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Forestry Commission**

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Opportunities for UK grown
timber: Wood Modification state
of the art review

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Executive Summary

This Client Report presents a review of the current state of the art for Wood Modification and identifies opportunities for UK grown timber. The study was funded jointly by DTI and the Forestry Commission. The DTI funding was part of the CD Framework project cc 2115 entitled "Best value from UK timber in construction" within Sub-project 3: Enhancing the performance of UK grown timber and improving its market opportunities through wood modification. It represents milestone 203343 due end August 2001. The Forestry Commission funding was through agreement PPD100 to review the status of wood modification and to assess its potential application for Sitka Spruce.

The aim of Sub-project 3 is to develop new methods for exploiting a range of environmentally and socially acceptable techniques for enhancing the resistance of timber to deterioration due to moisture, while improving their performance and fitness for purpose, and their application to the UK timber resource. In many European countries there has been considerable investment in the development of wood modification. Several of these processes have now been commercialised and the sale of imported modified timber has now begun. This represents both a threat to the use of home grown timber and a missed opportunity.

Key tasks

- To conduct a state of the art review of the literature and industrial best practice,
- To provide a thorough and practical evaluation of modification techniques,
- To identify strategic opportunities for potential transfer to home grown timbers.

Key outcomes

- Although the UK has fallen up to ten years behind the European state of the art there are still real opportunities for our home grown timbers and these are identified in this report.
- In the short term opportunities include wood polymer composites for hard wearing and stable parquet flooring
- In the short to medium term opportunities include: thermal modification, the use of reactive oils, chemical modification (acetylation) and enzymes to improve reagent penetration into spruce. This could establish UK timber in added value markets such as joinery and cladding for example

- In the longer term opportunities will be made available through the continuation and expansion of basic research and its application to industry practice. There are many potential wood modification agents that have not been evaluated including opportunities for creating innovative tailored materials by grafting stabilisers into the wood substrate.
- BRE has established and maintained good links to the companies and institutes involved in wood modification to ensure that there are excellent opportunities to exploit these technologies to add value to home grown timber.

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Introduction

The project is being carried out for DTI and the Forestry Commission. The DTI funding is part of the CD Framework project entitled "Best value from UK timber in construction" within Sub-project 3: Enhancing the performance of UK grown timber and improving its market opportunities through wood modification. The work is being carried out under contract number cc2115. The Forestry Commission funding is through agreement PPD100 to review the status of wood modification and its potential application to Sitka Spruce.

Wood for the construction and wood working industry has to meet many different requirements, depending on the application.

The highest qualities are used for:

- Window frames, exterior doors, timber facades, furniture and parquet flooring,
- hydraulic engineering, waterfront constructions and other exposed applications,
- timber construction.

The lower qualities are used for :

- pallets and packaging,
- as raw material for all kinds of board materials.

Depending upon its end use the timber needs good durability, dimensional stability, appearance, resistance to insect attack, strength, stiffness, hardness, low flammability, paintability, and glueability. In many cases home grown timber cannot meet these requirements. However, wood modification offers the potential to tailor the properties of the timber products to meet the requirements for end use.

Wood modification, by chemical reactions, physical, thermal or enzymatic means offers the potential for environmentally acceptable alternatives to commercial wood preservation. The objective is to exploit wood modification to improve the performance and market opportunities of UK grown timbers to meet market demands. Wood modification can provide home grown timber with a long service life and increased maintenance intervals. This report reviews the current modification technologies and their potential for UK home grown timber.

Description of the project

This DTI project aims to exploit and adapt innovative wood modification processes developed in other countries, to combine these with BRE's own expertise and apply them to the UK timber resource. Following this rigorous review of the state of the art for wood modification financed by both DTI and Forestry Commission, priority areas identified with the highest potential for success will be targeted for transfer into the UK market. The priorities will then be assessed and optimised for a UK demonstration of an improved durability-enhancing technology. The close engagement with co-operating companies and comprehensive dissemination activities planned for the wider industry will help to maximise take up and exploitation of the techniques developed during and beyond the project period.

The aim of this review is to provide a thorough background to the current state of the art for wood modification and then to identify opportunities for the UK, in particular for Sitka Spruce.

Abbreviations

ACE	Anti creep efficiency
ASE	Anti shrink efficiency
CCA	Copper/chromium/arsenic (wood preservative)
EDTA	Ethylene diamine tetra acetic acid
FTIR	Fourier transform infrared spectroscopy
GMA	Glycidyl methacrylate
LVL	Laminated veneer lumber
MAG	Malaic anhydride/glycerol
MF	Melamine formaldehyde
MUF	Melamine urea formaldehyde
MOE	Modulus of elasticity (stiffness measurement)
MOR	Modulus of rupture (strength measurement)
MMA	Methyl methacrylate
MW	Molecular weight
PEG	Polyethylene glycol
WIC	Wood inorganic composite
WPC	Wood polymer composite
WPG	Weight percent gain (a measure of the degree of wood modification)
WRE	Water repellent efficiency
UV	Ultraviolet
XPS	X-ray photo-electron spectroscopy

1. Background and motivation for wood modification

In order to understand the motivation for wood modification it is essential to understand the background to the past and present use of timber and the use of biocidal wood preservatives to enhance the durability of timber. This is explained in the following sections of this chapter. In general the motivation for wood modification comes from the increased environmental awareness and drive for sustainability in the world, and in particular within the European Community.

The drive for sustainability is in itself a drive for the use of timber, particularly European grown timber, in construction and manufacturing. Timber is a unique material in that it is completely renewable, CO₂ neutral, has good thermal performance and requires relatively little energy for its production, in particular when compared with other constructional materials. However, this being said there has been growing environmental pressure against the use of tropical hardwood from non-sustainable forests. These timbers have been used in many applications specifically for their high durability. To use alternative timbers from fast grown sustainable sources for these demanding applications generally requires them to be treated with preservatives to enhance their durability. In many European countries there is now also pressure against the use of traditional wood preservatives due to their leaching into water and difficulties with their disposal at the end of their life. In this respect considerable improvements have been made to traditional wood preservatives but the only way to completely overcome these issues is to find new non-biocidal ways to enhance the performance of sustainably grown timbers. This is where wood modification offers future solutions, some of which have recently been commercialised.

1.1 TRADITIONAL WOOD PRESERVATIVES AND THEIR USE

Wood is a major constructional material in the United Kingdom; timber and wood-based materials currently have a value of £2.5 billion in the UK alone, of which 80% is imported. This immediately highlights the importance of the more economical use of this resource on the UK's balance of payments. The majority of timber used in construction is softwood from managed forests in Europe, about 20% being home grown timber. Timber is widely used both in domestic buildings and in other areas such as agricultural commodities, fencing (particularly motorway fencing), sea defence and harbour works, and railways where it is usually required to remain sound and serviceable for many decades.

However, in many of these end uses, timber is liable to attack from wood-destroying organisms. The most important of these are the wood-destroying fungi (wet rot, dry rot and soft rot) which can invade the wood if it becomes wet, or even damp, for significant periods. Various insects, mostly beetles, also use wood as a food source, although high moisture contents are not always necessary for their attack. In the sea or in brackish waters timber can be attacked by marine borers which tunnel into the wood as a place of refuge. Some timbers have a natural resistance to these organisms but others, including many of the commonly used construction timbers, succumb easily to such attacks. For these latter timbers it is essential to apply a wood preservative in order to achieve the desired performance.

The older, central region of a mature tree trunk constitutes the heartwood whilst around it is a younger sap-conducting band known as the sapwood. In many timbers the heartwood can be distinguished as being darker in colour than the sapwood, but this is by no means a general rule. The sapwood of all timbers is very susceptible to attack by wood-destroying organisms but the heartwood varies in its resistance to attack (its natural durability) depending on the wood species. Some heartwoods are durable enough to perform satisfactorily in adverse conditions without preservative treatment, while others are no more durable than sapwood. In many instances when a tree trunk is converted to sawn stock, both sapwood and heartwood occur in the same piece of timber. Thus, even if the heartwood is durable, the presence of a significant proportion of sapwood requires the use of wood preservation.

Traditionally, where a long service life is required in hazardous conditions, tropical hardwoods such as iroko and greenheart, have been used. These timbers which make up much of the equatorial rainforest are now seen as scarce commodities from a threatened environment and their widespread use is being reviewed. Since wood preservation allows the use of perishable timbers in service environments where they would otherwise quickly degrade, the consumption of tropical hardwoods can be replaced by preservative-treated softwoods derived from well-managed and sustainable forests.

Long-term field trials using wooden stakes in ground contact (regarded as a very hazardous environment) have demonstrated that the use of appropriate wood preservative treatment can extend the life of such a commodity 10-20 times. For instance, Scots pine sapwood stakes, 50 x 50 mm in cross-section, fail after about four years in the field but similar stakes treated with certain wood preservatives are still sound after 60 or more years exposure. This means of extending the useful life of timber ensures a more effective and efficient use of this renewable resource. In addition, it provides greater opportunities to re-establish the world's forests which, in growing and thriving, ensure the long-term removal of carbon dioxide from the atmosphere.

Wood preservation can also be used to extend the life of timber already in service. Many buildings infested with wood-destroying insects can be successfully treated by the surface application of remedial fluids. Other components recognised as at risk from fungal attack can be treated where the infection is most likely to occur using solid implants or fluid injections of fungicidal preparations.

The European Committee for Standardisation, through the Technical Committee CEN/TC38, has adopted the following definition for a wood preservative.

Wood preservatives are active ingredient(s) or preparations containing active ingredient(s), in the form in which they are placed on the market, and which are, on the basis of the properties of their active ingredient(s), intended either to prevent wood-destroying or wood-disfiguring organisms (fungi, insects and marine borers) from attacking the wood and wood-based products or to combat an attack of these organisms.

Thus those preparations (such as paints and exterior wood stains) which provide a physical barrier between the wood and the surrounding environment are not regarded as wood preservatives and are not considered in this review.

In the UK, the use of wood preservatives is controlled under the Control of Pesticides Regulations 1986 (CoPR). Each year the Health and Safety Executive, who administer the CoPR for wood preservatives, publish a list of all those formulations given approval under the Regulations (HSE, 2000). This shows that there are about 30 different active ingredients currently included (some of which will be mixtures) although not all will be used in large quantities.

Wood preservation is a technology which is constantly developing. This is demonstrated by the changes in the active ingredients used. These changes may be initiated by shifts in availability, economics, efficiency or environmental considerations. In some cases, particularly in recent cases of environmental concern, such changes are demanded through legislation. While compounds such as mercuric chloride and DDT have long since ceased to be used, largely because safer and more effective systems were developed, more recently the insecticide dieldrin has been withdrawn from use by manufacturers and is no longer approved under the CoPR. The preoccupation with environmental concerns both through the CoPR and legislation evolving within the European Community has led to a restriction in the use of tri-n-butyltin compounds (now not available to the do-it-yourself market) and a derogation to a European Directive allowing the continued use of pentachlorophenol in the UK.

The trend has continued. The higher toxicity of the synthetic pyrethroids to insects coupled with a low mammalian toxicity has led to the widespread use of permethrin and cypermethrin in remedial treatment fluids. In addition, economics and difficulties in quality control have increased the use of synthetic copper and zinc carboxylates where previously the naphthenates derived from coal tar distillation would have been used. For the future, conventional wood preservation will continue using new biocides that are considered more environmentally acceptable than the traditional formulations. This will be in parallel with other methods of improving the performance of wood, including its durability. These alternative will use non-toxic materials, such as bulking agents and water repellents, or which modify the wood chemically so that it becomes unattractive to wood-destroying organisms (Kumar & Morrell, 1993).

1.1.1 Wood preservative formulations

Wood preservatives formulations may be conveniently divided into four main groups. These are:

1. Tar oils,
2. Water-borne biocides,
3. Organic solvent preservatives,
4. Emulsion preservatives.

1) Tar oils. These are blends of distillate oils. Those derived from coal tar with a boiling range from about 200°C to 400°C are collectively known as creosotes and are fully specified in British Standard BS 144. Coal tar creosotes are highly resistant to bacterial and fungal attack (Schmidt et al., 1991), and have been used for many decades in wood preservation. Other tar oils, mainly available to the do-it-yourself market, are derived from petrochemical tars or are diluted forms of true creosote.

Creosotes to BS 144, types 1 and 2, are applied industrially using vacuum/high pressure techniques to treat components such as railway sleepers and transmission poles to provide long-term protection in hazardous environments. Creosotes to BS 144, type 3, and the range of non-standard proprietary formulations are applied by superficial means, such as brushing and spraying, often as part of a maintenance programme, to commodities like domestic fencing.

2) Water-borne biocides. In the UK these consist mainly of inorganic compounds dissolved in water. The most common types are copper/chromium/arsenic (CCA) mixtures which are specified in BS 4072: Part 1. CCA mixtures are either salt based (copper sulphate, sodium dichromate, arsenic pentoxide) or oxide based (copper oxide, chromium trioxide, arsenic pentoxide). They used to be supplied as powders or concentrates for dilution at the treatment plant but are now more usually transported as pastes, again for dilution at the site of treatment. Although water-soluble, these mixtures react chemically when in the wood to become water-insoluble. They are only applied industrially and are used, like creosote, to treat a wide range of commodities where a high performance in hazardous conditions is required, for instance motorway fencing. In addition they are used to treat building timbers, such as domestic roof members, where economics rather than required effectiveness dominate. Ammoniacal copper zinc arsenate (ACZA) is replacing the use of oil borne preservatives particularly when treating Douglas Fir (Lebow & Morrell, 1994).

Treatment with boron compounds has always been included in the range of recommended treatment methods in the UK (see BS 5589, BS 5268 part 5) but has not been used extensively (Dickinson & Murphy, 1989). It is being reappraised as a useful preservative now that environmental considerations are taking greater prominence. Disodium octaborate is normally used, which remains water-soluble within the treated timber. Thus the timber has to be protected from the effects of leaching for the protection to remain effective. Timber treated in this way is used in relatively dry conditions where insect attack is considered likely or where the timber is protected by a surface coating.

A range of water-soluble biocides are used in the remedial treatment sector. Dry rot treatments include the sodium salts of pentachlorophenol or o-phenyl phenol and water-based do-it-yourself preparations contain a variety of quaternary ammonium compounds.

3) Organic solvent preservatives. These consist of a range of biocides, both fungicidal and insecticidal. Sometimes resins, waxes and co-solvents are added, dissolved in a light organic solvent such as white spirit or distillate, including acypetacs copper and zinc formulations (Hilditch et al., 1983) and AAC modified with copper (Drysdale, 1983). However, in some cases more than one active ingredient is used which can lead to alternative concentrations (BS 5707 part 1). Amongst the more recent suite of alternative active ingredients developed for wood preservation are 3-iodo-2-propynyl-N-butyl carbamate (IPBC) (Hansen, 1984), azaconazole (Valcke & Goodwine, 1985; Valcke, 1989), propiconazole (Goodwin, 1990), tebuconazole (Grundlinger & Exner, 1990), Isothiazalones (Nicholas et al., 1984; Leightley, 1990), tri(hexylene glycol) baborate, tri-iodo-allyl alcohol (Lee et al., 1990), TCMTB (Van den Eynde, 1990) and DNBP (Schnippenkoetter, 1988).

This group of preservatives is used industrially to treat exterior joinery, where it should be protected by a surface coating to ensure appropriate performance, and many internal building timbers such as roofing components and timber-frame studding. They may be used by the remedial treatment sector when the target infestation is regarded as relatively severe. They are also widely available to the do-it-yourself market where they are used to treat fencing, garden furniture and other commodities where a periodic surface application is regarded as beneficial.

4) Emulsion preservatives. Emulsion pastes containing insecticides and/or fungicides have been available for some time. They are used by the remedial sector to treat timbers of relatively large dimensions or those where surface treatment with a liquid is regarded as inappropriate. They are trowelled on to the surface and left for some time to soak slowly into the timber. Alternatively, they are sometimes injected under pressure into pre-bored holes or channels. Other paste formulations are applied in below ground bandages to transmission poles (Eaton & Hale, 1993), also providing effective, but not complete, protection to the above ground zone by protecting the most vulnerable zone of the pole (Morrell et al., 1994).

The increasing cost of organic solvents and concern that their evaporation from the wood after treatment may adversely affect the environment has led to the development of a variety of other emulsion formulations. Since the active ingredients are carried in the oil phase of these preparations, the biocides used are drawn from the same group as those used in the organic solvent formulations. Dilute oil-in-water emulsions were introduced into the remedial treatment sector as insecticidal formulations, and gained wide acceptance for use in all but the most severe infestations. This development led to similar preparations for the do-it-yourself market where fungicides and, sometimes, pigments were also included.

More recently micro-emulsions have appeared on the market which use even less organic phase than the dilute oil-in-water emulsions. The technology of their preparation is more refined providing a liquid which is more stable. They may also provide less health risk, allowing occupants of treated dwellings to return to their homes more quickly after remedial treatment. Evidence has been presented to indicate that micro-emulsions are similar to organic solvent borne formulations with respect to rates and depths of penetration (Dawson & Czipri, 1991; Czipri et al., 1992). In addition, the development of this technology offers the possibility of these formulations being used for the industrial pretreatment of selected timbers.

1.1.2 Treatment methods for traditional preservatives

Variations in the treatment method and techniques employed can cause considerable variation in a preservative treated products lifetime performance. The benefits of gas phase treatment are demonstrated through the penetration and distribution profiles revealing deeper penetration and more extensive distribution of product (Tillman, 1988). Improvements to pressure treatment processes to obtain deeper penetration of preservative include the oscillating pressure method (OPM) and the alternating pressure method (APM). Improvements still to be achieved include the recovery of light organic solvents

(LOS) from the treatments. OPM eliminates extensive dimensional distortions and the need for recovery of carrier or excess chemicals from the wood (Tillman, 1988).

Superficial treatment shows that dipping is better than brushing or spraying, as a result of the total immersion and slight penetration achieved. Numerous methods, reactions and techniques have been reviewed for the *in situ* treatment of timber with preservatives (Rowell, 1991; Takahashi, 1993). More advanced and potential techniques for wood treatability improvements include investigations into the use of enzymic pretreatment to initiate better penetration and fixation of preservative into Norway spruce (Militz, 1993b).

1.2 UTILISATION ISSUES

Despite extensive research into the science of wood preservation, it still seems that the conventional wood preservatives are preferred. However, the use of conventional preservatives is coming under increasing pressure through environmental considerations. The rising concerns about the environmental acceptability and safety of these biocides has been highlighted as a key issue of concern for a number of years (Hilditch, 1989). There is an increasing general desire to develop wood protection methods that are demonstrably safe for our environment and health, which deliver the high protective standards demanded for long-term timber utilisation and which are economically viable for general use.

1.2.1 Environment

Biocides leaching from preservative treated timber have been identified as a significant source of river pollution in certain areas (McNeill, 1990). Pesticides require stringent control during production, application, service lifetime and eventual disposal. As a recent example of this, European concerns on the polyphenol contents of creosotes prompted a legislation review on their future use. Assessments deemed that there should be no restrictions on creosote use, provided the benzo[a]pyrene content was <50ppm, and water soluble phenols content is limited to <3% (European Council Directive 76/769/EEC). Organotin compounds used in the marine environment as anti-fouling agents have been shown to have detrimental effects on the populations and reproduction of shellfish, in particular oysters and mussels. Organotin compounds were also easily bioaccumulated in fish, through the food chain. PCP and arsenic compounds are already banned from some European countries. This trend will increase, so there is considerable pressure on current preservatives with respect to their environmental acceptability.

Controlled release technology of preservatives was investigated to potentially reduce environmental pollution. Aspects based on the use of microcapsules were restricted by the size of the pores in the wood but found limited application in paints. Bioactive polymers in cell lumina and the bonding of biocides to cell wall polymers is another branch of this work, focusing on fluorophenyl isocyanates (Chen & Rowell, 1986). The controlled release of copper as a biocide from carboxylic acid 'soaps' fixed to cell walls, was highly successful (Pizzi, 1993). The copper was only released during humid conditions, when hydrolysis and dissociation occurred. It was also postulated that PCP could be used as the biocide in place of copper (Pizzi, 1993).

Environmental pressures have necessitated the development of Life Cycle Assessments (LCA) for preservatives and preservative-treated timber related to product manufacture, waste disposal and recycling potential. At the end of its service life treated wood becomes a waste product and interests lie predominantly in the ultimate fate of preserved wood and the associated environmental impact. An excessive accumulation of wood waste presents obvious problems. The proper use and recycling of wood products has to be addressed, along with its safe disposal and degradation after use (Evans, 1995). With the recycling or utilisation of second hand wood it becomes necessary to monitor the timber for trace elements (Börtitz & Wienhaus, 1991) since little may be known of its past. A variety of problems can be identified in the disposal of treated timber. Highlighted is the potential for the water soluble preservative elements in wood being introduced into the groundwater when the wood is stored or dumped. Alternatively, if the timber is incinerated contaminants in the smoke or the ash have to be considered. For instance, the combustion products of CCA treated wood include ash containing hexavalent chromium and gaseous arsenious acid (Fuse, 1988 from Takahashi, 1993). The effect on the environment of treated wood products have been assessed for three preservatives by Webb & Gjovik (1988). They found that (i) the small amounts of creosote lost were mostly biodegradable, proving a minimal health risk to humans, mammals and the environment, (ii) PCP from treated wood was not a significant hazard to the environment as the low levels in the immediate vicinity can be biodegraded by soil micro-organisms, and (iii) for CCA, water-borne arsenates controlled leaching through chromium fixation. They concluded that treated timber as land-fill was non-hazardous. Published reports on this subject have to be assessed carefully for in many cases the industry is reporting on itself and is unlikely to disclose major environmental problems.

Acknowledging preservative-treated timber as hazardous waste leads to two options for the industry; reduce the waste generation, or substitute safer, alternative chemicals for the traditional wood preservatives. The second option is where wood modification offers future prospects for the industry.

1.2.2 Health and Safety

Stringent health and safety regulations involved in the use of wood preservatives are administered in the UK by the Health and Safety Executive (HSE) who publish an annual list of wood preservative formulations approved for use (HSE, 2000). Exposure of treatment operators during application is often the most hazardous stage in the use of wood preservatives. European concerns to reduce the effect of wood preservatives on the environment, and to ensure the safe management of preservation treatment methods are reviewed regularly (Peek & Willeitner, 1993). In the USA the Environmental Protection Agency has regulations for the disposal of wood preservative waste (Talarek, 1988) and for treating facilities; it also provides guidelines on health and safety related to wood preservatives. It should be recognised that control is necessary, for like most biocides, those used in wood preservation can have physiological effects on users and people who come into contact with these chemicals after treatment if ingested in sufficient quantities (Reifenstein et al., 1990). However, this may not be confined to active ingredients for solvent emissions from treatment works have been scrutinised following a recent EC draft directive on VOC emissions. It has been suggested that significant improvements will be needed at preservation treatment plants if the proposed regulations are to be met (Coggins & Mouldrup, 1991).

1.3 CONCLUDING REMARKS

Although it can be demonstrated that wood preservation, as a technology, has progressed with time, the essential approach has remained the same, i.e. to select a biocide, dissolve it in a suitable solvent and allow the resultant solution to permeate the wood. There is considerable social and political pressure on the conventional approach to wood preservation. It is highly appropriate to take a long-term view of wood protection by examining the commercial potential of novel techniques of preserving and enhancing the durability of wood that could be environmentally more acceptable.

2. Methods of modification

2.1 INTRODUCTION

Four areas have been identified as having the potential to produce new methods for enhancing the durability and performance of wood while avoiding the use of conventional biocidal wood preservatives:

- Chemical modification
- Physical modification
- Thermal modification
- Enzymatic modification

A considerable amount of work has been carried out as small scale laboratory trials and tests. Much of the research has been piecemeal or unsystematic rather than comprehensive. However, from the many techniques that have been tested a few have been thoroughly researched in specific countries and have now been developed on a commercial or semi commercial scale.

This review gathers together the published information associated with these subject areas, identify the deficiencies and the opportunities for the UK in particular for our home grown timber.

Definitions for the various types of wood modification are currently being developed within the European Thematic Network for Wood Modification, which BRE is a member of. However, these definitions were not ready for inclusion in this report so previous definitions are used here.

2.2 CHEMICAL MODIFICATION

"Chemical modification is any chemical reaction between some reactive part of the wood cell wall component and a simple single chemical reagent, with or without catalysis, that forms a stable covalent bond."

(Rowell et al., 1988)

The essence of chemical modification is a reaction that produces a bond. In the majority of cases the reactive parts of the wood cell wall component are the abundant hydroxyl groups in the wood's polysaccharide molecules. The reaction results in a change in chemical configuration and molecular conformation that generally renders the wood no longer recognisable as a food source by biodegrading organisms, or no longer allows it to absorb water.

Chemical modification is widely accepted as an effective method of changing the properties of wood. These include many enhancements:

- increasing dimensional stability
- increasing resistance to biological attack
- increasing resistance to weathering
- improved acoustic properties

However, some of the other desirable properties of wood may be altered or lost by this modification. These include:

- reduction in tensile strength
- reduction in elasticity

The key is to maintain the woods desirable mechanical properties while improving its durability and water resistance.

In general, the principle of chemically modifying wood to enhance its biological durability can be described by several mechanisms (Kalnins, 1982):

- a) binding biologically active compounds to the wood structure so that they are able to interact with wood-destroying organisms;
- b) releasing biologically active breakdown products from the modified wood as a result of fungal enzyme action. These products would subsequently penetrate the fungal cell walls;
- c) blocking sterically the attack of fungal enzymes by large or polar essentially non-toxic groups, such as the acetyl group. Basically this confounds the "lock and key" principle by which many enzymes attack substrates;
- d) restricting water ingress into the wood structure and thereby maintaining low moisture content and a dimensionally stable material.

The wood can be rendered biologically resistant by preventing wood digestion by the fungus and/or rendering the wood hydrophobic. The basic principle is to alter the substrate so that the specific enzyme systems of the wood destroying organisms do not function on the modified wood (Rowell, 1982). Thus there is no need for the chemicals used in modification processes to be biocidal, thereby avoiding many of the current environmental concerns associated with conventional wood preservatives. The hydroxyl groups that occur commonly in the wood's organic polymers (cellulose, hemicelluloses and lignin) are the most reactive functional groups in wood. They also give the wood its hydrophilic character since water readily combines by hydrogen bonding to hydroxyl groups. As a result of the modification of these hydroxyl groups, the wood no longer has the capacity to bind to water molecules and thus has a greatly reduced hygroscopicity. This leads to improvements in integrity under weathering trials both visually and at the microscopic structural level (Dunningham et al. 1992). The improvement in dimensional stability and resistance to accelerated weathering trials was demonstrated for acetylated Radiata pine by Plackett et al. (1992). This reduction in the ability of the wood to take up water also reduces the ability of fungal colonies to establish themselves in the wood. Ideally fungi require wood with a moisture content greater than 17% to become established and decay the substrate.

Evidence that the chemical modification of wood improves photostabilisation was obtained in a comprehensive study of the photodegradation of modified wood (Kiguchi, 1992). These findings were contrary to the conclusions of earlier work on the effect of infrared and ultraviolet light on modified wood (Kalnins, 1984). Exposure of acetylated wood samples to ultraviolet and visible light demonstrated that a photostabilisation effect had been imparted to the

acetylated wood (Dawson & Torr, 1992) which minimised surface colour changes (Imamura, 1993a). Photodegradation of the surface of wood was also prevented by modification with a maleic acid/glycerol mixture (Fujimoto, 1992). The weathering of chemically modified surfaces of different degrees of acetylation, measured as weight percent gains (WPGs), showed improved resistance when measuring the tensile strength of thin strips with increasing WPG of modification (Evans et al. 2000). Colour stability in this study was not achieved and was also not achieved in surfaces modified with dicarboxylic acid anhydrides when artificially weathered (Evans 1998). Acetylating wood meal did not significantly affect colour changes on exposure (Ota et al. 1996) even though differences in photostability of esterified wood have been reported (Chang and Chang 2001). However, in other studies improved colour stability on exposure to UV light for modified sugi wood with acetic anhydride and butylene oxide was achieved. Despite the fact that the photo-oxidation occurring at the surface was similar as estimated by X-ray photo-electron spectroscopy (XPS), (Kiguchi 1997). Chemical modification did not improve the bonding strength or weathering resistance of the transparent coatings themselves. This suggests that the colour stability afforded by chemical modification is very timber species and reaction specific. Photostability of acetylated wood and its degradation through demethylation have been investigated by Hon et al. (1995).

The resistance of acetylated wood to biological decay in ground contact field test stakes suggests that 20% acetylated WPG is equivalent to approximately 4% CCA treatment. Acetylated wood only gives minor protection against marine borers (Brelid et al. 2000). The biological durability of straight chain alkyl anhydride modified wood has shown that acetic anhydride modified material at a WPG of 22% conferred biological durability over a wide range of European Standard fungal tests (Suttie et al. 1999; Forster et al. 1998; Forster et al. 1997) and insect tests (Suttie et al. 2000). Termite and fungal decay resistance have also been demonstrated by a number of other researchers (Singh et al. 1997). The biological resistance of chemically modified aspen composites of veneers and sawdust were significantly improved by the hot pressing stage of production (Timar et al. 1999).

The improvements of chemical modification on the acoustic properties of Sitka spruce was suggested to be the result of the formation of network structures (Chang and Chang et al. 2000). A summary of the structure and properties of chemically modified wood has been presented by Norimoto & Gril (1993), which included a comparison of anti creep efficiency (ACE) and anti shrink efficiency (ASE). The study also detailed the increase in specific Young's modulus compared with the increase in internal friction (to evaluate the effects of chemical treatment on acoustic properties of wood), and a comparison of modulus of rupture (MOR) with modulus of elasticity (MOE). It was noted that in order to

improve the hardness and abrasion resistance of timber it is necessary to have at least partial filling of the lumina.

The essential requirements of reagents for the chemical modification of wood were summarised by Rowell (1975). The reagents should:

- contain functional groups that react with hydroxyls,
- be non-toxic or non-carcinogenic to non-target life forms, and also non-corrosive,
- have a boiling point between 30°C and 150°C to aid easy removal of excess reagent,
- swell the wood to allow access to all reactive sites (this may require the use of solvents, such as pyridine),
- use catalysts that are mildly alkaline, have low boiling point and are non-toxic (e.g. tertiary amines),
- work in reaction conditions where temperatures are less than 120°C (simple and rapid reactions are the best),
- not produce by-products that have to be removed during reaction,
- form stable covalent bonds,
- graft hydrophobic components to the wood,
- react a single reagent with a single hydroxyl (the greater degree of substitution of wood components the better it is for durability),
- retain the desirable properties of untreated wood,
- be as cheap a possible as should the process.

It is necessary for the chemicals to swell the wood in order to facilitate the penetration of the reagent into the cell wall, and then it must react with the cell wall hydroxyl groups, preferably under mild conditions. Ideally the reactions should be rapid, form stable covalent bonds, produce no by-products and maintain the desirable structural properties of the untreated wood (Baechler, 1959; Rowell, 1975; Rowell, 1983). Such reactions can produce covalent bonds of the ether type (stable in acid and base conditions), acetal type (stable in basic conditions) and ester type. Bond strengths are in the order ether>acetal>ester.

Chemical modification of wood as a basis for enhancing the durability of wood is based upon the theory that fungal enzymes (e.g. cellulases) must directly contact the wood cellulose to degrade it, and that the substrate must have a

particular configuration for this to occur (Rowell, 1975). It has been shown that a simple chemical modification to the wood structure produced by the action of acids and bases resulted in an increase in fungal growth after washing with water. So any modification process has to be mild in pH to avoid permanent damage of the structure (Reinprecht, 1988).

The stability of modified wood, e.g. acetylated wood, to environmental changes is of great interest with regard to the commercial application of this technology. The dimensional stability can be tested by repeated water soak and oven dry cycles (Rowell & Ellis, 1978), which also gives an indication of the permanence of the conferred chemical modification. Similarly, Larsson & Simonson (1994) showed that acetylated spruce wood samples showed reduced deformation under moisture cycles. Rowell (1982b, 1992b) observed that the location of the reacted chemical in the cell wall polymers determined the effectiveness of the treatment for biological resistance and that the distribution of acetyl groups in acetylated wood was uniform. Imamura (1993a) reported that the morphological changes in wood exposed to weathering were reduced in 20% WPG acetylated wood, as was the colour change due to weathering.

The concept of degree of substitution (DS) can be used as a means of comparison of different techniques and substrates, instead of weight percentage gain (Kalnins, 1982). For comparable DS values it was reported that wood reacted with isocyanates and thioisocyanates had superior decay resistance to that reacted with acetic anhydride. The degree of substitution (DS) of the hemicellulose is thought to be the crucial factor in decay protection and dimensional stability (Rowell, 1982a,b). The effect of chemical modification is not one of direct toxicity but of reducing the ability of the wood to absorb moisture and altering the molecular configuration of the substrate to inhibit enzyme reactions (Rowell, 1982a).

Microdistribution of the modified hydroxyl groups is fundamental to the behaviour of the wood products. This has been identified as a key area for study in order to improve our knowledge of chemical modification of wood (Levy, 1994). For example, it is possible for a compound to bond preferentially to the hydroxyls of lignin rather than those of cellulose, and thus give enhanced resistance to decay by white rot fungi rather than brown rot fungi (Holland & Carey, 1992). Detailed investigations into the distribution of acetyl groups in acetylated whole wood used preparations of lignin, holocellulose, cellulose and hemicellulose isolated from pine wood and reacted with acetic anhydride have been documented (Rowell et al., 1994). Results indicated that all of the lignin hydroxyls had reacted, the hemicellulose hydroxyls less so and the holocellulose hydroxyls very much less so whilst the cellulose had not reacted. In solid wood at a weight percent gain (WPG) of 18% following reaction, all the lignin hydroxyls had

reacted and 20% of the holocellulose hydroxyls, conferring biological resistance to the sample. At a WPG of 8.5%, 80% of the lignin hydroxyls were substituted and biological attack occurred, which may indicate that lignin hydroxyl modification does not play a major role in the mechanism of resistance to attack (Rowell et al. 1994). The distribution of acetyl substituents in the polysaccharides of acetylated wood determined by NMR analysis, provided the basis for a discussion on the substitution of hydroxyls on different carbon atoms and its relationship to the weight gains associated with acetylation (Ohkoshi & Kato, 1992).

The permanence of modification reactions and reagents is being practically assessed through increasing numbers of field exposures of modified wood in accelerated field tests (EN252 and ENV12037) and also in commodity trials such as canal lining and window frames (Brelid et al. 2000; Beckers 1995).

The chemical modification of wood relies on the delivery of small reactive molecules into the wood cell wall structure. Often through impregnation or diffusion, and then a reaction or bond forming stage. The objective may be to produce a reaction through out the cross-section of a solid component, or to provide a protective envelope treatment. The key to optimising the reaction conditions is understanding the nature of the process and the constraints on the degree of substitution. For example, moisture adsorption thermodynamics of chemically modified wood clearly indicated a formation of bonds that restrict the swelling of the material and thus the restriction of further diffusion of unreacted reagent into the wood structure (Yasuda et al. 1995). The critical diffusion of reagent into the wood structure has been modelled based on Fick's Law and diffusion theory (Hill et al. 1997).

The reaction kinetics have been studied for the acetylation of solid wood (Hill et al. 1999) and cellulose (Ramsden 1997). The determination of activation energies of reactions allows the reaction conditions to be optimised to deliver the correct mechanical and biological durability properties of the reaction product. A step further used the degree of modification to model the effects of chemical modification on the dynamic mechanical properties of wood (Obataya et al. 1996).

A considerable variety of chemicals will react with hydroxyl groups the principal reagents are summarised in the following sections.

2.2.1 Acetylating reagents

The most widely studied and commercially exploitable reactions for chemical modification of wood involve alkylation and in particular acetylation, principally with acetic anhydride or acetyl chloride (Rowell, 1983). Acetic anhydride is a relatively cheap and small molecule that is reactive and has consistently demonstrated performance improvements when used to modify a range of timber species. It is the reagent for chemical modification that has reached semi-commercial status and has a industrial process developed for the production of acetylated wood. Carbon 13 NMR studies of acetylated wood show substitution of free sites occurs readily in the lignin (the most susceptible to damage of the wood polymerics) and not very much in the other carbohydrate structures. Rearrangement can then occur with the substituted lignin inferring network cross linking. (Boonstra et al. 1996).

Acetic anhydride and acetyl chloride produce ethanoic acid and hydrochloric acid respectively as by-products when reacted with wood and it was recognised that both of these compounds could have a detrimental effect on the wood's properties, for instance reducing the dimensional stability, as well as corroding metal attachments (Kumar et al., 1991).

Acetylation with acetic anhydride, in the presence of aniline gives increased WPGs and reduced reagent losses, compared to acetic anhydride alone. In addition the reaction produces acetanilide *in situ* which is a known biocide (Singh et al., 1992). It has been shown that the anti-shrink efficiency (ASE) of post acetylation aniline dip is greater than that for pre acetylation aniline dip, which is greater than that for samples of mango wood (*Mangifera indica*) without the aniline dip. The aniline improves the reaction stability, neutralises acidity, improves strength and resistance to corrosion (Singh et al., 1992). It is postulated that the use of aniline produces reactions other than acetylation which contribute to dimensional stability. This initial acylation of an aromatic nuclei of lignin occurs by direct attack of anhydride fragments on the aromatic nuclei, by a Fries rearrangement, or by both simultaneously (Pizzi et al., 1994). This leads to wood matrix cross linking. The stability of acetyl groups in acetylated wood to pH, temperature and moisture changes was extensively studied, revealing that pH 6 at 24°C and pH 4 at higher temperatures were the maximum stability conditions. The half-life of acetylated wood was estimated to be 30 years at pH 6 and 24°C with very little loss of acetyl groups (Rowell et al., 1992). Thus it could be used in situations where wood products would be exposed to high changes in humidity such as bathrooms and roof shingles (Rowell et al., 1993).

An alternative approach is to use thioacetic acid (Singh et al., 1979), which produces hydrogen sulphide gas as a by-product. This can then be scrubbed

out of the waste gases and recycled to produce the more thioacetic acid a considerable improvement. However, all excess thioacetic acid must be removed after reaction as it is a known depolymerising agent for lignin. The draw back of the procedure is highlighted by the low WPGs obtained, the highest being 8% (Kumar & Kohli, 1985). Thioacetic acid reduced the hygroscopicity more than acetyl chloride, but was less effective at maintaining the dimensional stability for similar acetyl substitution levels (Kumar et al., 1991).

2.2.2 Other anhydrides

A range of straight chain alkyl and other anhydrides have been studied experimentally as agents for chemically modifying wood. These include propionic, butyric, valeric, hexanoic and heptanoic straight chain anhydrides (Hill et al., Jones 1995, Suttie et al. 1999) and succinic and octenyl succinic anhydrides (Hill and Mallon 1998). Other alkyl anhydrides that have been studied include propionic anhydride and hepta-decenylsuccinic anhydride (Codd et al., 1992). A study of the effects of alkyl chain length on the anhydride for the alkylation of wood (Jones, 1995) reported that a decreasing percentage of the hydroxyl groups react as the alkyl chain length of the anhydride is increased, for equivalent reaction times. Many anhydrides become too expensive to make the process commercially viable, including valeric, hexanoic and heptanoic anhydrides. WPG was demonstrated to be an excellent indicator of dimensional stability, regardless of anhydride chain length. It appears that improvements in dimensional stability are due to a bulking effect. This has been demonstrated by the ASE and volumetric swelling coefficient (S%) both varying with WPG independent of alkyl chain length (Hill & Jones, 1995).

2.2.3 Anhydride and epoxide oligoesterification

An oligomer is based upon 3 or 4 monomer units. Oligoesterified wood based upon anhydrides and epoxides showed greater resistance to biodeterioration and weathering, and improved mechanical properties (Matsuda et al., 1988, 1992, 1993). Maleic anhydride (MA) and phthalic anhydride (PA) do not form durable ester bonds but further reaction of MA or PA esterified wood with epichlorohydrin (ECH) yields oligoesterified wood, a highly dimensionally stable and durable product (Kumar, 1994). Oligoesterified wood prepared with phthalic anhydride and ECH showed greatly improved termite and decay resistance (Murakami et al., 1993), and was assessed as having higher compressive and flexural strengths, greater chemical resistance, improved electrical insulation properties and a much lower water absorption thus making it potentially a valuable industrial material (Matsuda, 1993). The unreacted reagent solution is removed by heating the oligoesterified blocks while applying a vacuum.

2.2.4 Alkylation in combination with other treatments

There are some common features between chemically modified wood and wood treated with blocking agents, for instance the process may involve a two step formation of a chemically bonded wood-methacrylate composite through initial chemical activation of wood fibres followed by co-polymerisation of poly(methyl methacrylate) to the activated fibre (Banks et al., 1992).

A combination of wood-polymer composite (WPC) and acetylated wood technologies has been attempted by esterifying wood with anhydride, impregnating the modified wood with glycol methacrylate (GMA) and then curing it by heating to achieve a cross-linked, oligoesterified wood with improved dimensional stability (Ueda et al., 1992). Carboxymethylation of wood may be achieved using an ethanol-water reaction medium of chloroacetic acid, which is impregnated and heat treated (Nakano et al., 1990). The introduced side chains increased with increasing concentration of ethanol, independent of temperature.

Acetylation of oil palm and rubber wood gave a greater improvement in dimensional stability per weight gain than polymerisation of monomers *in situ* (Ibrahim & Razak, 1991). Wood modified by reaction with succinic anhydride and then treated with copper sulphate solution resulted in only a small amount of bound copper, but good dimensional stability and effective protection against all wood-destroying organisms - whereas succinylated wood alone was not resistant to brown rot fungi (Dunningham & Parker, 1992). Another demonstration of copper as a fungicide used with novel modification techniques of wood is reported by Pizzi (1993), utilising copper carboxylic acid 'soaps' thermal fixed to cell wall components.

2.2.5 Isocyanates

Isocyanates have been thoroughly investigated as candidate modifying agents, due to their reactivity and small molecular size. However, more recently the commercial importance of the modification process has been doubted due to the poor environmental profile and health and safety restrictions associated with isocyanates.

Reactions with isocyanates (Rowell & Ellis, 1979; Rowell, 1984), thio-isocyanates (Kalnins, 1982; Chen, 1992b) and chlorosulphonyl isocyanate (Chen, 1994b) have been studied. Martins and Banks (1991) found that n-butyl and phenyl isocyanates imparted fungal resistance characteristics to the wood and reduced the hygroscopicity. Isocyanates react rapidly with wood yielding urethane bonds and achieving WPGs of 40% in 20 minutes. The reactions can

be so swift that precautions are required to ensure that the tracheid walls do not split. The low molecular weight isocyanates tend to react with the cell walls while the high molecular weight isocyanates tend to fill the cell lumens like a resin (Kumar, 1994). To obtain the optimal reduction in the water sorptive properties of wood requires modification with molecules not significantly larger than water. The reaction to form urethane bonds between diphenylmethane diisocyanate, perfluoroalkyl ethanol and the wood produced a stable modified wood product that maintained water repellence (Engonga et al. 1999). The observation that n-butyl isocyanate reduced the equilibrium moisture content of wood more than phenyl isocyanate also suggests that molecular size and conformation may be important (Martins & Banks, 1991). Studies of the resistance of wood chemically modified with isocyanates demonstrate that protection against certain fungi species only occurs if the holocellulose fraction showed substantial changes due to modification (Williams and Hale 1999).

The smaller loss of alkoxy bonded chemical from wood reacted with epichlorohydrin suggested that the ether bond is more stable than the sulphonate bond, which is important when considering the permanence of induced properties such as stability and decay resistance (Chen, 1994b). The stability of the bond between the fungicidal group (in this work para-toluene sulphonyl isocyanate) and the wood plays a more important role in the permanence of the fungicidal groups in the modified wood than the hydrophobicity of the fungicidal group alone (Chen, 1992b). The use of diisocyanate gave better cross-linking and improved dimensional stability, and thus an increase in conferred decay resistance (Chen, 1992a).

Fluorine substitution in the phenyl ring of phenylisocyanate increased the fungal resistance of the modified wood compared with the unsubstituted compound, illustrating improvements that can be achieved through minor modifications of the reacting chemicals (Chen et al., 1990). Fluorine was also the active component of the controlled release technology of fluororphenyl isocyanates as highly effective wood modifiers and conferrers of improved bioresistance (Chen & Rowell, 1986).

2.2.6 Formaldehyde

Reaction with formaldehyde creates a bridge across two adjacent hydroxyls in the wood substrate. This process of forming oxymethylene (oxane) bridges between hydroxyls is termed formalisation. Formalisation was observed to impart a greater dimensional stability to Sitka spruce samples than acetylation (Kameyama et al., 1994). A WPG of only 2% increased greatly the fungal resistance of the substrate (Kumar, 1994; Stevens et al., 1979). Inoue et al. (1992) showed that the compressive deformation of wood could be permanently

fixed by cross-linking with formaldehyde. However, the mechanical properties of cross-linked wood were adversely affected, the strength and stiffness being reduced. Rowell & Konkol (1987) found that treatment with formaldehyde resulted in the crushing and bending strengths of wood being reduced. The impact bending strength may be reduced by up to 50% and the abrasive resistance is reduced as well, probably as a direct result of the action of the strong acid catalyst hydrolysing the cellulose.

Formaldehyde cross-linked wood was compared with resin polymer-impregnated wood and 13 other wood treatments for vibrational properties (Akitsu et al., 1993a,b; 1992; 1991). The studies demonstrated that chemically modified wood, when creating improved dimensional stability, retains the vibrational properties of the wood, and thus may have potential in the manufacture of musical instruments. Trioxane and tetraoxane in the vapour phase in the presence of metallic catalysts depolymerises to formaldehyde. A similar reaction in wood, catalysed with sulphur dioxide and $\text{Fe}_2(\text{SO}_4)_3$, was found to improve its hygroscopicity and its acoustic properties for musical instruments (Yasuda et al., 1993). Medium density fibreboard has been treated with formaldehyde to improve decay resistance and dimensional stability (Norimoto & Gril, 1993).

Other reagents can provide the stabilising feature of cross-linking associated with formaldehyde reaction and, equally, this cross-linking can provide improvements in hygroscopic and acoustic properties (Minato & Yasuda, 1992; Yusuf et al., 1995). Dimethylol compounds with metal salt catalysts provide cross-linking when cured at 90 to 100°C, imparting highly improved dimensional stability to the wood (Nicholas & Williams, 1987). Dimethylol dihydroxyethylene urea with a WPG of 15% conferred biological resistance against *Coniophora puteana*, and was also leach resistant (Videlov, 1989). Cross-linking reagents and wood modification using non-formaldehyde reagents, includes modification with glyoxal, glutaraldehyde and dimethylol dihydroxy ethyleneurea (DMDHEU), catalysed by sulphur dioxide (Yasuda & Minato, 1994a,b).

2.2.7 Epoxides

Epoxides (alkylene oxides) reacted with wood confer an effective reduction in biodeterioration and in the shrinking and swelling properties of the modified wood (Rowell, 1982). Wood modified with epoxides is recommended for internal wall materials, where improved dimensional stability and low hygroscopicity is important, in addition to increased plasticity for forming or wood bending (Norimoto & Gril, 1993), demonstrated by the reduced ACE values of epoxide modified wood. The reaction with epoxide is demonstrated to be highly moisture sensitive (Rowell & Ellis, 1984a), predominantly using butylene oxide (BO) and propylene oxide (PO) catalysed with triethylamine (Rowell & Ellis, 1984b). PO and BO enhanced with a cross-linking agent trimethylol propane trimethacrylate

(TMPTM) controlled the hygroscopic dimensional changes in paper birch, imparting a high degree of dimensional stability at low loadings (Guevara & Moslemi, 1984). The reaction between epoxide and wood hydroxyl groups has been shown to be a combination of bond forming with the wood and self-polymerisation. The reactions with wood hydroxyls did not occur under particular conditions. Reactions were entirely homo-polymerisation that resulted in a bulking effect and the observed dimensional stabilisation (Cetin & Hill 1999).

Ethylene oxide has been used as a gas and reacted with wood at atmospheric pressure, though the product performance was not as good as acetylated wood for biological resistance (Kumar, 1994). Fumigation with ethylene oxide was demonstrated as being effective at controlling basidiomycetes, *Anobium punctatum* and *Hylotrupes bajulus* in wooden artifacts, both as a remedial treatment and a preventative treatment. The indication was for its application to entire infested buildings (Unger et al., 1990).

The manufacture of modified wood has now reached the stage where specific epoxides are used that have biocidal or fire retardant properties (such as organo-phosphorous monomers) attached to them. These "tagged-on" compounds are taken into and bound in the wood structure (Rowell & Chen, 1994). Epichlorohydrin was reacted with pentachlorophenol to produce a "new epoxide" prior to reaction with timber samples. The potential for future developments of epoxide modified wood lies with these specifically designed epoxides.

2.2.8 Acrylonitrile

Acrylonitrile and wood produces cyanoethylated wood when reacted in the presence of an alkali catalyst (Rowell, 1983), the product being very stable dimensionally and decay resistant (Kumar, 1994). A WPG of 15% increased the service life of field stakes by 100%, however, leaching in hot water reduced this effect completely suggesting that there are weaknesses with the modification system. It has been suggested that the decay resistance of cyanoethylated wood may be associated with the observation that thiamine (Vitamin B1), which is necessary for fungi to utilise organic nitrogen, is destroyed in alkaline conditions (Holland & Carey, 1992). In addition brown rot fungi utilise acidic conditions for the decay of wood which may be delayed by the alkaline catalysts involved in acrylonitrile modified wood.

2.2.9 Non hydroxyl reactions

In addition to the reactive hydroxyl groups of the polysaccharides and lignin, the carbonyl groups in wood polymers are capable of reacting. The versatility of the predominant hydroxyls in their ability to react with modifying molecules, especially those that impart hydrophobicity and resistance to enzymic attack, resulted in the carbonyl group reactions receiving little research attention. However, experimental work on the reaction of polysaccharide carbonyl groups with phenylhydrazine demonstrated an increased resistance to fungi at a degree of substitution of only 0.0037 (Thomas, 1955).

2.2.10 Silylation

Silicates are naturally present in many timber species. This is thought to influence the durability of the resulting timber and experiments have been conducted with organo-silanes with alkyl side chains (see also 2.3.4). Organo-silane modified maritime pine was produced through the esterification reaction effectively grafting the organo-silane into the wood. Good dimensional stability was observed through a bulking effect (Sebe and Jeso 2000).

2.2.11 Other reactions

Reactions of iron (III) compounds with the constituents of wood (Ntshlele et al., 1994), can occur via many different pathways. The ferric ion could be forming a complex with the lignin constituents or reacting with the carbohydrates imparting water repellency and dimensional stability to the timber. However, surface degradation during natural weathering of radiata pine samples treated with ferric chloride and ferric nitrate was noted, showing enlargement of pit apertures combined with micro-checking. The electrochemistry of iron in association with oxalic acid has been identified as fundamental in the degradation of wood by brown rot fungi (Hyde & Wood, 1995 in press). Treatment with chromium oxide reduced this degradation (Evans et al., 1994), and this may be due to effects on the electropotential of iron.

Wood chemically modified with tetrafluoromethane gas plasma showed improved water repellency (Matsui et al., 1992). The mechanism involves a surface modification of wood in a fluorine containing gas plasma, adding fluorine atoms to the woods surface, maintaining the same appearance and surface characteristics of the samples. Modified surfaces were reported as being very stable after repeated water soaking events.

2.3 PHYSICAL MODIFICATIONS

This approach is based upon the premise that the exclusion of moisture from the wood by blocking available pathways, will prevent increases in moisture content and thus the utilisation of the timber by wood destroying organisms. The structure of softwood may be regarded as a collection of tubes (50-70 μ m in diameter) stacked vertically. These tubes (tracheids) are connected by valves (pits) that allow the transfer of fluids through the wood structure. The tracheids exert a capillary action on water, drawing it into the wood structure. To avoid this occurring the water can be blocked physically from entering the wood tissue and there are several ways of achieving this. The most basic ways of achieving this are through a physical barriers such as pole sleeves that are wrapped around the end of a commodity such as a transmission pole before it is erected. This prevents moisture movement into the end grain of the pole and moisture movement laterally into the pole near the ground line. In addition brush applied end grain sealants can be applied to the end grains of timber joinery prior to assembling the joints. This provides protection against moisture ingress by providing a physical barrier.

2.3.1 Water Repellent Formulations

Water repellent materials impregnated into the wood have often been studied as systems in association with surface coatings. Coatings and finishes containing polymeric alkyd and acrylic resin are the best primers for protection against weathering (Valcarel & Barra, 1989). They are, however, not truly hydrophobic and do allow the molecular diffusion of moisture into the wood. Future developments are likely to rely on a "double barrier" water repellent system combining a migrating polyolefin and a non-migrating high molecular weight fatty acid (Eaton & Hale, 1993). Feist (1990) compared the weathering performance of painted wood with and without pre-treatment with water repellent preservatives. Noted improvements in the performance of substrates were reported for southern pine wood and plywood, when water repellent preservative treatments were used the paint holding characteristics improved. It has been reported that solvent-borne primers are highly effective at increasing the in service life and performance of window joinery (Miller et al., 1987).

Chromium trioxide (Cr VI) emulsions in polyester alkyd wood varnishes have been demonstrated to improve the water resistance of the wood surface (Pizzi, 1990b). The mechanism is by a durability enhancement from the cross-linking between lignin, CrO₃ and alkyd resin. A mechanism that is associated with phenol fixation by chromium salts to wood, imparting protection against light degradation (Raknes et al., 1988).

Water repellent formulations (WRF) using oleoresin and gum rosin from Aleppo pine (*Pinus halepensis*) were compared with paraffin wax and synthetic resin (Voulgaridis, 1993). It was concluded that the natural product combinations were as successful as the synthetic resins, as *water excluders*. They conferred significant protection to beech, poplar and pine sapwood against liquid water uptake. This type of approach has links with section 4.4 and the use of natural extractives in timber preservation.

Water repellent efficiency (WRE) defined by Rowell & Banks (1985) is:

$$\text{WRE} = \frac{D_c - D_t}{D_t} \times 100$$

D_c = water uptake of control during exposure in water for t hours

D_t = water uptake of treated sample during exposure in water for t hours

WRE for various wood species after acetylation was 34-45% and for acetylated wood subsequently impregnated with a water repellent formulation (3% paraffin wax, 15% linseed oil, 82% white spirit) it was 69-80%. Poplar had the highest WRE in a water soak test lasting 72 hours (Hafizo_lu & Yildiz, 1990). The combination of polymer and water repellent used as a stabilising system, together with boron-based biocide imparted excellent properties to southern pine (Barnes et al., 1992).

Water repellent treatments using organophosphorus and silicon compounds, gave a twofold to threefold reduction in water absorption (Pokrovskaya et al., 1990). Other workers have explored the use of poly(hydride siloxane) (Sidorov et al., 1989) and organo-cyclosiloxane (Telysheva et al., 1991) to modify the water repellency of wood, with some success. For example polyethylhydride siloxane with tetrabutoxytitanium as an additive reduced water adsorption by a factor of 3.2 when brushed on to Scots pine sapwood (Velikanova et al., 1989).

2.3.2 Resin Impregnation

This method of maintaining a low moisture content for wood during service has long been practised using simple waxes and resins as additives to organic solvent preservatives. The principal disadvantage in using such an approach is that the additives do not persist and the water repellent effect disappears after a few years service. Current thinking under this heading might include consideration of the wide range of hydrophobic chemicals now available and of placing them selectively within a timber component where they would be most effective. Thus the joint zones of a window frame are most vulnerable to water ingress and this could be reduced long-term by the application of a range of materials from simple paint formulations to synthetic resins and water repellent derivatives from tree bark.

Wood treatments with resins have been widely studied, including the utilisation of epoxy resins, phenolic resins, melamine resins, urea resins, polyurethane prepolymers and unsaturated polyesters (Pittman et al., 1994). New principles for enhancing durability using waterborne resins impregnated into wood are described by Rapp and Peek (1995). The application of resin impregnated timber to produce a hard-wearing and durable finish has been applied to parquet flooring market in Germany. With polymethylmethacrylate, WPGs of approximately 160% produces a highly water repellent composite as the lumina are filled, but the dimensional stability is lower than other modified wood materials as the polymer is not in the cell walls. This material (acrylic wood) demonstrates good mechanical properties and is used in parquet flooring, sports equipment and musical instruments (Rowell & Konkol, 1987).

Polyethylene glycol (PEG) is a water soluble polymer that is introduced into wood by diffusion, which can be accelerated by increasing the temperature and concentration of the PEG solution. WPGs of 25-30% have been reported; the PEG remains water soluble, so it can leach out after drying. Impregnation with PEG imparts very good dimensional stability, reflected through ASE values, and reduces checking during drying. Impregnation with PEG-10,000 is similar in physical terms to the introduction of paraffin wax (Norimoto & Gril, 1993). The impregnated wood is usually finished with a surface coating to seal in the glycol. It has been used in archaeology to treat water-logged wood, as in the recent Mary Rose project (Stevenson, 1995), and generally to treat cross-section plaques and table tops, rifle stocks, and green wood sections for bowls and other turnings (Rowell & Konkol, 1987).

Yellow pine impregnated with melamine formaldehyde (MF) and melamine urea formaldehyde (MUF) resins produced a greatly enhanced dimensional stability, and resistance to weathering and fire (Pittman et al., 1994). MF resins are extremely weather and water resistant, stable to ultraviolet light and have excellent fire retardant properties. However, some of the mechanical properties of timber may be diminished by resin treatment, due to the rigid and brittle nature of the cured resin in wood. This slight detrimental effect can be overcome by using blends of resins (MUF and MF). When the resins are cured *in situ* the process may be regarded as similar to the production of a wood polymer composite (see section 2.3.3).

Water based water repellents for treatment of wood were investigated including a comparison of pine resin and linoleic acid based repellent, that imparted similar water repellency properties as a commercially available organic solvent based treatment. The water exclusion test was based upon repeated soaking and drying, including a freezing stage to allow for efficacy assessments over a much reduced period of time. The water based pine resin showed an even distribution in the impregnated surface, most of the linoleic acid was in the rays as paraffin wax tends to be (Ostberg & Englund, 1992). Again illustrating links with section 4.4 and the use of natural extractives as preservatives, and the non-exclusivity of the four approaches to wood modification.

Phenol formaldehyde (PF) resin can penetrate the wood cell walls, resulting in an improvement of the electrical insulatory properties, heat resistance and decay resistance. The dimensional stabilisation of particleboards and of surfaces of solid wood result in good performance mechanically and may be worth commercial application (Norimoto & Gril, 1993). PF resin has been used to impregnate veneers for plywood, while particleboards achieved improved dimensional stability and biological resistance with the introduction of a low molecular weight phenolic resin in aqueous solution; termites were unable to digest the material (Kajita & Imamura, 1993).

Melamine resins have been progressed as resin treatments for wood to improve durability and hardness in applications such as parquet flooring (Rapp & Peek 1996). The differences in the retention of resin is determined by the type of resin impregnated and in turn indicates the degree of anti shrink efficiency (ASE) that will be conferred to the final product. The resins have the ability not only to exclude moisture from the timber but also to interfere with some of the fungal degradation mechanisms.

Copper carboxylic acid 'soaps' of fatty acids of vegetable oil, rosin and synthetic unsaturated polyester resins were tested as wood preservatives (Pizzi, 1993). In long-term durability ground contact field trials the systems were found to have a 25 year efficacy, the carboxylic acid 'soaps' were fixed by heating or UV radiation. The copper was the acting fungicide, although PCP could be used, and was released from the carboxylic acid group under hydrolysis. This is a highly controlled release of fungicide when the wood is most likely to be under attack from fungi. The ramifications for environmental concerns are highly positive, as the treatment is strongly fixed to the cell wall, natural product based and the fungicide is released primarily when needed (Pizzi, 1993).

2.3.3 Wood Polymer Composites (WPC)

The potential applications for many WPC materials has already been established. Economics has restricted this approach to specialist applications, but the use of special monomers which incorporate the ability to polymerize with the inclusion of a biocidal moiety may offer promise for the future. In addition, the little studied WIC materials seem to have an interesting potential. From an environmental perspective and looking at the recycling of WPCs, the focus should be on non-petroleum source monomers and on ways of using forestry waste, such as bark and leaves as sources of suitable molecules.

Polymer impregnated woods and wood polymer composites are potentially very useful but costly to produce. There is scope for the production of particular WPCs for specific end uses. Reviewers of WPCs have considered the value of these materials (Lala et al., 1980), and the mechanical properties acquired by the wood by their inclusion (Akkanen et al., 1972). More recently the emphasis has been on the use of WPCs in modifying panel products such as MDF, OSB and LVL. Wood polymer material has been extensively reviewed in general by Meyer (1984), and with particular reference to tropical hardwoods by Noah & Foudjet (1988) and Yap et al. (1990).

WPCs are formed by impregnating wood with a monomer and curing or polymerising the monomer *in situ* by gamma-radiation, or catalyst and heat (Schneider, 1994). The monomer (usually a non-polar compound which will not penetrate the wood cell walls) is vacuum impregnated into the wood and later polymerised *in situ*. The polymer then resides exclusively in the lumina, unlike the chemical modification systems where the introduced materials actually react in and with the cell walls. The inclusion of a plastic in this way makes the product highly water repellent, while improvements to dimensional stability are relatively low (Rowell & Konkol, 1987). However, impregnation of beech (*Fagus sylvatica*) with dimethylol resin resulted in increased density, dimensional stability and mechanical durability (Militz, 1993a).

Swelling due to moisture uptake may be reduced if the polymer, resin or monomer penetrates the cell walls as phenol formaldehyde resin does. Observed rates of swelling for WPCs are considerably slower than untreated wood, however some polymers are hygroscopic allowing an increased swelling at high humidity (Ellis, 1994). Wood-polystyrene composites have shown no deterioration in mechanical strength after 14 years in soil contact (Lutomski, 1993). The inclusion and reaction of phenol-formaldehyde (PF) resins, proceeds via a condensation polymerisation or a free radical polymerisation process involving vinyl monomers (Kumar, 1994). PF resins located in the cell walls produces a dimensionally stable composite from condensation polymerisation, while vinyl monomers are non-polar and fill only the lumina thus water can still be taken up in the latter case of free radical polymerisation and effect product dimensional stability. A 10% polymer loading of the cell walls with PF resin gives good decay resistance (Furuno et al., 1992). The cell lumina can be filled with a polymer resin that will block water ingress and maintain the wood moisture content below the levels required for fungal decay. More recent techniques have involved the incorporation of boric acid into the resin mix for impregnation giving even greater biological resistance to the wood (Ryu et al., 1992b). The product was more effective against white rot fungi than brown rot as in many chemical modification trials (Imamura, 1993b).

There are numerous examples of wood polymer composites in the literature. The biological resistance of acrylic copolymer wood was reported by Fujimura et al. (1993a,b) while acryl-high-polymer 3 was found to provide improved durability and dimensional stability with a cross-linked epoxy polymer (Fujimura and Inoue, 1991). Wood impregnated with para-halophenyl para-tolyl sulfonamides increased resistance to brown and white rot fungi when the halogen was iodine or fluorine, but not for chlorine or bromine (Chen, 1994b).

Wood impregnated with a thermosetting resin which penetrates the cell walls (typically PF at 25-30% weight gain) and is then dried at 90°C and cured at 155°C, gives a product called Impreg in the USA (Rowell & Konkol, 1987). The polymerised PF is water insoluble. Creating veneers in this way and then forming a ply board under compression produces a PF-impregnated material known as Compreg. This is used commercially for dies, winding jigs, drilling jigs etc. (Rowell & Konkol, 1987).

Partially polymerised epoxy resin was vacuum impregnated into wood, having been mixed with a hardener compound, to produce a highly water repellent barrier for veneers (Rowell & Konkol, 1987). Urea formaldehyde resin has been used to modify alder and beech wood (Gal'Perin and Ignatovich, 1991). Though the imparted properties are highly species dependent, some species are more

difficult to treat than others (Noah & Foudjet, 1988). Brebner et al. (1988) showed that WPCs exhibited species dependent mechanical properties. Ellis (1994) demonstrated that WPCs could reduce water sorption characteristics while Schneider (1994) showed they impart improvements in finishing ability and hardness. A WPC incorporating bis-n-tributyltin and creosote imparted even further enhanced biological decay resistance (Ravindran et al., 1988). Wood treated with PF resin incorporating boric acid and then heat cured showed improved biological resistance at lower resin loading than when using resin alone (Ryu et al., 1992b). Using mixtures of resins and biocides is potentially a more economical method of producing improved wood than using resins alone.

Vinyl monomers (ethylene, propylene, vinyl chloride, vinyl acetate, vinylidene chloride, acrylonitrile, methylmethacrylate, styrene etc.) impregnated into wood and then followed by free radical polymerisation, induced by either heat and catalyst systems or gamma-irradiation, have been applied commercially. WPCs can be produced to meet specific requirements by blending monomers. Lucite or Plexiglas incorporated into wood has produced a WPC, which has been used for products including parquet flooring, sports equipment, musical instruments, knife handles and office equipment. It has been argued that in these cases the improved physical properties justify the higher cost (Meyer, 1982).

Methyl methacrylate (MMA) may be impregnated and then polymerised *in situ* by irradiating with gamma-radiation (Gibson et al., 1966; Schaudy et al., 1982; Thomas et al., 1993). This compound when polymerised in the wood gave improved mechanical properties and surface quality and is used in architectural features, sporting goods, crafted objects, furniture etc. Wood impregnated with partially polymerised epoxy resins yielded dramatic increases in hardness and abrasion resistance; the product has been used in wooden boat hulls, outer plywood veneers and for strengthening decayed wood (Norimoto & Gril, 1993).

MMA mixed with other monomers and polymerised by radiation has induced a higher degree of bonding and increased the dimensional stability and water resistance of the treated wood (Simunkova, 1991). Such WPCs are known commercially as "Acrylic wood" in the USA. Currently these WPCs are three times as expensive as untreated wood, but provide much better durability, e.g. for flooring in heavy traffic areas. The inclusion of a polymer which will increase tensile strength and dimensional stability may reduce the problems associated with rapid-grown low-density timber, such as home-grown Sitka spruce, some of which arise during the drying process. Applications in fibreboard products and polymer fibre composites, to reduce water absorption and swelling of wood fibre have been reported by Youngquist et al. (1992). In addition applications for composite boards from esterified aspen fibres were reported by Clemons et al. (1992). WPCs have also been used in imparting better sound insulation

properties with rubber chip and wood particle boards (Ohsawa et al., 1992). Stable covalent bonding has been identified as the key to the durability of exterior finishes, and a radical stimulated method of coupling alkyd resins to wood has been shown to improve considerably this bonding and thus its durability (Pizzi, 1990a). Le'Loch & Pizzi (1995) have reported the covalent fixation of styrene in wood.

Polymerisation initiators have been identified as having effects on the dimensional stability, static bending strength and rate of polymerisation of the introduced monomer when styrene was produced *in situ* in wood (Lawniczak, 1989).

Also of interest are hot-pressed wood blocks impregnated with maleic anhydride and glycidyl methacrylate (GMA) which produced cross-linked oligo-esterified wood with very good dimensional stability (Ueda et al., 1994). Such a product has strong links with section 4.2.4.2 (chemically modified wood). Maleic anhydride/glycerol (MAG) acylation of wood, where cross-linking the MAG between cellulose chains is the proposed mechanism, provided highly improved water resistance and mechanical strength of cellulose when studied in isolation with MAG oligomers (Uraki et al., 1994). This involved the reaction of two compounds, one with three-functional groups (glycerol) and a second with two-functional groups, to form a three dimensional polymer (Fujimoto et al., 1992).

A WPC produced from sugar maple (*Acer sacchaum*) with a vinyl monomer displayed increased mechanical properties and reduced moisture effects (Brebner et al., 1988; Schneider et al., 1989, 1990). Lower water vapour differential coefficients and reduced adsorption characteristics for WPCs were reported by Hartley & Schneider (1993). A water repellent, fluorinated monomer impregnated into pine wood samples and polymerised gave a WPC with similar improvements in properties (Abdel-Mohdy & El-Sawy, 1991).

Cocos wood (*Cocos nucifera*) and styrene monomer, which was deposited mainly in the thin-walled parenchyma gave a WPC which was considerably stronger and more decay resistant than the wood alone (Lawniczak et al., 1993). An unsaturated polyester and styrene mix impregnated at low initial moisture content gave better improvements in hardness of the resultant WPC for *Shorea contorta* and *Anthocephalus chinensis* (Carandary, 1989).

The application of a natural system of simple disaccharides called trehalose, could form a WPC of a most intriguing form. Trehalose occurs in cryptobionts - organisms that display hidden life or suspended animation (Rosner, 1995). It has been identified as preserving biological chemicals at elevated temperatures and humidities for an indefinite period of time. The system is elucidated as embedding proteins in a highly stable trehalose glass, which can continuously lose water (Rosner, 1995).

Clearly to improve the properties of WPCs, techniques must be developed which provide data leading to a greater understanding of how the absorbed polymer is distributed within the wood constituents. Tangiguchi (1993) established the relationship between the polymer loading and the imparted strength of the product material. An accurate technique for measuring the uptake of polymer by the sample, measured the increase in weight using the changes of the oscillation frequency of a piezoelectric quartz crystal which was dependent on weight changes of the electrode (Fujimora et al., 1994). It has also been demonstrated that the density and the position of the sample in the tree both influence the performance of the WPC formed from aspen (*Populus tremuloides*) and styrene. The greatest dimensional stability was found with a sapwood sample with maximum polystyrene content (Lawniczak, 1994).

The wide variety of monomers available and many methods employed to produce WPCs has emphasised the interest of these materials as high performance, lignocellulosic composites (Rowell, 1991; 1992 a,b). There are numerous specialist applications, and a great potential for more should the simplicity of the production process be improved.

2.3.4 Wood Inorganic Composites (WIC)

Wood/inorganic composites (WIC), or wood/mineral composites can be created by impregnating wood samples with sodium silicate (see also 2.2.10), or by soaking them in saturated solutions of aluminium sulphate, calcium chloride, barium chloride or boron compounds. Aluminium sulphate and boron compounds produced good composites that were dimensionally stable, able to exclude moisture, fire resistant, decay resistant and had improved bending strengths (Furuno et al., 1991; Furuno, 1992).

Silicic acid monomer solution, produced from a silicic acid aqueous solution subjected to cation exchange, may be impregnated into wood forming silicic acid gels that improve the dimensional stability and the water resistance (Yamaguchi, 1994a,b). This is a single stage process and consequently simple and inexpensive. It is also a non-toxic, and thus a more environmentally acceptable

method of impregnation to gain improved dimensional stability. The Sol-Gel process for the preparation of WIC, uses alkoxysilanes and ultrasonic radiation. A 15-30% WPG of silica gel, formed in the cell walls, improved dimensional stability (Ogiso & Saka, 1993). WIC produced by treating the wood with 3-isocyanatepropyl triethylsiloxane then tetraisopropyl titanate, fixed titanium dioxide in the lumina and promoted binding with the cell walls (Saka & Yakake, 1993).

An alternative WIC preparation method utilised the double diffusion process. The wood was first impregnated with water and then soaked in a solution containing barium or calcium cations, followed by a second soaking in a solution containing SO_4^{2-} or HPO_4^{2-} anions. The unreacted material was removed by further soaking in water, then the WIC was dried. Biodegradation tests demonstrated that BaHPO_4 in the wood was very effective in enhancing resistance to biodegradation, a WPG of 13% protecting the wood from decay fungi and termites. However, lower WPG values need investigating for economic reasons if the commercial application of this material is to be realised (Tsunoda et al., 1992). WIC produced by the double diffusion process imparted high fire resistant properties (Hirao et al., 1992). WIC treated veneers made into laminated veneer lumber at a WPG of 25% inhibited biological attack, although a WPG of nearly 100% was required to improve fire resistance (Takahashi, 1993). Extension of research into WIC and different inorganic chemicals looks promising.

2.4 THERMAL MODIFICATION

Many methods of thermal modification of wood have been reported in the literature. All the processes have in common a feature of heating wood to temperatures in excess of 200°C for several hours. Differences are noted in the medium of heat transfer, the method of reducing oxygen attack at elevated temperatures and the batch processing steps. The first articles concerning wood heat treatment are from the 1920's. After this the method has been developed in Germany (Giebeler 1983), France (Dirol & Guyonnet 1993), Finland (Viitaniemi 1997) and the Netherlands (Boonstra et al. 1998; Tjeerdsma et al. 1998). Heating wood in a restricted atmosphere induces the formation of cohesive structures between the cell wall components, chemical alterations and to a certain extent degradation. Heat treatment improves the dimensional stability and water repellency, abrasion, and permeability to water vapour. Heat treatment also darkens the timber although the density remains almost unchanged. The product is more brittle than the starting substrate and requires very sharp blades for machining.

Thermal treatments of wood rely on changes to the polysaccharides occurring. The molecular structure of the cell wall constituents changes during heating, in particular lignin and hemicellulose breakdown and start to form new water insoluble polymers. Characterisation of thermally modified wood revealed the molecular changes in structure that resulted in wood performance improvements (Tjeerdsma et al. 1998). Acetic acid liberation from the hemicelluloses and the catalysis of carbohydrate cleavage reduces the degree of polymerisation. Auto-condensation of lignin then leads to an increase in cross-linking and consequent dimensional stability and decreases in hygroscopicity. If the heat treatments are conducted in the presence of oxygen then major damage can result in breakdown of the cellulose as well. As a result 'shielding gases' are required to protect the cellulose from breaking down and rearranging, this is nitrogen in the case of the French retification process from dry wood and more typically it is the steam generated from heat treating wet or green wood. The heat treatment of timber requires the correct balance to be struck in delivering desirable durability enhancements with minimum loss in strength (Kamdem et al. 1999). It is this aspect of heat treated wood that defines the end uses of the product to those applications where large structural loads will not occur, such as garden fencing, window joinery and outdoor furniture.

The extent of the change in timber properties during heat treatment depends on:

- the maximum temperature and the maximum length of the actual heat treatment period,
- the temperature gradient,
- the maximum duration of the entire heat treatment,
- the use and amount of water vapour,
- the kiln drying process before the actual heat treatment,
- the wood species and its characteristic properties (Syrjanen 2001)

2.4.1 Heat treatment

Non-durable softwoods have been the principal focus of heat treatments in Europe but many timber species have been heat treated including albizzia (Sudiyani et al. 1999) and eucalyptus species (Santos 2000).

The development of a heat treatment process at industrial scale using a mild pyrolysis process (Gohar 1998) and other heat treatments have been developed in France where the process of heating dry wood to temperatures above 200°C in an inert atmosphere is called retification and the product is called retified wood (Vernois 2001). There are four plants manufacturing this product in France and more are expected to come on stream in the next few years. Heat treatments have also been developed in France where the process of heating wet wood to 230°C provides a saturated steam atmosphere for protection of the wood (Vernois 2001), similar to the process developed in Finland.

The process developed in Finland in the 1990s uses water vapour derived from the timber moisture content as the shielding gas to prevent deleterious breakdown of the wood structure. The product is called ThermoWood. The timbers are typically pine, birch and sometimes spruce species that can be treated green or kiln dried. The three stages are the temperature rise, the treatment stage and the cooling phase which are all carefully controlled in relation to the core temperature of the timber. The process liberates small amounts of acetic acid and phenolics which requires acid resistant stainless steel vessels to be used for treatments (Jamsa & Viitaniemi 2001). Temperatures between 180°C and 250°C are used to alter the physical and chemical properties of wood permanently. The changes that occur on heating wood and producing the modified product can be monitored using Fourier transform infra red spectroscopy (FTIR). Kotilainen et al. (2000) provides an

introduction to the handling of the FTIR data by principle component analysis. A summary of research on heat treatments in Finland is provided by Syrjanen & Kangas (2000) and the effect of heat treatments on the properties of spruce is provided by Viitanen et al. (1994).

The properties of timber that are changed by heat treatments include:

- colour, which changes to dark or mid brown, but is not UV stable
- the equilibrium moisture content, which is reduced by 50%
- the shrinking and swelling, which are also reduced by 50-90%
- the biological durability out of ground contact, which is improved
- the mechanical properties, which are reduced by up to 30% (Jamsa & Viitaniemi 2001).

Long-term natural weathering of coated ThermoWood has shown encouraging performance as a cladding product and coating performance is not adversely effected by the heat treated substrate (Jämsä et al. 2000).

2.4.2 Hydrothermal treatment

Steaming or heating wood in a compressed state improves hardness but results in slight decreases in other mechanical properties. It also produces a slight darkening in colour and no recovery of set (Inoue et al., 1993). The compression of wood while heating (170°C) causes lignin flow (in effect a rearrangement of the cementing material between the cellulose fibres) to relieve the internal stresses. This greatly reduces the tendency of wood to swell when wet and increases the strength. This product (Staypak) is used commercially for tool handles, mallet heads, jigs and dies in the United States (Rowell & Konkol, 1987). Heating wood under vacuum without compressing it still causes lignin flow and increases in stability, though the strength decreases. This product (Staywood) is not commercially used (Rowell & Konkol, 1987).

The "Plato-process" developed in the Netherlands for thermal modification of non-durable timber species involves a hydrothermal treatment followed by a drying and curing stage (Boonstra et al. 1998). This process produces a material with greater dimensional stability and improved durability aspects (Tjeerdsma et al. 1998). In the "Plato-process" the hydrothermal treatment is a two stage process, firstly the green wood is heated in aqueous solution to 200°C, where the pressure reaches 20bar and selective depolymerisation occurs. In the second

stage the aldehydes and phenols react once more with each other creating a polymer network (Hekhuis 1996). Characterisation of thermally modified wood including the cross linking and rearrangements at molecular levels that occur upon heating during the "Plato-process" are reported by Tjeerdsma et al. (1998).

Heat treatments have also been conducted in combination with a conventional wood protection chemical and the report of biological resistance of steam compressed wood that had been pre-treated with boric acid (Yalinhilic 1999). Though the added value through performance improvements of these composite treatments is not known.

2.4.3 Hot-oil treatment

Using oil to transfer heat to the wood and protect it from damaged at high temperatures has been used in a number of simple treatments, an example is fence posts treated in hot tall-oil (complicated mixtures of natural pine oils extracted from forestry waste) baths in Finland (Nurmi 2000). Promising results have been achieved using these tall oils but this work is hindered by the vast number of derivatives that could potentially be used and the quality control and performance of treated batches of material. On the other hand it is a very simple and accessible way of treating timber to generically enhance timber durability, perhaps with an application in more remote communities.

A hot-oil treatment has been commercially developed and patented in Germany using vegetable oils, such as rape seed oil, as the heat transfer agent (Rapp & Sailer 2001). Oil-heat treatment of Scots pine and spruce improved the dimensional stability and biological resistance of the product (Sailer et al. 2000). Natural plant oils lend themselves to the oil-heat improvement of wood from an environmental point of view and because of their physical and chemical properties. As renewable raw materials they are CO₂ neutral. The use of other plant oils, such as, sunflower oil, soybean oil, or even tall oils their derivatives, in addition to drying oils such as linseed oil, have also been investigated. The smoke point and the tendency to polymerisation are important for the drying of the oil in the wood and for the stability of the respective oil batch. The oil becomes thicker during repeat treatments because volatile components evaporate, the products arising from decomposition of the wood accumulate in the oil and change its composition. This obviously leads to improved setting of the oils and slight other changes in the surface characteristics of the treated wood.

2.5 ENZYMATIC MODIFICATION

Enzyme laccase is a recently developed bonding of lignocellulosic fibres through oxidation of phenolic compounds. During the reaction phenoxy radicals are formed in the lignin component of lignocellulose while oxygen is reduced to water. Substitution of synthetic adhesives for boards and panels using an enzyme treatment has both environmental and economical advantages.

The reaction mechanism can be described by a parallel mechanism of direct oxidation of lignin on the fibre surface and a phenol/phenoxy cyclic mediator process of dissolved phenolic compounds in the suspension liquid. No other radical species than phenoxy radicals can be found during laccase catalysed oxidation of wood fibres.

Fibreboard with good mechanical properties can be made from laccase treated fibres and a higher surface compatibility can be observed. The bonding strength appears to correlate with the amount of stable radicals in the lignin matrix.

Enzymatic treatments have also been developed in Austria and Germany to assist in the treatment of timbers with low permeability such as spruce. This can assist with both traditional wood preservation and wood modification. Initial results showed that penetration into the wood was improved considerably but results were too variable. Recent work has shown that sterilisation of the wood prior to the enzymatic treatment can give good, uniform penetration into the wood (spruce).

3. Commercial status of modification

3.1 OVERVIEW

To date modified woods form a very small percentage of the commercial market for wood. The high cost of most of the production methods limits it to special end uses, where paying more for the product is acceptable. However, this is likely to change in the short and medium term future. Wood modification will never completely replace current wood preservatives or the use of tropical hardwood, but will effectively offer a new range of "modified species". The full commercialisation of modified wood has begun to occur through thermally treated wood.

The status of wood modification has been described on four levels (Beckers & Militz, 1999):

Level 1:	Small scale laboratory experiments
Level 2:	Larger scale laboratory experiments Field tests Product evaluation
Level 3:	Pilot plant Technological and economic feasibility Industrial implementation
Level 4:	Industrial production

Level 1: Small scale laboratory experiments

Many different types of wood modification treatments have been evaluated using small scale laboratory experiments. These include:

- Thermal treatment
- Enzymatic treatment
- Methylation
- Epoxidation (EO, PO, BO, EpCl)
- Aldehyde treatment
- Anhydride treatments
- Isocyanate treatments
- Acid chloride treatments
- Carboxylic acid treatments
- Oxidation
- Silylation

These experiments identified the treatments that have been developed further. However, it must be stressed that there is still considerable potential to discover new modifying agents that might be suitable for the treatment of UK grown timbers both as solid wood and for wood based panels. There is still a real need for further fundamental research.

Even the most advanced wood modification systems are still in an early state of commercialisation. There are knowledge gaps including mechanisms of modification and analysis of the modified material for quality control purposes.

Level 2: Larger scale laboratory experiments, field tests and product evaluation

Several modification methods have progressed to this level. These include:

- Thermal treatment
- Epoxidation
- Formaldehyde treatment
- Acetylation (both solid wood and fibres)
- Fibre treatment with maleic anhydride
- Isocyanate treatments

At this stage of development additional knowledge gaps are exposed. These include: material properties of modified wood (mainly related to gluing and painting), potential for use in board products, and process development.

Level 3: Pilot plant, technological and economic feasibility, and industrial implementation

Only acetylation, thermal modification and formaldehyde treatment have reached this stage of development.

Acetylation

Acetylation of solid wood has been developed in the **Netherlands** over the last 7-10 years. A £2 million pilot plant has been built at the Akzo Nobel site in Arnhem. This development involved 65 companies from The Netherlands, Germany and Switzerland. The pilot plant has been thoroughly tested and is being used to generate material for various end use demonstrations. The predecessor to this plant was used to produce products including canal linings and window joinery (Beckers et al. 1995).

The up-scaling work is almost complete and a decision on a full industrial plant to produce 50,000 m³ of timber is expected this year.

Acetylation of fibres has been developed to a similar scale in **Sweden**. This development has been more secretive but a very large pilot plant was opened last year at a Swedish paper mill. The pilot plant has the potential to modify fibres for paper or wood based panels.

There is also an industrial plant for acetylation in **Japan** but its status is not known.

Thermal modification

Pilot plant work on a **hydro-thermal treatment** (the Plato process) has been completed in the Netherlands, and thermal modification of fibres has also been developed at a pilot plant level.

Pilot plant work on **retification** (thermal treatment) has been completed in **France**.

Pilot plant work has been completed on several different **thermal treatments** in **Finland**, these include Stellac and ThermoWood.

A hot oil treatment for garden timber has been completed in **Germany**.

Formaldehyde treatment

A formaldehyde treatment has been developed in **Germany** and is used for parquet flooring.

This stage of development becomes increasingly complex. Issues include the effect of up-scaling, processing technology, equipment design and requirements and quality standards.

Level 4: Industrial production

To date only thermally treated wood is currently being produced industrially, although acetylation could potentially follow very soon if key developments are given the go ahead.

Thermal modification

Pilot plant work on **hydro-thermal modification of solid wood** was completed in the **Netherlands** some time ago. A **full industrial plant** capable of producing 50,000 m³ of timber has now been completed and start-up production has begun. There have been some teething problems with initial production and sales.

Eight industrial thermal modification plants have now been established in **Finland**. Commercial production began in 2000 and this is anticipated to increase exponentially from now on! Most of these plants are now owned by

large Forestry based corporations. These products are already being marketed in the UK.

Approximately **ten thermal modification plants** have been set-up in **France**. Commercial production has begun and plants in other EU countries are planned.

The **hot oil treatment** in **Germany** is used to commercially produce timber which the company uses to produce garden furniture, fencing and pergolas.

The main issues at this stage relate to market acceptance/penetration as well as the mismatch between the current standards for timber compared to the properties of modified wood.

Note: There have been **NO developments in the UK**

3.2 ADDITIONAL INFORMATION

3.2.1 Chemically modified solid wood

Chemically modified wood has been broadly studied and numerous field evaluations of performance have been conducted across the world from India (Panda & Panda 1995), The Netherlands (Militz et al. 1997), Sweden (Brelid 1999), USA (Rowell 1995) China (Zhang et al. 2000) and the UK (Forster et al. 1998, Suttie et al. 2000). Rowell concluded (1975) that chemical modification of wood is only likely to prove fruitful for a specific end use rather than as a general material. This showed foresight, as today the employment of chemically modified wood is still in relatively specialised fields (Rowell & Konkol, 1987). Advances in this field have arisen through a strong commodity focus. During the the development of chemical modification in The Netherlands the practical potential for chemically modified wood was reviewed by Militz et al. (1997) and its scope for application in Ireland was assessed (Birkinshaw 1998).

Formaldehyde chemical modification of wood is used commercially for parquet flooring in Germany. It has also been experimentally used to increase the wet strength of paper (Rowell & Konkol, 1987). Reaction with formaldehydes and epoxides can reduce the mechanical properties of the wood and further research is required in the selection of different catalysts and reduced treatment parameters. Isocyanates have less reported problems (Holland & Carey, 1992). Modification of cell wall at molecular level (i.e. not filling only the lumena) is required to effect the ASE and ACE which is usually associated with molecular bulking, cross-linking or a combination of the two. Mechano-sorptive creep of PEG impregnated or esterified (epoxide treated) wood is increased because of the hydrophilic nature of the bulking agent that is not counterbalanced by cross-linking (Norimoto et al., 1992), thus yielding high ASE values. This plasticising action is important and may render epoxide modified wood unsuitable for load bearing structural members.

Chemically modified wood has been developed and used in several applications including;

- Acetylated solid wood laboratory durability trials provided the basis for the field trials of acetylated cladding with different coatings, acetylated garden wood, sea water exposure and canal linings (Beckers et al. 1995).
- Chemically modified wood as a thermoplastic material, using biodegradable plasticisers has been used to produce moulded trays and

boxes (Honma et al., 1992). It is also possible to plasticise wood using ammonia and mechanical compression, particularly on low density timbers, though there is limited reported evidence (Shiraishi, 1993).

- Musical instruments made from formaldehyde cross-linked wood improved dimensional stability, retains the vibrational properties of the wood. Similar reaction in wood, catalysed with sulphur dioxide and $\text{Fe}_2(\text{SO}_4)_3$, was found to improve its hygroscopicity and its acoustic properties for musical instruments (Yasuda et al., 1993).

When considering the processes for the chemical modification of wood, the toxicity and corrosiveness of the compounds concerned and the overall costs should be addressed. Compounds that react with hydroxyl groups are not selective and will attack all hydroxylated natural material including animal tissues, thus treatment plant operators should take especial precautions to avoid excessive contact with the reactants. Processing costs at the moment are high. The cost of producing acetylated flakeboard is over three times that of producing conventional flakeboards, such as waferboard and OSB. This suggests that products for structural members and panels, which are all relatively inexpensive materials, are unlikely to be acetylated before use at current costs. However, as the commercial process develops and production costs are reduced so the cost of the material will become more competitive with conventional treated material. This cost balance might not be an issue in some European countries if current attempts to prohibit certain wood treatments are successful. This would mean that modified wood would only need to be price competitive with tropical hardwoods. The high value end use categories do suggest many applications for acetylation technology (Youngquist & Rowell, 1988).

More recent studies of applications have concentrated on accelerating and improving the extent of reaction. Anhydride modified wood has been prepared without the use of solvents (Zhang et al. 2000). Whilst the use of specific solvents have provided catalytic effects as well. The potential of tertiary amine catalysts to improve the acetylation of wood showed that pyridine acts as a solvent and a catalysts for the acetic anhydride reaction with wood (Hill et al. 2000). The dielectric properties of wood were determined to be suitable for microwave heating and confirmed in small scale trials for the acceleration and reaction of acetic anhydride in wood to produce and modified material (Brelid et al. 1999). Acetylation of solid wood using microwave heating in laboratory scale experiments show an acceleration of the reaction phase and an acceleration of the by product removal phase (Brelid 1999).

However, by far the most commercially prominent development has been the development of acetylation for solid wood in The Netherlands, reported in Section 3.1.

3.2.2 Chemically modified wood-based panels

Wood-based panel products such as OSB, chipboard and medium density fibreboard, offer particular advantages because in this form the wood provides a relatively large surface area for penetration and reaction. This may enable panel products to be used in service environments currently prohibited to them.

A promising area for chemically modified products is in the manufacture of MDF. British Petroleum, the manufacturers of acetic anhydride, developed a pilot plant (Kumar, 1994). The production of acetylated wood fibre on a commercial pilot plant scale with a relatively simple, no solvent or catalyst process is described (Sheen, 1992). A consistent level of acetylation was achieved, although prospects for full scale industrial production were not realised due to the very high cost of production which was passed on as a high end cost of the board materials.

Acetylated wood products may be applied to internal walls of bathrooms, to sign boards, roof shingles and other situations where constant dampness is an element of service life. An LVL product has been prepared where acetylation, using sodium acetate as a catalyst, was applied prior to hot pressing (Takahashi, 1993). Alternatively the application of acetylated wood products has been combined with WPC for flooring, violins, sounding boards in stereo speakers, and piano pin blocks. Maleic acid-glycerol treatment has been used to obtain permanent set after wood bending and improved dimensional stability of particleboards (Norimoto & Gril, 1993).

Chemical modification of wood can create new challenges in subsequent processing. For example, acetylation of wood reduces its hydrophilic property, thus presenting potential problems in the use of water-borne adhesives that have strong attractions to wood hydroxyl groups. Water-borne adhesives tend to be incompatible with acetylated wood, resulting in poor wetting and penetration of the adhesive. A structural assessment of acetylated and unmodified laminates made from Scandinavian pine and spruce highlighted four cold setting adhesives as suitable for laminate construction as these maintained the structural integrity of the laminated product (Vick et al., 1993).

Panel products made from fibres or flakes of timber that might be acetylated before being manufactured into a board have commercial implications for the UK markets. It would appear that reconstituted panel products, such as medium density fibreboard (MDF), oriented strand board (OSB) and flakeboards, provide a very real and suitable avenue for the application of chemical modification to wood technology. This is principally because the practical problems of modifying wood are greatly reduced when using small chips or fibres instead of solid

blocks. Enormous benefits could arise from improvements in these products. Chemical modification applications to fibre boards can reduce water absorption and swelling of wood fibre and polymer fibre composites (Youngquist et al., 1992). The manufacturers of panel products are very keen to see modification processes succeed as their products are notoriously difficult to treat with conventional preservatives (Mitchoff & Morrell, 1991). Production costs could accept and incorporate the increased costs of modification at present provided the processes are developed and tailored to the end-products.

Fibres of *Populus tremuloides* treated with poly(methylene polyphenyl isocyanate) and then coated with polystyrene showed improved mechanical properties and dimensional stability under extreme conditions (Maldas et al., 1990). Composite boards produced from esterified aspen fibres showed similar improvements (Clemons et al., 1992). This highlights the connections between the areas of chemically modified wood being used in wood polymer composite manufacture. Low density fibreboard manufactured from acetylated fibres was more dimensionally stable than the equivalent board made from steam treated fibres (Rowell et al. 1995).

Particleboard adhesives are entering the technology of fast curing PF resins (Yazaki et al., 1994b). Often particleboard adhesives have preservatives added to them to improve their properties (Khatilovich & Maksimenko, 1990), such as arsenic trioxide added to phenol formaldehyde (PF) resin adhesive in plywood (Shukla & Joshi, 1992). Wood modification has excellent potential in applications for reconstituted wood-based products, especially by way of a simple one-step dip treatment process for acetylation (Rowell et al., 1986). Simple non-catalysed systems are a viable way of improving industrially the dimensional stability and biological resistance of board products (Rowell et al., 1987; Rowell & Plackett, 1988; Mahlberg, 1989).

Water adsorption is a serious problem with board products, causing swelling and irreversible release of compressive stresses in the boards (Kajita & Imamura, 1993). However, acetylated low density particle boards performed more like solid wood and MDF treated by formalisation using tetraoxane and sulphur dioxide catalysis produced similar results (Kajita & Imamura, 1993). Increased dimensional stability, strength and improved finishing qualities were imparted to aspen fibre acetylated by ketene gas, acetic anhydride, then formed into acetylated MDF using PF resin (Rowell et al., 1991a). The use of ketene gas (CH₂CO), produced from the pyrolysis of acetone, adds on to polysaccharide units producing no byproducts, acetylating the wood (Rowell et al., 1991a). Flakeboards that are acetylated to 15-17% WPG are highly resistant to fungal attack and tunnelling bacteria, and also swell in water at greatly reduced rates (Rowell et al., 1987; Rowell & Plackett, 1988). Acetylated flakeboards with a PF

adhesive resin, show lower moisture contents, improved dimensional stability and improved biological decay resistance (Hadi, 1992). The chemical treatment of wood for improved dimensional stability via acetylation, liquid and vapour phases, has very strong implications for the flakeboard manufacturing process (Rowell, 1989). Previously, Sheen (1992) reported on the industrial process of producing acetylated wood fibre using acetic anhydride. However, by far the most commercially prominent development has been the development of acetylation for wood in Sweden, reported in Section 3.1.

The vapour phase preservative treatment of manufactured wood-based board materials including particleboards, MDF, aspen wafer boards and OSB has been investigated using esterified borate in the vapour phase to obtain complete impregnation (Murphy & Turner, 1989). A relatively rapid and complete penetration of boards with trimethyl borate (TMB) was achieved, with 0.5 % w/w boric acid equivalent providing complete protection in fungal decay tests.

3.2.3 Physical modifications and wood polymer composites

WPCs find applications in the production of musical instruments where a demand for high dimensional stability is required; they also impart excellent and permanent vibrational properties. Vibrational properties have been demonstrated for methyl methacrylate and isocyanate impregnated wood cured by gamma-radiation (Schaudy et al., 1982), and generally for chemically modified and resin impregnated wood (Akitsu et al., 1993; 1992; 1991).

Polymer impregnation of wood as a means of preserving the wood has been used in marine archaeology and the treatment of timbers in ships of historic interest. In treating the Tudor ship the *Mary Rose*, a PEG solution was sprayed onto the constantly wet oak timbers. The molecular weight (MW) of the polymer being used is highly significant. It has been estimated that if the process includes spraying PEG polymers (MW 200) for 15 years, this will thoroughly penetrate the timbers, and that subsequent spraying of PEG MW 4000 for 5 years will penetrate the decayed surface layer and bulk it out, providing both dimensional stability and greater hygroscopicity (Stevenson, 1995). The permeation of the PEG can be monitored at the cellular level using a non-destructive method, thus correct MW polymers can be calculated for the complete permeation of the sample (Stevenson, 1995). Ethylene diamine tetra acetic acid (EDTA) pre-treatment of the wood removes free iron and aids PEG penetration.

Understanding the compatibility of phases in WPC production might have the possibility of using chemically modified wood (more hydrophobic). This is more

compatible with polymeric material, also grafting to the wood surface and the use of radical initiators might also be used (Hill 2000).

Schneiders review (1994) recommended the study of polymerisation reactions in wood with a view to developing chemical formulations and curing processes specifically for wood, as he concluded that monomers reacted differently in wood during polymerisation than in isolation in a reaction vessel. He also noted that treatment fluids might separate out into individual constituents as the wood acts chromatographically. Properties of WPCs, such as elasticity, could be predicted from a combination of the spectral characteristics of the wood and polymer; the rheological behaviour of the WPC could be predicted from a knowledge of the volume share of the individual components (Poliszko, 1990).

From an environmental standpoint, attention should focus on the development of WPCs using both wood and plastic from renewable resources, particularly non-petroleum source monomers such as furfuryl alcohol derivatives (Schneider, 1994; Ryu et al., 1992a). The economical use of forestry resources is important and composites from recycled materials such as wood fibre and plastic composites are attractive (Rowell et al., 1991b).

The potential applications for many WPC materials has already been established. WIC materials seem to have an interesting and promising future. From an environmental perspective and looking at the recycling of WPCs, the focus should be on non-petroleum source monomers and on ways of economically using forestry resources (Sasaki et al., 1993).

3.2.4 Thermal modification

Markets will continue to grow as demonstration of the materials properties are pursued. The environmental profile of heat treating timber and the potential for reuse of forestry waste products to generate the heat for the treatment plant will be future issues. The markets for oil-heat treated timber are likely to open up in the UK. Of the modification processes that are applied to timber to improve appearance, dimensional stability and durability the heat treatments are most commercially developed. The initial products manufactured using heat treated timber are:

- Cladding boards
- Window frames
- Garden furniture
- Fencing

- Decking timbers

Some of these products are beginning to appear in the UK market supplied through the Finnish treaters into UK timber merchants.

4. UK Opportunities

4.1 INTRODUCTION

Modification of wood and fibre materials will extend the market opportunities for UK grown wood and wood based products. Particularly in applications where it is subjected to the weather or moisture. This will enhance the use of renewable resource (home grown) wood which is also good from a CO₂ point of view since an increase in life span of wood products reduces the amount of CO₂ in the atmosphere. Expanding the possibilities for the use of home grown timber will also provide more work for industries related to the UK wood sector. The possibilities to use timber with originally a lower natural durability and performance will stimulate the use of UK grown timber species instead of importing American, Asian or African species, thus improving the forestry chain within the UK. A major innovation will be that fast growing softwood can be turned into durable timber with good dimensional stability.

The technology of Modification of wood and fibres has only recently started to be commercialised and in addition to conventional timber application many additional novel materials and applications can be envisaged. For example:

- Modified veneers could be used for the production of high quality plywood boards.
- The treatment of wood particles could lead to water resistant OSB (oriented strand board), particleboard, MDF and HDF.
- The changed wood colour gives new aesthetic possibilities.

The treatment of fibres opens up almost unlimited application fields like extrusion and moulding of products, new insulation materials etc.

The use of Wood Modification could improve the properties of UK grown timbers. Depending upon the technique used the potential improvements include: durability, dimensional stability, equilibrium moisture content, anti shrink efficiency, paintability and fire performance. This could achieve better utilisation of the increasing volumes of UK grown timbers, increasing their service life and increasing the market they can access.

The UK was a key player during the early stages of Wood Modification development in Europe (University of Wales and BRE). However, in the UK there

has been relatively little pressure to replace the use of energy intensive and fossil fuel based construction materials using more environmentally sustainable and renewable materials, such as wood. There has also relatively little pressure on the use of existing biocide based wood preservatives and on non-sustainably grown tropical timbers compared to other developed countries in Europe.

The legislative and consumer pressures in European countries including The Netherlands, Germany, France, Denmark, Finland, Sweden, and Belgium have meant that innovative and sustainable technologies for enhancing the performance of wood (including durability) have received considerably more attention than they have in the UK. Some of these technologies are now very advanced and the UK has fallen up to ten years behind the current state of the art.

Some of these technologies have already begun commercial production, in particular the thermal treatments, and sales of heat treated timber of unknown source have come on line in the UK during 2001. It is known that these companies have already targeted the UK as a market into which they will sell their timber.

This technology gap makes very concerning reading for the UK situation and the future UK production of timber, particularly if we fail to seize the opportunity to catch up with these technologies. At present this represents both a missed opportunity for UK home grown timber and a threat to potential future markets. This project aims to **begin** the reversal of this situation.

If European legislation follows the majority of developed European countries it is possible that in the future it will become difficult to sell timber treated with many of the preservative systems that are currently used to treat home grown timbers.

Although the UK is now a long far behind the current state of the art this does NOT mean that there are not real opportunities for the UK. BRE and the University of Wales, Bangor have maintained a presence in European developments and there are real opportunities to partner with the existing companies and institutes to tailor and develop wood modification techniques specifically for our home grown timbers and specific products.

4.2 OPPORTUNITIES FOR HOME GROWN TIMBER

4.2.1 Thermal modification

It is clear from the information presented in this document that it is the thermal treatments that offer the most immediate commercial opportunities. Since this technology is now so advanced in three European countries there seems to be little to be gained from re-inventing the wheel and developing completely new heat treatments for UK grown timbers. The opportunities for UK timber arise through partnering with the European companies and research institutes who have developed these technologies. There are advantages and disadvantages to the different systems developed in each of the three countries. Where possible opportunities will be sought to evaluate treatment of home grown timbers using the different techniques. BRE is already involved in negotiations to facilitate these opportunities. However, it must be remembered that the different countries and companies have different motivations to assist or resist the transfer of these technologies to the UK.

The Dutch heat treatment process (Plato) is very advanced but is also highly dependant upon capital investment. As with several wood modification systems the primary species modified with this process is radiata pine. This indicates that it could be suitable for modification of Scots pine but its application to UK spruce is unknown. This is also a process that is not likely to ever be set-up at individual sawmillers facilities. It is more likely to require a centralised larger scale plant. In the favour of this process could be the motivation of the Dutch industry since there is no competition to sell Dutch home grown timber into the UK so there could be potential to develop this process for use in the UK through a licensing agreement.

Finish systems are mainly owned by large scale Finish forest based corporations. There is a strong motivation to sell treated Finish grown timber into the UK but there is likely to be little motivation to assist in the development of UK timber, but there is one exception. BRE has already made contact with this company. Since the Finish systems have all be developed with the motive of value adding to Finish grown timber, including spruce, it is considered that these process should have been developed to work with Norway spruce so there is a good chance that the processes could be adapted for UK grown spruce.

At this French system seems to be the most promising of the heat treatments for transfer to UK spruce. The main reason for this is that the process is less capital intensive and would be more suitable for development at individual sawmills. This would make it more attractive for the UK timber processors. Good contacts have been established to this company and the initial feedback is that

modification of spruce or Scots pine could be possible. Trials on UK timbers are currently being negotiated by BRE.

These process must be considered for the UK panels sector as well as for solid wood. The cost issues for wood-based panels will be equally, if not more important than for solid wood, but there are also considerable gains that could be achieved in panel performance.

4.2.2 Hot oil treatments

These treatments are a variation on thermal modification. A patent is held in Germany, which covers some uses of hot oil. However, there is more scope for innovation in this area and this presents opportunities for the UK to catch up with its European competitors. Again specific opportunities exist through partnering, BRE will bring these opportunities to the UK sawmilling industry.

One possibility for the use of hot oils is to use tall oils (pine oils). Considerable work has been carried out on the use of Finnish tall oils for wood modification. This could offer long term possibilities for UK timber. The main difficulty is to identifying and separate out which of the several hundred components should be used for wood modification.

4.2.2 Acetylation

Acetylation of Irish spruce has been evaluated in the Netherlands. There were problems relating to uneven penetration of the wood. To successfully acetylate solid spruce a pre-treatment would be required. Enzymatic treatments might offer the long-term solution if the high costs could be resolved but there could be more immediate possibilities for Scots pine.

An acetylation plant would be very expensive and complex to set up. It is essentially a cross over between the chemical industries and the timber industry. This process could NOT be carried out by a conventional sawmill. However, there could be an opportunity set -up of a site in UK or to supply timber to The Netherlands.

Although there are problems for the acetylation of solid spruce, these could potentially be overcome for wood-based panels. The large scale of the UK wood panels industry means that there could be possibilities to use acetylation for treatment of fibres, particles/chips and flakes. This should not be ignored.

4.2.3 Enzymes

Enzymes potentially show excellent technical possibilities for UK spruce. Unfortunately the process is slow and the need for sterilisation would be expensive. This added to the relatively high costs of wood modification processes becomes a very expensive treatment for timber. This could only be economically feasible if dramatic savings could be made.

4.2.4 Additional opportunities

Another process that could offer potential to UK timbers is the impregnation with cellulose. This has been developed in New Zealand but could potentially be applied to home grown timber.

There are also methods that can be used to increase surface hardness. These include formaldehyde modification and isostatic compression. Increasing the hardness of home-grown softwood would could increase their use for flooring enable new markets to be exploited such as joinery and furniture.

4.2.5 Sustainability and recycling

Wood modification offers the UK opportunities to meet environmental objectives both for materials in use but in particular at the end of life. Although modern wood preservatives have achieved considerable improvements in their environmental performance with regard to leaching of chemicals they still cause a problem at the end of life. Traditional wood preservatives contain potentially toxic substances (e.g. Copper, Tin, Chromium, Arsenic). Contamination by metals in these prevent the full environmental benefit being achieved from wood since even if it is burned for energy the ashes will contain higher concentration of these chemicals and these ashes will have to go to landfill.

For modified wood there are no such problems and at the end of life the wood can be consider in the same way as virgin wood.

5. Conclusion and recommendations

- In order to sustainably use fast grown timber for demanding applications requires the use of wood preservatives to enhance their durability. Attention is increasingly focussed on non-biocidal ways of enhancing the durability of timbers to overcome issues relating to end of life and during life environmental issues. This is where wood modification offers future solutions.
- In many European countries there is considerable environmental and consumer pressure on the use of: fossil fuel based materials, non sustainably sourced tropical hardwoods and biocidal based wood preservatives. This has lead to considerable investment in the development of wood modification techniques.
- The different wood modification techniques have been developed to different levels, but for most advanced techniques commercial production has begun and products are now being advertised for sale in the UK to a market that is NOT prepared for these products.
- Currently the production of modified wood is very small compared to the consumption of timber in Europe. However, the production of some of these products is anticipated to increase exponentially. This represents both a threat and a missed opportunity for UK grown timber at a time when home grown timber production is set to increase up to ~17 million m³ per year within 15 years.
- Despite the UK's lack of investment in wood modification compared to other European countries there are still real opportunities to exploit these technologies to add value to home grown timbers.
- The opportunities for UK timber arise through partnering with the European companies and research institutes who have developed these technologies. BRE together with the University of Wales have represented UK interests in European developments, which has kept the door open for UK companies to adapt techniques for use with home grown timbers.
- The market opportunities through wood modification apply to both solid wood and to wood based panels.

- Effort should focus on raising the value of spruce as the predominant species in the UK. However, Sitka spruce is one of the more difficult species to modify due to its low permeability and many wood modification systems have not been tested on a spruce substrate. Investment will be needed to make this possible.
- The different forms of wood modification enable wood species to be tailored to suit the performance requirements of the end product. For example for parquet flooring the modification could be tailored to gain maximum improvement in dimensional stability, hardness and wear resistance or to stabilise the colour/appearance whilst for external joinery biological durability will be of greater importance.
- The focus of wood modification treatments needs to be the creation of wood and wood based products that are fit for purpose. The process can be tailored to produced a modified product with a specific service life for its intend use.
- At present there are no recognised standards for the performance of modified wood, which performs differently to both naturally durable timber and preservative treated timber. Performance data on all forms of modified wood will be urgently required as the commercial importance of these products accelerates. In all cases there is a need for the development and testing of demonstration products within the UK.
- In addition to the many wood modification techniques that have so far been evaluated or developed there are many more yet to be discovered. The only way that the UK will be able to discover new techniques to add value to UK grown timber will be through investing in basic research in this area.
- Wood modification can add value by being product specific, for example specific epoxides can be used that have biocidal or fire retardant properties (such as organo-phosphorous monomers) attached to them. These "tagged-on" compounds are taken into and bound in the wood structure.

Additional specific conclusions can be broken down into the different forms of wood modification as discussed within the report.

- **Chemical modification** in particular acetylation could have real advantages for UK grown timber. This needs to be determined through evaluation of UK species and in particular the development and testing of demonstration products. In particular the chemical modification of strands, chips or fibres could enable exterior wood-based panels to be produced with superior durability and dimensional stability, opening up new markets for these materials. There are some limitations for the chemical modification of spruce due to its low permeability but the use of enzymatic treatments might offer a solution to this. At this stage it is believed that chemical modification will be focused at higher value end uses where dimensional stability and durability are particularly important. For example, acetylated wood can be used in situations where wood products would be exposed to high changes in humidity and moisture ingress such as bathrooms, window joinery and roof shingles.
- **Physical modification**, such as wood plastic composites are likely to be used where good dimensional stability and wear resistance are particularly important. Simple moisture exclusion, such as sealing end grain prior to assembly have an important role in extending the service life of timber commodities. Also, the use of special monomers which incorporate the ability to polymerise with the inclusion of a biocidal moiety may offer promise for the future. From an environmental perspective the focus for wood polymer composites should be on non-petroleum source monomers and on ways of using forestry waste (such as bark and leaves) as sources of suitable molecules. Wood polymer composites with improved wear resistance and colour stability are suited for use in high value end markets such as parquet block flooring.
- **Thermal modification** offers real potential for UK grown timber, in particular the process developed in France. There is also good potential to exploit the use of thermal treatments that use hot oils since this area has considerable scope for innovation. Possibilities in this area are currently being negotiated. In general thermally modified wood will be targeted at higher value added, non structural applications such as cladding, window joinery, garden furniture and decking.
- **Enzymatic treatments** could offer new possibilities for spruce by enhancing its permeability. This could apply to both wood modification and traditional wood preservation allowing even penetration of reagent into the wood substrate.

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