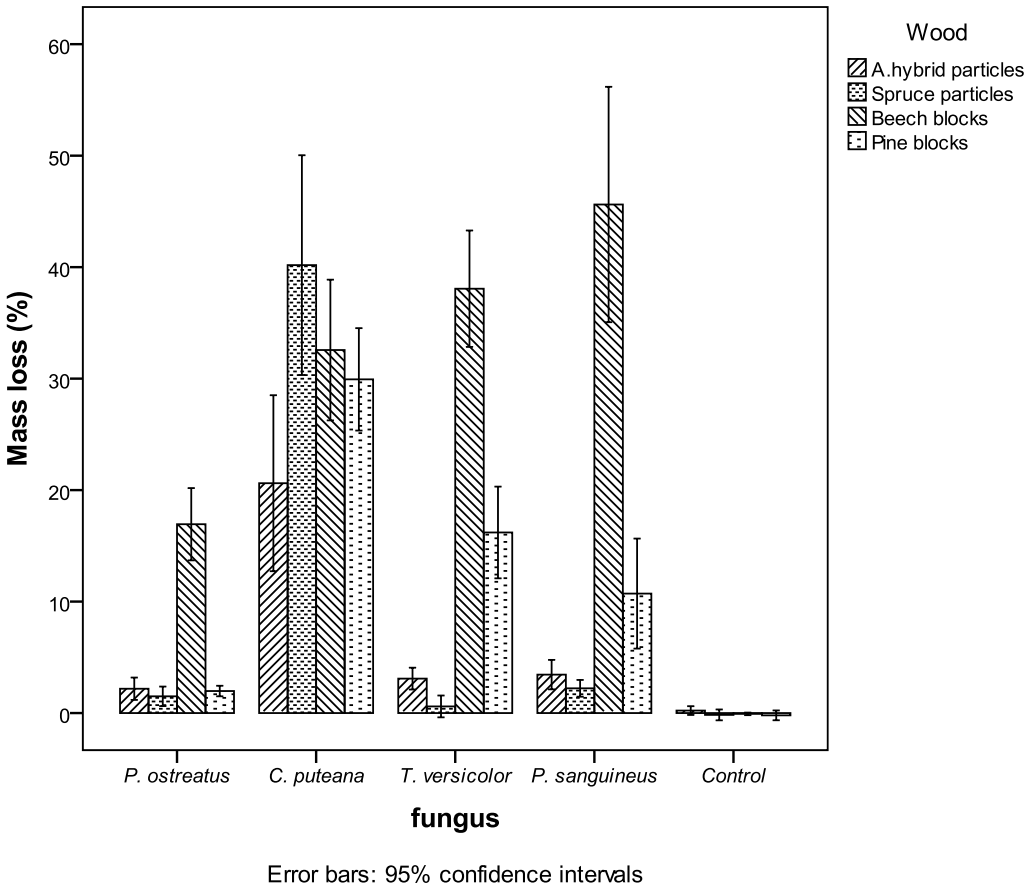


Figure 5.4: Mass loss wood particles, beech and pine due to decay fungi

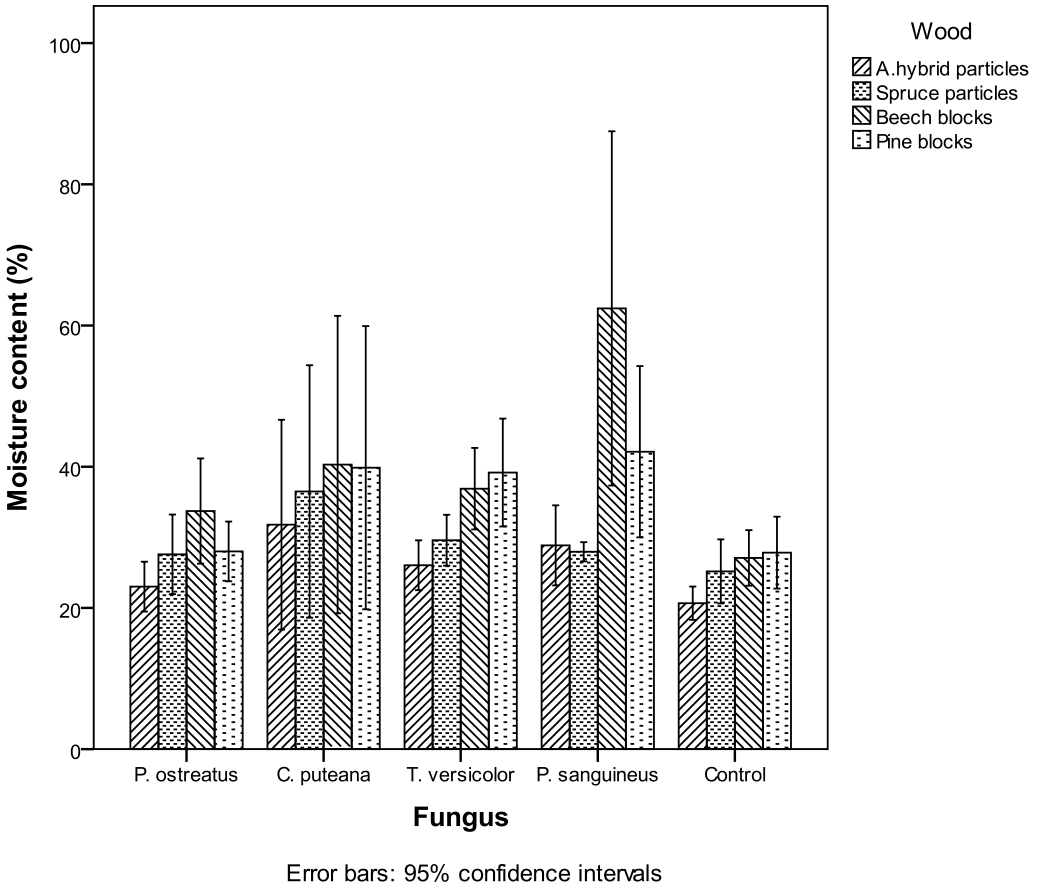


Figure 5.5: Moisture content of wood particles, beech and pine after fungi test

5.3.3 Decay of particleboards

Internal bond strength. Exposure to the moist conditions of the fungal decay test resulted in losses of 82% of the original internal bond strength with the UF resin, 48% for the MUF resin and the PF resin bonded board only lost 9% (NS) of its original IB strength (Table 5.2). Exposure to the fungi caused significant damage to the boards and in some instances very low strength values were recorded especially in UF bonded samples. Very low IB values were also recorded for the MUF resin ranging from 4-9% of the original values after fungal exposure. No significant changes in IB values were found with PF bonded boards due to *T. versicolor* and *P. sanguineus* but decreases of 38% and 53% occurred with *C. puteana* and *P. ostreatus* respectively.

Overall the IB strength after fungal exposure was significantly affected by the resins rather than the type of wood. Boards bonded with PF resin showed superior IB strength for each exposure. Boards bonded with MUF resin only had slightly higher IB

strength than those bonded with UF resin when exposed to *P. ostreatus*; this was not significant with the other fungi.

Table 5.2: Internal bond strength of particleboards after fungal exposure

Board	Internal bond (MPa)				
	Sterile control	*P. ostreatus*	*T. versicolor*	*P. sanguineus*	*C. puteana*
Acacia hybrid UF	0.17 c (0.04)	0.00 c (0.01)	0.03 c (0.01)	0.00 b (0.00)	0.00 b (0.00)
Acacia hybrid MUF	0.66 b (0.04)	0.12 b (0.05)	0.09 bc (0.02)	0.05 b (0.01)	0.02 b (0.02)
Acacia hybrid PF	0.91 a (0.19)	0.48 a (0.09)	1.06 a (0.14)	1.06 a (0.34)	0.63 a (0.07)
Recycled wood UF	0.11 c (0.24)	0.03 bc (0.01)	0.02 c (0.004)	0.004 b (0.005)	0.002 b (0.005)
Spruce MUF	0.57 b (0.22)	0.12 b (0.04)	0.27 b (0.16)	0.11 b (0.02)	0.007 b (0.006)

In parentheses is standard deviation

Value with different letter within the same column is significant different at 95% level

Mass loss. In terms of mass loss the PF bonded *Acacia* hybrid boards had minimum mass losses (Figure 5.6, raw data in appendix Table 5), ranging from 1.1 to 8.3% whilst those from the UF and MUF bonded boards ranged from 14.9 to 37.3%. The PF bonded board exposed to *P. ostreatus* showed only 8.3% weight losses but with *T. versicolor*, *P. sanguineus* and *C. puteana*, the mass losses were considered minor, i.e. less than 3%. The mass losses of MUF bonded boards were similar to UF bonded boards although *C. puteana* caused slightly lower mass losses. The mass losses of *Acacia* hybrid boards bonded with UF and MUF resins were less than recycled wood and spruce when exposed to *P. ostreatus* and *C. puteana*. The UF and MUF boards had higher mass loss than spruce caused by *T. versicolor*.

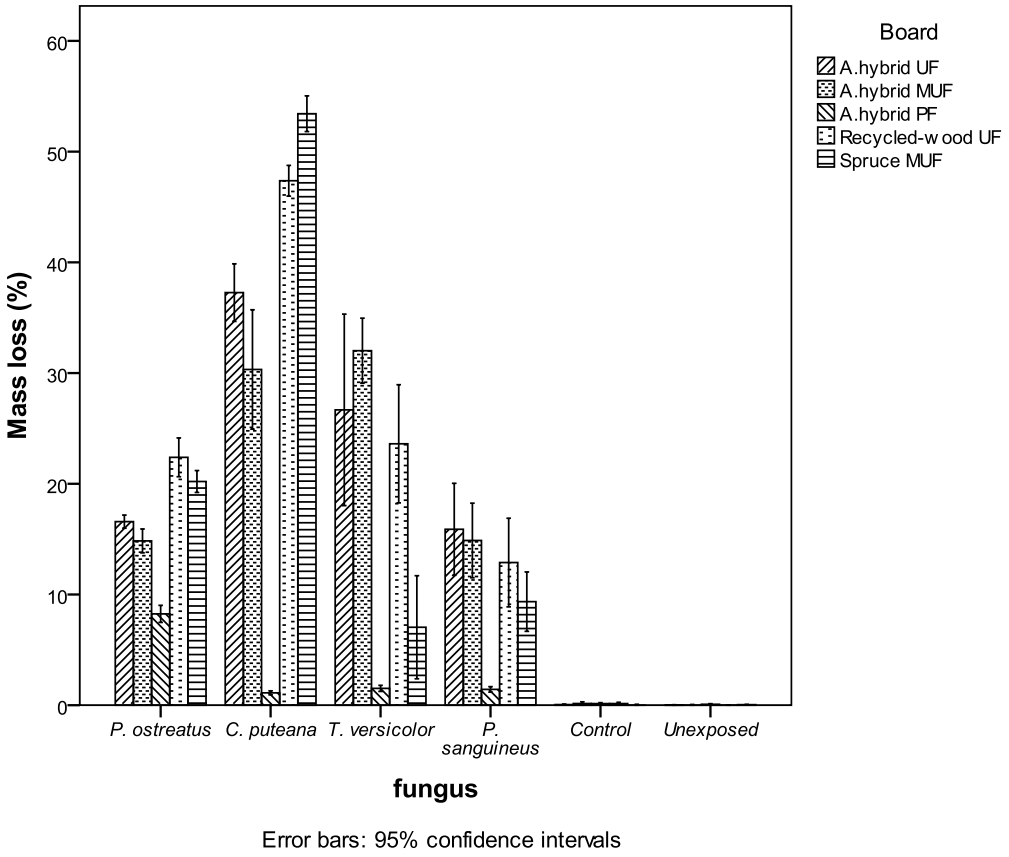


Figure 5.6: Mass loss of particleboards exposed to decay fungi

The MC of the *Acacia* hybrid boards after 16 weeks exposure (Figure 5.7) varied considerably. The sterile control boards increased in moisture to at least 23%, sufficient for decay and in all of the fungal exposure tests higher moisture contents in the region of 32 to 52% were recorded. Wet vermiculite, used for *P. ostreatus,* effectively gave a high MC (68 - 74%) in the boards. In one series, that of the MUF bonded boards exposed to *T. versicolor*, the moisture contents were similar to those of *P. ostreatus* (66 and 68% respectively). The moisture contents were highly varied in boards thus mostly were not significantly different between the boards and fungal treatments.

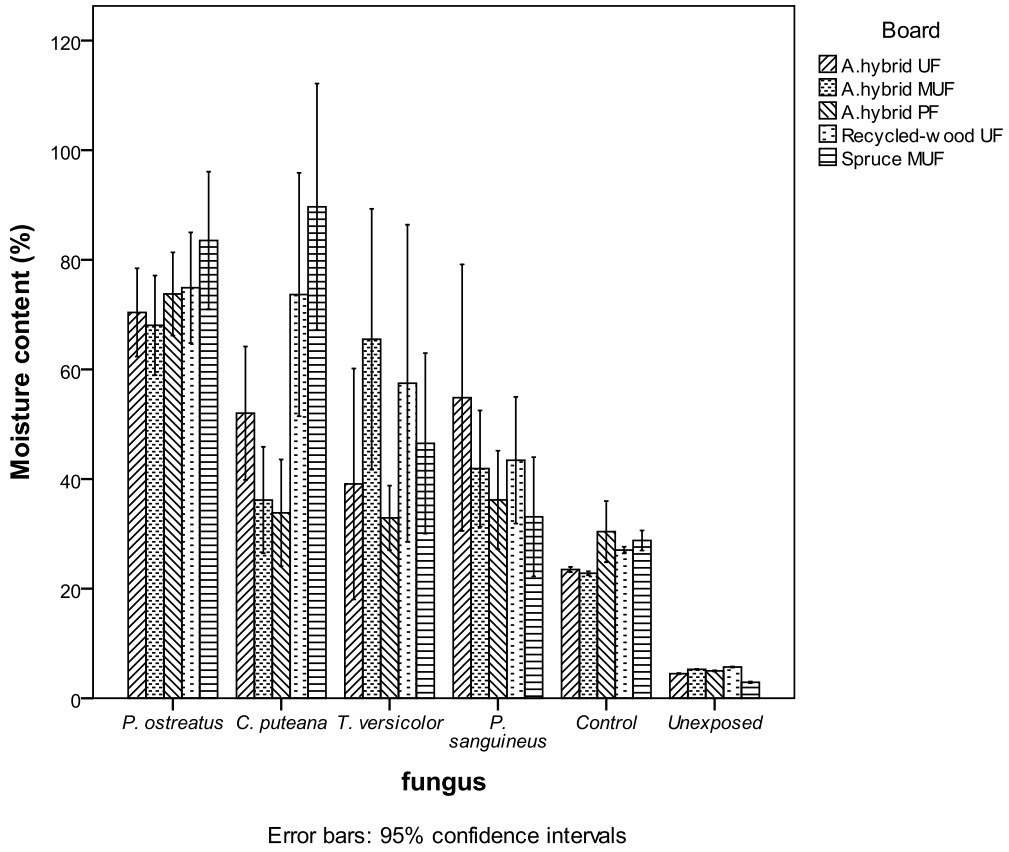


Figure 5.7: Moisture content of particleboards from *Acacia* hybrid, recycled wood and spruce at the end of the fungal test

Thickness swelling. Thickness swelling of *Acacia* hybrid boards due to decay ranged from 7.5 to 73% (Figure 5.8). The swelling was highest in UF bonded boards (33 - 73%) followed by MUF (24 - 42%); little swelling occurred with PF boards (7.5 - 12%). Wetting in the sterile control exposure followed a similar order (UF, 33% > MUF, 28%, ns) with low swelling occurring in the PF (8.8%) bonded boards. Swelling of UF resin bonded boards was severe with *P. ostreatus* (73%) exposure followed by *P. sanguineus* (57%). The swelling of UF board due to *T. versicolor* and *C. puteana* showed no significant difference to the control (33%). Similar trends but to a lesser extent were observed in MUF bonded boards and the greatest amount of swelling (42%) was caused by *P. ostreatus*. Thickness swelling was also obvious in the PF bonded boards exposed to *P. ostreatus*. Swelling of PF bonded boards exposed to the other fungi was not different to the sterile control exposure.

Thickness swelling due to decay of *Acacia* hybrid boards with UF resin was higher than recycled wood except when exposed to *T. versicolor*. The swelling decreased by using MUF resin even though they were not as good as the spruce boards. Changes in

thickness of decayed spruce boards were not significant when compared to the sterile control. Reduction in thickness was seen in boards exposed to *C. puteana*. After 16 weeks, the unexposed *Acacia* hybrid boards bonded with MUF and PF resin had less thickness increment than the recycled wood and spruce.

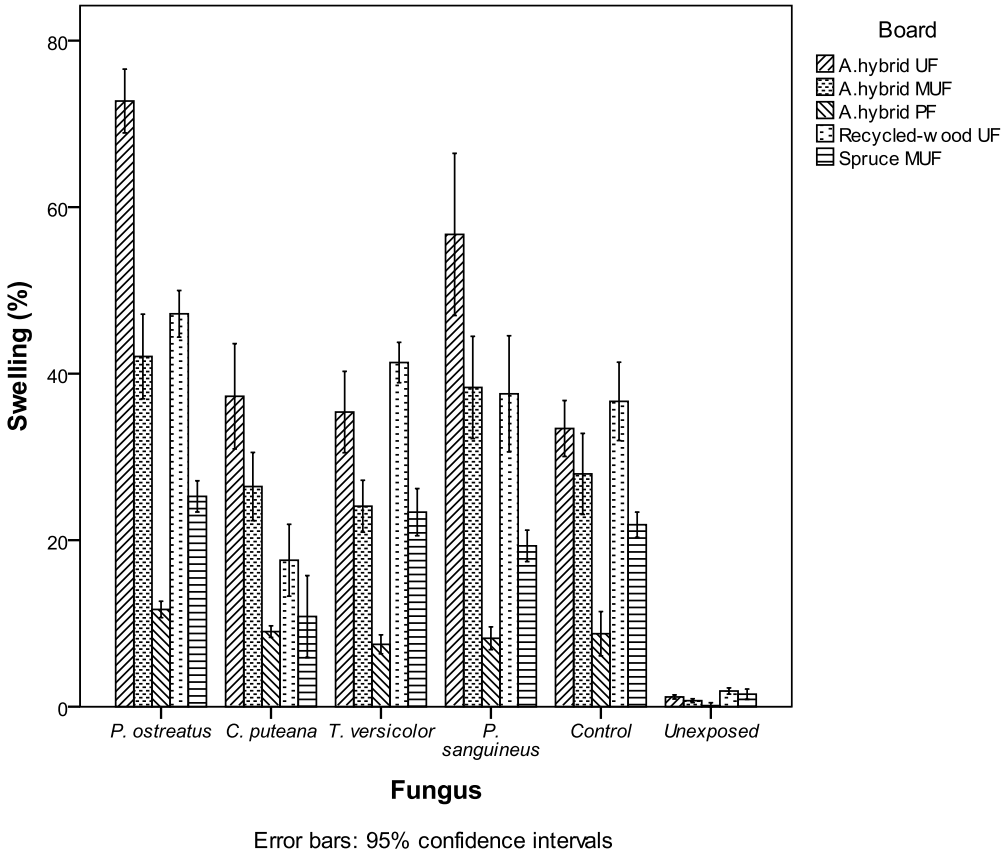


Figure 5.8: Thickness swelling of particleboards due to fungal test

Expansion of the *Acacia* hybrid boards due to exposure over the sterile malt-agar medium was between 0.6 to 1.7% with the highest values from UF bonded boards (Figure 5.9). Urea formaldehyde bonded boards also had the highest expansion when exposed to white rot fungi (*P. ostreatus*, *T. versicolor*, *P. sanguineus*) followed by the MUF and PF bonded boards. Within the UF board, high expansions were suffered with *P. ostreatus* (2.8%) and *P. sanguineus* (2.6%) whereas expansion with *T. versicolor* was no different to the control. The expansion of UF board due to *C. puteana* was lower than the control because of wood shrinkage, a normal feature of brown rot decay. The expansion of board bonded with MUF resin showed no significant difference between white rot exposure and sterile control conditions. Slight, but not significant shrinkage occurred in the board exposed to the brown rot. The expansion of PF boards due to

decay exposure was about 0.6% - 0.8% which was not significantly different to controls.

Even though the *Acacia* hybrid boards of UF and MUF resin had decay expansion due to *P. ostreatus* and *P. sanguineus*, the values were similar to recycled wood and spruce respectively (Figure 5.9). The expansion of *Acacia* hybrid due to *T. versicolor* exposure was significantly less than recycled wood and spruce boards which is similar to the sterile control samples. Severe shrinkage of the recycled wood and spruce boards with *C. puteana* exposure resulted in very significant reduction in length and width.

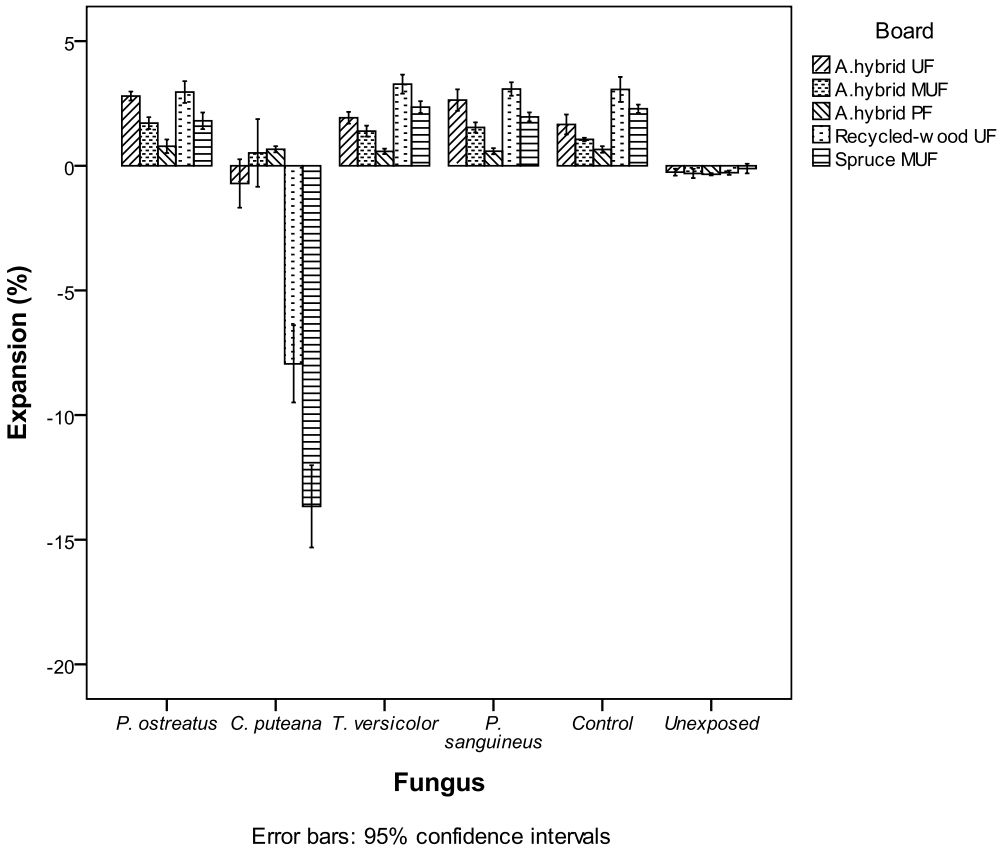


Figure 5.9: Expansion of particleboards from *Acacia* hybrid, recycled wood and spruce due to fungal test

Discussion. In UF and MUF bonded boards, mass losses due to decay were severe in boards exposed to *C. puteana* and *T. versicolor* followed by *P. sanguineus* and *P. ostreatus*. Conversely the swelling and expansion of the boards were considered high with *P. sanguineus* and *P. ostreatus* rather than *C. puteana* and *T. versicolor*. The use of wet vermiculite cannot be connected to the deteriorations since MC of the boards with

vermiculite was not different. On the other hand, PF bonded board with vermiculite had higher MC than the other PF bonded boards. PF bonded boards had significant losses in IB, mass loss and swelling when exposed to *P. ostreatus*.

Both brown rot and white rot fungi caused severe loss of IB strength of the boards (Table 5.2). In the case of PF bonded boards IB strength decreased due to *C. puteana* (brown rot) and *P. ostreatus*. The loss due to *P. ostreatus* is correlated to high MC as discussed above. Past studies indicate that wood decay by brown rot fungi usually caused greater losses in wood strength than white rot fungi (Pechman and Schaile 1950; Henningsson 1967; Sexton et al. 1993). Brown rots rapidly reduce wood strength early in decay process, while white rots caused slower progressive decrease in wood strength (Zabel and Morrell 1992). Wood strength loss by brown rot fungi is closely related to degradation of hemicellulose components (Winandy and Morrell 1993). Hemicellulose sidechains, such as arabinose and galactose degrade in early stages of decay. Main-chain hemicellulose carbohydrates such as mannose and xylose degraded in later stages.

Despite of brown rot fungi caused slight higher mass loss than white rot fungi (Figure 5.6), changes in swelling of the boards (Figure 5.8) has not showing particular trend, whereas shrinkage in size (Figure 5.9) was observed due to brown rot fungus decay.

In the case of boards with PF resin, a considerable amount of IB strength is retained as attributed from low decay in the board. The board has low IB strength (0.48 MPa) due to *P. ostreatus* which in parallel with the mass loss value (8.2%). On the other hand in board exposed to *C. puteana* even though lower mass loss recorded (1.1%) the IB was relatively low too (0.63 MPa).

Acceptable properties of particleboard can usually be produced with PF resin at 6% loading (Hann et al. 1963). At high resin loadings, besides a binder role, excessive PF might react within the particles and thus enhance board properties. The resin forms as a bulked product where the chemicals were probably not attached to the cell wall components but formed insoluble polymers which do not leach out in water (Rowell and Banks 1985). The hygroscopicity, swelling and susceptibility of the wood to biodegradable organisms would thus be reduced. It was suggested that the wood preserving effects of PF resin is influenced by the molecular weight of the resin used

because this will affect the resin penetration into the wood cell walls (Ryu et al. 1993). The penetration of resin into wood cell walls was investigated by Furuno et al. (2004) using light microscopy, scanning electron microscopy and electron probe x-ray microanalysis, and found that PF resin components with low and medium molecular weights penetrated into the cell walls thereby contributing to the enhancement of dimensional stability and decay resistance in the impregnated wood.

Besides *P. ostreatus*, reduction in IB strength of PF bonded board was when the board exposed to brown rot fungus (*C. puteana*). This could be improved by increasing the resin loading as suggested by Kajita and Imamura (1991) since the use of 15% PF (low molecular weight) loading controlled the mass loss of 600 kg m^{-3} particleboard from the brown rot fungus *Tyromyces palustris.* Mass losses due to white rot fungus *Trametes versicolor* were controlled at 5% resin incorporation.

Relationships of swelling and expansion to mass loss of *Acacia* hybrid boards exposed to decay fungi were evaluated (Figure 5.10 and 5.11). Weight loss of boards exposed to *P. ostreatus* has strong regression to swelling and expansion of the boards (r^2 = 0.838, 0.744). Mass loss of boards exposed to *C. puteana* and *T. versicolor* did not have any linear relationship with the swelling but had negative and positive correlation respectively to the boards' expansion (Table 5.3). The mass loss was significantly correlated with the swelling and expansion of boards exposed to *P. sanguineus*.

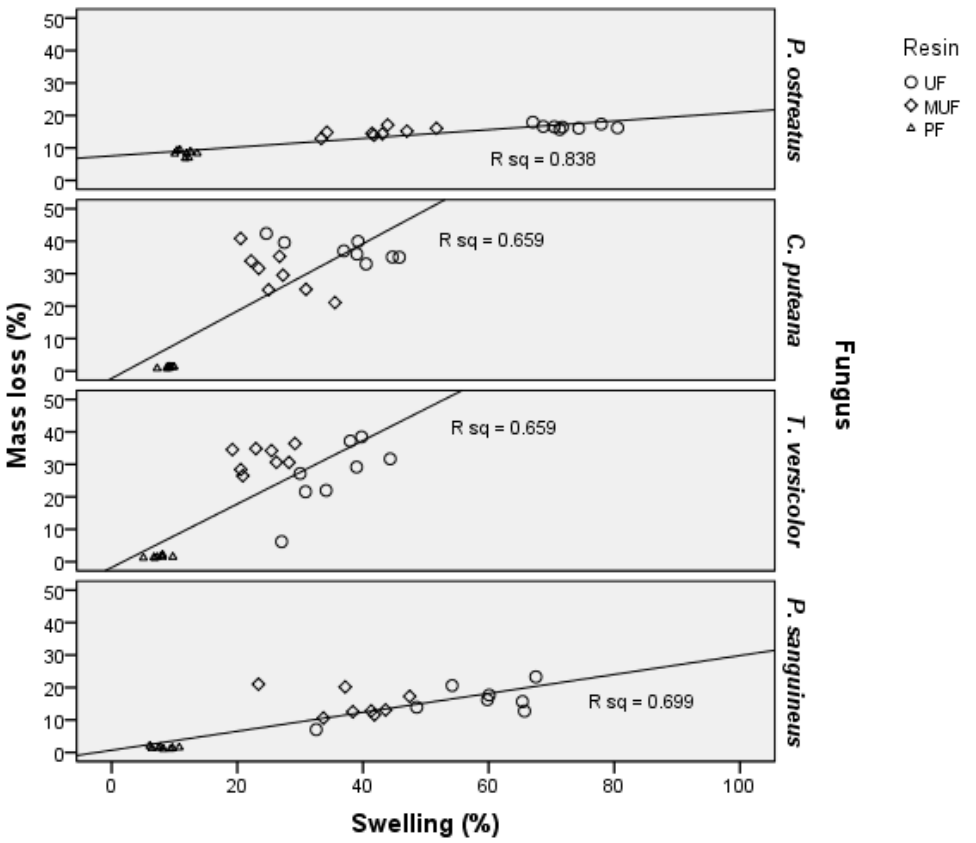


Figure 5.10: Linear relationship of mass loss and swelling of *Acacia* hybrid particleboards

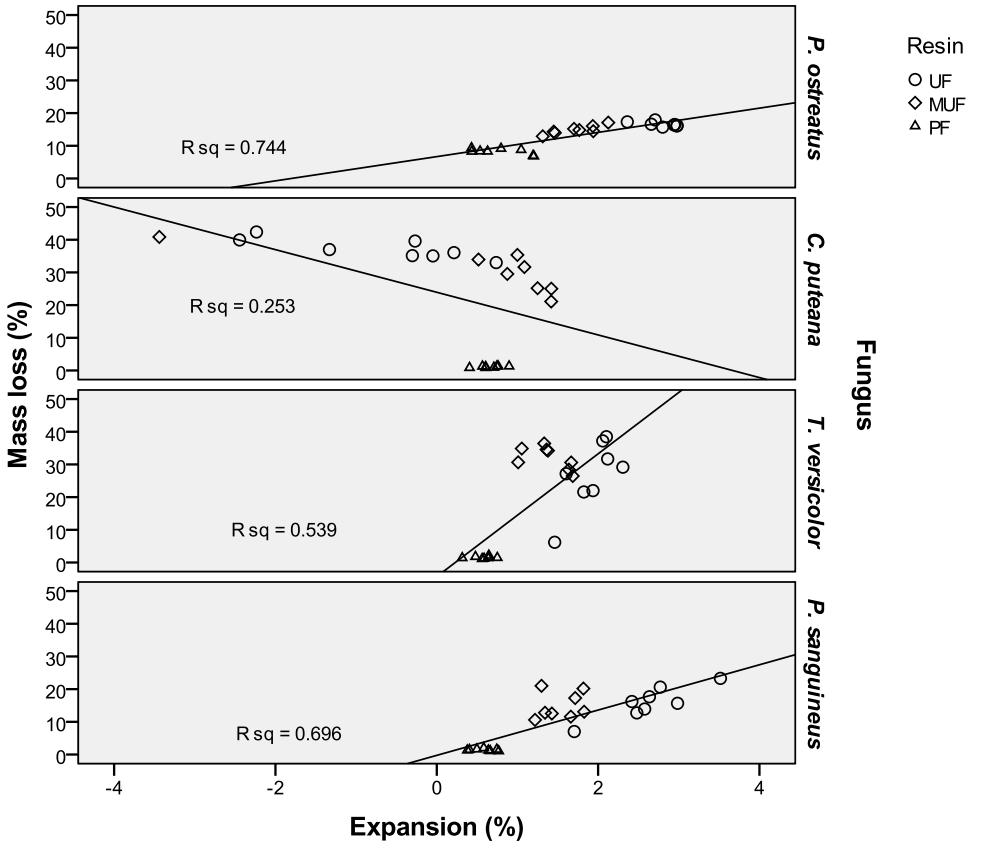


Figure 5.11: Linear relationships of mass loss and expansion of *Acacia* hybrid particleboards

Table 5.3: Pearson correlation of decay values of *Acacia* hybrid particleboards

Correlation	*P. ostreatus*	*C. puteana*	*T. versicolor*	*P. sanguineus*
Mass loss - swelling	0.915 **	0.812 **	0.812 **	0.836 **
Mass loss - expansion	0.863 **	-0.503 *	0.770 **	0.834 **

** = significant at 0.01 level, *= significant at 0.05 level

The virulence test showed that the fungi can be used for decay study. The wood particles had significant weight loss caused by *C. puteana* and relatively small due to white rot fungi. Particleboards showed high mass loss due to *C. puteana*. Decay due to white rot fungi was more apparent in the boards than in the particles form. This study indicates that boards from *Acacia* hybrid were susceptible to decay fungi. The decay was minimised by applying phenol formaldehyde resin in the boards.

5.4 Conclusions

The internal bond strength of boards with UF and MUF resins strongly deteriorated due to decay fungi. *T. versicolor* and *C. puteana* caused severe loss in weight of the boards. Thickness swelling and shrinkage resulting from decay was high in boards bonded with UF resin followed by MUF. The PF bonded board had high decay resistance except when exposed to *P. ostreatus*. Internal bond strength of the boards degraded as result of decay by the brown rot fungus, *C. puteana*.

The relationship between mass loss and thickness changes of *Acacia* hybrid boards caused as a result of decay exposure to *P. ostreatus* and *P. sanguineus* was measured. The *Acacia* hybrid boards have better TS and IB strength than the recycled wood and spruce. Nevertheless apart for PF bonded boards, no trend differences were seen on the boards due to fungal decay.

The weight loss of *Acacia* hybrid boards caused by *P. ostreatus* and *C. puteana* was less than the recycled wood and spruce boards. The PF resin significantly improved the moisture resistance in the boards and thus the resistant of the board to fungi decay.

CHAPTER 6

EFFECT OF *ACACIA* HYBRID EXTRACTIVES ON WOOD GLUING WITH UREA FORMALDEHYDE RESIN

6.1 Introduction

Wood used in particleboard may interact with the resin system to give enhanced or reduced bonding properties with a resultant positive or negative influence on the board properties. Apart of the wood physical characteristics, this can be attributed to non-structural components or extractives, which are mostly tannins, polyphenols, essential oils, fats, resins, waxes, gums, starch and other simple metabolic intermediates (Maloney 1977). *Acacia* hybrid was found to produce particleboard with better physical and mechanical strength properties compared with recycled wood (Table 4.4, 4.8). Extractives contents of the wood are suspected to have some role in wood gluing thus enhanced the board properties. According to Hoong et al. (2009) bark tannin from *Acacia mangium* (one of the parent species of *Acacia* hybrid) can be applied for wood adhesive use. It was hypothesised that the extractives from the *Acacia* hybrid had a significant resin interaction which enhanced bonding and performance. A series of experiments were made to examine if any interactions occurred, including redistribution of the extractives during pressing.

This part of the study aims to investigate the effect of extractives from *Acacia* hybrid on wood gluing. This was achieved by measuring the extractive interactions with the thermoset glue i.e. urea formaldehyde resin. Specific objectives of this chapter as follow:

1. To determine the effect of *Acacia* hybrid extractives on wood gluing with urea formaldehyde resin by shear test.
2. To evaluate the properties of urea formaldehyde resin added with *Acacia* hybrid extractives by infrared spectrometry and thermal behaviour analysis.

6.2 Automatic Bonding Evaluation System (ABES)

Automatic Bonding Evaluation System (ABES) was developed to help understand strength development of an adhesive under various conditions (Humphrey 1993). The system is a compact device for forming and immediately testing adhesive bonds between wooden veneers. It consists of interconnected mechanisms for pressing together test samples to form an adhesive bond between the samples, and for pulling apart the bonded parts while measuring the maximum force required to break the adhesive bond. The system allows for accurate control of bonding pressure, platen temperature and bonding dwell time besides good alignment of the lap shear samples (Wescott et al. 2007).

According to Humphrey (1993) the system works by applying adhesive to overlapping portions of a two-part sample located between opposing press heads of the bond testing device. The press heads then press together the overlapping portions for a specific period of time while heating the test sample to a preselected temperature. The system precisely maintains the temperature while bonding the sample at a preselected pressure. A load cell measures the shear force required to separate the bonded test pieces.

A rapid and reproducible small-scale testing procedure for efficiently screening new adhesives system from bio-based materials can be developed by employing ABES instrument (Frihart et al. 2009). Increase in breaking load independent of press time of the urea formaldehyde resin can be observed (Stefke and Dunky 2006). Higher breaking load at short press time is achieved by varying the hardeners.

Lecourt et al. (2003) studied the use of ABES and thermal mechanical analysis (TMA) as forecasting systems of wood bonding effectiveness. The modulus of elasticity has been shown to be correlated mathematically with internal bond of the particleboard with tannin adhesives. The kinetic response of urea formaldehyde based adhesives has been studied using differential scanning calorimetry (DSC) and ABES (Heinemann et al. 2002). Activation energy values were derived from the former and compared with isothermal bond strength development data collected using the latter. The results suggest that the ABES could be more sensitive to small differences in adhesive formulation than DSC.

In contrast to the standard ABES procedure where wood bonding is tested directly after pressing to evaluate reactivity kinetics of adhesives, measurements by Stöckel et al. (2010) on the urea formaldehyde based adhesives formulated for particleboard were carried out in a universal testing machine after several days of storing and complete curing.

6.3 Materials and methods

6.3.1 Materials

The urea formaldehyde (UF) resin was obtained from Dynea, UK. It had 68% solids content, viscosity 420 cp (at 25 °C) and a free formaldehyde content 0.15%. The *Acacia* hybrid extractives were from extraction experiments using hot water and methanol. Details of the extractions and extractives properties have been mentioned in Chapter 3. The extractives used were A80, A100, A120, A160, AA, and AM.

6.3.2 Properties of urea formaldehyde resin

6.3.2.1 Buffering capacity

Buffering capacity of the resin was determined according to Stefke and Dunky (2006). The resin was diluted with deionised water to obtain 100 g solutions with solids content of 50% followed by titration to pH 3.0 with 0.5 M sulphuric acid. A Hanna pH meter (model pH 204) calibrated with buffer solutions at pH 4.0 and 7.0 was used to measure pH values. The titration process was carried out at room temperature. The process was repeated with UF resin added to *Acacia* hybrid extractives (A100) (4.00 g, 1% solids content) and deionised water (3.96 g) respectively followed by titration.

6.3.2.2 Gel time

Gel time was measured as the time taken by the resin from the onset of heating till completely gelled. The gel time of UF resin and *Acacia* hybrid extractive mixture was determined by adding 2.5 g of solids resin with hardener (ammonium chloride, 0.5% w/w, 1% solids) and extractive (1% w/w, 1% solids) in a test tube (15 x 148 mm) before

being heated at temperature 100 °C in silicone oil. The mixture was stirred regularly. The gel time was performed on *Acacia* hybrid extractives A80, A100, A120 and A160 from Chapter 3. Control sample gel time was determined by replacing the extractive with deionised water (99% of extractives amount). The effect of temperature was evaluated by measuring gel time of extract A100 at 60 °C and at 100 °C temperature. Three replicates were conducted for each gel time sample.

6.3.3 Evaluation of ABES instrument

Urea formaldehyde resin was mixed with deionised water (99% of extractives [0.5% w/w, 1% solids]) and stirred. The mixture (0.0212-0.0218 g) was applied to the end-most 5 mm (Stefke and Dunky 2006) of a beech veneer (120 x 20 x 1 mm) before been overlapped with another veneer as in Figure 6.1 (Heinemann et al. 2002). The joints were pressed between heated blocks at a temperature of 110 °C (Stöckel et al. 2010) and press pressure 54 kg cm^{-2} for 30, 35, 40, 60, 70, and 80 s, cooled for few seconds and pulled apart in the shear mode. Ten replicates were done for each sample.

The breaking load of the glued veneers increased with increasing press time (Figure 6.2). Thirty seconds of press time was insufficient for the resin to polymerise. The process was intensive between 40 s where resin became sticky thus holding the veneers. Complete polymerisation at 110 ^{o}C temperature occurred after 70 s. Press time for bonding urea formaldehyde resin can be reduced by adding hardener such as ammonium chloride in the resin mixture (Stefke and Dunky 2006).

It was found that the glued veneers tend to slip from grip while being pulled for shear determination at breaking load of over 254 N. The machine has breaking load error 20 N when tested with blank samples (unglued veneers). Therefore modification of the test procedure is suggested in 6.3.4.

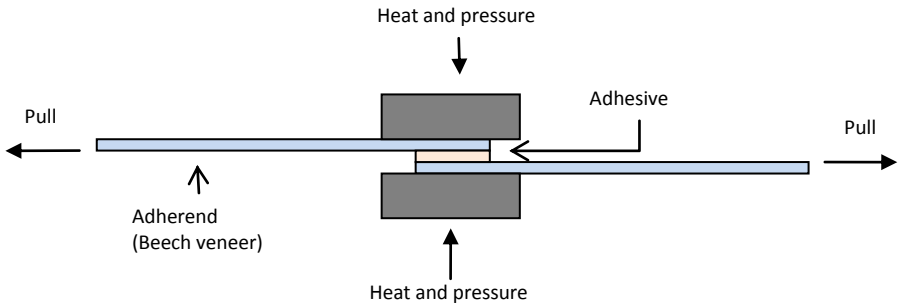


Figure 6.1: Schematic diagram of ABES tensile test

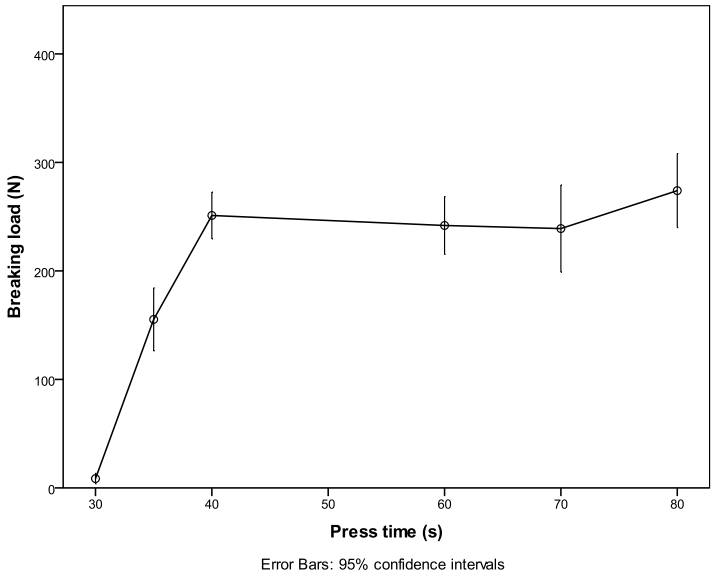


Figure 6.2: Breaking load of glued beech veneers against pressing time in ABES instrument

6.3.4 Shear strength of UF resin with *Acacia* hybrid extractives

Wood gluing strength of UF resin mixtures was determined on tangential sliced beech veneer strips of 120 mm length, 20 mm width and 1 mm thickness obtained from The BioComposites Centre. ABES instrument was used to glue the veneers.

Hardener (ammonium chloride, NH_4Cl) was incorporated into the resin to ensure complete polymerisation within 80 s. The resin mixture was spread on beech veneers at 5 x 20 mm area as above, before being pressed and heated at 110 °C respectively for 80 s (or stated otherwise) using ABES. They were then cooled down with a metal plate (Stöckel et al. 2010), conditioned at relative humidity 65% and temperature 20 °C for 3 days, followed by shear strength determination using Instron universal testing machine

(model 4301, 5 kN capacity) at a crosshead speed of 10 mm min^{-1} (Frihart et al. 2009; Wescott et al. 2007).

The UF resin stock was stored in cold environment in order to minimise polymeric changes.

6.3.4.1 Urea formaldehyde resin with extract A100

Efficiency of *Acacia* hybrid extractives to UF resin was evaluated by mixing the resin with extract A100. Details of the mixtures are summarised in Table 6.1.

Table 6.1: Shear test details of UF resin with extract A100

No	UF on veneer (g)	Resin mixture		Press time (s)
		Extractives	Control	
1.	0.0208	UF[a] + NH_4Cl[b] + A100 (0.5% w/w, 2%)	UF[a] + NH_4Cl[b] + H_2O (98% of A100)	40, 60, 80
2.[c]	0.0208	-	UF[a] + NH_4Cl[b] + H_2O (98% of A100)	60
3.	0.0193	UF[a] + NH_4Cl[b] + A100 (2% w/w, 4%)	UF[a] + NH_4Cl[b] + H_2O (96% of A100)	60, 80
4.	0.0188	UF[a] + NH_4Cl (1% w/w, 10%) + A100 (1.5% w/w, 4%)	1) UF[a] + NH_4Cl (1% w/w,10%) 2) UF[a] + NH_4Cl (1% w/w,10%) + H_2O (96% of A100)	80

[a] UF resin at 68% concentration
[b] NH_4Cl at 10% concentration, 0.5% from UF solids
[c] Veneers were pre-spread with A100 (0.0150 g, 2%) and water (0.0147 g) respectively
All veneers were pressed at 110 °C

6.3.4.2 Urea formaldehyde resin with extract A80, A100, A120, A160, AA, and AM

The effect of extraction methods to wood gluing was determined by mixing UF resin with extract A80, A100, A120, A160, AA and AM. Details of the mixture are summarised in Table 6.2.

Table 6.2: Shear test details of UF resin with extract A80, A100, A120, A160, AA, and AM

No	UF on veneer (g)	Resin mixture		Press time (s)
		Extractives	Control	
1.	0.0158	A80, AM mixture = UF[a] + NH_4Cl[b] + extractives (1.5% w/w, 2%)	UF[a] + NH_4Cl[b] + H_2O (98% of extractives)	60, 80
2.	0.0158, 0.0205	A80, A100, AA mixture = UF[a] + NH_4Cl[b] + extractives (1.5% w/w, 7%)	UF[a] + NH_4Cl[b] + H_2O (93% of extractives)	80
3.	0.0205	A80, A100, A120, A160 mixture = UF[a] + NH_4Cl (0.5% w/w, 10%) + extractives (1.5% w/w, 8%)	UF[a] + NH_4Cl (0.5% w/w,10%) + H_2O (92% of extractives)	80

[a] UF resin at 68% concentration
[b] NH_4Cl at 10% concentration, 1% of UF solids
All veneers were pressed at 110 °C

6.3.5 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy analysis was performed on the urea formaldehyde resin samples using Bruker FTIR spectrometer between 500 and 4000 cm^{-1} wavelength before thermal analysis.

6.3.6 Thermal analysis

Thermal studies of urea formaldehyde resin samples were carried out using TGA-DSC instrument (SDT Q600). Samples (14 mg) were placed in alumina crucible. Each sample was heated from ambient to temperature up to 500 °C at heating rate 5 °C min^{-1} under a nitrogen atmosphere. Continuous records of sample temperature, sample mass and heat flow were taken.

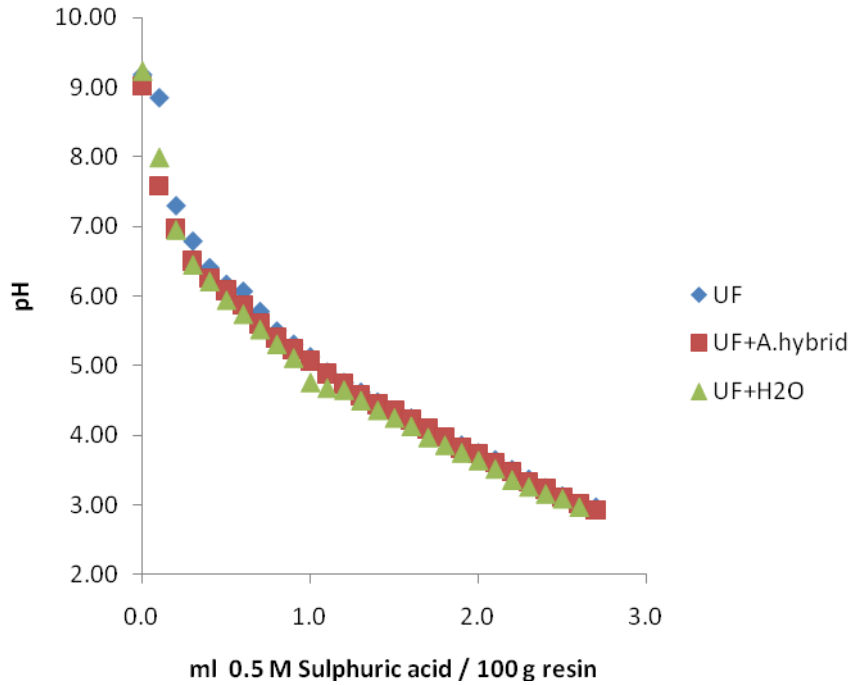
6.3.7 Statistical analysis

Statistical software, SPSS version 16 was used to determine mean, standard deviation, mean difference and error bar of the data.

6.4 Results and discussion

6.4.1 Buffering behaviour and gel time of UF resin

The pH and buffering behaviour of UF resin are shown in Figure 6.3. The UF resin was alkaline with pH 9.18. Addition of *Acacia* hybrid extractives and water did not change the buffering behaviour of the resin. Buffering behaviour of the resin is negligible since only a small volume of acid (less than 2.8 ml) was needed to reduce the pH to 3. The initial pH of the resin was slightly decreased when extractives were added. This is expected because the wood is acidic as shown in previous chapter. Differences between the mixtures were not obvious and when the pH turned 6 the values were nearly similar. Even though the water mixtures had a slightly higher initial pH of 9.23, the values decreased more than others as the titration proceeded and finally needed only 2.4 ml of acid to achieve pH 3. A slight increase in resin temperature was observed due to the exothermic hardening reaction at lower pH. The increase however has no influence on buffering behaviour of the UF resin, as also seen by Stefke and Dunky (2006).



UF = urea formaldehyde resin

Figure 6.3: Buffering behaviour of urea formaldehyde resin

The gel time test indicates that the UF resins require at least 1.19 minutes to gel at temperature 100 °C (Table 6.3). Addition of *Acacia* hybrid extractives into the resin slightly prolonged the gel time from 1.19 (control) to 1.27 (A100) minutes. The gel time at the lower temperature (60 °C) was slow especially in the presence of extractives. It took 5.4 minutes for the extractives resin to gel as compared 4.1 minutes for the control UF resin.

Ammonium salts (chloride or sulphate) are usually used as curing agent for UF resin (Pizzi 2003). The hardener releases the acid thus decreases the pH of the resin and accelerates curing. The ammonium ion of the hardener reacts with the free formaldehyde in UF resin to release the acid as follows:

$$4NH_4Cl + 6HCHO \rightarrow 4HCl + (CH_2)_6 N_4 + 6H_2O \quad (6.1)$$

Since most of wood extractives are acidic, it is expected to reduce gel time of a urea formaldehyde resin. However, it was found that the extractives have different ways in affecting the gel time. Slay et al. (1980, cited in River et al. 1991) reported that extractives obtained from pressure refining of five hardwoods and pine decreased the gel time of a urea formaldehyde resin when added in small amounts, addition of 6 to 9% alcohol soluble fractions shortened gel time by 70%, whereas water soluble fractions had less of an effect.

Extractives that are insoluble in the adhesive solvent system could cause more adhesion problems than extractives that are soluble. Narayanamurti et al. (1962, cited in River et al. 1991) found that extractives of teak that are insoluble in water and this adversely affected the setting of UF resin whereas the hot water soluble extractives of *Acacia* did not interfere with the UF resin curing.

The quantity of hardener has an effect on curing of UF resin and wood mixes. Xing et al. (2004) found that with an ammonium chloride concentration of ≥0.4% the gel time of UF resin increased when added with poplar and spruce particles (of bark and wood), whereas at lower concentrations of hardener (≤0.2%) the gel time decreased when added with the particles.

The pH and acid buffering capacity of hot water extracts from crop materials were significantly higher than softwoods and increased the gel time when added into the resin (Hague et al. 1998). So based on the acid buffering capacity of *Acacia* hybrid wood (Chapter 3), UF resin buffering behaviour in Figure 6.3, and finding by Narayanamurti et al. (1962, cited in River et al. 1991), the hot water extractives of *Acacia* hybrid could have no effect on the gel time of UF resin even though a slight increase on the gel time was recorded (Table 6.3). However the gel time measurement was done manually. More accurate results would be expected using a gel time meter.

Table 6.3: Gel time of urea formaldehyde resin and *Acacia* hybrid extractives mixtures

Additives	Gel time (mins.)	
	60 °C	100 °C
Control	4.06 (0.18)	1.19 (0.05)
A80	-	1.25 (0.02)
A100	5.41 (0.08)	1.27 (0.01)
A120	-	1.24 (0.02)
A160	-	1.25 (0.01)

In parentheses is standard deviation

6.4.2 Wood gluing of UF resin added with extract A100

Effect of *Acacia* hybrid extractives from 100 °C water extraction (A100, 2% solids, 0.5% w/w) on UF resin was determined by shear strength determination of glued beech veneers at 40, 60 and 80 s press times. Results indicate that the samples have shear strength of more than 4 MPa (Figure 6.4, raw data in appendix Table 6). All the glued samples were fully polymerised after ABES pressing even at a low press time of 40 s. Ammonium chloride hardener was effective to ensure full resin cure. Increasing the press time from 40 s to 80 s had no significant effect. Hence the A100 extractive used had no positive effect on the shear values.

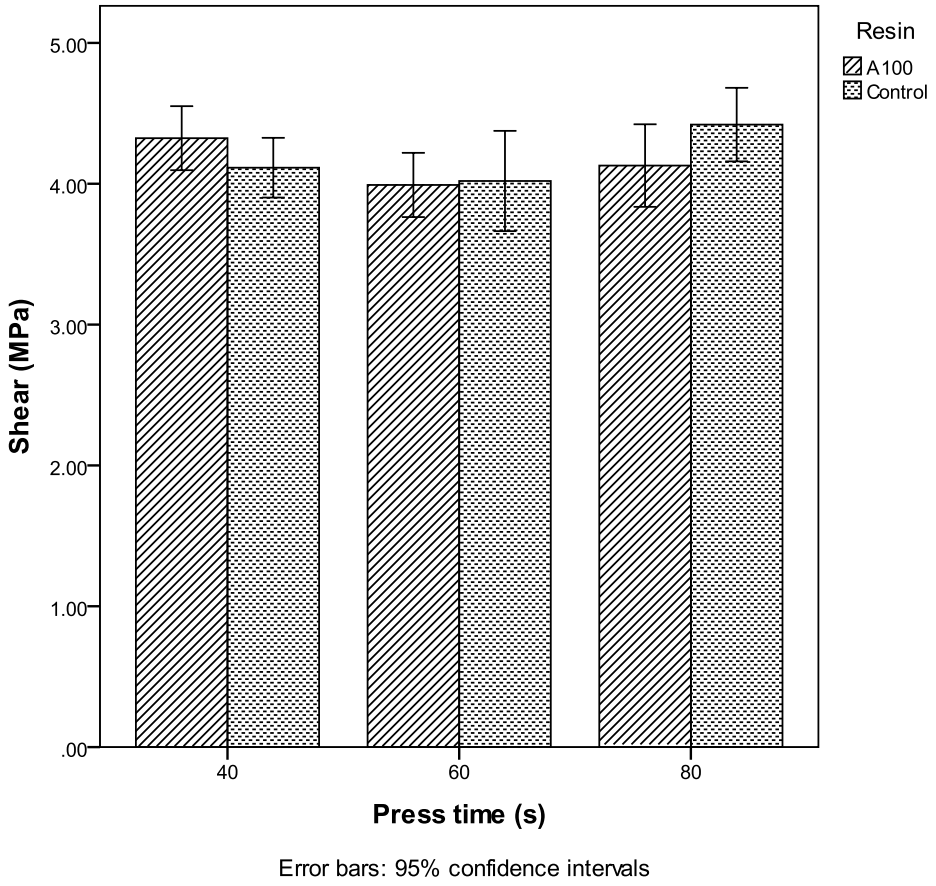
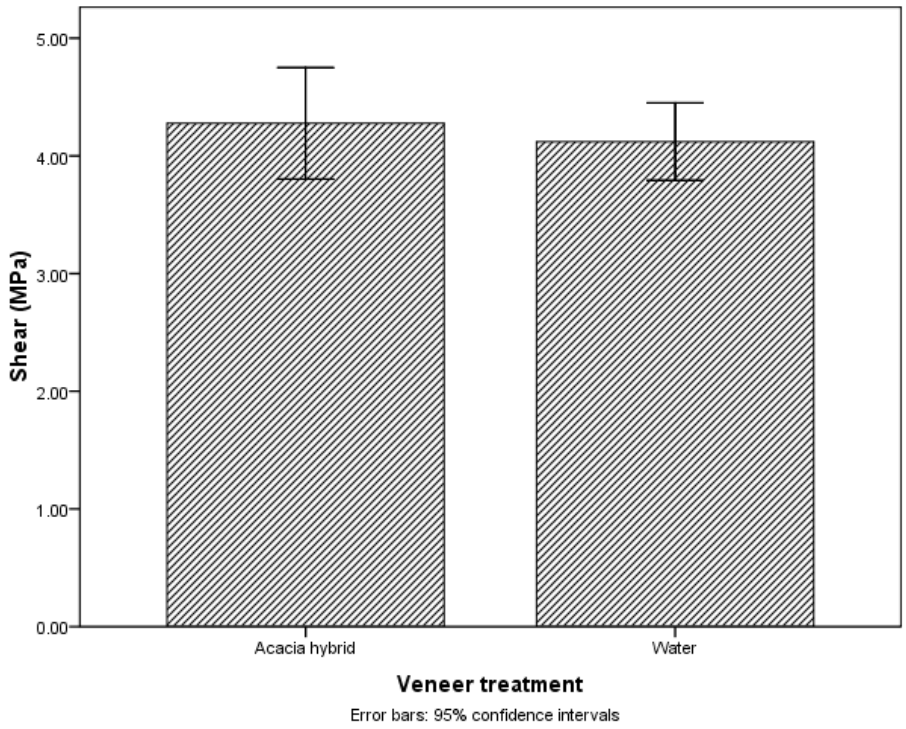


Figure 6.4: Shear strength of beech veneers bonded with urea formaldehyde resin (UF) added with *Acacia* hybrid extractives (A100, 2% solids)

Bonding of extractive treated veneers with UF resin was examined. The extractives (0.0150 g) and water (0.0147 g) were spread on to veneers before the veneers were air-dried and conditioned at ambient conditions. The treated veneer was then spread with UF resin before been overlapped with another treated veneer. The veneers were pressed at 110 °C for 60 s. Shear tests indicated that no significant difference between treatments (Figure 6.5, raw data in appendix Table 7), similar to the results in Figure 6.4. Incorporation of extractives onto beech veneers did not improve shear strength of the UF bonded veneers.



Note: veneer treatment done by pre-spread with A100 (0.0150 g, 2%) and water (0.0147 g) respectively followed by air dry

Figure 6.5: Shear value of treated veneers bonded with urea formaldehyde resin

The extractives were concentrated further to 4% solids. Repetition of the test showed an improvement in shear strength over the control when pressed for 60 s but when pressed for 80 s there was no difference between treatments and similar values to the 60 s pressing with extractive treatment were noted (Figure 6.6, Table 6.4, raw data in appendix Table 8).

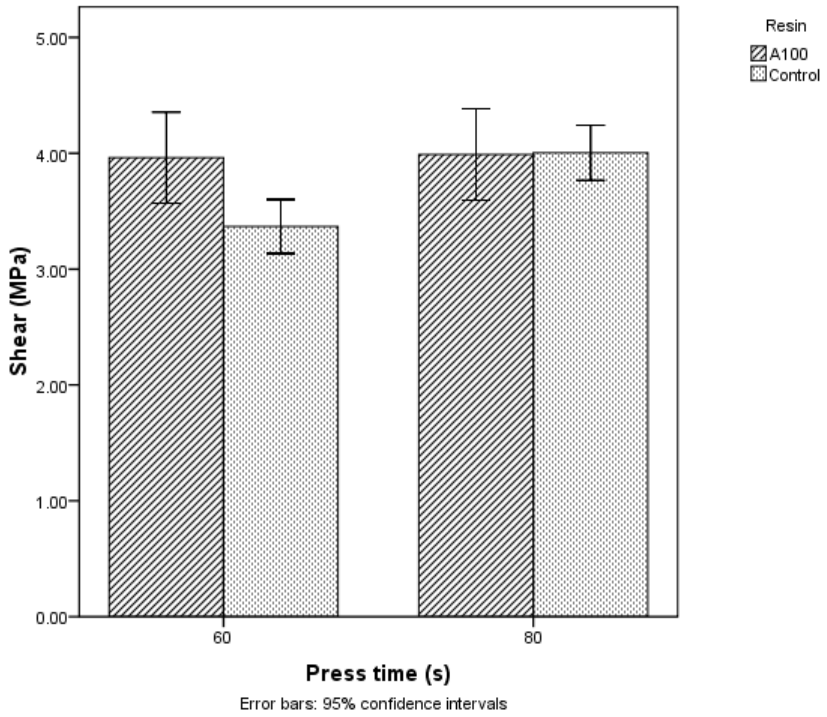


Figure 6.6: Shear value of veneers bonded with urea formaldehyde resin added with *Acacia* hybrid extractives (A100, 4% solids)

Table 6.4: Statistical comparison of shear value of veneers bonded with urea formaldehyde resin added with *Acacia* hybrid extractives (A100, 4% solids)

Press time (s)	Resin	Mean shear* (MPa)
60	A100	3.96 a
	Control	3.37 b
80	A100	3.99 a
	Control	4.00 a

*Mean values with same letter are not significant different at 95% confidence levels

In the above experiments, the amount of water in resin was levelled so to have similar viscosity between the resins under comparison. The drawback with this is that the resins became less viscous and thus could penetrate deeper into the veneer, which consequently affect shear strength. The effect of water addition to the UF resin is summarised in Figure 6.7 (raw data in appendix Table 9). Three sets of resins were tested: resin only, resin with aqueous extractives, and resin with water to compensate for the aqueous extractives. The amount of solids UF applied to the veneers was standardised at 0.0188 g. The results showed that the UF resin alone has a high shear value of 6.45 MPa, and addition of the aqueous extractives and water to the resins

decreased the shear strength to 4.47 and 4.16 MPa respectively. This indicates that the amount of water in UF resin has a significant effect on the gluing of beech veneers as supported by statistical data in Table 6.5. Even though the concentration of extractives had been increased (1.5% w/w, 4% solids) and higher percentage of hardener (1% w/w) was used, the effect of the extractives, if any, on wood gluing was not seen.

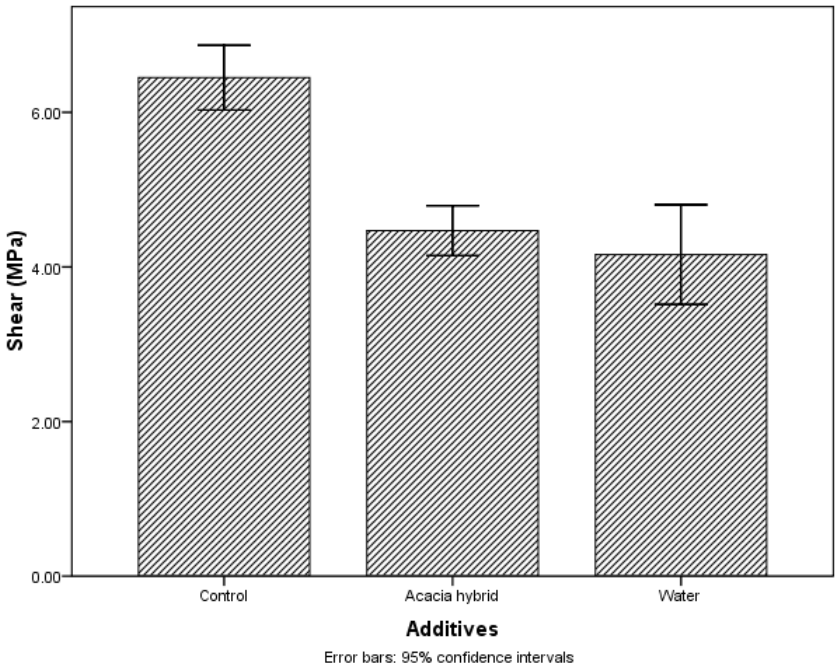


Figure 6.7: Shear strength of veneers bonded with urea formaldehyde resin with aqueous additives

Table 6.5: Statistical comparison of shear strength of veneers bonded with urea formaldehyde resin with aqueous additives

Resin	Mean shear* (MPa)
Control	6.45 a
Acacia hybrid	4.47 b
Water	4.16 b

*Mean values with same letter are not significant different at 95% confidence levels

6.4.3 Wood gluing of UF resin added with extract AA, AM, A80, A100, A120 and A160

The shear strength of beech veneers glued with UF resin with *Acacia* hybrid extractives from 80 °C water extraction (A80) and methanol extraction (AM) had been determined

(Figure 6.8, Table 6.6, raw data in appendix Table 10). The shear strength of veneers with extract A80 resin was 4.4 MPa at press time 60 s. The resin was fully polymerised after 60 s because increasing the press time to 80 s had not improved the strength. Addition of extract A80 increased the bonding strength of UF resin, however the increment was not significant. Methanol extracted *Acacia* hybrid extractives have been compared with extract A80. The methanol extractives had low solubility with water and were thus handled at 1:8 methanol to water ratio. Shear strength of the methanol extractives was lower than the extract A80 even though the difference was not significant. Failure related to resin bonding was observed in few test veneers. Further testing of the methanol extractives was abandoned due to its low water tolerance.

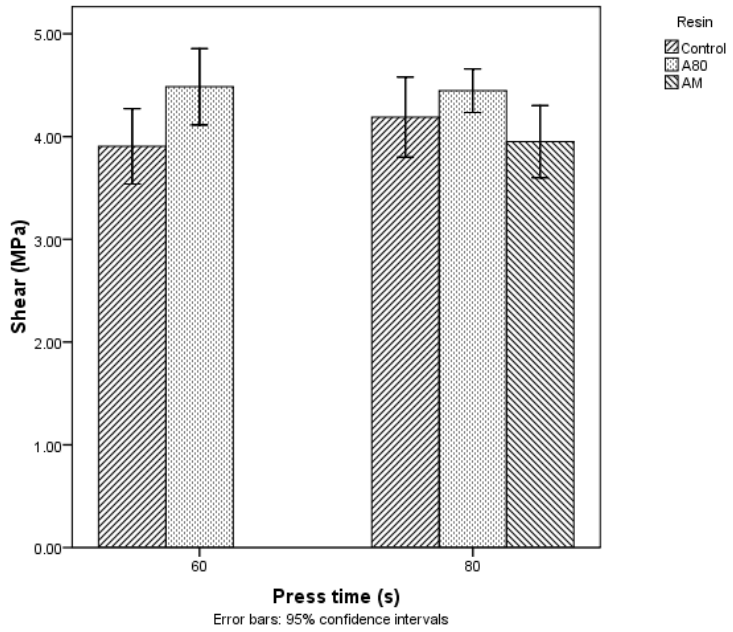


Figure 6.8: Shear strength of veneers bonded with urea formaldehyde resin with *Acacia* hybrid extractives (A80 and AM)

Table 6.6: Statistical comparison of shear strength of veneers bonded with urea formaldehyde resin with *Acacia* hybrid extractives (A80 and AM)

Press time (s)	Resin	Mean shear* (MPa)
60	Control	3.90 b
	A80	4.48 a
80	Control	4.19 ab
	A80	4.44 ab
	AM	3.95 ab

*Mean values with same letter are not significant different at 95% confidence levels

Extract A80 has been investigated with extract A100 and AA at a higher concentration (7%). Extract AA was obtained from the water extraction of *Acacia* hybrid using an autoclave with the intention of extracting at a temperature of over 100 °C. Pressure achieved was 4 bar, giving about 142 °C. The amount of urea formaldehyde solids on the veneers was applied at two doses, 0.0158 and 0.0205 g. High shear strength between 5.7 and 8.2 MPa were recorded from the veneers (Figure 6.9, raw data in appendix Table 11). The shear strength of veneers with UF resin was significantly higher when added with extract A80 (Table 6.7). The strength however was not significantly different between the three extractives. A similar trend of higher shear values was observed at higher amount UF solids (0.0205 g). The UF resins with high concentration extractives (7%) and 1% hardener had a short pot life i.e. only 1.5 hours as compared to resin mixtures of Figure 6.8. It became viscous more quickly than the previous resin mixtures. The resins were thicker and more difficult to spread on veneers. Shear strength of the veneers showed high variation as a result.

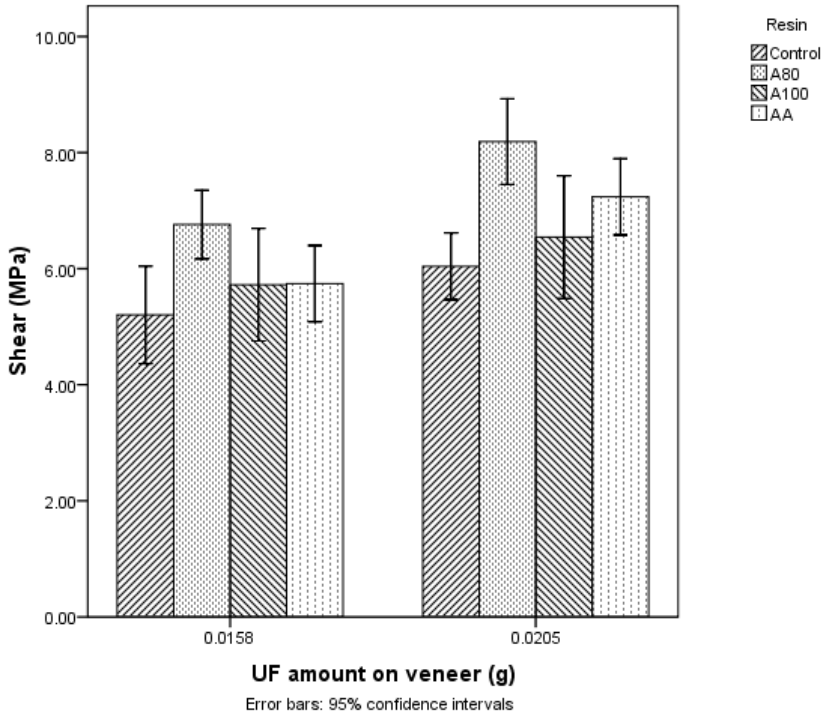


Figure 6.9: Shear strength of veneers bonded with urea formaldehyde resin with 1.5% w/w 7% *Acacia* hybrid extractives (A80, A100 and AA) at 1% w/w 10% ammonium chloride

Table 6.7: Statistical comparison of shear strength of veneers bonded with urea formaldehyde resin with *Acacia* hybrid extractives (A80, A100 and AA)

UF solids (g)	Extractives	Mean shear*(MPa)
0.0158	Control	5.20 d
	A80	6.76 bc
	A100	5.72 cd
	AA	5.74 cd
0.0205	Control	6.04 bcd
	A80	8.19 a
	A100	6.54 bcd
	AA	7.24 ab

*Mean values with same letter are not significant different at 95% confidence levels

In the next experiment, the shear strength of UF resins extractives mixtures was determined the same day to ensure the similarity of resin polymer properties. Ammonium chloride hardener was applied at 0.5% instead of 1% of the dry-resin weight in order to lengthen resin pot life. The extractives were used at high concentrations (8%, 1.5% w/w). Two sets of hot water extractives, A120 and A160, extracted at temperatures of 120 and 160 °C respectively using Parr reactor were used alongside the extracts A80 and A100. The UF resin had significantly higher shear strength (5.2 MPa) when used with extract A80 (Figure 6.10, raw data in appendix Table 12). The shear strengths of extract resin mixtures A120 were lower than extract resin mixture A80 and was not significantly different to the control (Table 6.8). The shear strength did not improve when extract A160 was added to the UF resin. The extract A160 possibly has no effect on the resin properties. The shear strength of veneers in Figure 6.10 were relatively lower than values in Figure 6.9 besides have smaller standard deviation as result from low amount of hardener used which made the resins less viscous and has longer pot life.

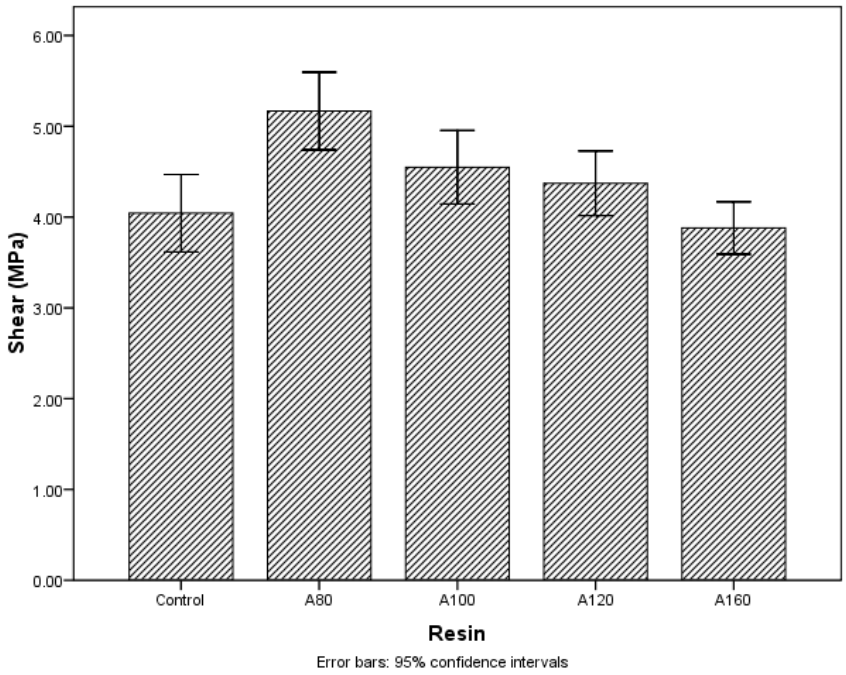


Figure 6.10: Shear strength of veneers bonded with urea formaldehyde resin with 1.5% w/w 8% *Acacia* hybrid extractives at 0.5%w/w 10% ammonium chloride

Table 6.8: Statistical comparison of shear strength of veneers bonded with urea formaldehyde resin with 1.5% w/w 8% *Acacia* hybrid extractives at 0.5%w/w 10% ammonium chloride

Extractives	Mean shear* (MPa)
Control	4.04 bc
A80	5.17 a
A100	4.55 ab
A120	4.37 bc
A160	3.88 c

*Mean values with same letter are not significant different at 95% confidence levels

The extractives of wood may contain a significant proportion of phenolic compounds which could react with any free formaldehyde available in the formaldehyde-based resin, thus modifying the resin and producing for example a urea-tannin-formaldehyde resin. The use of extractives in wood gluing has been investigated by a few researchers. Hoong et al. (2009) fortified extractives (tannin) from the bark of *A. mangium* with phenol formaldehyde resin and used it as adhesive for plywood which had shear strength that met the requirements of international standards. Pizzi (1979)

mixed tannins with urea formaldehyde resin for plywood adhesive. The resin system prevented water deterioration in the product and attained good mechanical properties. The amount of reactive phenols in extractives could be related with stiasny number as shown in Chapter 3. Extracts A80 and A100 have high stiasny numbers at 46 and 43% respectively which indicate high amounts of phenols. Even though the quantities of reactive phenols in extracts A80 and A100 were not much different, the extract A80 produced better shear strength when added into the UF resin (Figure 6.9, 6.10).

6.4.4 FTIR and TGA-DSC analysis of UF and *Acacia* hybrid extractives

Mixtures of urea formaldehyde resin (68% solids) and *Acacia* hybrid extractives (A80, 8.8% solids) were analysed by FTIR and TGA-DSC. Composition of the mixtures is shown in Table 6.9. Ammonium chloride (10% solids) was used as hardener.

Table 6.9: Composition of *Acacia* hybrid extractives and urea formaldehyde resin mixtures for FTIR and TGA-DSC analysis

	Composition (%, w/w)			
	Urea formaldehyde	Extractives	Water	Hardener
1. Control	87	-	10	3
2. *Acacia* hybrid	86	10	1	3

The thermogravimetric behaviour of urea formaldehyde (UF) resin and *Acacia* hybrid extractive mixtures are shown in Figure 6.11. The thermogram typically showed gradual weight loss of the samples as temperature increased. The *Acacia* hybrid mixture had two subtle changes at temperatures between 63 to 350 °C suggestive of initial and secondary decomposition. The control resin showed one apparent change at temperature between 240 and 340 °C. This singular weight loss is similar to that observed for UF resin by Singha and Thakur (2008) and Xu et al. (2009) whereas two apparent weight losses were reported by Siimer et al. (2010). The subtle changes of *Acacia* hybrid are supported by the endothermic curve which showed peaks at temperatures of 77 and 227 °C besides a small endothermic curve at 165 °C (Figure 6.12). The weight loss of the control resin is accompanied by an endothermic curve starting at 207 °C followed by an exothermic and several endothermic heat flows between 236 and 272 °C.

The slight weight loss of control resin at the temperatures of up to 200 °C was possibly due to minor formaldehyde emission and from water evaporation formed by condensation reactions whereas the major loss at temperatures of between 240 and 340 °C could be caused by structural decomposition of the polymer (Xu et al. 2009; Hirata et al. 1991). In the *Acacia* hybrid resin, there could be some decomposition in the extractives besides formaldehyde emission and water evaporation which caused apparent weight loss starting at temperature 63 °C and at endothermic temperature 77 °C followed by the degradation of cured extractives resin starting at 217 °C. Intensive decomposition of the extractives possibly occurred at the higher temperature. This is supported by Sun and Sun (2001) who measured significant weight loss of extractives from wheat straw at a peak temperature of 370 °C, and by Gaugler and Grigsby (2009) on tannins structural decomposition at peak temperatures between 250 and 320 °C.

The yield of char of *Acacia* hybrid mixture was 11% which is lower than the control (15%). Besides having slight lower amount of UF in the mixture (Table 6.11), the extractive containing resin has a slightly higher structural decomposition which decreased the char recovery.

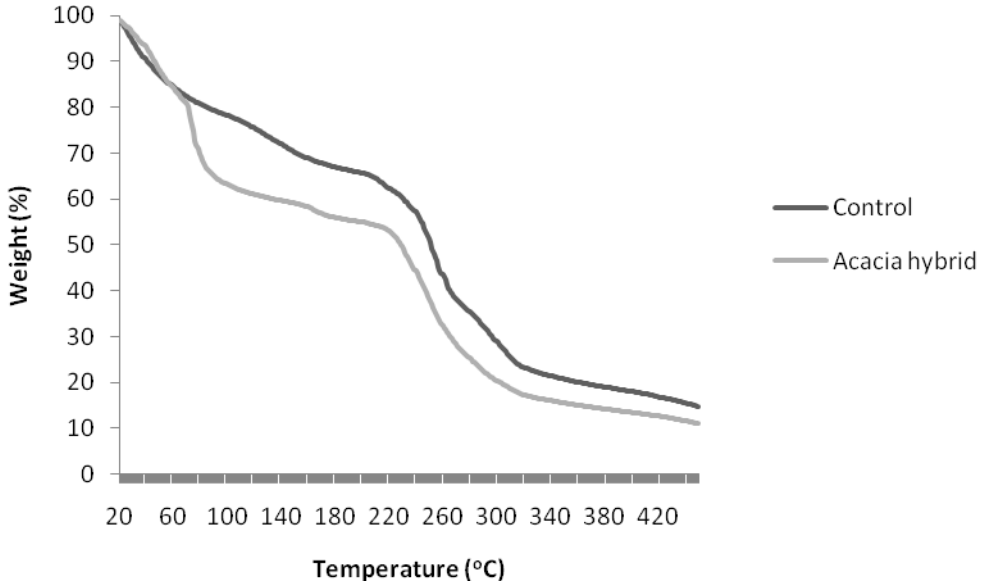


Figure 6.11: Thermal gravimetric analysis of urea formaldehyde resin mixed with *Acacia* hybrid extractives

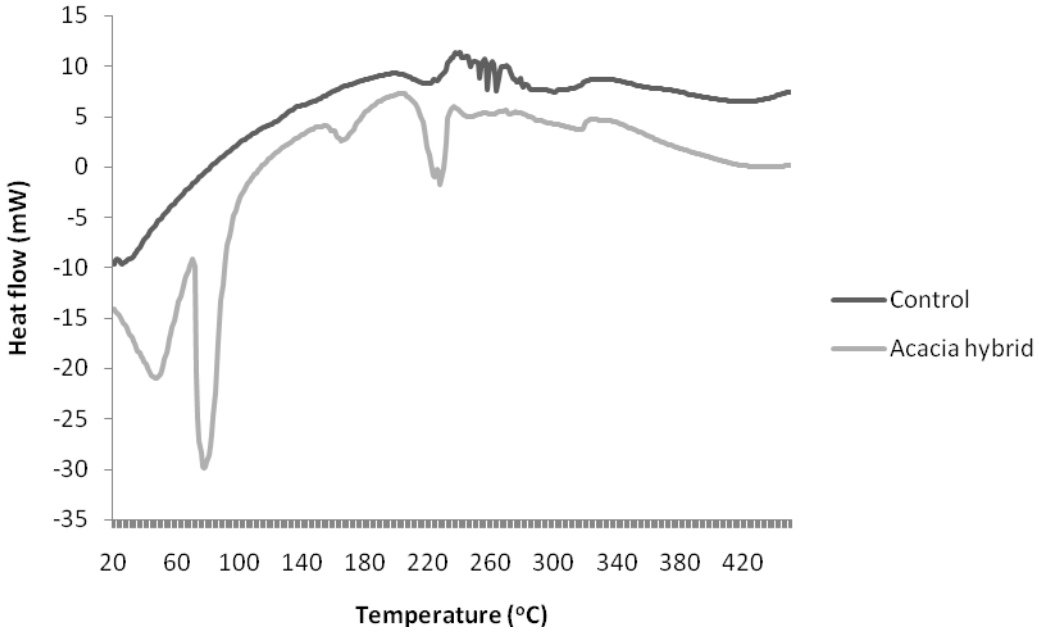


Figure 6.12: Differential scanning calorimetric analysis of urea formaldehyde resin mixed with *Acacia* hybrid extractives

The *Acacia* hybrid extractive containing resin had an identical FTIR spectrum to the control (UF) resin (Figure 6.13). All the basic structural peaks of UF resin appeared in both spectra and these have similar peak intensities (Osemeahon and Barminas 2007). The only difference is the peaks between 2370-2300 cm^{-1} in the control resin spectra which are not present in the extractive containing resin. The peaks are due to the presence of amide (Edoga 2006). In the spectra of control resin, the broad peak stretching between 3611-3140 cm^{-1} is due to N-H stretching of primary aliphatic amines or O-H of methylol urea, 2963 cm^{-1} is due to $–O-CH_3$, 1648 cm^{-1} is due to C=O stretching of primary amide, 1463 cm^{-1} is due to C-H bending of methylene bridge, and 1000 cm^{-1} is due to C-O stretching of methylol group (Park et al. 2003; Osemeahon and Barminas 2007). Details of the peaks are shown in Table 6.10.

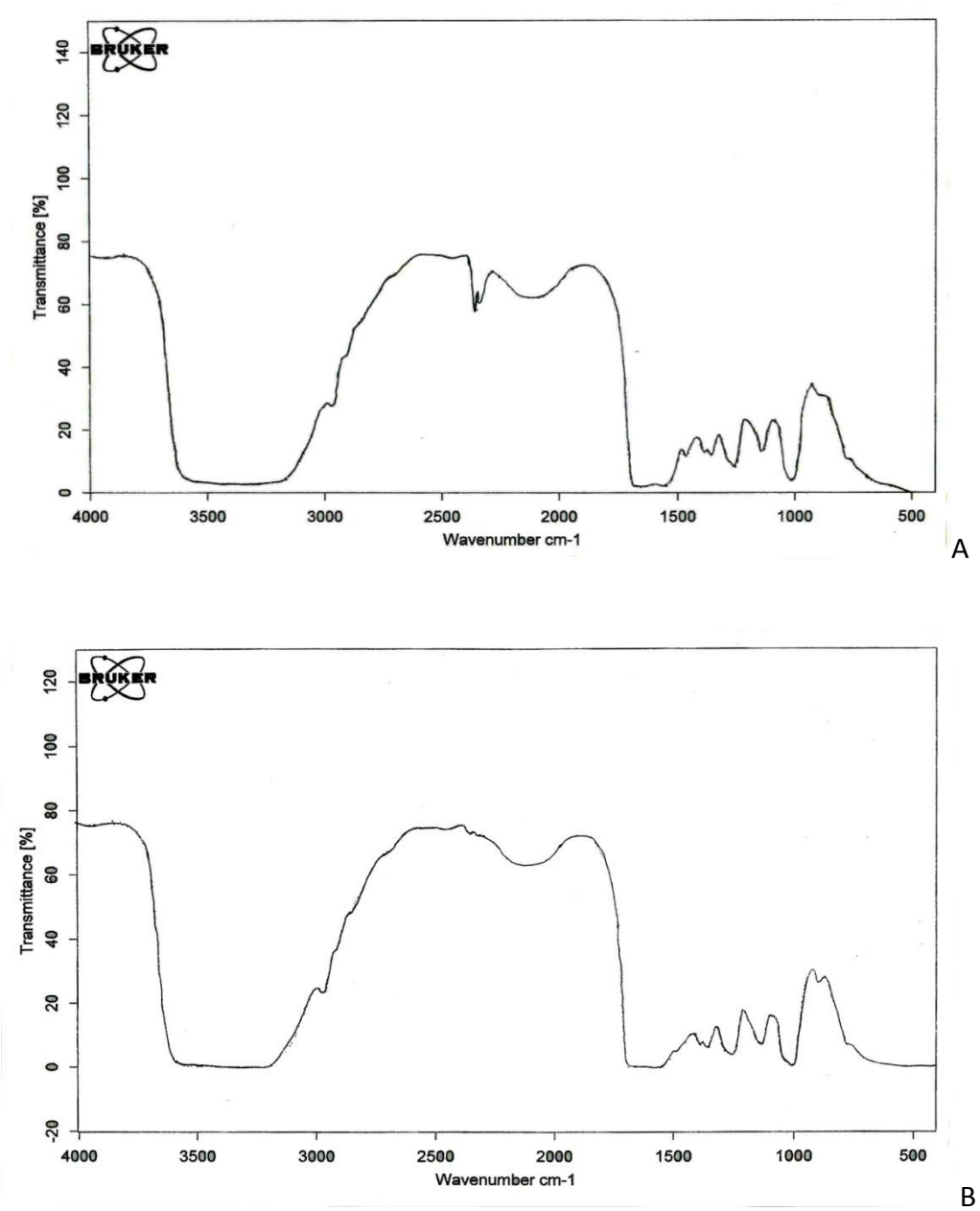


Figure 6.13: FTIR spectra of urea formaldehyde resin (A) and urea formaldehyde resin added with *Acacia* hybrid extractives (B)

Table 6.10: Absorption band of FTIR spectra of Acacia hybrid extractives mixtures

Absorption (cm^{-1})		Chemical structure assignment	reference
Acacia hybrid	Control		
3574-3167	3611-3140	NH stretching of primary aliphatic amines	Park et al. 2003
2963	2963	-O-CH_3, aliphatic ethers	Park et al. 2003
2370	2352	Presence of primary and/or secondary amide	Edoga 2006
1648	1648	C=O stretching of primary amide	Park et al. 2003

1537	1537	C-N stretching of secondary amines	Park et al. 2003
1443	1463	C-H bending in NCH_2N, CH_2O, OCH_3	Park et al. 2003
1389	1370	C-H mode in CH_2 and CH_3	Park et al. 2003
1259	1333	C-N stretching of CH_2-N	Park et al. 2003
1130	1111	C-O stretching of aliphatic ether	Park et al. 2003
1018	1000	C-O stretching of methylol group	Park et al. 2003
907	796	N-H bending of primary aliphatic amines	Park et al. 2003

6.5 Conclusion

The alkaline urea formaldehyde resin has a low buffering capacity to balance the acidity of the wood. Addition of *Acacia* hybrid extractives into the resins slightly reduced the resin pH but did not affect the buffering capacity behaviour overall. The gel time of UF resin was 1.2 minutes and the addition of extractives into the resin did not affect the gel time.

Several shear tests to determine the effect of *Acacia* hybrid extract A100 to the UF resin were carried out. Tests showed that the shear strength of the veneer glue bond with UF resin was unchanged (4 MPa) even with the addition of 2% w/w extract A100 into the resin. The total water content in the resin strongly affected the veneers bonding. The effect of water addition to the shear bond strength was reduced by using a higher extractive concentration of up to extract A80, 8% solids (5.2 MPa). However, the extract A100, A120 and A160 did not affect the shear strength even at high extractive concentrations. The effect of extractives on the UF resin is likely to be influenced by the amount of reactive polyphenols as suggested by stiasny value.

The thermal analysis showed subtle changes in the behaviour the UF resin at temperatures between 240 and 340 °C, which might be caused by the structural decomposition of UF polymer. Two subtle changes were shown by the extractive containing resin. Initial changes at temperature of 63 °C may be due to a slight change or reaction by the extractives, besides the formaldehyde emission and water condensation that caused significant weight loss of the mixtures. The secondary change was possibly due to the degradation of cured resin and extractives. The FTIR spectra showed that both UF resin and extractives mixtures have similar basic structural peaks as owned by typical urea formaldehyde resin.

CHAPTER 7

MATRIX-ASSISTED LASER DESORPTION/IONISATION TIME OF FLIGHT (MALDI-TOF) ANALYSIS OF *ACACIA* HYBRID EXTRACTIVES

7.1 Introduction

The results of Chapter 6 suggested that the hot water extractives of *Acacia* hybrid affected the bonding of veneers glued with urea formaldehyde resin. The extractives consist of polyphenols which possibly contribute to wood adhesion (Hoong et al. 2011) whereas the thermal extraction has influence on yield and composition of the extractives (Duan et al. 2005; Makino et al. 2009).

Therefore the objective of this part of study is to analyse the composition of hot water extractives of *Acacia* hybrid by mass spectrometry equipment i.e. matrix-assisted laser desorption/ionisation.

7.2 Matrix-assisted laser desorption/ionisation (MALDI) mass spectrometry

One of the problems of analysis of extractive is the identification of the complex mixture of compounds present. Chromatographic systems such as GC and HPLC can separate compounds but precise identification of the molecules present relies on the use of standards or the use of a variety of techniques for structural elucidation, including mass spectrometry to give molecular masses and nuclear magnetic resonance (NMR).

Mass spectrometry is an analytical technique measuring mass-to-charge ratio of ions from atoms which have lost or gained electrons. The mass spectrometer usually consists of ion source, mass analyser and detector. The ion source will generate ions from the sample which will be separated according to mass-to-charge ratios by the mass analyser and then detected by the detector. The information will be analysed by data analyser and presented as a mass spectrum. Analysis of polymeric samples using early mass chromatography technique is difficult since polymers are not volatile and ionised polymerstend to fragment (Staal 2004). Alternative mass spectrometry

techniques are those that can place ionised polymers in a gas phase without degrading the polymers and this is in essence what MALDI-TOF achieves.

Matrix-assisted laser desorption/ionisation time of flight is a kind of mass spectrometry with soft ionisation technique which enables the introduction of intact high molar mass polymers into the gas phase. The method allows desorption and ionisation of varying size molecules thus can provide a vast amount of information about structure of a sample of polymers, its molecular weight and molecular weight distribution.

In MALDI-TOF analysis, sample is mixed with a matrix molecule, placed on an electrically conducting target such as stainless steel plate and dried to form a crystalline mixture (Kempka 2005). The steel plate is placed in a vacuum and energy from short laser pulse is applied to the sample and matrix (Figure 7.1). The matrix will absorb the photon energy and transfer it to the sample which will be ionised through the capture of a proton, a metal ion or some other species to form positively or negatively charged ion adducts (Montaudo 1995). The ions will enter into the flight tube that housing the ions optics and the detector providing a fixed distance through which the ions travel under height vacuum (Siuzdak 1996; Ghirardo 2004). The ions travel down the flight tube at constant speed depending on their mass – heavier ions takes longer time to reach the detector, or stated simply, separates the molecules. At the end of the flight, a detector converts the ions to signals which are processed by the computer to produce mass spectra showing molecular mass to charge ratio (x-axis) and abundance value (y-axis) measures as the relative intensities.

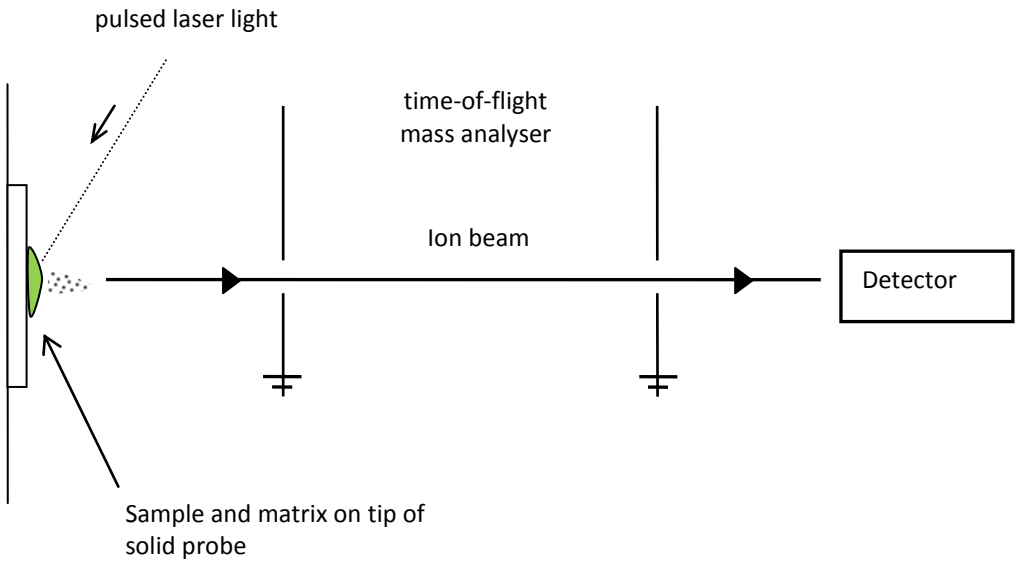


Figure 7.1: Schematic diagram of MALDI-TOF (Siuzdak 1996)

7.3 Materials and methods

7.3.1 Sample preparation for MALDI-TOF analysis

Acacia hybrid extractives (A80, A100, A120 and A160) were dissolved with deionised water to make a 5 mg/l concentration. 2,5-Dihydroxy benzoic acid (DHB) was used as matrix solution. The sample was mixed with the matrix solution at a volumetric ratio of 1:1 before deposited (1 µl) onto a steel target had been pre spread with DHB. The steel target was deposited into MALDI-TOF instrument after the mixture evaporated.

7.3.2 MALDI-TOF mass spectrometry

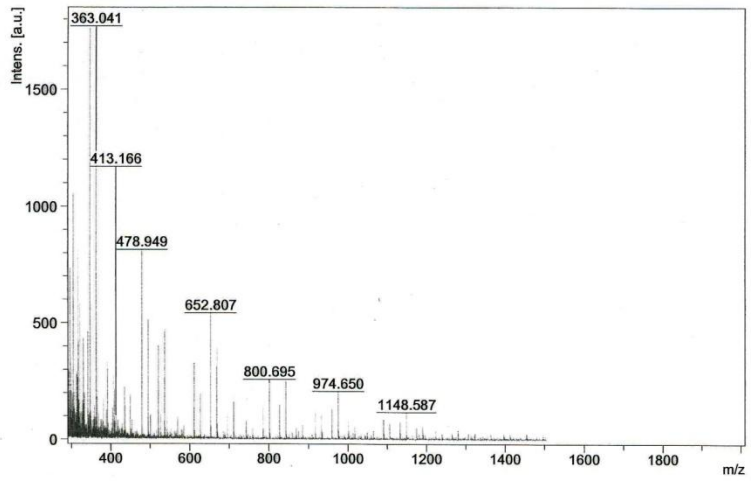
The MALDI-TOF spectra were acquired using Bruker Reflex III instrument equipped with a pulsed nitrogen laser with a wavelength of 337 nm, and the duration of the laser pulse was 3 nm. The MALDI-TOF conditions are as follows: laser intensity 2178, accelerating voltage 20.0 kV, linear mode operation, and extraction delay time 200-800 ns. The instrument was operated in the positive ion mass mode. The calibration has been conducted with a polyethylene glycol (PEG) standard. The spectra were processed and analysed from a sum of shots using Bruker Daltonics Flex Analysis software.

7.4 Results and discussion

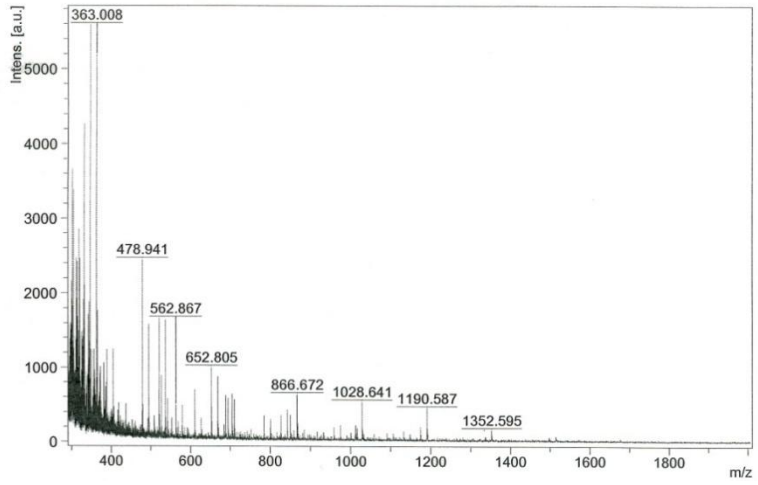
7.4.1 Mass spectra of extract A160

The MALDI-TOF mass spectra of hot water *Acacia* hybrid extractive A160 showed peaks of ionised components between 200 and 1500 Da (Figure 7.2a). Increasing the laser power at 30 and 60% varied the peak intensities which was useful for component identification (Figure 7.2b and 7.2c).

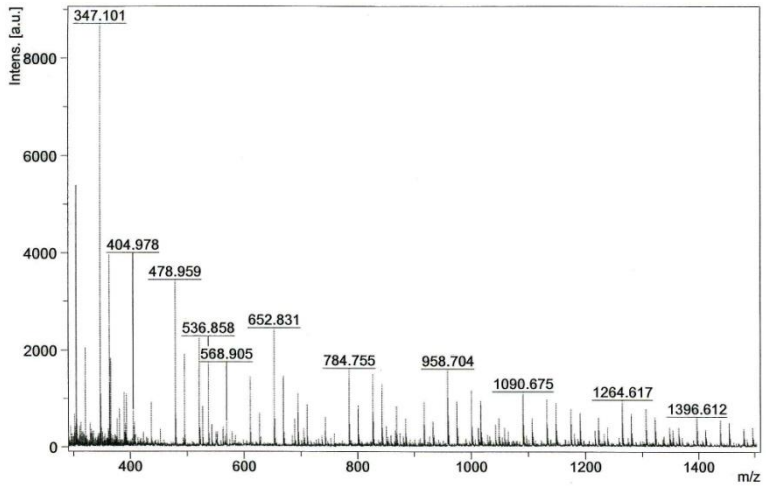
The spectrum at 60% power revealed a series of ion peaks with 162 Da difference at K^+ and Na^+ adducts. The $[M+K]^+$ and $[M+Na]^+$ peaks were identified through 16 Da mass difference of the peaks which represent K and Na atom mass difference. The 162 Da difference is usually due to the fragmentation of glycosyl unit,$C_6H_{10}O_5$, i.e. a hexose (Figure 7.3) which can be calculated to be 162.058 Da (Jung et al. 2010; Price et al. 2011; Teleman et al. 2003). Details of the ionic peaks of the series are shown in Table 7.1. By assuming the existence of dimer (Hex_2), the primer compound has a molecular mass of 180.028 (365.086 - 162.058 - Na) or 179.849 (381.005 - 162.058 – K) which resemblance hexose repetitive unit, $C_6H_{12}O_6$. Eight repetitions of hexose has been recorded from Figure 7.2b. The primer hexose was not detected on the spectrum which suggests that the compound exists at least at dimer level. Most of the hexose was observed as Na^+ and K^+ adducts. The only protonated peak seen was a hexamer, at 990.6 Da. The intensity of the ionic peaks decreased as the molecular mass increased. The octamer (Hex_8) produced an ionic peak only i.e. $[M+K]^+$ at 1352.595 Da. Further observation of the spectra indicated two consecutive small peaks after Hex_8 with peak difference of about 162 Da respectively which was not recorded by the Bruker analysis software. The peaks could be of $[M+K]^+$ of nonamer (Hex_9) and decamer (Hex_{10}) calculated at 1514.653 and 1676.711 Da respectively.



A



B



C

Figure 7.2: MALDI spectra of extract A160 (A), extract A160 at 60% laser intensity (B), and extract A160 at 30% laser intensity (C)

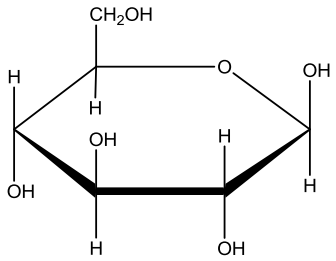


Figure 7.3: Example of hexose molecule, $C_6H_{12}O_6$ (glucose)

Table 7.1: Hexose fragmented peaks from extract A160 (60% power)

Hex_n	Unit	$[M+H]^+$	$[M+Na]^+$	$[M+K]^+$
Hex_2	Dimer	N	365.086	381.005
Hex_3	Trimer	N	526.893	542.836
Hex_4	Tetramer	N	688.779	704.727
Hex_5	Pentamer	N	850.721	866.672
Hex_6	Hexamer	990.603	1012.682	1028.641
Hex_7	Heptamer	N	1174.639	1190.587
Hex_8	Octamer	N	N	1352.595

N = not available

At 30% increment of MALDI-TOF laser power, the ionic peaks of hexose had decreased intensity while another group of peaks either emerged or intensified (Figure 7.2c). The peaks have apparent repetitive mass difference of 132, 42 and 174 Da which judging from the isotope is caused by C-H-O groups (Figure 7.4). The repetitive moieties were due to acetyl xylo-oligosaccharides based on spectrum by Kabel et al. (2002b) (Table 7.2). Even though extract A160 had ionic components of less than m/z 1500, the peaks within were complex which enabled component detailing. The spectrum consists of peaks with K^+ and Na^+ adducts identified from the 16 Da mass differences. Mathematical examination of the spectrum indicates that the peaks were inter-related. Apparent peaks were marked and used for grouping which produced six groups of peaks (E, D, C, B, A and Y) (Table 7.3, raw data in appendix Table 13). Within the group, the peak had a 174 Da difference than the peak next or before which indicate the addition or loss of an acetyl xylose unit (XylAc, 42 + 132). Most of the peaks have 132 Da difference with the above peak within the same table column which indicates xylos (Xyl) fragmentation. The peaks had 42 Da differences which related to acetyl functional group (Ac). Most of the measured peaks were comparable with the calculated values. Nevertheless group E had slight deviation than the calculated values

probably due to weak ionic components. Infect last peak of $[M + K]^+$ of group E was not detected even though the $[M + Na]^+$ peak appeared.

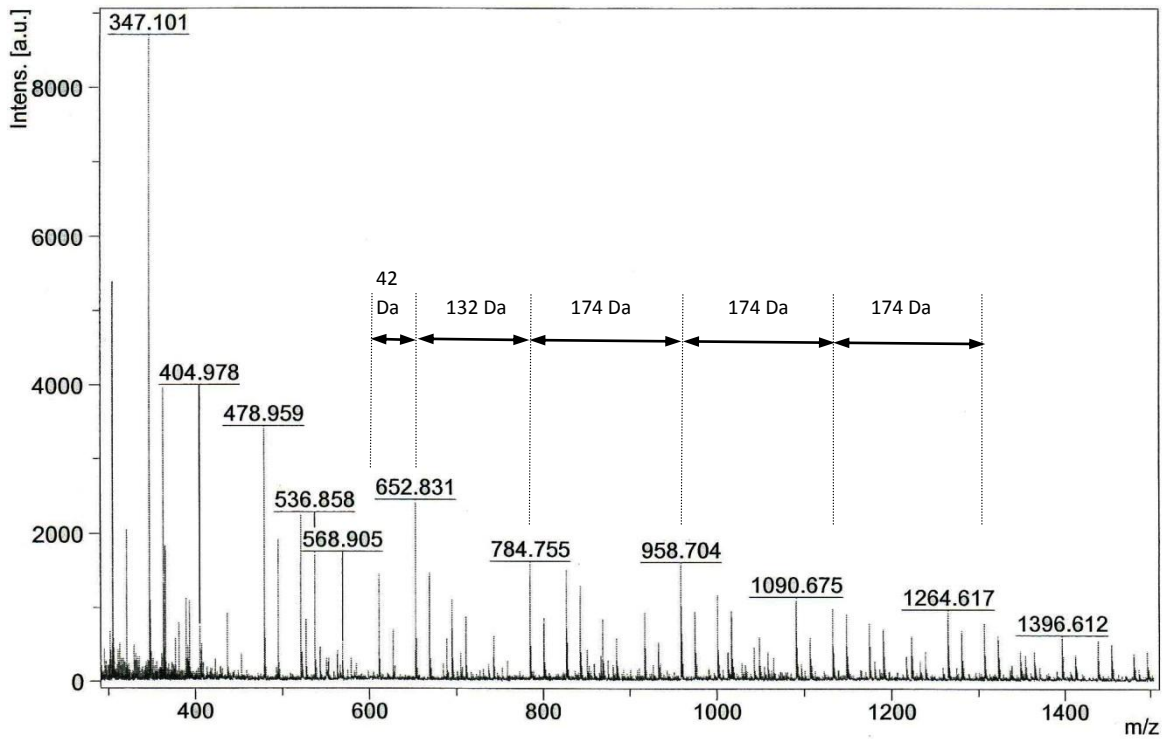


Figure 7.4: Repeating unit of mass spectrum A160 at 30% power increment

Table 7.2: Comparison of MALDI spectra of acetyl xylo-oligosaccharides fragment from extract 160 and Eucalyptus wood (Kabel et al. 2002b)

Eucalyptus $[M+Na]^+$ (Kabel et al. 2002b)	A160 (Observed M ionic)
479	478.959
521	520.920
563	562.888
611	610.862
653	652.831
695	694.807
743	742.791
785	784.755
827	826.739
869	868.724
917	916.717
959	958.704
1001	1000.700
1049	1048.694
1091	1090.675
1133	1132.660

1175	1174.649
1223	1222.630
1265	1264.617
1307	1306.607
1349	1348.598
1397	1396.612
1439	1438.605
1481	1480.605
1529	N
1571	N
1613	N

N = not available

Table 7.3 Sodium and potassium fragmented peaks of extract A160 spectrum at 30% laser intensity

A. $[M+Na]^+$

Group	0	1	2	3	4	5	6	7
E	-	-	389.0	562.9	742.8	916.7	1090.7	1264.6
D	-	**347.1**	**520.9**	694.8	868.7	1042.7	1216.6	1396.6
C	305.1	**479.0**	**652.8**	**826.7**	**1000.7**	1174.6	1348.6	-
B	437.0	**610.9**	**784.8**	**958.7**	**1132.7**	**1306.6**	1480.6	-
A	568.9	742.8	916.7	**1090.7**	**1264.6**	1438.6	-	-
Y	704.8	874.7	1048.7	1222.6	1396.6	-	-	-

B. $[M+K]^+$

Group	0	1	2	3	4	5	6	7
E	-	-	405.0	578.8	758.7	932.7	1106.6	N
D	-	**363.0**	**536.8**	710.8	884.7	1058.7	1238.6	1412.6
C	321.0	**494.9**	**668.8**	**842.7**	**1016.6**	1190.6	1364.6	-
B	452.9	**626.8**	**800.7**	**974.7**	**1148.6**	**1322.6**	1496.6	-
A	578.8	758.7	932.7	**1106.6**	**1280.6**	1454.6	-	-
Y	710.8	884.7	1064.7	1238.6	1412.6	-	-	-

N = not available

The arrangement of acetyl xylose based on peak groups of Table 7.3 could be as shown in Figure 7.5. Some components consist entirely of acetyl xylose repeating unit which attached with each other with starting unit has an additional hydrogen atom. Starting molecule of group D has molecular mass ion of 347.1 Da which probably of acetyl xylose (XylAc, 174 Da) and xylose sugar (Xyl_1, 150 Da) besides Na^+ (23 Da). Components with Na^+ have starting molecule of 305 Da which consist of Xyl_1 and Xyl. Further addition of xylose to $[M + Na]^+$ 305 Da component produced basic molecules at 457,

569 and 705 Da respectively. Similar explanation applied to $[M + K]^+$ mass. The components could vary further with addition of acetyl and xylose unit in many ways.

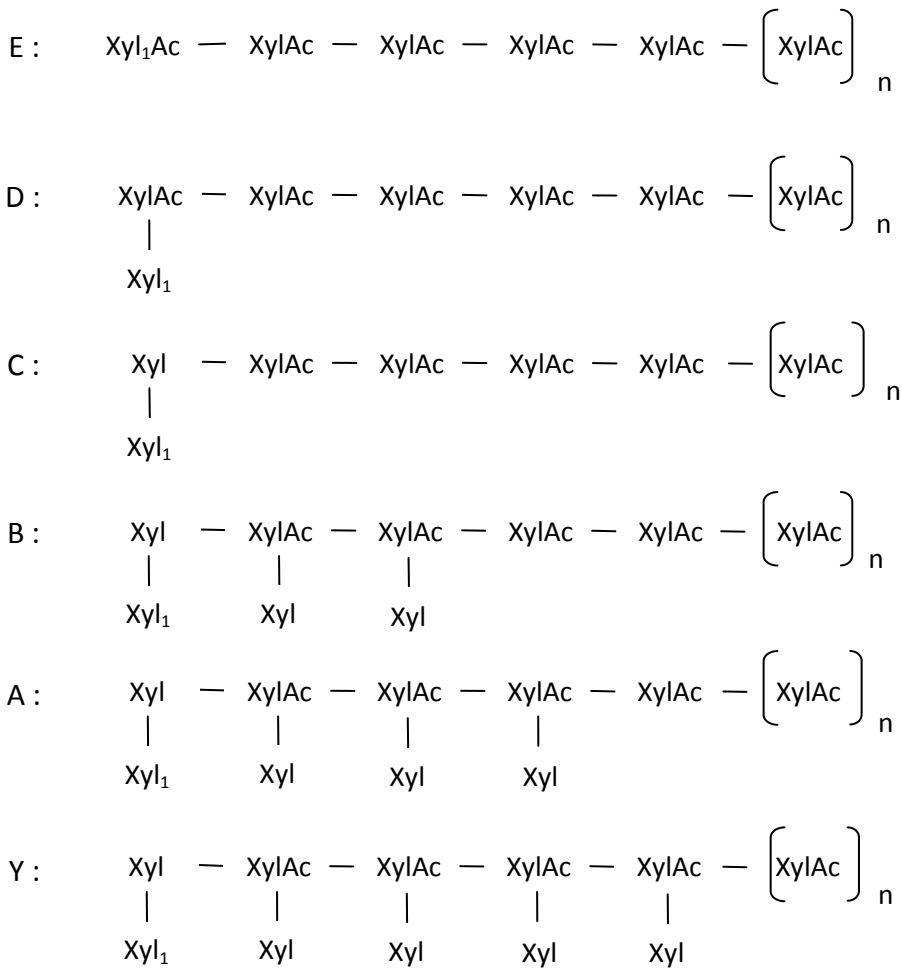


Figure 7.5: Suggested arrangements of acetyl xylo-oligosaccharides components of extract A160

Xylo-oligosaccharides (XO) are sugar oligomers originated from lignocellulosic materials such as wood which have xylan as main hemicellulose polymer. When *Acacia* hybrid wood were heated in water at high temperature (and pressure), catalytic action of hydronium ions from the water ionisation generate acetic acids (Vázquez et al. 2005). The heterocyclic ether bonds of xylan backbone then cleaved to give compounds of low polymerization degree. The XO is possible to be further hydrolysed to sugar. The percentage or quality of XO produced is depending on xylan resources (Kabel et al. 2002a). Xylan from brewery's spent resembles that of wheat bran which mainly substituted with arabinose residues. Xylan from hardwoods is an acetylated 4-*O*-methyl-α-D-glucuronoxylan which almost without any arabinose substitution.

Kabel et al. (2002b) obtained acetylated XO besides gucuronic acids and hexose from hydrothermally treated *Eucalyptus* wood. Presence of diacetylated XO was confirmed by Reis et al. (2005) on acetylated neutral and acidic XO obtained by partial acid hydrolysis of *Eucalyptus globulus* wood glucuronoxylans. Xylo-oligosaccharides substituted with arabinose were released from arabinoxylan from barley and brewery's spent grain (Kabel et al. 2002a). The presence of diacetylated XO was not found in *Acacia* hybrid by the observation in Table 7.3 and Figure 7.5. The wood has high possibility of producing XO without arabinose substitution.

Xylo-oligosaccharides are potential to be used in pharmaceuticals, agricultural products, and food applications (Vázquez et al. 2005; Reis et al. 2005). As food additives and neutraceuticals, XO caused prebiotic effects from their ability to modulate intestinal function (Moure et al. 2006). The raw XO can be refined by physicochemical treatments.

Pair peaks 1174-1013, 1013-851, 867-705, 705-543, 689-527, and 569-407 Da of Figure 7.2C have 162 Da differences which could be of hexose unit loss. Double hexose moiety losses were detected on XO components at ionic peak 851 and 543 Da respectively. Ohbuchi et al. (2009) have analysed XO from eucalyptus and reported the presence of branched hexose and suggested that the hexose may be of galactose based on finding by Shatalov et al. (1999). Similar findings reported by Spina et al. (2000).

The hexose in Table 7.1 could be of basic components residue resulted from the hydrolysis of *Acacia* hybrid at high temperature. It has no structural linkage with the XO. Identification of the hexose is difficult where one is relying on the mass spectrum alone, since it cannot discriminate between different isomers such as galactose, mannose and sucrose as hexose (Kubota et al. 2008).

7.4.2 Mass spectra of extract A80, A100 and A120

The ionic peaks of *Acacia* hybrid extract A80 mass spectrum were almost identical to peaks of extract A100 (Figure 7.6 and 7.7). The mass spectra of extract A120 had a number of close peaks with biggest mass recorded at 1018 Da (Figure 7.8). The poly ethylene glycol (PEG) standard was used as reference and the peaks were identified in

Figure 7.8 by 44 Da mass difference which corresponds to the presence of fragment with formula OCH_2CH_2 (Dale et al. 1996; Ayorinde et al. 2000; Chamrad et al. 2003). The peaks are: 665, 709, 754, 797, 842, 887, 930, 974 and 1018 Da. The PEG was identified on extract A80 and A100 mass spectra as a single peak at 797 Da.

The repeated fragment of 74 Da was observed between 1149 and 1965 Da in A80 and A100 spectra respectively (Figure 7.6 and 7.7). It is highly unlikely that the fragment is from dimethylsiloxane, C_2H_6SiO, from organosilicon polymer which had numerous isotopes. This is not naturally present and could not have contaminated the samples (Maziarz et al. 2002; Bour et al. 2010; Yan et al. 2002; Henkensmeier et al. 2004). It is suggested that the peaks are fragments of carbon-hydrogen-oxygen isotope ions rather than a styryl (Quirk et al. 2007) nor a polyglycerol (Haag et al. 2000) as shown in Figure 7.7.

Most of the peaks in extract A80, A100 and A120 mass spectra are possibly from phenolic compounds besides the PEG. This is likely because reactive phenols were detected as a significant component in the extractives (see stiasny values in Chapter 3). The existence of polymeric phenols in the form of polyflavonoid tannins was observed in the MALDI-TOF spectra of *Acacia mearnsii, A. mangium* and *A. confusa* (Pasch et al. 2001; Hoong et al. 2010; Wei et al. 2010).

The 74 Da repetitive units possibly attached to non repetitive compound mixtures which have massive ionic mass at 1149 Da and partly consist of phenolic compounds. There is possibility that the ionic peaks of A80 and A100 have 148 Da (74 x 2) repetitive fragments between 1149 and 1965 Da caused by at least 2 groups of ionic molecules. One of the groups had an extra 74 Da unit with possible K^+ adduct ionic peaks at 1223, 1373, 1521, 1670, 1817 and 1965 Da. Another group had ionic peaks at 1150, 1297, 1446, 1594, 1743 and 1891 Da. The fragment could be of ferulic acid glycoside moiety which linked to lignan macromolecules (Mattinen et al. 2009; Struijs et al. 2009). The formation of lignan polymers is expected with presence of laccase in which carboxylic acid group is eliminated from the ferulic acid of the lignans. The mass equation of the repetitive unit as follow: 194.06 Da (ferulic acid) – 43.99 Da (CO_2) – 2 ($2H^+$) = 148 Da. The structure of ferulic acid is shown in Figure 7.9.

Lignans are a group of propyl phenolic dimer compounds found in plants. There are many types present in both aglyconic and glycosylated forms as a result of reduction, oxidation, dehydrogenation and addition reactions (Struijs et al. 2009). Examples of lignans are

secoisolariciresinoldiglucoside which abundant in flaxseed (Mattinen et al. 2009) besides pinoresinol, isolariciresinol, matairesinol, *p*-coumaric, sinapic, ferulic acids and ferulate ester (Ford et al. 2001), others such as furanoid lignans, arctigenin and hydroxyarctigenin (Konno et al. 1990; Marco et al. 1992). Lignans found present in phenolic compounds from hot water extraction of plants together with lipophilic substances, diglycerides, resin acid, carbohydrates and lignins (Sun et al. 2003; Örså et al. 1997; MacLean and MacDonald 1967; Ho et al. 2007). The extraction temperature varied between 80 and 190 °C (Sun et al. 2003; Ho et al. 2007). For lignan isolation, the plants are defatted with n-hexane followed by ethanol extraction (Struijs et al. 2009). According to Örså et al. (1997) lignans are released from heartwood rather than sapwood of spruce wood.

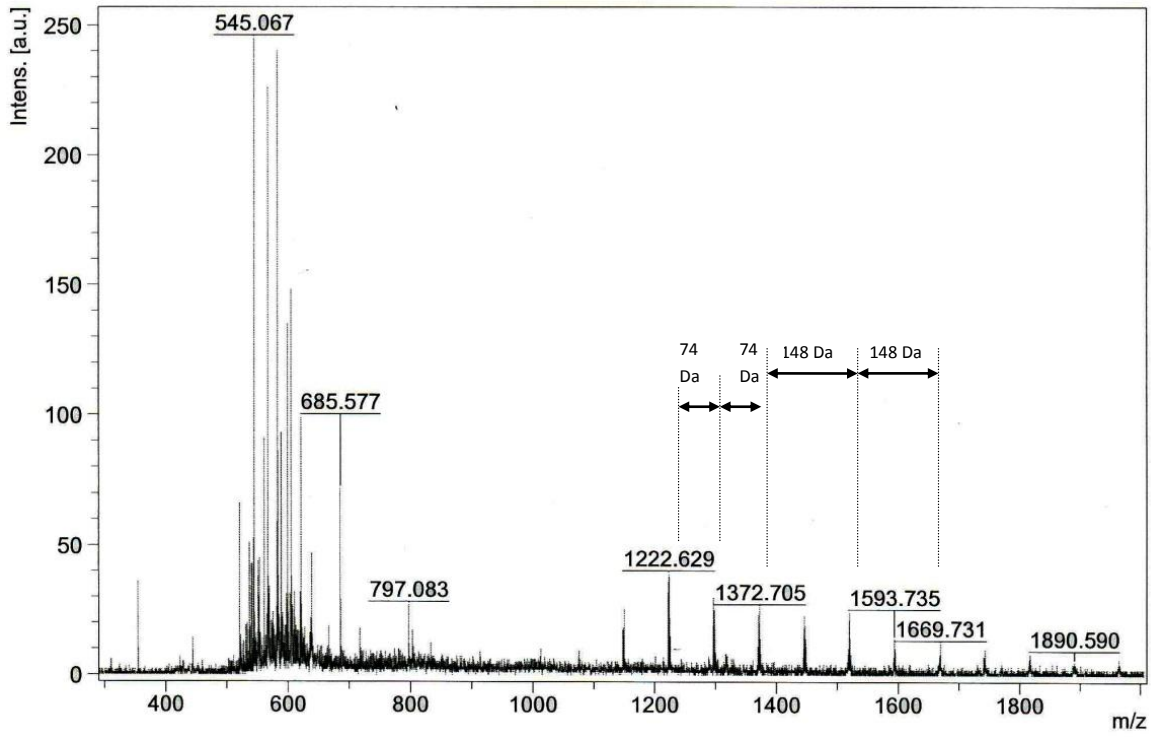


Figure 7.6: MALDI spectrum of extract A80

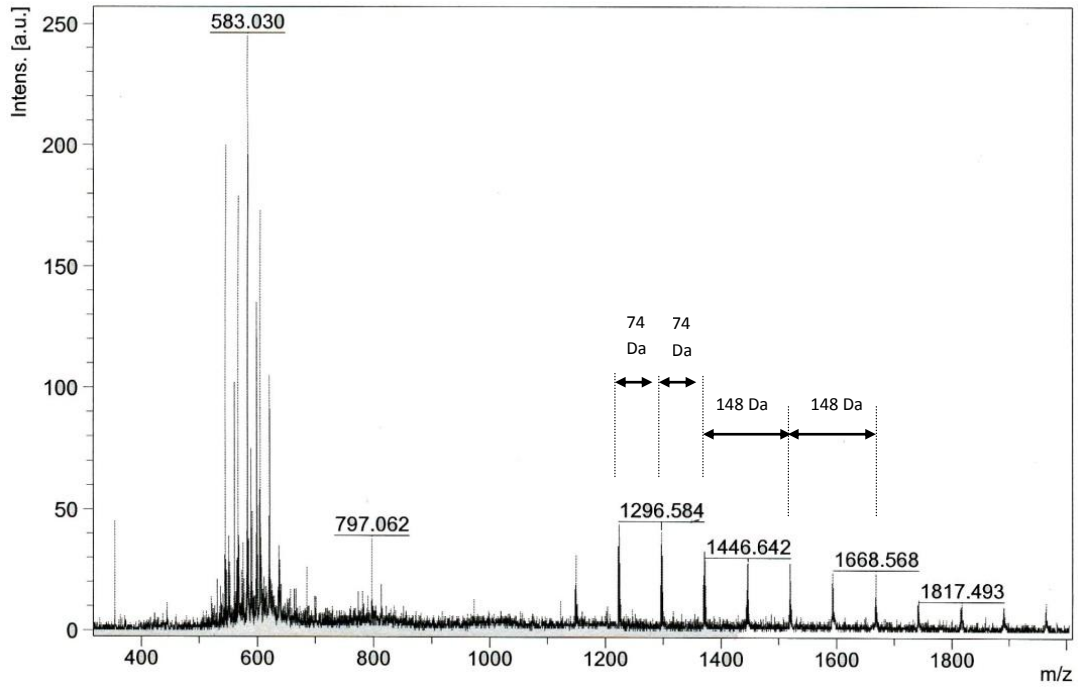


Figure 7.7: MALDI spectrum of extract A100

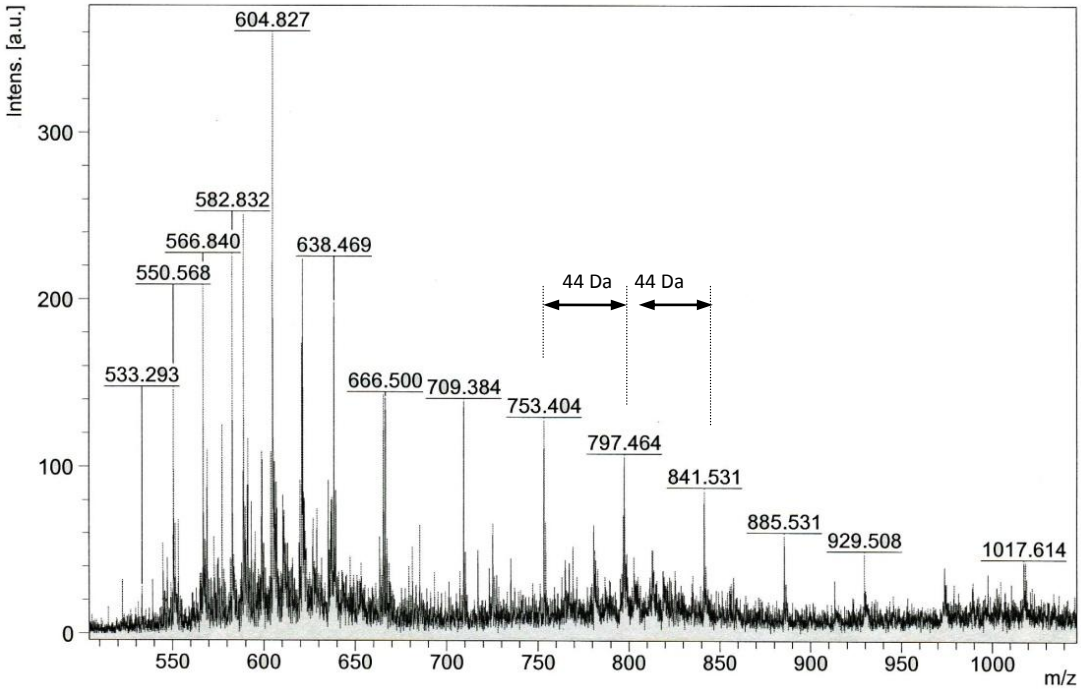


Figure 7.8: MALDI spectrum of extract A120

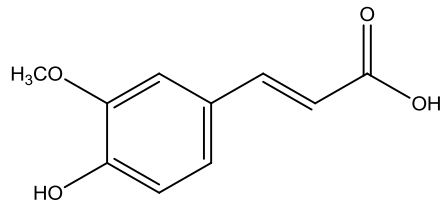


Figure 7.9: Ferulic acid structure

The low molecule mass of extract A80, A100 and 120 were measured by MALDI-TOF between 354 and 797 Da originated from monomers and non repetitive macromolecules (Figure 7.6 – 7.8). The peaks had been linked to molecular mass of known polyphenols (Table 7.4). Four apparent molecular mass with H, Na and K ionic peaks were noticed and labelled as compound A, F, C and B. Compound A had intense peaks at 545, 567 and 583 Da in A80 and A100 spectra even though absent of protonated peak in A120 mass spectrum. It had molecular weight of 544 Da. Compound B and C showed peaks of H, Na and K adducts in all the spectra for 582 and 566 Da molecular mass respectively. The compound C was not immediately noticed because of shared peaks. The ionic peaks of Compound F (molecular weight 560 Da) were apparent in A80 and A100 spectra but absent of H and K adducts peaks in the A120 spectrum. Compound G was observed with $[M+Na]^+$ 621 Da peak besides protonated peak (A80 and A100) and K adduct (A120). Compound D and E had two ionic peaks in the A80 and A120 spectra, and had only one peak from $[M+K]^+$ in extract A160. Some compounds exist as single ionic peak labelled as compound H, J, K, L, M, N, Q and R.

An oxygen unit (16 Da) difference was observed between compounds on series of compounds D-A-F-M and E-C-B-G. By expecting compound A has molecular formula $C_{26}H_{24}O_{13}$ (Matsuzaki et al. 2010), the molecular formula of compound D is calculated as $C_{26}H_{24}O_{12}$, compound F as $C_{26}H_{24}O_{14}$, and compound M as $C_{26}H_{24}O_{15}$. Compound G was possibly $C_{27}H_{34}O_{15}$ (Bae et al. 1994). Therefore compound B has lack an oxygen atom than compound G determined as $C_{27}H_{34}O_{14}$, compound C as $C_{27}H_{34}O_{13}$, and compound E as $C_{27}H_{34}O_{12}$. Compound L lack a carbon (12 Da) than compound E to give molecular formula of $C_{26}H_{34}O_{12}$.

Compound A has similar mass weight with galloyl glycoside known as guavinoside A which first isolated by Matsuzaki et al. (2010) from methanol extract of

Psidiumguajava L. Compound B has 582 Da mass weight similar to phyllaemblicin A, an ester glycoside reported by Zhang et al. (2000). Other phenolic molecules that have same mass weight with formula $C_{33}H_{26}O_{10}$ are biflavonoid (2'',3''-Dihydrorobustaflavone 7,4',7''-trimethyl ether) (Lin et al. 2000), flavonoid (5,3'-Dibenzoyloxy-3,6,7,4'-tetramethoxyflavone) (Díaz et al. 2003), and flavonol glycoside (4`-*p*-hydroxybenzoylisorhamnetin-3-O-α-L-rhamnopyranoside) (Gohar et al. 2009). Compound C has 566 Da molecular mass and calculated to has molecular formula of $C_{27}H_{34}O_{13}$ which similar to armaoside (a lignan glycoside), *erythro*-1-(4-O-*β*-D-glucopyranosyl-3-methoxyphenyl)-2-{2,6-demethoxyl-4-[(E)-formylvinyl] phenoxyl} propane-1,3-diol (Yuan et al. 2005), brunneogaleotoside (Kirmizibekmez et al. 2004), and arbortristoside A (Rathore et al. 1989). The molecular mass of compound F was 560 Da which identical to the mass of 13'-Hydroxy mahuannin A ($C_{30}H_{24}O_{11}$) reported by Rawat et al. (1998), ellagic acid derivatives 4,4'-*O*-dimethylellagic acid 3-(2'',3''-di-*O*-acetyl)-α-L-rhamnoside ($C_{26}H_{24}O_{14}$) (Ito et al. 2002), and galloyl glucoside of molecular formula $C_{26}H_{24}O_{14}$, iriflophenone 2-*O*-(6-*O*-galloyl)-β-D-glucopyranoside (Lee et al. 2010).

The molecular mass of compound D could be related to galloyl glycoside $C_{23}H_{28}O_{14}$ of 8-*O*-Galloyl desbenzoylpaeoniflorin (Tanaka et al. 2000) besides $C_{26}H_{24}O_{12}$ molecule, lack one oxygen atom than compound A resemble toiriflophenone 2-*O*-[6-*O*-(4-hydroxybenzoyl)]-β-D-glucopyranoside (Lee et al. 2010). The compound G mass was similar in weight to 3-O-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-catechin (Bae et al. 1994) and $C_{27}H_{34}O_{15}$ tannin (Okuda et al. 1983).

Compound H, J and Q have molecular weight of 331, 484 and 636 Da and suggested as simple gallotannin or galloyl glycoside known as 1-O-galloyl-β-D-glucopyranose, di-O-galloyl-β-D-glucopyranose, and tri-O-galloyl-β-D-glucopyranose respectively. Gallotannins formed when gallic acid esterifies and binds with polyol carbohydrate such as glucose.

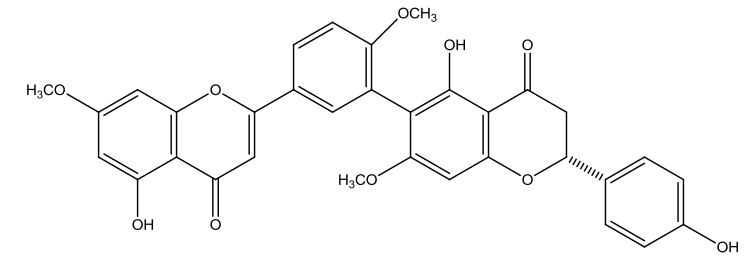
The 538 Da compound was similar in weight with amentoflavone ($C_{30}H_{18}O_{10}$) (He et al. 2008) and lignan glycosides known aslanicepside A and lanicepside B ($C_{26}H_{34}O_{12}$) (Zhou etal. 2007). Lignan glycoside $C_{27}H_{34}O_{12}$ has same molecular weight with compound E

(Machida et al. 2009) whereas ellagic acid 4-*O*-β-D-3’’,6’’-di-*O*-acetylglucopyranoside has same weight as compound M (Gallo et al. 2006).

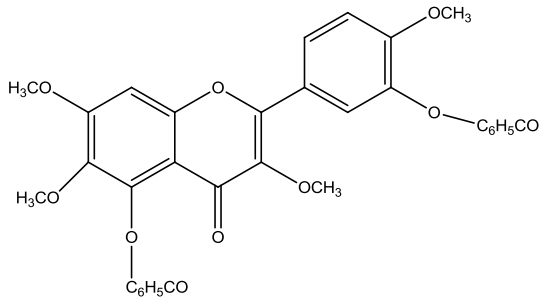
Table 7.4: Possible components in extract A80, A100 and A120 based on MALDI spectra

Comp.	Mw.	Peak				Compound with similar molecular weight		
		Adduct	A80	A100	A120	Name	Formula	Reference
H	332	Na	N	354	354	1-O-galloyl-β-D-glucopyranose	$C_{13}H_{16}O_{10}$	Gao et al. 2008
J	484	K	N	N	523	di-O-galloyl-β-D-glucopyranose	$C_{20}H_{20}O_{14}$	Gao et al. 2008
K	498	Na	521	N	N	Diospyroside B (5,8-dihydroxy-2-methyl[1,4]naphthoquinone-5-O-β-xylopyranosyl (1→6)-β-glucopyranoside)	$C_{22}H_{26}O_{13}$	Cai et al. 2000
D	528	Na	551	N	551	8-*O*-Galloyl Desbenzoylpaeoniflorin	$C_{23}H_{28}O_{14}$	Tanaka et al. 2000
		K	567	567	567	Iriflophenone 2-*O*-[6-*O*-(4-hydroxybenzoyl)]-β-D-glucopyranoside	$C_{26}H_{24}O_{12}$	Lee et al. 2010
L	538	Na	561	561	N	Amentoflavone	$C_{30}H_{18}O_{10}$	He et al. 2008
						Lanicepsides A [(2β,3α,4β)-α-[4-(β-D-glucopyranosyloxy)-3-methoxyphenyl]tetrahydro-2-(4-hydroxy-3-methoxyphenyl)furan-3,4-dimethanol]. Lanicepsides B [(2β,3α,4β)-2-[4-(β-D-glucopyranosyloxy)-3-methoxyphenyl]tetrahydro-α-(4-hydroxy-3-methoxyphenyl)furan-3,4-dimethanol]	$C_{26}H_{34}O_{12}$	Zhou et al. 2007
A	544	H	545	545	N	Guavinoside A	$C_{26}H_{24}O_{13}$	Matsuzaki et al. 2010
		Na	567	567	567			
		K	583	583	583			
E	550	H	551	N	551	(7*S*, 8*R*)-5-methoxydehydrodiconiferyl alcohol 4-*O*-β-D-glucopyranoside	$C_{27}H_{34}O_{12}$	Machida et al. 2009
		K	589	589	589			
F	560	H	561	561	N	13'-Hydroxy mahuannin A	$C_{30}H_{24}O_{11}$	Rawat et al. 1998
		Na	583	583	583	4,4'-*O*-dimethylellagic acid 3-(2'',3''-di-*O*-acetyl)-α-L-rhamnoside	$C_{26}H_{24}O_{14}$	Ito et al. 2002
		K	599	599	N			
						iriflophenone 2-*O*-(6-*O*-galloyl)-β-D-glucopyranoside	$C_{26}H_{24}O_{14}$	Lee et al. 2010
C	566	H	567	567	567	Armaoside	$C_{27}H_{34}O_{13}$	Yuan et al. 2005
		Na	589	589	589	Brunneogaleotoside	$C_{27}H_{34}O_{13}$	Kirmizibekmez et al.

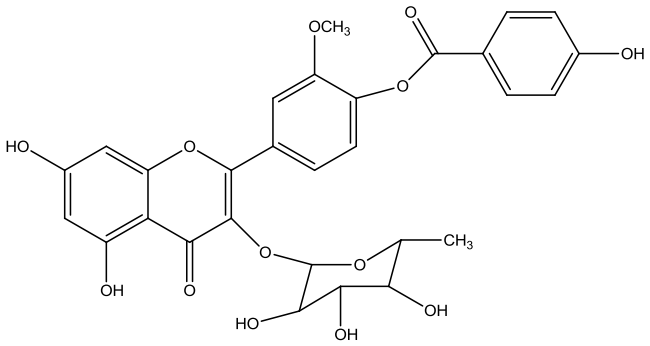
		K	605	605	605			2004
						arbortristoside A	$C_{27}H_{34}O_{13}$	Rathore et al. 1989
M	576	Na	599	599	N	4-*O*-β-D-3’’,6’’-di-*O*-acetylglucopyranoside	$C_{26}H_{24}O_{15}$	Gallo et al. 2006
B	582	H Na K	583 605 621	583 605 621	583 605 621	Phyllaemblicin A	$C_{27}H_{34}O_{14}$	Zhang et al. 2000
						2’’,3’’-Dihydrorobustaflavone 7,4’,7’’-trimethyl ether	$C_{33}H_{26}O_{10}$	Lin et al. 2000
						5,3'-Dibenzoyloxy-3,6,7,4'-tetramethoxyflavone	$C_{33}H_{26}O_{10}$	Diaz et al. 2003
						4`-*p*-hydroxybenzoylisorhamnetin-3-O-α-L-rhamnopyranoside	$C_{33}H_{26}O_{10}$	Gohar et al. 2009
N	594	Na	N	619	N	kaempferol rutinoside	$C_{27}H_{30}O_{15}$	Frison-Norrie and Sporns 2002
G	598	H Na K	599 621 N	599 621 N	N 621 638	3-O-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-catechin	$C_{27}H_{34}O_{15}$	Bae et al. 1994
Q	636	H	N	N	638	tri-O-galloyl-β-D-glucopyranose	$C_{27}H_{24}O_{18}$	Gao et al. 2008
R	647	K	686	N	N	Trigalloylquinic acid	$C_{28}H_{23}O_{18}$	Clifford et al. 2007



A



B



C

Figure 7.10: 582 Da molecular weight compounds: 2’’,3’’-Dihydrorobustaflavone 7,4’,7’’-trimethyl ether (A), 5,3'-Dibenzoyloxy-3,6,7,4'-tetramethoxyflavone (B), and 4`-*p*-hydroxybenzoylisorhamnetin-3-O-α-L-rhamnopyranoside (C)

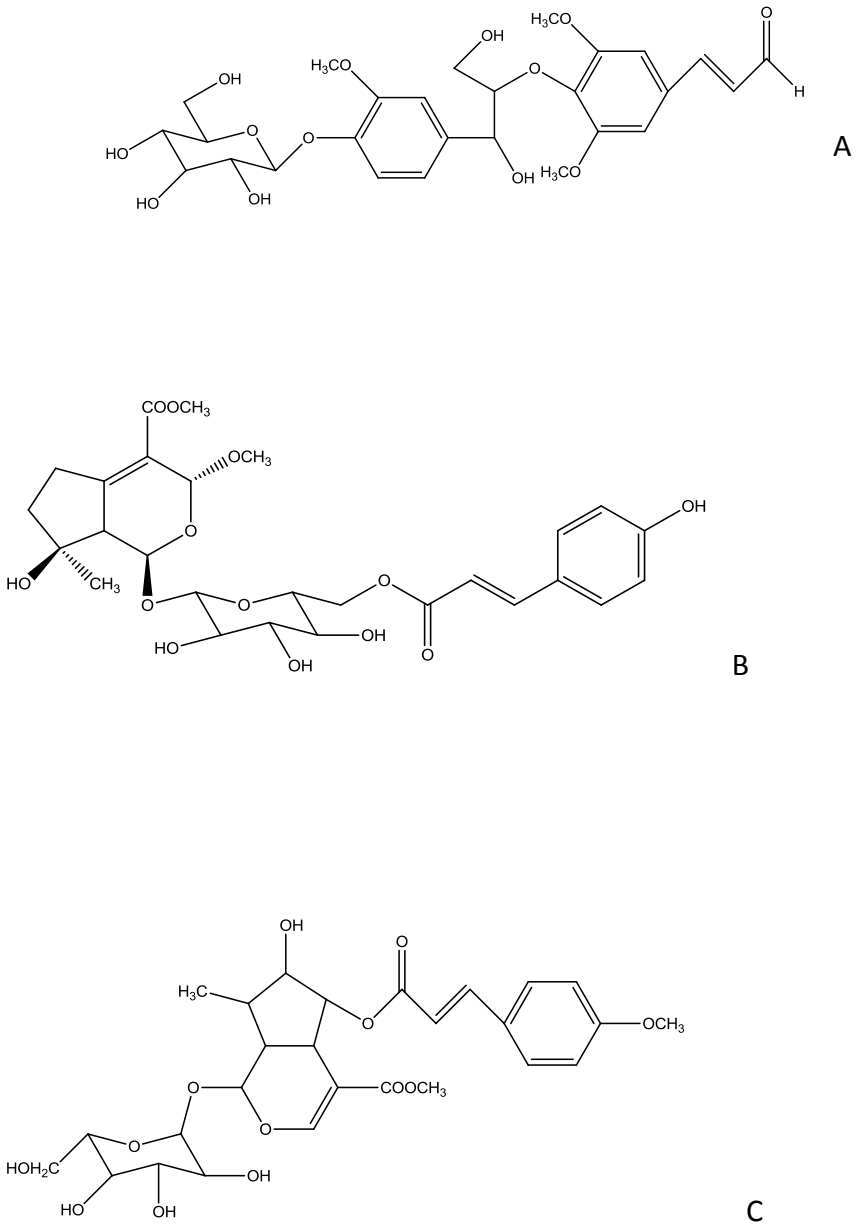
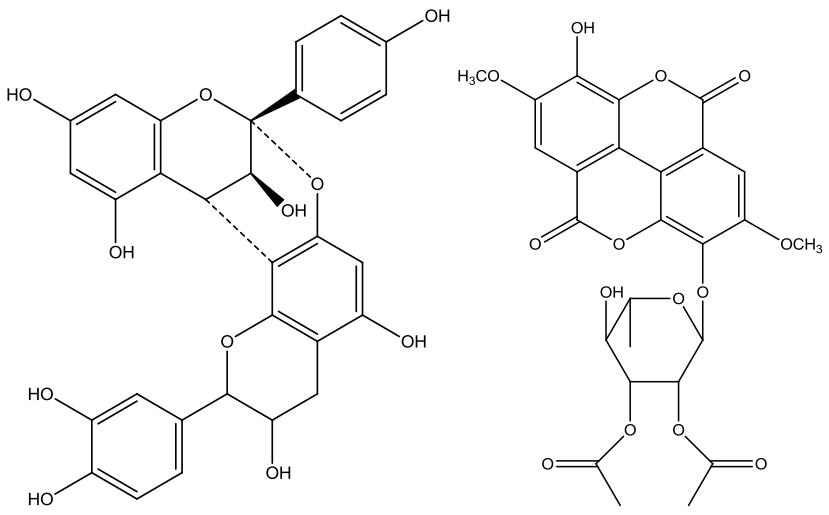
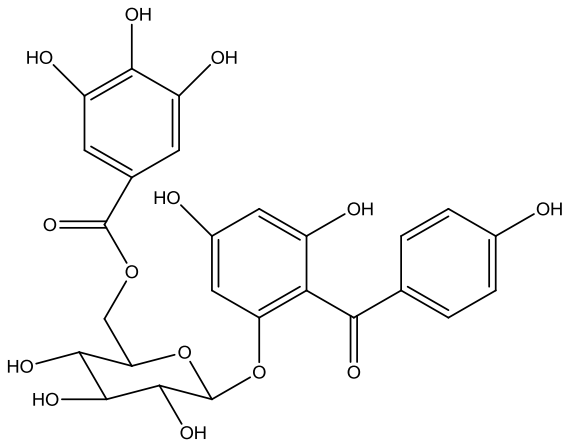


Figure 7.11: 566 Da molecular weight compound: *erythro*-1-(4-O-*β*-D-glucopyranosyl-3-methoxyphenyl)-2-{2,6-demethoxyl-4-[(E)-formylvinyl] phenoxyl} propane-1,3-diol (A),brunneogaleotoside (B), arbortristoside A (C)

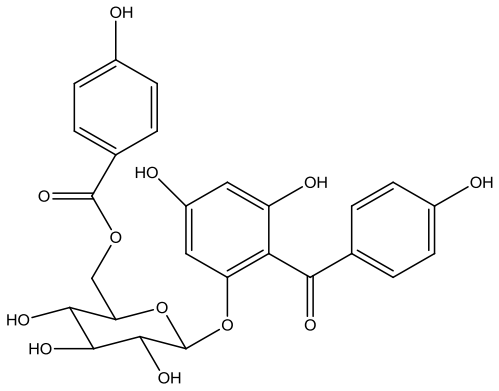


(A) (B)

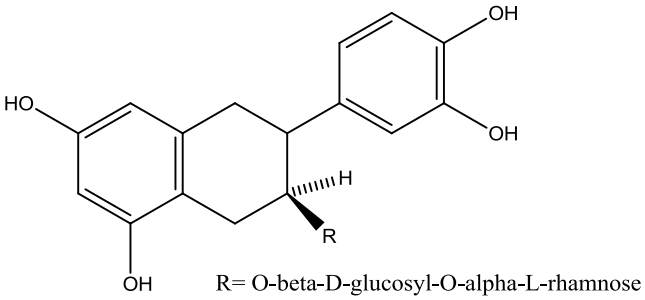


(C)

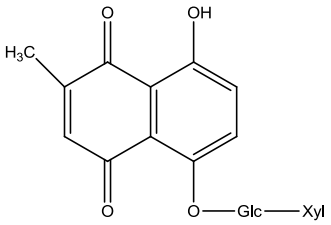
Figure 7.12: 560 Da molecular weight compound: 13'-Hydroxy mahuannin A (A), 4,4’-*O*-dimethylellagic acid 3-(2’’,3’’-di-*O*-acetyl)-α-L-rhamnoside (B), and iriflophenone 2-*O*-(6-*O*-galloyl)-β-D-glucopyranoside (C)



(A)



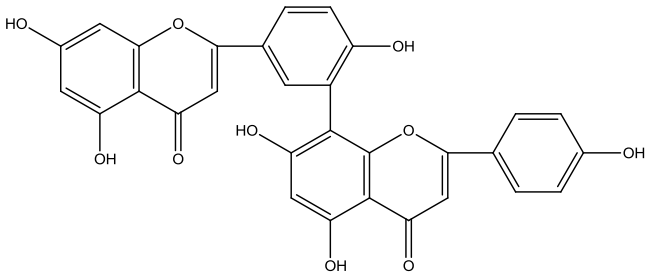
(B)



(C)

Figure 7.13: Iriflophenone 2-*O*-[6-*O*-(4-hydroxybenzoyl)]-β-D-glucopyranoside (A), 3-O-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-catechin (B), and 5,8-dihydroxy-2-methyl[1,4]naphthoquinone-5-O-β-xylopyranosyl (1→6)-β-glucopyranoside (C)

(A)



(B)

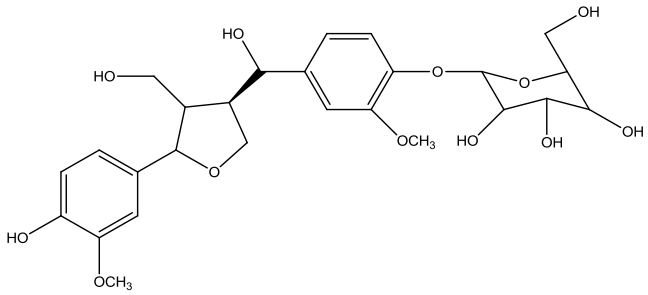


Figure 7.14: 538 Da molecular weight compound: Amentoflavone (A), and (2β,3α,4β)-α-[4-(β-D-glucopyranosyloxy)-3-methoxyphenyl]tetrahydro-2-(4-hydroxy-3- methoxyphenyl)furan-3,4-dimethanol (B)

The *Acacia* hybrid extractives of extract A80, A100 and A120 possibly contained simple polyphenols known as hydrolysable tannins which is phenolic compounds usually in the form of pyrogallol and ellagic acid, and esters of sugar, mainly glucose, with gallic and digallic acids (Pizzi 1983b).

Unlike the above results, polymeric polyphenols known as condensed tannins from *Acacia* species had been detected using MALDI-TOF. The tannins usually consist of groups of repetitive units to make high molecule size such as up to 2400 Da for the case of mimosa tannins (Pasch et al. 2001).

Condensed tannins from mimosa (*Acacia mearnsii*) and *A. mangium* were predominantly consisted with prorobinetinidin with repeat unit of 288 Da combined with profisetinidin (272 Da) and prodelphinidin (304 Da) as shown in Figure 7.15 (Pasch et al. 2001; Hoong et al. 2010). The condensed tannins from *A. confusa* contained high percentage of procyanidin combined with propelargonidin and prodelphinidin (Figure 7.16) (Wei et al. 2010).

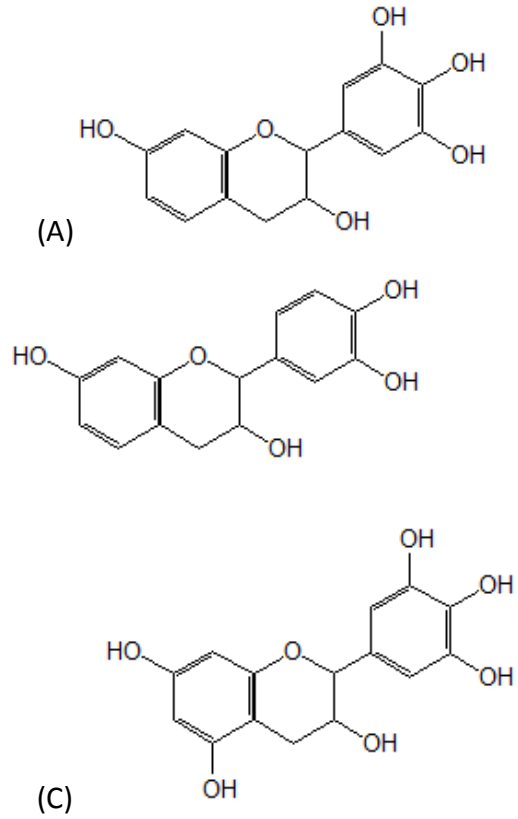
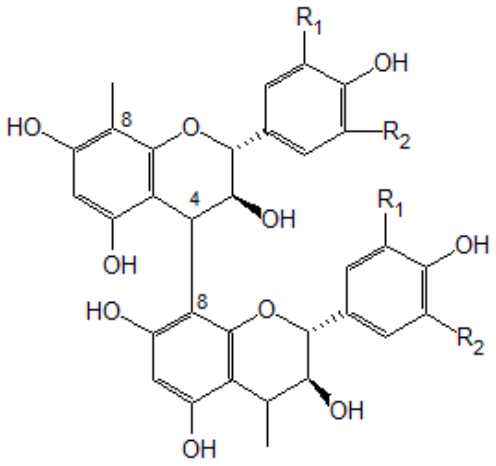


Figure 7.15: Repetitive polyphenols in condensed tannins of *A. mearnsii* and *A. mangium*: (A) prorobinetinidin, (B) profisetinidin and (C) prodelphinidin (Pasch et al. 2001; Hoong et al. 2010)



Procyanidin: R_1 = OH, R_2 = H

Propelargonidin: R_1 = R_2 = H

Prodelphinidin: R_1 = R_2 = OH

Figure 7.16: Condensed tannins *in A. confusa* at C4-C5 linkage (Wei et al. 2010)

Two flavonoids have been found in *A. mangium* which are 2,3-*cis*-3,4',7,8-tetrahydroxyflavanone and teracacidin (Tachi et al. 1989; Pietarinen et al. 2004). Eight

flavonoids have been identified in *A. auriculiformis* heartwood, all having 4',7,8-hydroxylation pattern, and include isoteracacidin (the 2,3-*cis*-3,4-*trans* isomer) and 4',7,8-trihydroxyflavanone, in addition to the two reported for *A. mangium* (Drewes and Roux 1966).

Methanol extracts of *A. mangium* and *A. auriculiformis* contained three flavonoids (2,3-trans-3,4',7,8-tetrahydroxyflavanone, teracacidin, and 4',7,8-trihydroxyflavanone) which were purified and identified by nuclear magnetic resonance spectroscopy by Barry et al. (2005) (Figure 7.17). Besides, melacacidin compound was identified from the extracts by comparing with known compounds from *A. melanoxylan*.

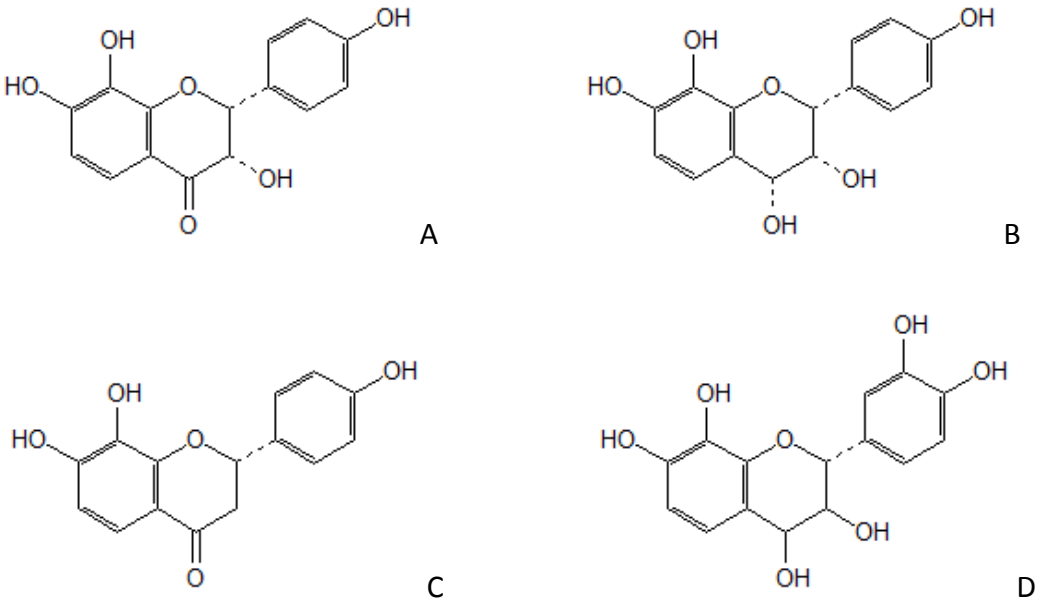


Figure 7.17: Flavonoids from methanol extracts of *A. mangium* and *A. auriculiformis*: 2,3-trans-3,4',7,8-tetrahydroxyflavanone (A), teracacidin (B), 4',7,8-trihydroxyflavanone (C) and melacacidin (D) (Berry et al. 2005; Kar 2003)

7.5 Conclusion

The characterisation of *Acacia* hybrid extractives was performed using MALDI-TOF mass spectrometer. Analysis showed that the chemical contents of the extractives were varied. Extracts obtained between 80 and 120 °C contained compounds with molecular weight between 332 and 647 Da. The compounds were probably of simple polyphenols primarily of galloyl glycosides, lignan glycosides and flavonoids. Four

major compounds were considered with molecular weights of 544, 560, 566, and 582 Da. The A80 and A100 extracts contained polymers with repetitive unit of 74 or 148 Da which is likely from ferulic acid of lignans. The extract A160 obtained at high temperature, produced two different compounds than the others. Hexose polymers with up to eight repetitive units were observed with 162 Da fragment unit at 60% laser power. Another group of ionic peaks found when the laser power was reduced to 30%. The peaks had a similar trend as obtained by Kabel et al. (2002b) and have 174 Da fragmentation identified as acetylxylose. A total of six groups of acetylxylo-oligosaccharides were identified from the spectrum of extract A160. The results suggested that high extraction temperature (160 °C) affected the composition of the extractives. This is supported by extractives recovery data in Chapter 3.

CHAPTER 8

FINAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

8.1 Final discussion

In this work exceptional performance was noted in boards made from *Acacia* hybrid furnish. The boards have high physical (TS, water absorption) and mechanical (IB, MOE and MOR) strengths surpassing boards of recycled wood and spruce. The high strengths could be related to the wood itself. It was hypothesised that this could be explained by resin-extractive interactions.

In field studies, *A. auriculiformis* and *Acacia* hybrid trees appear to have better resistance to decay than *A. mangium* as reported by Lee (2002). This is supported by Mihara et al. (2005) in which extractives of *A. auriculiformis* showed higher antifungal activity than *A. mangium*. *Acacia auriculiformis* contained higher levels of flavonoids i.e. 3,4',7,8-tetrahydroxyflavanone and teracacidin with antifungal capability. The flavonoids content in *A. auriculiformis* was about five times higher than *A. mangium* (Barry et al. 2006). Decay test of the wood showed that the decay resistance of *A. mangium* to *T. versicolor* and *G. trabeum* are of moderately resistant and not resistant depending on the wood sources (Salmiah and Amburgey 1993). *Acacia auriculiformis* showed 2% weight loss in heartwood and 22% in sapwood due to decay by *Schizophyllum communie* (Ashaduzzaman et al. 2011). In contrast particleboards from *Acacia* hybrid were susceptible to decay fungi. The decay decreased when *Acacia* hybrid boards were bonded with phenol formaldehyde resin. Besides as acting as binder, part of the resin might be polymerised in the wood giving some degree of water resistance. Particleboards deteriorate when exposed to decay fungi under suitable conditions (moisture content above 20%, suitable temperatures and aeration, mineral nutrients) except by applying treatments to the boards (Imamura et al. 1986; Kajita and Imamura 1991; Clausen et al. 2001; Nemli et al. 2005).

Extraction work was done to the wood in order to evaluate the resin–extractive interactions. The extraction temperature of hot water *Acacia* hybrid extractives

effected the extractives composition. The amount of reactive polyphenols was high when the extraction temperature less than 100 °C and decreased at higher temperature. This is supported by study by Makino et al. (2009) on the bark of four tropical species which showed that the yield and total polyphenolics content of the extracts increased with increase in extraction temperature from 20 to 100 °C. The total polyphenolics at 100 °C from the barks were between 5.3 and 14.2% based on Folin-Ciocalteu method. The total sugar contents were almost constant at 20-80 ^{o}C but increased substantially at 100 °C. Water extraction at 80 °C was suggested to produce polyphenols with low sugar content.

Duan et al. (2005) suggested optimum conditions for the extraction of tannins from bark at time 30 min, temperature 140 °C, and water volume 75 ml (for 1 g wood meal). The total phenols content obtained under these conditions was 25.3% (Folin-Ciocalteu method). The phenolic contents markedly reduced with increased temperature to 180 °C suggesting that too high a temperature leads to conversion or degradation of the polyphenols. In the *Acacia* hybrid study, the amount of reactive polyphenols was markedly reduced at lower temperature (120 °C) probably due to longer time applied i.e. 2 hours.

Analysis of the hot water *Acacia* hybrid extractives using MALDI-TOF suggests that low temperature extractives (A80) may consist of simple polyphenols primarily of non repetitive galloyl glycosides, lignans and flavonoids. No polymeric polyphenols in the form of condensed tannins oligomers were observed. The composition of polyphenols depends on the extract solvent and the type of wood. Foo (1984) isolated flavonoids and condensed tannins from the heartwood of *Acacia baileyana* from methanol extraction. Few flavonoids have been obtained from the methanol and acetone extracts of *A. mangium* heartwood and knot (Tachi et al. 1989; Pietarinen et al. 2005), whereas Barry et al. (2005) isolated three flavonoids from methanol extracts of *A. mangium* and *A. auriculiformis* heartwood. Polymeric condensed tannins mostly occur in the bark of *Acacia* species and can be easily extracted by using hot water. Six types of proanthocyanidin dimers from the bark of *Acacia mearnsii* have been isolated by hot water (Duan et al. 2005). The characteristics of condensed tannins oligomers have been identified from hot water extractives of *A. mangium* bark (Hoong et al. 2010).

Addition of *Acacia* hybrid extractives with urea formaldehyde resin improved the gluing of wood veneers to some extent. This only occurred using extract A80 at high percentage of solids (8%). The availability of polyphenols in the extractives might contribute to additional bonding property by reacting with UF resin components. This possibly happened at initial stage of the resin curing during free formaldehyde emission and water condensation as supported by the TGA spectra (Figure 6.11). Subtle weight loss occurred probably as result from the reaction between the polyphenols and UF components.

The polyphenols of wood extractives have the potential for use as or as components of adhesives. Mostly were in the form of condensed tannins preferably due to its chemical suitability (polymeric structure) besides commercially available at vast volume (Pizzi 1982). The tannins were mostly available from the bark of mimosa, quebracho and radiata pine (Kim and Kim 2003), and have been used industrially for the manufacture of exterior wood panels (Trosa and Pizzi 2001). Physical, chemical and mechanical properties of pine and wattle tannin based adhesives have been extensively studied (Kim and Kim 2003; Kim et al. 2003). Acceptable properties of plywood have been successfully produced with phenol formaldehyde binder fortified with sulfited tannin from the bark of *A. mangium*.

According to Pizzi (1982), the reaction of condensed tannins with formaldehyde is normally expected on flavonoid (flavan-3-ols) units. The nucleophilic centres of the A ring of flavonoid unit tend to be more reactive than those found on the B ring due to the vicinal hydroxyl substituents which cause general activation in the B ring without any localized effects as those found in the A ring. Formaldehyde reacts with tannins to produce polymerisation through methylene bridge linkages to reactive positions of the flavonoid units, mainly at the A rings. The reaction of hydrolysable tannins with formaldehyde is different to condensed tannins due to structural differences. The hydrolysable tannins are mixtures of simple phenols such as pyrogallol and ellagic acid, and of esters of sugar, mainly glucose with gallic and digallic acids. Their chemical behaviour is similar to that of simple phenols toward formaldehyde.

Therefore the reactions of polyphenols of *Acacia* hybrid extractives with UF resin components probably occur in two ways as explained by Pizzi (1982). The non

repetitive flavonoid units possibly interact with formaldehyde at A rings of the flavonoid to produce methylene bridge linkages (Figure 8.1), whereas the galloyl glucoses react with formaldehyde as simple phenols (Figure 8.2). Since the flavonoids and other polyphenols were largely non polymeric, the methylene linkages molecules could have short chains and fewer branches. The methylolated phenols were condensed (Garro Galves et al. 1996; Takano et al. 2008) to produce polymers which explains the subtle weight loss occurring in the resin mixtures shown in TGA spectrum.

Besides the reaction of polyphenols with formaldehyde, there also a possibility of interaction of polyphenols with the urea formaldehyde resins producing polyphenol-urea formaldehyde condensates as suggested by Pizzi (1979). The interaction however involves several stages which are quite complex.

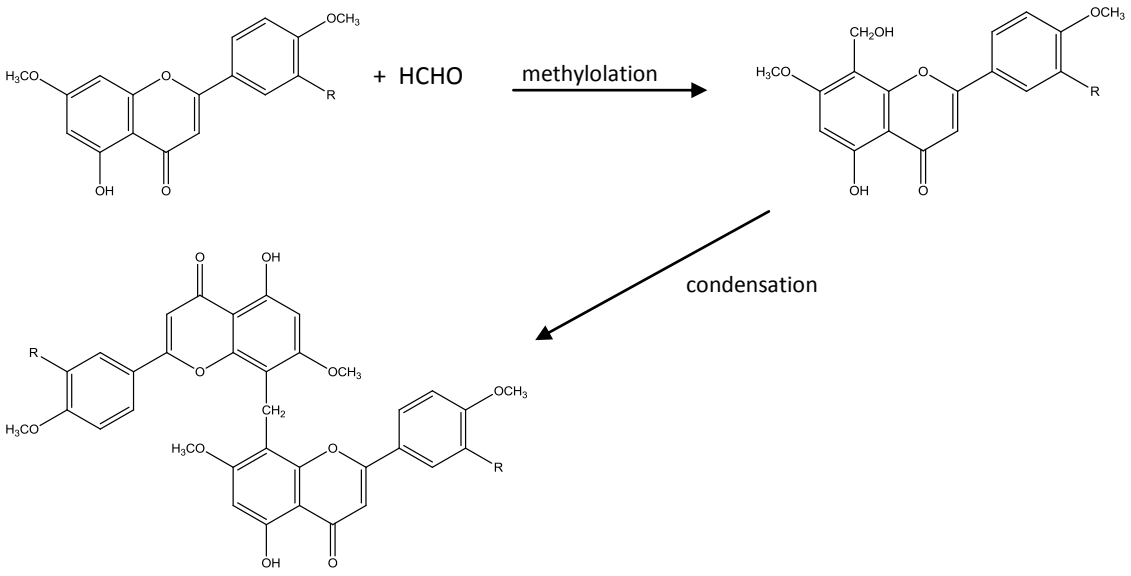


Figure 8.1: Example of flavonoid (flavones) and formaldehyde reaction

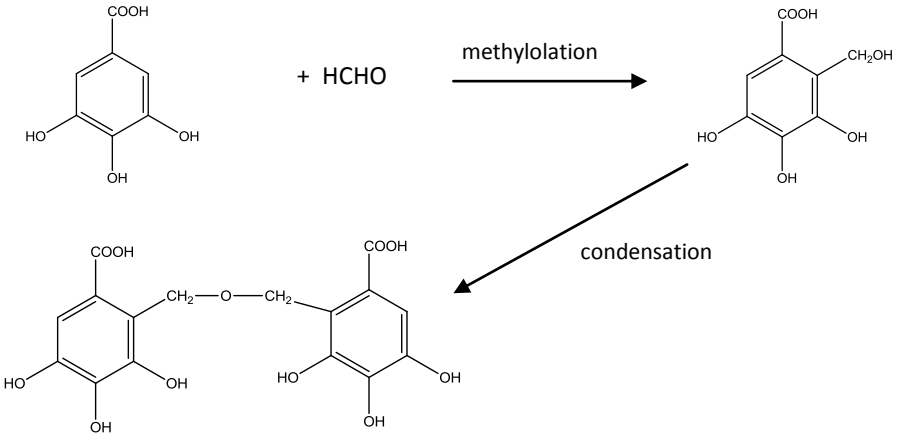


Figure 8.2: Example of simple phenol (gallic acid) and formaldehyde reaction

8.2 Conclusions

The wood of *Acacia* hybrid wood has been successfully processed and turned into particleboards. The wood has medium density of 446 kg m^{-3} which within the value reported by previous researchers. It has good dimensional stability as compared to pine and has low buffering capacity which would not cause difficulty when applied with acid sensitive adhesive.The amount of reactive polyphenols in hot water extractives of *Acacia* hybrid decreased at extraction temperatures of 120 °C and over.

Particleboard from *Acacia* hybrid with urea formaldehyde resin binder showed better physical and mechanical properties than the recycled wood board. Although the increased slenderness ratio of *Acacia* hybrid particles would have had an effect on the MOE and MOR of the panels, it should be noted that the internal bond strength of the *Acacia* hybrid particleboard was higher than that of the recycled wood. Particleboards with melamine urea formaldehyde and phenol formaldehyde resins as binder and spruce material were compared with the boards of urea formaldehyde resin. The *Acacia* hybrid boards bonded with UF, MUF and PF resins have better moisture resistance than the boards from recycled wood and spruce. Board bonded with PF resin has better moisture resistance followed by board with MUF resin. The *Acacia* hybrid boards have high IB strength using the resins.

Decay tests of the boards showed that better decay resistance was achieved when the boards were bonded with PF resin compared to boards with UF and MUF resins. The

PF board was dimensionally stable and has high degree of internal bond strength even after decay fungi exposures. The only small deterioration in PF board properties observed when exposed to *P. ostreatus* and *C. puteana*. Besides gluing the wood, some of the PF resin possibly impregnated into the wood to give some degree of resistance to moisture thus to decay fungi too. It is concluded that the type of resin or treatment applied have important role to improve decay resistance of particleboard rather than the type of wood itself.

Investigation of the effect of extractives to urea formaldehyde resin for wood gluing was carried out. The UF resin has low buffering capacity which indicates the resin's stability for use as a wood binder. Addition of *Acacia* hybrid extractives has not affected the resin acidity as well the gel time. The shear strength determination of beech veneers was influenced by the total water content in the UF resin mixtures. Significant improvement in shear strength showed after the *Acacia* hybrid extractives (extract A80) was added into the UF resin at concentration of 8%. It is suggested that the amount of reactive polyphenols in extractives has some contribution to wood gluing.

Reaction of *Acacia* hybrid extractives with UF resin is suggested from the thermal gravimetric analysis which showed that the UF resin has significant weight loss when added with the extractives (extract A80). This is supported by the exothermic peaks temperature shown in the DSC spectrum. Analysis with the FTIR spectrophotometer has not showed anything peculiar with the mixture's structural peaks.

Analysis of *Acacia* hybrid extractives with MALDI-TOF mass spectrometry revealed that composition of the extractives varied with the extraction temperature. The high temperature extraction (160 °C) contained hexose polymers and acetyl xylo-oligosaccharides. The A80 and A100 extractives had polymers with 74 Da or 148 Da repetitive units in which the later could be of ferulic acid. The A80, A100 and A120 extractives has small molecular weight ionic peaks which could be related to simple polyphenols of galloyl glycosides, lignan glycosides and flavonoids.

Reaction of non repetitive polyphenols with formaldehyde possibly occurred that produce additional bonding in the wood as shown by shear strength test. The reaction could be between flavonoid unit and simple phenols with the free formaldehyde in UF

resin which involved the methylolation and condensation processes as shown in Figure 8.1 and Figure 8.2. This is supported by the significant initial weight loss in the UF and extractives mixture during the thermal analysis.

8.3 Recommendations

Further study is suggested to investigate the extractives constituents of *Acacia* hybrid using extraction solution others than water such as hexane and methanol. The extractives could be isolated by column chromatography then identified using mass spectrometry, HPLC and nuclear magnetic resonance.

Besides for wood gluing, the isolated extractives of *Acacia* hybrid could be evaluated for decay resistance and antioxidant potency. The effect of heartwood and sapwood should be considered. Extractives with antioxidant capable molecules are capable of inhibiting the oxidation of other molecules. Oxidation reactions can produce free radicals which in turn can start chain reactions and consequently cause damage if occurs in a cell. Antioxidants terminate these chain reactions by removing free radical intermediates and inhibit other oxidation reactions.

The effect of extraction temperature to the compositions of water extractives can be investigated. The compositions include reactive polyphenols (stiasny method), total phenols (Folin-Ciocalteu method), glucose contents, lignin, and cellulose contents. It is expected to get variation in the extractives compositions as the temperature varied. Therefore suitable extraction parameters for specific components isolation can be suggested.

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APPENDICES

Table 1: Distribution and dimension of *Acacia* hybrid and recycled wood particles

	Particles[3]	Mesh opening (mm)						
		x>3.35	3.35> x>2.8	2.8>x> 1.4	1.4>x> 1.0	1.0>x> 0.6	0.6>x> 0.25	x<0.25
Distribution (%)	AH	11.1	6.5	39.8	15.6	21.2	4.8	1.0
	RW	4.0	11.0	62.4	11.7	8.9	1.0	0.5
Length[1] (mm)	AH	30.91	25.60	16.83	10.40	8.18	-	-
	RW	24.14	18.29	14.57	9.30	7.31	-	-
Width[1] (mm)	AH	3.43	3.26	2.55	1.02	0.92	-	-
	RW	3.10	3.07	2.36	1.25	0 .80	-	-
Thickness[1] (mm)	AH	0.98	1.07	1.13	0.63	0.43	-	-
	RW	1.76	1.80	1.32	0.63	0.43	-	-
Slenderness ratio[1,2]	AH	38.23	26.95	16.05	17.62	20.10	-	-
	RW	14.53	11.10	11.68	16.09	17.72	-	-

[1] Average of 20 particles. [2] Slenderness ratio is length over thickness of individual particles

[3] AH = *Acacia* hybrid, RW = recycled wood.

Table 2: Immersion of particleboards of Acacia hybrid, spruce and recycled wood

Board	Thickness swelling (%)		Water absorption (%)	
	2 hour	24 hour	2 hour	24 hour
Acacia hybrid UF	2.69 c (0.32)	11.22 c (1.34)	0.83 cd (0.74)	18.78 cd (2.35)
Acacia hybrid MUF	1.89 cd (0.64)	7.49 cd (1.52)	0.25 d (1.12)	15.81 d (4.44)
Acacia hybrid PF	0.68 d (0.55)	5.15 d (1.28)	4.16 c (2.38)	24.60 c (4.55)
Recycled wood UF	5.97 b (1.14)	23.94 b (4.96)	5.30 b (1.30)	43.87 b (7.21)
Spruce MUF	25.21 a (2.75)	28.42 a (3.00)	73.42 a (4.63)	83.74 a (3.84)

In parentheses is standard deviation.
Number with same letter within the same column is not significantly different at 95% confidence levels.

Table 3: Mass loss of decay wood particles compared to beech and pine

Wood	Mass loss (%)				
	P. ostreatus	*T. versicolor*	*P. sanguineus*	*C. puteana*	Control
Acacia hybrid particles	2.18 b (1.20)	3.09 c (1.17)	3.45 b (1.58)	20.62 b (9.44)	0.22 a (3.17)
Spruce particles	1.50 b (1.05)	0.60 c (1.17)	2.22 b (0.90)	40.18 a (11.79)	-0.16 a (0.39)
Beech	16.94 a (3.88)	38.06 a (6.25)	45.62 a (12.63)	32.56 ab (7.55)	-0.07 a (0.09)
Pine	1.98 b (0.56)	16.20 b (4.92)	10.72 b (5.90)	29.93 ab (5.49)	-0.21 a (0.35)

In parentheses is standard deviation.
Number with same letter within the same column is not significantly different at 95% confidence levels.

Table 4: Moisture content of decay wood particles compared to beech and pine

Wood	Moisture content (%)				
	P. ostreatus	*T. versicolor*	*P. sanguineus*	*C. puteana*	Control
Acacia hybrid particles	23.01 b (4.22)	26.04 c (4.23)	28.56 b (6.79)	31.79 a (17.76)	20.67 b (1.90)
Spruce particles	27.59 ab (6.74)	29.59 bc (4.32)	27.96 b (1.62)	36.49 a (21.39)	25.17 ab (3.65)
Beech	33.72 a (8.92)	36.89 ab (6.91)	62.42 a (30.01)	40.30 a (25.20)	27.08 a (3.17)
Pine	28.00 ab (5.06)	39.17 a (9.14)	42.12 ab (14.51)	39.86 a (23.99)	27.82 a (4.10)

In parentheses is standard deviation.
Number with same letter within the same column is not significantly different at 95% confidence levels.

Table 5: Mass loss of particleboards exposed to decay fungi

Board	Mass loss (%)					
	Control	Sterile control	*P. ostreatus*	*T. versicolor*	*P. sanguineus*	*C. puteana*
Acacia hybrid UF	0.001 (0.050)	0.06 (0.06)	16.58 (0.71)	26.68 (10.34)	15.89 (4.97)	37.27 (3.11)

Acacia hybrid MUF	-0.001 (0.081)	0.15 (0.18)	14.84 (1.29)	32.02 (3.51)	14.88 (4.03)	30.32 (6.45)
Acacia hybrid PF	0.08 (0.06)	0.14 (0.09)	8.25 (0.92)	1.52 (0.33)	1.43 (0.30)	1.12 (0.22)
Recycledwood UF	-0.02 (0.05	0.15 (0.13)	22.39 (2.09)	23.61 (6.38)	12.89 (4.79)	47.37 (1.66)
Spruce MUF	0.05 (0.03)	-0.05 (0.16)	20.20 (1.18)	7.04 (5.57)	9.35 (3.21)	53.42 1.93

Table 6: Shear strength of beech veneers bonded with urea formaldehyde resin (UF) added with *Acacia* hybrid extractives (A100)

Time (s)	Resin	Mean (MPa)	N	Std. Deviation
40	A100	4.3236	11	0.33842
	Control	4.1140	10	0.29645
60	A100	3.9914	11	0.33940
	Control	4.0195	10	0.49760
80	A100	4.1291	9	0.38132
	Control	4.4200	10	0.36491

Table 7: Shear value of treated veneers bonded with urea formaldehyde resin

Treatment	Mean	N	Std. Deviation
Acacia hybrid	4.2767	10	0.66180
Water	4.1209	9	0.42849

Table 8: Shear value of veneers bonded with urea formaldehyde resin added with *Acacia* hybrid extractives (A100, 4% solids)

Time (s)	Resin	Mean (MPa)	N	Std. Deviation
60	A100	3.9618	9	0.51206
	Control	3.3677	9	0.30367
80	A100	3.9888	8	0.47205
	Control	4.0037	10	0.33272

Table 9: Shear strength of veneers bonded with urea formaldehyde resin with aqueous additives

Resin	Mean (MPa)	N	Std. Deviation
Control	6.4502	6	0.39970
Acacia hybrid	4.4705	6	0.30702
Water	4.1608	6	0.61404

Table 10: Shear strength of veneers bonded with urea formaldehyde resin with *Acacia* hybrid extractives (A80 and AM)

Time (s)	Resin	Mean (MPa)	N	Std. Deviation
60	Control	3.9047	6	0.34946
	A80	4.4848	8	0.44388
80	Control	4.1884	6	0.37167
	A80	4.4459	5	0.17036
	AM	3.9501	5	0.28284

Table 11: Shear strength of veneers bonded with urea formaldehyde resin with *Acacia* hybrid extractives (A80, A100 and AA)

UF solids (g)	Extractives	Mean (MPa)	N	Std. Deviation
0.0158	Control	5.2033	6	0.79962
	A80	6.7604	6	0.56364
	A100	5.7238	6	0.92423
	AA	5.7420	6	0.62728
0.0205	Control	6.0410	6	0.54698
	A80	8.1887	6	0.70235
	A100	6.5433	6	1.00747
	AA	7.2371	6	0.62484

Table 12: Shear strength of veneers bonded with urea formaldehyde resin with 1.5% w/w 8% *Acacia* hybrid extractives at 0.5%w/w 10% ammonium chloride

Resin mix.	Mean (MPa)	N	Std. Deviation
Control	4.0431	8	0.50974
A80	5.1678	8	0.51131
A100	4.5488	8	0.48470
A120	4.3709	8	0.42496

A160	3.8791	8	0.34574

Table 13: MALDI spectra sodium and potassium fragmented peaks of extract A160

A. Calculated $[M + Na]^+$of A160

	0	1	2	3	4	5	6	7
E			389	563	737	911	1085	1259
D		347	521	695	869	1043	1217	1391
C	305	479	653	827	1001	1175	1349	
B	437	611	785	959	1133	1307	1481	
A	569	743	917	1091	1265	1439		
Y	701	875	1049	1223	1397			

B. Calculated $[M + K]^+$of A160

	0	1	2	3	4	5	6	7
E			405	579	753	927	1101	1275
D		363	537	711	885	1059	1233	1407
C	322	496	670	844	1018	1192	1366	
B	453	627	801	975	1149	1323	1497	
A	585	759	933	1107	1281	1455		
Y	717	891	1065	1239	1413			