Densification of Wood.

The influence of hygrothermal treatment on compression of beech perpendicular to gain

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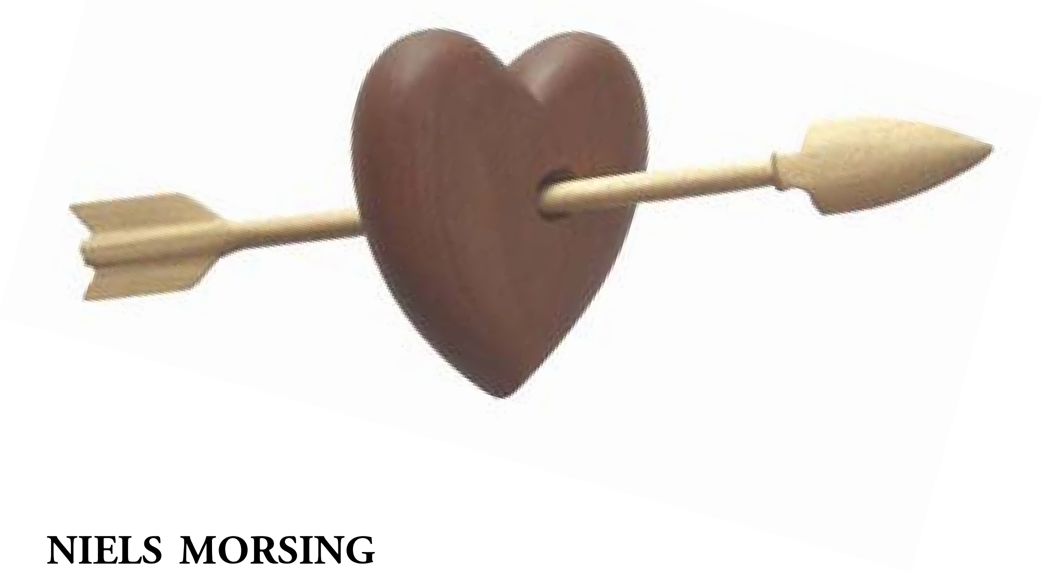

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Niels Morsing

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Preface

The present report is submitted in partial fulfilment of the requirements for obtaining the degree of Ph.D. The work was carried out at the former Building Materials Laboratory[1]under supervision of Dr. Preben Hoffmeyer.

The author wishes to express his sincere thanks to Dr. Preben Hoffmeyer for his support and guidance during the project.

Thanks to the staff at the former Building Materials Laboratory for invaluable help in experimental work. Thanks are particular directed towards Mrs. Ulla Gjøl Jacobsen. Also thanks to the staff at Fritz Hansen Eftf. A/S for providing the material for the work, to Per Skovholt for his support, and to Inger Mann Nielsen for fruitful discussions and company during study tours in the United States and Japan.

I am deeply indebted to the staff at Wood Research Institute, Kyoto University, especially to Dr. Inoue, Dr. Norimoto and Dr. Morooka. Their hospitality, inspiring discussions and patience during three study tours are most appreciated.

The project has been possible thanks to an initiative from Skandinavisk Industries A/S. The financial support for the work was provided by Skandinavisk Industries A/S and the Danish Agency for Development of Trade. The support is gratefully acknowledged.

Gentofte 1997.09.30

Niels Morsing

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[1] From 1996 merged with Department of Structural Engineering to form a new institute:
Department of Structural Engineering and Materials (BKM).

Summary

A study of compressed (densified) beech is presented. The main objective is to investigate the combined effect of temperature, steam pressure, time, and moisture content on the compression of beech perpendicular to the grain. A better understanding of these parameters can contribute to the improvement of the existing methods for densification of wood with respect to springback, dimensional stability and hardness.

The dissertation comprises 10 chapters, of which Chapter 3-7 represents the main experimental work. These chapters is structured to reflect the 4 stages identified in making compressed wood: Softening, Compression perpendicular to the grain, drying, and eliminating springback.

Softening

Existing knowledge on wood softening and degradation through hygrothermal treatment is reviewed applying theories from the polymer technology.

Both short-term and long-term tests were performed on specimens inside an autoclave[1]. The purpose of the short-term tests was to study the effect of hygrothermal treatment (steam) on the compression response (stress-strain). The purpose of the long-term tests was to study stress-relaxation and creep. In addition to these tests a study of the dynamic mechanical properties using a vibration test method inside an autoclave[1] is presented.

All mechanical tests applied showed a good agreement between the property investigated (stiffness) and the softening/degradation condition. Such tests, therefore, are useful in quantifying the softening/degradation condition of wood. A dramatic reduction in elastic modulus and dynamic modulus (stiffness) is identified. The main reduction is seen in the beginning of the steam treatment.

The results from the mechanical tests indicate that the principle from polymer technology of time temperature superposition can be applied to the data. However, it is found that degradation mechanisms at high steam pressures dominate the compressive behaviour. Consequently the WLF (Williams-Landel and Ferry) equation can not be applied. It is proposed to evaluate the mechanical properties for the range of conditions of service expected and display them graphically (master curve and shift factors) for the prediction of a particular mechanical response.

Springback

Methods for eliminating the memory effect incorporated in the compressed wood is reviewed and experimentally examined. This effect, known as springback, manifests itself in excessive swelling when the compressed wood is exposed to moisture and heat. The experiments focus on heat treatment of the compressed wood (in oven or hot-press) or steam treatment (in an autoclave).

The experimental study includes a very promising method of eliminating springback, called ***hygrothermal treatment in a closed system***. The closed system consists of a hot-press equipped with a Viton sealing to prevent the moisture from evaporating. A steam pressure is developed by the moisture inside the wood when the wood is compressed.

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[1] The experiments were carried out at BKM, DTU, Denmark

It is demonstrated that springback can be completely eliminated, and that steam treatment greatly reduces the time to eliminate springback. Springback is avoided by the accelerated stress-relaxation from steam treatment identified in the mechanical tests.

It is assumed that the elimination of springback for ***steam treated wood*** is the result mainly of the breaking of primary bonds responsible for the memory effect in wood. Based on the basic theory on wood polymers it is expected that a slight rubbery flow of lignin and a formation of bonds in new positions takes place when the wood is cooled.

Conversely it is assumed that the elimination of springback for ***heat treated wood*** is the result of thermal degradation of the hygroscopic components in the cell wall (hemicellulose and lignin).

Properties

The properties of compressed beech with respect to its physical and mechanical properties are examined. An important experimental effort is the attempt to quantify the dimensional stability of compressed wood.

It is demonstrated that both hardness and dimensional stability are improved by either heating or steaming compressed wood in the compressed state. The table below shows characteristics of the steam- and heat treatments under conditions where springback is eliminated. The dimensional stability of compressed wood is investigated using sorption tests at different relative humidities.

Characteristics of compressed beech under conditions where springback is eliminated.

Characteristic:	Heat treatment	Steam treatment
Elimination of springback	190°C, 20 hours	190°C, 15 min.
Hardness[1]	+20%	+100%
Dimensional stability[1]	+20%	+10%

[1] Compared to ordinary beech

It is shown how the process of densification may be optimised using the knowledge obtained in the experimental part and using the theory of time temperature correspondence from polymer technology.

It is hoped that the new knowledge presented in this thesis can form the basis for further work in the area of densification of wood. Such work should be focusing on specific end-uses of the product and include considerations on economical aspects of the treatment.

Sammenfatning

Nærværende rapport indeholder et studie i densificering af bøgetræ. Hovedformålet er at undersøge den kombineret effekt af temperatur, damptryk, tid, og fugtindhold på komprimering af bøg vinkelret på fiberretningen. En bedre forståelse for disse parametre vil medvirke til optimering af de eksisterende metoder til densificering af træ med hensyn til "springback", dimensionsstabilitet og hårdhed.

Rapporten er organiseret i 10 kapitler, hvor kapitel 3-7 repræsenterer den vigtigste eksperimentelle del. Disse kapitler er opbygget således, at det afspejler de forskellige trin identificeret ved fremstilling af komprimeret træ: Blødgøring, komprimering vinkelret på fiberretningen, tørring og eliminering af springback

Blødgøring

Eksisterende viden om blødgøring af træ og termisk nedbrydning gennemgås med baggrund i teorier hentet fra polymerteknologien.

Korttids- og langtids tests er gennemført inde i en autoklave til undersøgelse af hygrotermisk påvirkning (dampning) af bøg under komprimering. I tillæg til disse forsøg er gennemført et studie af, hvorledes de dynamisk mekaniske egenskaber påvirkes af damp. Der er i disse forsøg anvendt en "vibrationsmetode".

Alle de nævnte mekaniske tests viste en god sammenhæng mellem de undersøgte mekaniske egenskaber og "blødgøringsbetingelserne". Forsøgene viste en dramatisk reduktion i både det elastiske E-modul og det dynamiske E-modul. Reduktionen var størst i begyndelsen af dampbehandlingen. Testene har vist sig nyttige til karakterisering af træs blødgøringstilstand.

Resultaterne fra de mekaniske test indikerer, at temperatur-tid superpositions princippet kendt fra polymerteknologien kan anvendes på dataene. Det er dog fundet, at nedbrydningsmekanismer dominerer ved høje damptryk. WLF-ligningen (Williams-Landel and Ferry) kan således ikke anvendes. Det foreslås i stedet, at de mekaniske egenskaber bestemmes for de betingelser, der forventes anvendt i "praksis" og, at de derefter vises grafisk (master kurve og forskydningsfaktorer), til forudsigelse af et specifikt mekanisk respons.

Springback

Metoder til eliminering af de mekaniske spændinger (træets hukommelse), der opstår ved komprimering gennemgås og undersøges eksperimentelt. Denne effekt, kendt som springback, viser sig ved kraftig svelning når det komprimeret træ efterfølgende udsættes for høj relativ luftfugtighed (eller vand) og høj varme. Eksperimenterne fokuseres på varmebehandling (i en ovn eller varmepresse) eller dampbehandling (i en autoklave) af det komprimeret træ.

Den eksperimentelle del inluderer en meget lovende metode til eliminering af springback, kendt som hygrotermisk behandling i et lukket system. Det lukkede system består af en varmepresse udstyret med en Viton gummiring, der forhindrer fugt i at slippe væk fra træet under opvarmning. Når træet komprimeres dannes et damptryk inde i træet.

Det vises, at springback kan fjernes fuldstændigt, og at dampbehandling reducerer den nødvendige tid til eliminering af springback. De mekaniske test har vist, at springback undgås ved den accelererede spændings-relaxation, der opstår under dampbehandlingen. Det er bl.a fundet, at komprimering i et lukket system ved 190°C i 10 minutter eliminerer springback.

Det antages, at eliminering af springback for dampbehandlet træ er et resultat hovedsageligt af nedbrydning af de primære bindinger, der er ansvarlige for hukommelseseffekten i træet. Det må forventes, iflg. polymerteorien vedrørende termoplastiske materialer, at ligninen er i en gummiagtig tilstand på grænsen til en flyde tilstand og, at der dannes nye primære bindinger i den deformerede tilstand når træet afkøles.

Omvendt forventes, at eliminering af springback for varmebehandlet træ er resultatet af termisk nedbrydning af de hygroskopiske komponenter i cellevæggen (hemicellulose og lignin).

Egenskaberne

De fysiske og mekaniske egenskaber er grundigt undersøgt. En vigtig eksperimentel part er forsøget på at kvantificere dimensionsstabiliteten af komprimeret træ. Dimensionsstabiliteten er bl.a undersøgt ved anvendelsen af sorptionsforsøg ved forskellige relative luftfugtigheder.

Både træets hårdhed og dimensionsstabilitet er forbedret ved enten opvarmning og ved dampning i den komprimeret tilstand. Tabellen nedenfor viser karakteristiske egenskaber for dampbehandlet henholdsvis varmebehandlet træ under betingelser, hvor springback er elimineret.

Tabel Karakteritika for komprimeret bøg under betingelser, hvor springback er elimineret.

Egenskab:	Varme behandling	Damp behandling
Eliminering af springback	190°C, 20 timer	190°C, 15 min.
Hårdhed[1]	+20%	+100%
Dimensionsstabilitet[1]	+20%	+10%

[1] Sammenlignet med ubehandlet træ.

Det er i rapporten vist, hvordan densificeringsprocessen kan optimeres med henblik på forbedring af egenskaberne ved at bruge teorien omkring tid-temperatur sammenhængen, der kendes fra polymerteknologien.

Det videre forløb

Forhåbningen er, at den tilegnede viden, som er præsenteret i nærværende rapport, danner grundlag for videre arbejde inden for emnet densificering af træ. Dette arbejde bør koncentreres omkring specifikke anvendelser af produktet og inkluderer overvejelser vedrørende økonomien i den pågældende behandling.

1. Introduction

1.1 Background

Wood exhibits a number of extraordinary properties compared to other materials. It has an excellent workability and good mechanical properties - in summary it can be considered as being "light and strong". In addition, it has a beautiful appearance and radiates warmth. For these reasons it is widely used for applications such as furniture, structures, interior panels, flooring etc.

However, wood as a material has several undesirable properties that need to be improved in order to use the material more effectively and to extend its field of application. These include: Dimensional instability due to its hygroscopic nature, discoloration and degradation by exposure to UV-light, inhomogeneous mechanical properties, biological degradation etc.

The density is the single most important property of wood. Increasing the density of wood (densification) enhances its mechanical properties.

Shrinkage and swelling limit the use of wood for structures, e.g. flooring. Structures need to be designed to accomodate dimensional changes. Furthermore, cracking often occur, because the tensile strength of the fibres across the grain is exceeded.

This study is directed at the above-mentioned research areas and defines its topic within a combination of densification and improving dimensional stability of wood.

A pilot-study with the aim of reviewing methods of dimensional stabilisation and improving mechanical properties was carried out (Nielsen and Morsing, 1992). It was concluded that wood can be densified either by compression or by filling of lumen with a monomer, that is subsequently cured *in-situ* (Wood-Polymer-Composites).

The present study is concentrated on the first method, compression of wood perpendicular to the grain, known as compressed wood or densified wood (both expressions are used frequently in the present report).

Compressed wood swells to a higher degree merely due to the increased density. However, it will also tend to loose its compressed state as the result of the memory effect, known as springback. Consequently, compressed wood has to be subjected to by a stabilising treatment. The memory effect, which is considered the main problem of compressed wood and will be extensively investigated. In the present study the compression of the wood is combined with a hygrothermal treatment. Main emphasis is placed on the effect of steam treatment.

The combination of compression and hygrothermal treatment was chosen for two reasons. Firstly, due to the increasing environmental concern it does not seem appropriate to start a project dealing with hazardous chemicals. Secondly, recent results from Japan have demonstrated a promising method of eliminating springback by the use of steam treatment at high steam pressures.

Different species respond differently to the process of densification, with respect to both hardness and dimensional stability. This difference can mainly be attributed to the variations in structure and chemical composition. For the present study, *beech* was selected. Beech is the most important species for solid wood flooring in Denmark. Beech is characterised by large dimensional changes when exposed to changes in relative humidity and a higher hardness than most softwoods.

The effect of wood densification on coniferous woods is even more pronounced for softwoods than for hardwoods due to the lower density of softwoods. The method of densifying wood could therefore also be applied to coniferous woods intended to be used for structural purposes, for furnitures etc.

Since densification improves a number of important mechanical properties, it was introduced commercially before the densification mechanisms involved were really understood. The early attempts did not consider the effects of softening and stability, and for that reason none of the products were put into continuous use. Although subsequent research on plasticization and on the causes and elimination of springback has led to improved products, the techniques have not been further developed.

1.2 Scope of the present study

Objective
The main topic of the present study is the investigation of the combined effect of temperature, steam pressure, moisture, compression pressure and time on the compressive behaviour perpendicular to the grain of beech. A better understanding and control of these parameters will help optimising the methods for densification of wood, with respect to springback and dimensional stability.

It is intended that the dimensional stability and the hardness is improved without damaging the wood structure severely and thus maintaining the desirable properties of wood.

Method
In order to achieve the objective the following tasks were undertaken:

1. A critical review of methods for improving mechanical properties and dimensional stability was carried out. This was done in a pre-study which is not a part of the study reported here. Reference is made to (Nielsen and Morsing 1992).

2. A literature survey on densification of wood by compression perpendicular to the grain. Reference is made to (Morsing 1994). Parts of this study are included and the study is therefore not needed as a background for reading the present report.

3. Study of the stages in making compressed wood separately and in combination, involving:

- The hygrothermal behaviour of wood (including softening and degradation) and its influence on the mechanical response perpendicular to the grain (stress-strain relationship, creep, stress-relaxation, dynamic modulus).

- Examination of methods to avoid hygrothermal recovery of compressed wood. Emphasis is placed on the effect of hygrothermal treatment.

4. Determination of the physical and mechanical properties obtained by varying the parameters, time, temperature/pressure, and moisture. Main emphasis is placed on the behaviour regarding moisture and hardness.

It is hoped that the new knowledge obtained as part of the project may form the basis for an industrial production of compressed wood.

1.3 Outline of the report

The dissertation is organised in ten chapters, where Chapters 4-7 represents the main experimental work.

A literature survey on the structure and properties of beech is presented in Chapter 2.

The method of making densified wood and the stages involved are introduced in Chapter 3. This chapter includes a literature survey on densified wood and reviews the basics of wood softening (plasticization) and thermal degradation. The compressive behaviour of wood is treated with respect to hygrothermal softening and degradation.

Chapter 4-7 includes the experimental part, which focus on the stages required for making densified wood. It comprises the below mentioned four experiments:

Chapter 4:
Experiment 1. The influence of steam on the mechanical response: This experiment studies the effect of hygrothermal treatment (steam) on the short-term and long-term mechanical response (stress-strain relationships in short-term tests, creep and stress-relaxation) in static tests inside an autoclave. Corresponding with these tests a study of the dynamic mechanical properties using a frequency test method inside an autoclave is carried out.

Chapter 5:
Experiment 2. Hygrothermal recovery: This experiment studies the memory effect.

Chapter 6:
Experiment 3. Fixation of compressive deformation of beech by hygrothermal treatment. This experiment studies the influence of various hygrothermal treatment on the springback. The experimental study includes a very promising method of eliminating springback, called hygrothermal treatment in a closed system. This is a process where the wood is compressed and fixed in a closed system with subsequent cooling while in the compressed state. The elimination of springback is thought to be caused by the accelerated stress-relaxation as identified in experiment 1. It is the result of the thermo-plastic behaviour of the wood components.

Chapter 7:

Experiment 4. Properties of compressed wood: This experiment studies the relationship between density (compression set) and the properties of compressed beech. The experiment includes a study of the influence of hygrothermal treatment (steam or heat) on the physical properties. An important experimental effort is the attempt to quantify the dimensional stability of compressed wood.

The experimental work was carried out at Department of Structural Engineering and Materials (BKM) at the Technical University of Denmark and at the Wood Research Institute (WRI), Department of Property Enhancement of Wood at Kyoto University. Studies of the compressive behaviour of wood when exposed to steam, were carried out in Japan, while the dynamic tests and experiments nos. 2-4 were carried out in Denmark.

2. Beech wood - structure and properties

Beech is a common species in most of Europe. Its northern borderline passes through Scotland and the south of Norway. The southern borderline passes through the Pyrenees and Sicily. The western border is the Atlantic Ocean and the eastern borderline is at Bosporus and the Ukraine.

Beech is mainly used for furniture, desktops, etc.. As a structural material the uses are more limited. However, in Denmark beech is used for solid wood flooring produced at Junckers Industrier A/S in Køge.

In the following an introduction to the special features of beech structure is presented. The section includes an outline of the chemical composition of wood. Furthermore the physical and mechanical properties of beech are introduced.

2.1 Structure

Macro- and ultrastructure

Beech (*fagus sylvatica*) has a diffuse-ring porous structure, with little difference between springwood and latewood. No relationship is found between the width of growth rings and the density (Moltesen 1988). Figure 2.1 shows a micrograph of a cross section of beech at 100x magnification.

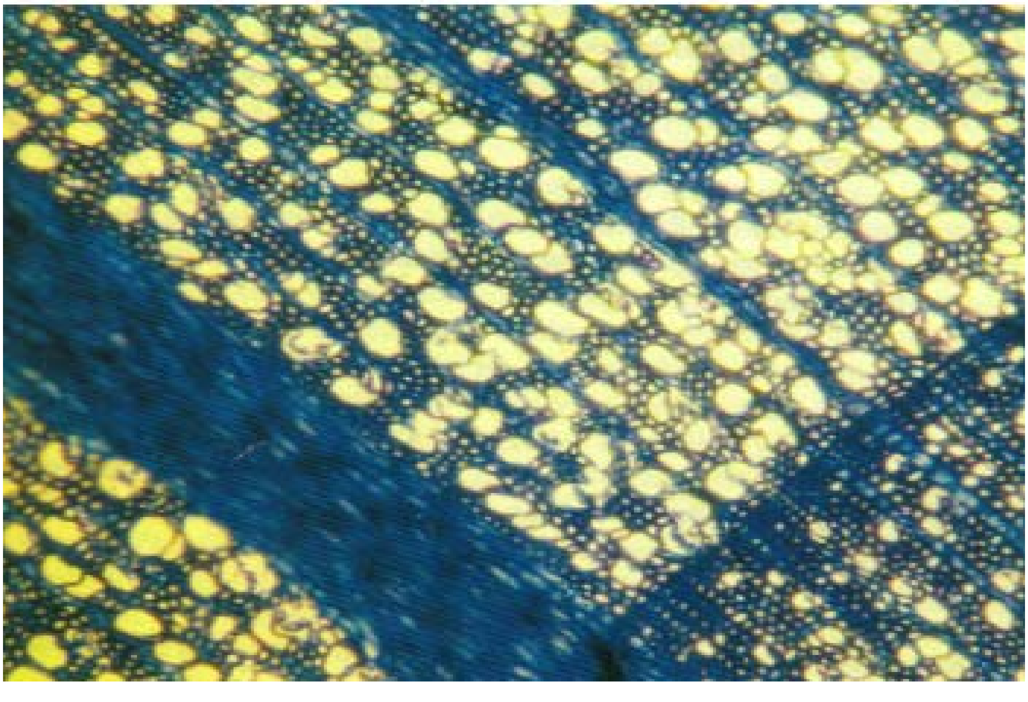

Figure 2.1 Micrograph of beech cross section. Magnification 100X, (Junckers Industrier, 1996).

The differences in composition and morphology of fibres in softwoods and hardwoods have a large impact on the compressibility. The ratio between the fibre length and the fibre diameter has a dominant influence on the flexibility of the fibre which will be reflected in the compressive behaviour.

Table 2.1 shows the difference in composition of fibers in the major Danish hardwood species and Norway spruce (*picea abies*). Compared to other hardwoods beech has a relatively low amount of tracheids fibers. Beech can be recognised without optical aids by the rays which are seen on the tangential surface as long brownish spots of up to 10 mm length.

Table 2.1 Percentages of cell types in beech compared to other hardwoods and spruce (Fengel et al., 1984, Moltesen, 1988).

Wood species	Cell type percentages (volume)			
	Vessels	Tracheids	Rays	Parenchyma
Beech	31	37	27	5
Oak	8	58	29	5
Ash	12	62	15	11
Birch	25	65	10	0
Spruce		95	5	1-6

Beech is a short fibroid species. Tracheid fibers have a length of app. 0.6-1.3 mm in hardwood while the length is 1.7-3.7 mm in softwood. The diameter is almost the same app. 20 - 40 μm for softwoods and 15-20 μm for hardwoods. The length of hardwood vessels are 300-700 mm and the diameter is 5-100 μm.

Chemical structure

Wood consist basically of the three polymers: cellulose, hemicellulose, and lignin. The chemical composition of the cell wall plays a key role in the thermally activated chemical processes softening and degradation and has an important influence of the compressive behaviour of solid wood.

The exact composition and amount of the polymers in beech is uncertain. Kürcherner & Karacsony (1961) have given the following figures:

Cellulose: 49%
Hexosanes: 14%
Pentosanes: 22%
Lignin: 15%

The lignin content in hardwoods is somewhat lower than found in softwoods.

Cellulose $(C_6H_{10}O_5)_n$ is a high molecular and well defined polymer composed purely of anhydroglucopyranose linked to each other by β-1,4-glycosidic bonds, (Figure 2.2). Therefore, cellulose can be described as a linear-polymer glucan with a uniform chain structure. Each molecule contains from 8000 to 15000 glucose monomers depending on their origin. The cellulose chains are 0.25 to 5μm long. Accordingly, the molecular weight varies widely ($5\cdot10^4$-$2\cdot10^6$g/mole). The type of bonding causes the molecules to be flat and ribbon-like, and it allows the formation of internal hydrogen bonds which stabilise the molecule. The molecules may be situated parallel to each other and form hydrogen bonds between themselves. They can crystallise and produce aggregates called microfibrils. According to the rosette theory (Giddings et al. 1980, Herth et al. 1984) each microfibril contains 36 chains, lying side by side. 40-50 percent of the mass of wood is cellulose.

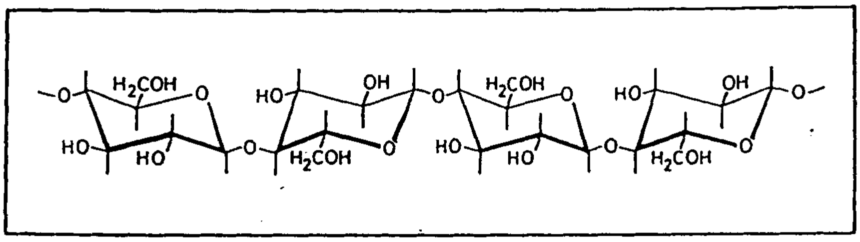

Figure 2.2 Cellulose (adapted from Fengel et al., 1984).

Cellulose microfibrils are partly crystalline and partly amorphous with a degree of crystallinity of app. 60%. The exact nature of the arrangement of glucan chains within the microfibrils is still a point of controversy and several models have been suggested. The models differ mainly in the presentation of the less ordered amorphous parts, cf. Fengel et al. 1984. The mode of synthesis is thought to be the basis of the crystallisation: Complexes of cellulose-synthesizing enzymes are embedded in the plasmalemma in the form of rosettes (Giddings et al. 1980, Herth et al. 1984).

The bonding within the cellulose and in the microfibril is of relevance for many of the properties of wood. Covalent bonding both within the glucose rings and between the rings to form the chains contributes to the high axial tensile strength of wood. Laterally within a microfibril the cellulose chains are bonded by hydrogen bonds and van der Walls forces.

Due to the unbranched nature and high degree of crystallinity, cellulose is insoluble in most solvents. Swelling of cellulose may however occur, which in the case of most polar solvents results in hydrogen bonding of solvent molecules in between the cellulose chains. The swelling is mostly highly dependent on temperature. Water can be bound by hydrogen bonds to the hydroxyl groups on the surfaces of microfibrils. But it cannot penetrate the crystalline cellulose, since the hygroscopic hydroxyl groups are mutually satisfied by hydrogen bonding within this region.

Hemicelluloses are non-cellulosic polysaccharides with a low degree of crystallization. Contrary to cellulose the hemicelluloses are often branched polysaccharides. In addition, they usually have much smaller molecular chains attaining degree of polymerization values in the range of only 200. Large deviations between hemicellulose in softwood and hardwood are recognized. However, in both softwood and hardwood the hemicelluloses amount to approximately 20-30% of the dry wood weight.

Hemicellulose is composed of various sugar units. These sugar units can be subdivided into groups such as pentoses, hexoses, hexuronic acids and deoxy-hexoses. The main portion of the hardwood hemicellulose is a xylan of the type 0-acetyl-4-0-methylglucurono-β-D-xylan, cf. Figure 2.3. The sugar units are often sidegroups of this main chain.

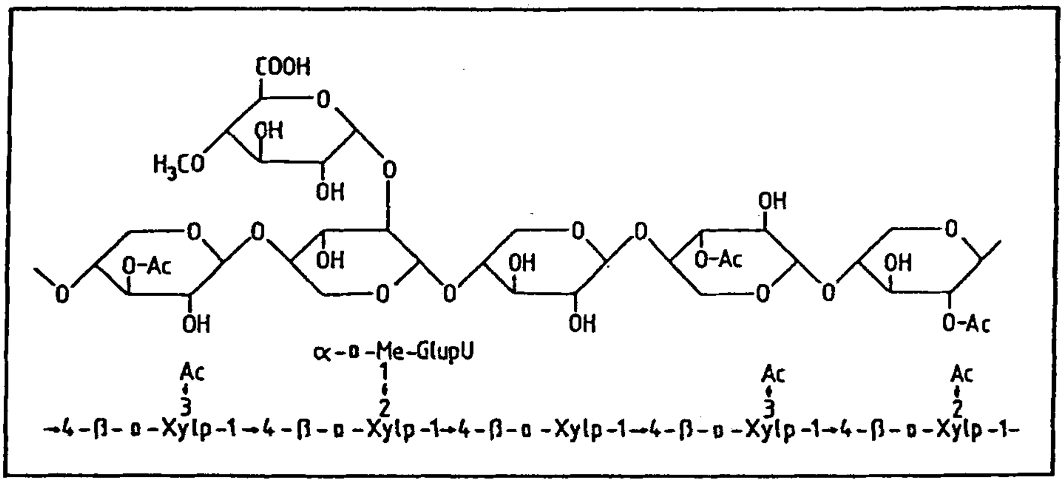

Figure 2.3 Partial structure of 0-acetyl-4-0-methylglucuronoxylan, from hardwood, (adapted from Fengel et al., 1984).

As shown in the figure the OH-groups of the xylan mainchain (C2 and C3) are partially acetylated. The 4-O-methylglucuronic acid residues are linked to the main chain by α-1,2-linkages. On an average the hardwood xylans contain one uronic for each ten xylose residues, however, the distribution of acidic residues is found to be highly uneven.

Due to the heterogeneous and branched nature with many sidegroups, hemicellulose form a predominantly amorphous substance with easy access to OH-groups and other reactive groups. Hemicelluloses are therefore relatively hydrophilic and sensitive to thermal degradation.

Lignin is a three dimensional high molecular polymer mainly consisting of phenylpropane units which dictate a completely amorphous and highly cross-linked network. Due to its cross-linked nature lignin is quite stable and relatively hydrophobic compared to cellulose and hemicellulose.

The lignin structure cannot be described by a simple combination of one or a few monomeric units or by one or a few types of linkages. Therefore, the lignin structure is still a matter of controversy. Several models have been suggested. The structural concept of hardwood lignin as ed by Nimz, (1974) is illustrated in Figure 2.4.

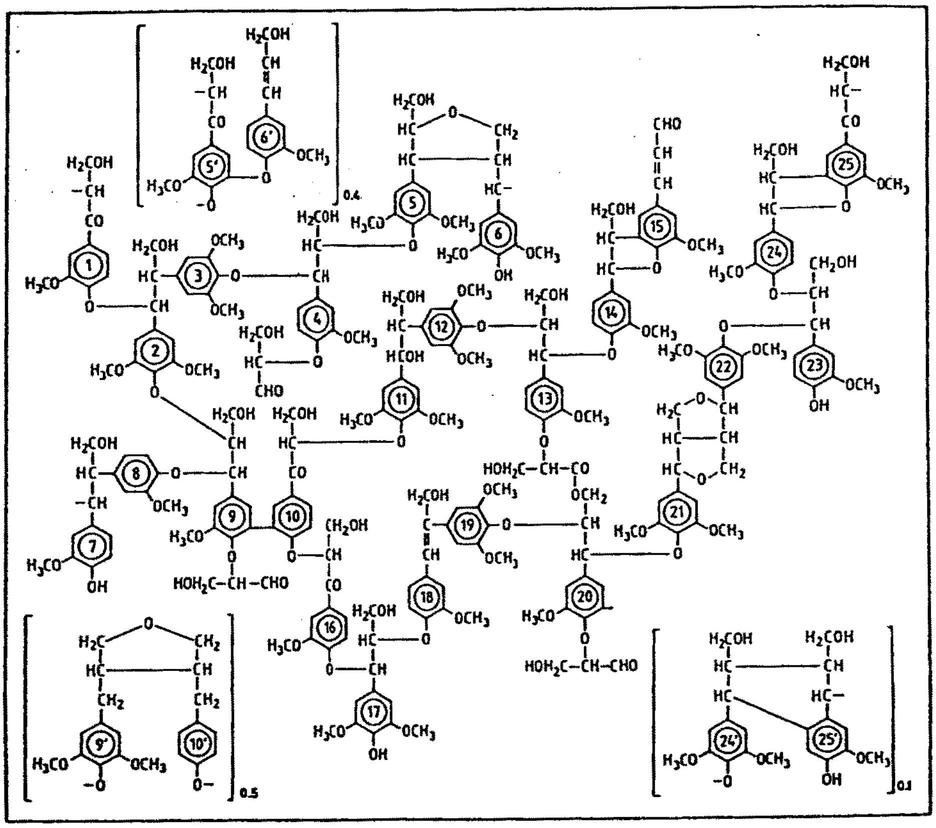

Figure 2.4 A partial structure of hardwood lignin (adapted from Fengel et al. 1984).

Lignin-polysaccharide linkages: An element contributing to the complex structure of lignin is the existence of lignin-polysaccharide linkages. True covalent bonds between lignin and the polysaccharides have been detected in many woods. In addition a possibility of multiple secondary interactions (hydrogen bonding, van der Walls forces etc.) exists. The compounds formed by the covalent linkages are referred to as LCC's (Lignin-carbohydrate complex) or LPC's (Lignin polysaccharide complex). The polysaccharides involved may be both hemicelluloses as well as cellulose, yet the former seems to be by far the most abundant (Fengel et al., 1984).

The results obtained by Eriksson (1980) indicate that lignin is bound to all kinds of sugar units in the hemicelluloses. Linkages to the side-chain units seem to be the rule. The most dominant types of LPC's are believed to be ether linkages, ester linkages and glycosidic-like linkages. Direct evidence of the latter has not yet been proven (Koshijima et al., 1976).

The linkages between lignin and polysaccharides have presumably a high impact on the compressive behaviour, particularly on the processes of softening and degradation.

Distribution of the components within the cell wall: Different models have been proposed as to how the constituents are organised in the cell wall, one such model is shown in Figure 2.5. The model should be taken with great caution since the risk of over-simplifying is very high.

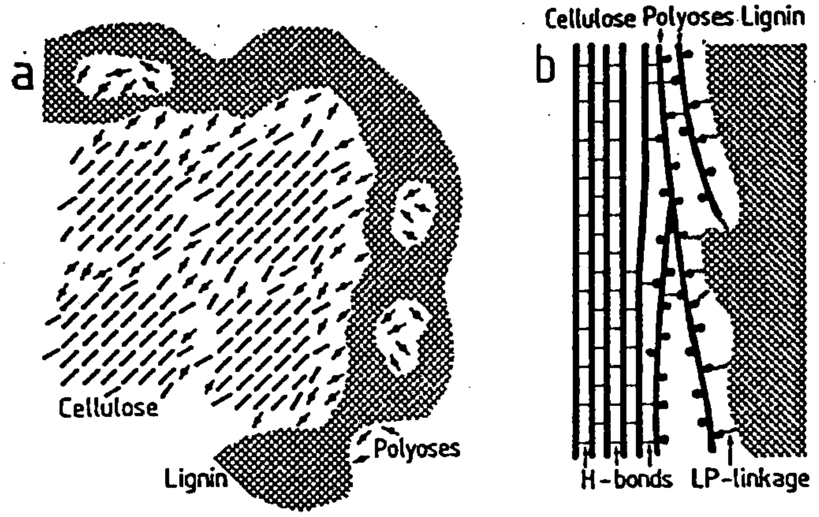

Figure 2.5 A model of the association of cellulose, hemicellulose (polyoses) and lignin in the wood cell wall with reference to the presence of less ordered cellulose molecules and the linkages at the interfaces in transverse (a) and longitudinal view (b), (Fengel et al. 1984).

2.2 Properties

The average dry-density of Danish beech is about 680kg/m^3 with a minimum of about 560kg/m^3 and maximum of about 820kg/m^3. The density of beech in Germany is found to be at the same level (Andersen et al., 1955).

As a consequence of the high density and the low level of extractives beech has a high drying shrinkage. From green to oven-dried state the shrinkage is app.:

Axial: 0.3 %
Radial: 5.8%
Tangential: 11.8%
Volume: 17.9 %

A sorption isotherm, which represents the relationship between moisture content, ω, and relative humidity, is shown for beech in Figure 2.6.

The traditional way to define moisture content, ω, is to express it in terms of its ovendried weight: $\omega = ((W_m - W_o)/ W_o) * 100$ %, where W_m is the weight of wet wood, W_o is the weight of ovendried wood, and ω is the moisture content (%).

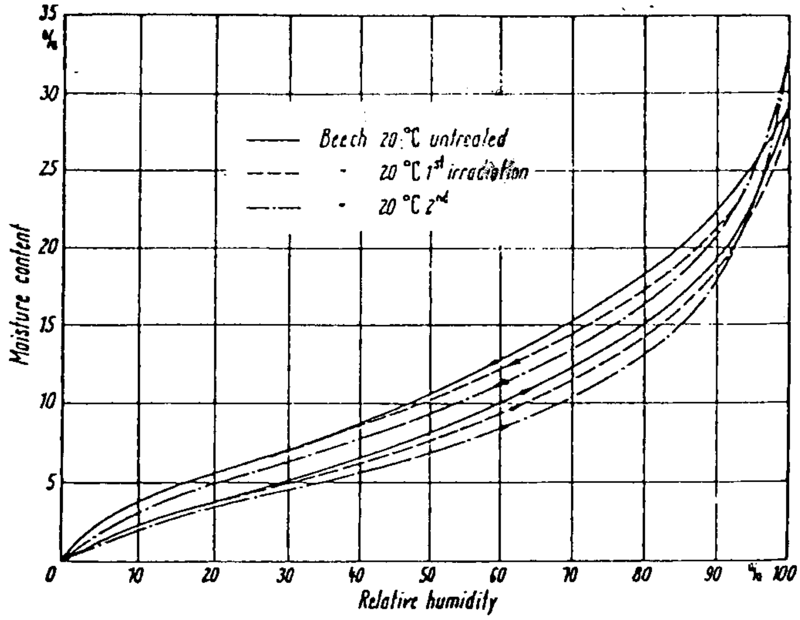

Figure 2.6 Sorption isotherms for beech at 20°C. The solid line is for untreated wood (adapted from Weichert, 1963).

By chemical processes it is possible to separate the cell wall components and measure their sorption isotherms. Figure 2.7 shows sorption isotherms for the components separately and for solid wood. The chemical processes most likely effect the orignal structure of the components and thus the moisture uptake. However, the tendency is clear, lignin shows the lowest moisture uptake, while hemicellulose shows the highest.

Volumetric swelling as a function of moisture content for different wood species, including beech is shown in Figure 2.8. The volumetric swelling tends to be linear with a moisture content in the range 5-20%.

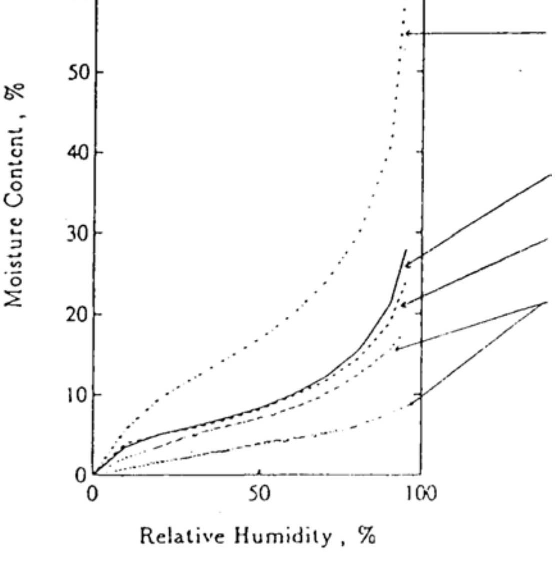

Figure 2.7 Adsorption isotherms of wood and the wood constituents at 25°C:. Two curves are shown for

lignin prepared in two different ways (Cristensen et al. 1959).

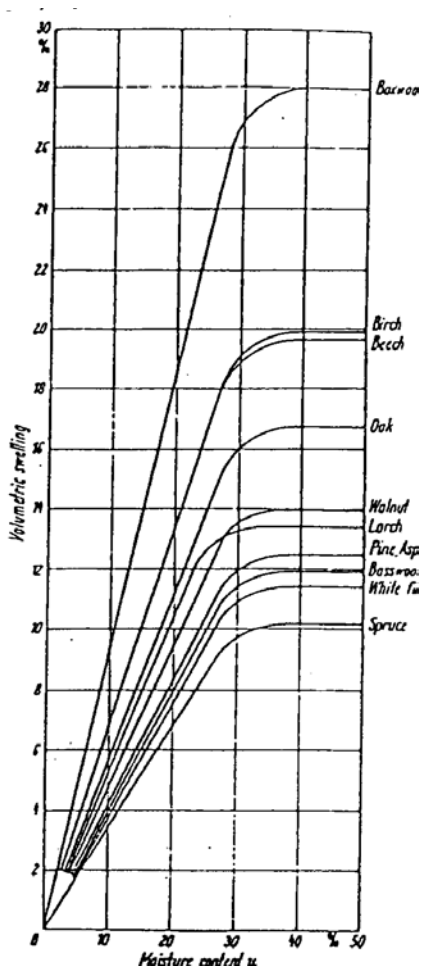

Figure 2.8 Volumetric swelling as a function of moisture content for different wood speciess (adapted from Mörath,1932).

2.3 Dimensional stability

The term dimensional stabilisation refers to mechanical or chemical modifications that reduce the tendency of wood to shrink and swell. The literature in this field was reviewed by Nielsen and Morsing (1992) with special reference to chemical modification. Methods found in the literature can be related to one of the following five groups.

1. Laminating of anisotropic sheets.
2. Applying water resistant surface and internal coatings to retard moisture adsorption or moisture loss.
3. Reducing the hygroscopicity of the components.
4. Bulking the fibres with chemicals, thus reducing their capacity for water.
5. Cross-linking the cellulose chains of the fibres so that their separation by water is minimised.

Different methods for quantifying dimensional stability are proposed in the literature. Most methods are based on the principle of comparing the swelling in water of treated wood with the swelling in water of untreated reference wood. Another method is to compare the swelling of treated wood with the swelling of untreated wood when the relative humidity is changed.

The term most frequently used for quantifying dimensional stability is the ASE (anti-swelling-efficiency). ASE is defined as,

$$\mathrm{ASE} = \frac{S_1 - S_2}{S} \cdot 100\ (\%) \qquad 2.1$$

where S_2 is the volumetric swelling coefficient of treated wood and S_1 is the volumetric swelling coefficient of untreated wood. The volumetric swelling coefficient is calculated from,

$$S = \frac{V_2 - V_1}{V_1} \cdot 100\ (\%) \qquad 2.2$$

where V_1 is the volume in dry condition and V_2 is the volume in wet condition.

Another term is MEE (moisture exclusion efficiency) that expresses the reduced moisture content from a given treatment,

$$\mathrm{MEE} = \frac{\omega_1 - \omega_2}{\omega_1} \cdot 100\ (\%) \qquad 2.3$$

where ω_1 is the moisture content of untreated wood and ω_2 is the moisture content of treated wood.

The MEE is often illustrated by an isotherm, where equilibrium moisture contents at different relative humidities are illustrated.

3. Densification of beech by compression perpendicular to the grain

3.1 Introduction

The method of making densified wood and the stages involved are introduced in Chapter 3. The chapter contains a literature survey on densified wood and reviews the basics of wood softening (plasticization) and thermal degradation. The background section also outlines the influence of hygrothermal treatment of wood on compression perpendicular to the grain.

3.2 Background

It is useful to explore the extreme situations in order to understand the extraordinary compressive behaviour of wood. Two elegant illustrations of extreme wood densification came to the authors knowledge during visits at the Wood Research Institute at Kyoto University in Japan.

The first one, an elegant example of densification provided by "Cupido's Arrow", an artistic product developed by Dr. Inoue. A wooden arrow has pierced a wooden heart and cannot be separated because of the thickness of the arrow and the "feathers". Heart and arrow do not originate from the same wood block. The understanding of this apparent mystery involves fundamental aspects of the wood structure.

Four steps are required to make Cupido's Arrow (Fig 3.1): 1) one end of a wooden plank is saturated with water and heated; 2) the softened end is densified by hot-pressing; 3) it is kept compressed until drying is completed and recovery prevented; at this stage the plank made of a densified end and a remaining non-densified part is cut into the shape of an arrow without the head; so that the heart can be introduced; 4) the densified end is heated again in boiling water in order to provoke its swelling by hygrothermal recovery; the final geometry of the arrows head is obtained by shaping the swollen end.

The second example is illustrating an ideal situation of wood forming, cf. Fig. 3.2. Logs are pressed into a square and thus the waste material at the sawmill is minimised. The technical objective of this example is a more efficient usage of raw materials which naturally come in shapes inconvenient for industrial production.

The logs are heated in green condition in a large microwave heater. The logs are compressed in this heated and moist condition, at a pressure as low as 1 MPa. The technique was developed at the Nara Experimental Research Station by Dr. Kobayashi and is in a preliminary state. However, in Japan there has been a great interest of the process, which has been patented. The basic concept of the process is of course absurd unless it is possible to stabilise the wood in the compressed shape.

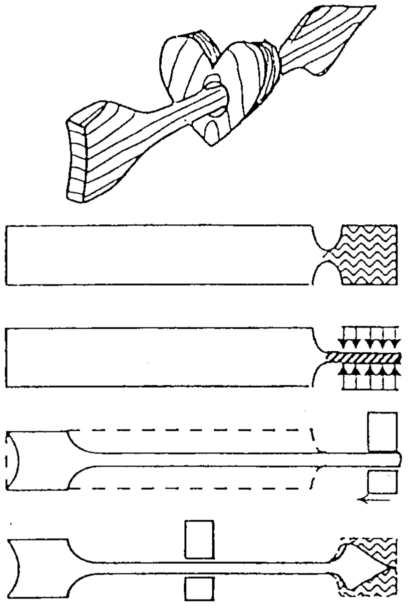

Figure3.1 The Cupido arrow, Inoue (1994)

As exemplified by the Cupido arrow the processing technique of densifying wood requires four steps:

1. Softening or plasticization of the cell wall
2. Compression perpendicular to the grain in the softened state
3. Setting by cooling and drying in the deformed state (drying set)
4. Springback (hygrothermal recovery) or fixation of the deformed state

3.2.1 Softening and compressive behaviour

Hygrothermal treatment results in considerable changes of the compressive behaviour of wood. This is explained by its viscoelastic nature. At the molecular level the mechanical response of a viscoelastic material is time dependent in a partial reversible way (softening) or in connection with permanent modifications of chemical nature (degradation).

Time-dependent chemical processes are typically thermally activated. Furthermore in hygroscopic polymers, such as wood, the softening or degradation mechanisms depend on moisture content and moisture variations. In other words, hygrothermal treatment of wood will soften or degrade the wood structure and highly influence the mechanical response perpendicular to the grain.

The phenomena of softening and degradation of wood are reviewed in detail in Section 3.4.

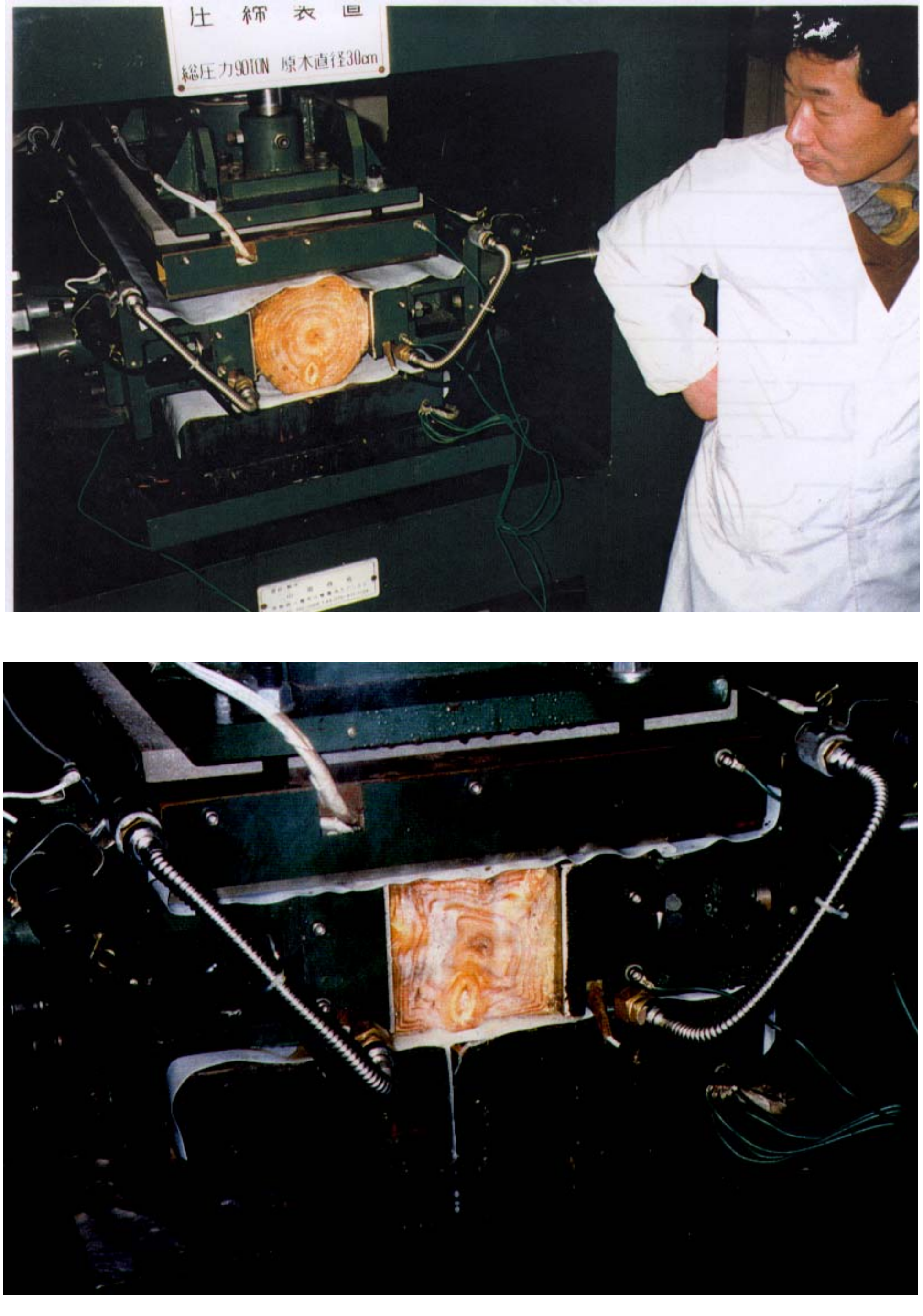

Figure 3.2 Square logs: Above Dr. Kobayashi the inventor (photograph Morsing,1993).

3.2.2 Springback and drying set

It is a well known fact that when wood is dried in a compressed state more hydrogen bonds will be formed and the deformed state will be maintained, known in the following as drying set or compression set (C_s).

The degree of compression set, C_s is expressed as:

$$C_s = \frac{l_o - l_c}{l_c} \cdot 100\ (\%) \qquad 3.1$$

where l_o and l_c are the thicknesses in oven-dry condition before respectively after compression

The cross-links (primary bonds) in lignin and crystalline regions of cellulose tie the chains together at widely spaced points length-wise and will resist movement. When the wood is compressed the chains tend to order; but the cross-links and the microfibrillar framework provide a rheological memory which correspond to the original shape due to primary bonding. The deformed state will, however, be held in place until the hydrogen bonds are separated, e.g., by moisture and heat.

When the compressed wood is immersed into water both swelling of the cell wall and softening (breaking of secondary bonds) of the constituents occur. The latter allow the internal stresses, introduced during compression, to be relieved, resulting in springback, as shown by the Cupido arrow. On drying, the dimension increase due to swelling, is lost in the form of shrinkage. The remaining irreversible increase of dimensions is due to recovery of compression set or "springback", known as recovery of set, R_S .

The recovery of set, R_S, can be expressed as (Seborg et al., 1945; Stamm, 1948; Inoue et al.,1991):

$$R_s = \frac{l_r - l_c}{l_o - l_c} \cdot 100\ (\%) \qquad 3.2$$

where l_r is the thickness in wet condition after the recovery test.

It is important to bear in mind that the basic difference between the two terms springback (recovery of set) and anti-swelling-efficiency (ASE, cf. Eq. 2.1) is that recovery of set matches the initial oven-dried state with an oven-dried state after water soaking. ASE matches an initial oven-dried state with a wet state after soaking in water.

Inoue et al. (1992) examined the hygrothermal recovery of set versus compression set of sugi (*cryptomeria japonica*). They found that compression of set has no influence on recovery of set. This was also concluded by Stamm (1948) based on measurements on birch laminates.

Arima (1975) found that the magnitude of the applied compressive load, has a significant impact on the rate of recovery.

It appears that an increased temperature during immersion in water causes release of internal stresses to a higher extent (Arima, 1975). It might be considered that this is due to an increased softening of the constituents.

This phenomenon was investigated by Inoue et al. (1992), who examined the effect of re-softening the matrix after compression on the recovery of set. Specimens were compressed in a wet condition at temperatures ranging from 20°C to 100°C.

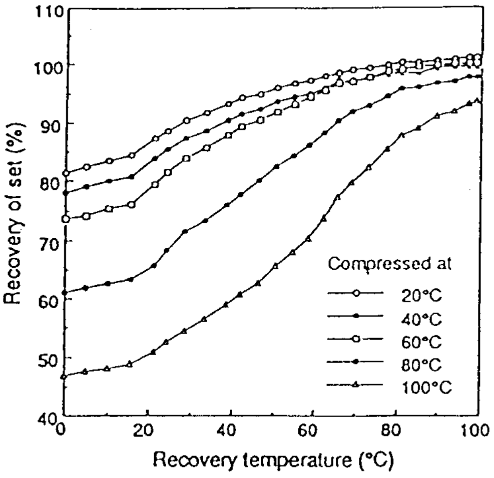

Figure 3.3 The effect of temperature on the recovery of set in water saturated condition (Inoue et al., 1992).

Figure 3.3 shows diagrams of the recovery from water soaking at different recovery temperatures. The influence of the recovery temperature on the recovery of set is significant. The specimens reach about 90% of their original thickness at the temperature at which the specimens were initially compressed. Inoue (1992) concluded that the compression set only recovers its initial shape when the wood is re-softened under the same conditions that it was softened during compression. Less recovery will occur if the compressed wood is exposed to less severe swelling conditions.

3.2.3 Permanent fixation of the compressed state

Ordinary untreated compressed wood is subject to a large amount of "springback" when exposed to moist conditions. It is therefore desirable to find conditions under which it can be compressed without the accompanying strong tendency for it to recover its original dimensions.

The mechanisms involved in eliminating springback are closely related to the mechanisms known from dimensional stabilisation of wood (Nielsen & Morsing, 1992). Three basic mechanisms of fixing the compressive deformation can be identified:

The *first mechanism* is to prevent the wood from being re-softened by changing the hygroscopicity of the cell wall and thus making the cell wall inaccessible to water.

The *second mechanism* is to form covalent crosslinks between the wood components in the deformed state.

The *third mechanism* is to release the elastic stresses and strains stored in the microfibrils and matrix during compression.

3.3 A literature survey on densification of wood

The following presents a literature survey on methods for making densified wood. The section is arranged in two parts. The first part deals with methods based on compression accompanied by a hygrothermal treatment. The second part deals with methods based on compressing accompanied by a chemical treatment.

The advantages of compressed wood have been known for more than 100 years and extensive research has been carried out. The concept of compressing wood to improve the properties started at the end of the 19th century. The first patents dealing with compressed wood in United States were: Sears, 1900; Walch and Watts, 1923; Oleheimer, 1929; Brossmannes, 1931; Esselen, 1934; and Olson 1934. These patents were concerned almost entirely with the mechanics of compression and did not adequately consider plasticization or stability of the products. Densification of wood was introduced commercially before the phenomena involved were really understood. Consequently, none of the patents were put into continuous use.

Subsequent research on plasticization of wood and on elimination of “springback” have led to improved products. During the period from 1930 to 1960 many attempts were made to alter wood properties. These attempts include heat treatment and different chemical treatments, involving bulking of the cell wall using polar chemicals.

Lately world wide interest on densification of wood is increasing due to increasing competition from other materials. Furthermore the quality of structural wood is decreasing as a consequence of harvesting fast grown woods.

3.3.1 Hygrothermal treatment

3.3.1.1 Heat-stabilised wood in a hotpress, “Staypak”

Compressed solid wood was introduced in Germany in the early thirties (Kollmann, 1936) and marketed under the tradename “Lignostone”. The product was compressed in a hot-press and stabilised by heat-treatment. A similar product of laminated compressed wood was marketed under the tradename “Lignifol”.

In US a similar product was introduced during World War II (Seborg et al., 1945). It was marketed under the tradename “Staypak”. The pressure applied in the production depends on density, moisture content and temperature of the wood species. At 160°C and 12% moisture content Seborg et al. (1945) found that a specific gravity of 1.3 could be achieved at a pressure of 10-17 MPa on birch laminates depending on the plasticizing conditions. For some hardwoods a pressure of about 24 MPa is required according to Mendoza (1976).

Figure 3.3 shows that moisture and heat during compression has an impact on recovery. Several researchers have investigated this phenomenon (e.g. Seborg et al., 1945; Saito, 1973; Arima, 1975; Suematsu, 1980).

Figure 3.4 gives a plot of recovery of set versus the heating temperature for parallel-laminated yellow poplar (Seborg et al., 1945). The specimens were compressed at approximately 1.4 MPa at three different moisture contents for either 5 or 30 minutes. The figure shows that higher temperature and moisture content and longer time of pressing decreases recovery from compression. It should be noticed that when the moisture content and temperature is increased, then the heating time becomes less important.

Seborg believed that the large reduction in "springback" is due to a breakdown of secondary hydrogen bonds, and subsequent release of stresses introduced in the matrix and microfibrils.

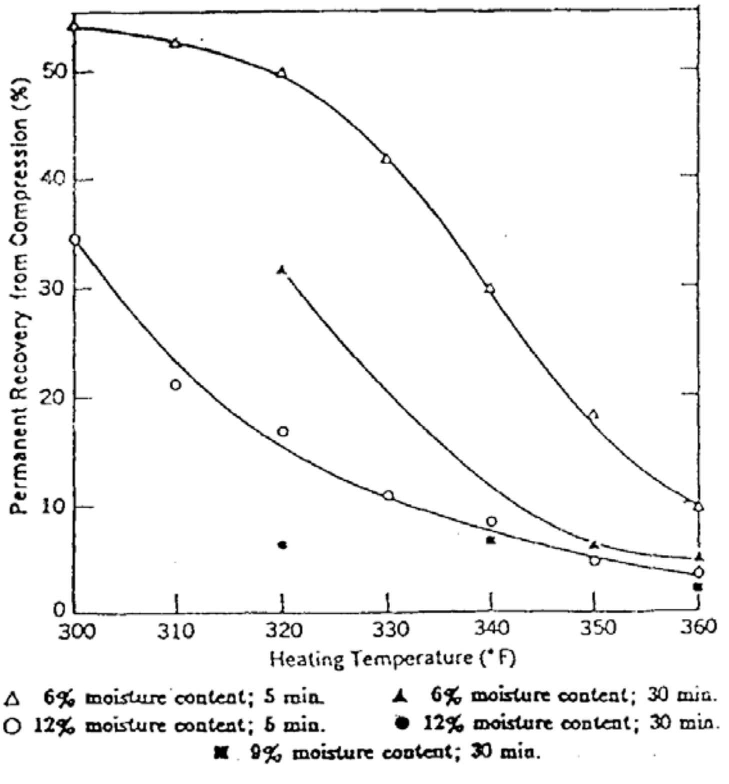

Figure 3.4 Recovery of set versus heating temperature in a hot-press and moisture content for parallel laminated birch (Seborg et al. 1945).

Under high pressures, there is a tendency for solid wood to spread laterally. To prevent this, "Staypak" should be restrained in lateral direction when making "Staypak" from solid wood.

When heated to temperatures above 100°C for prolonged time there is a tendency for "Staypak" made of solid wood to loose moisture from the free faces of the wood, especially the end grain. By the time the temperature has risen to that necessary to plasticize, the moisture content may have dropped below the minimum level of plasticization. This can be detected from the colour change of the wood because there will be some non-darkened zones at the ends of the wood. These zones will "springback" like ordinary compressed wood. The problem can be eliminated by compressing at temperatures below 100°C and subsequently increasing the temperature of the platens in the compressed state. For the same reasons it is important to cool the material in the press before unloading. Otherwise the wood will springback in the hot state (Seborg et al., 1945).

"Staypak" has strength properties considerably greater than those of normal wood. The increased values are in general proportional to the density. Table 3.1 gives the strength properties of parallel laminated birch in comparison with normal wood and "Compreg", cf. next subsection dealing with chemical treatments.

Because of the high density and hardness of "Staypak" it is necessary to use special wood working tools. It can be turned on a lathe, using metal working tools, with better precision than for normal wood. Machine speeds should be lower than for cutting and shaping normal wood.

Table 3.1 Coefficients comparing parallel-laminated Birch for "Staypak" and "Compreg" under conditions that minimises "springback" with untreated wood (Stamm 1964).

Characteristic property	"Staypak"	"Compreg"
Specific gravity	2.1	2.0
MOR	1.9	1.7
MOE	1.9	1.5
Toughness	0.9	0.7
Izod Impact	1.1	0.4
Hardness	10	12

3.3.1.2 Wood heat stabilised in an oven

The temperature in the heat treatment applied in making "Staypak" is not sufficiently high for long enough periods of time to give dimensional stability. The high degree of compression greatly reduces the rate of swelling and shrinking, but it in no way affects the final equilibrium dimensional changes. It will swell the same absolute amount as uncompressed wood and three times as much based on the reduced dimensions. It should therefore not be used for outdoor purposes, (Seborg et al., 1945).

Heating compressed wood for prolonged time can be used for stabilising the product. Inoue et al. (1991) tried to improve the dimensional stability by dry-heating sugi *(cryptomeria japonica*) for prolonged time in the compressed state. They found that the recovery depends on heating temperature and heating time. Dry heating required 20 hours at 180°C to avoid "springback". However, the heat-treatment affected the strength properties and gave rise to a colour change of the final product (cf. Table 3.2). The colour change of heated wood is a severe drawback for industrial applications. Furthermore the long treating time is a problem.

The stability established to the cell wall because of high temperature treatment changing the hygroscopicity is considered to contribute to the fixation of the compressed state.

Heat treatment of the wood substance at elevated temperatures changes the hygroscopicity, as a result of thermal degradation. This is verified in Figure 3.5 where recovery of set is compared with the dimensional stability of wood (ASE) for uncompressed wood. Similar results were found by Saito (1973). Heat treatment (200°C, 2hr) after pressing in a hot-press reduced springback of the specimens to about one-fifth.

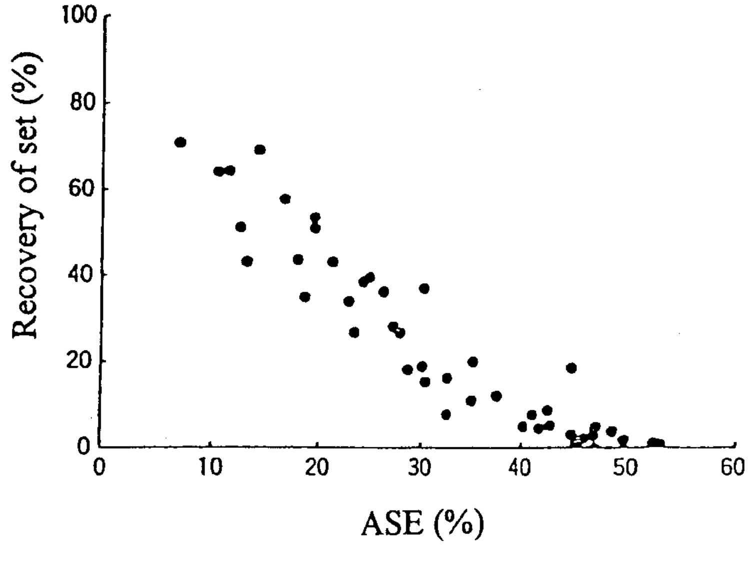

Figure 3.5 Recovery of set versus dimensional stabilization (ASE) for heat treated specimens in an oven after compression (Inoue et al. 1991).

3.3.1.3 Steam stabilized compressed wood

Steaming wood in the deformed state has proved to be an effective method for permanent fixation as shown by Stamm (1946). Based on the work of Stamm, Inoue (1991) developed a technique by which compressed wood from sugi was fixed in a metal frame and steamed in the compressed state. Figure 3.6 shows the influence of steam pressure and time on the recovery of set.

Inoue et al. (1993) propose that fixation of the compressed wood structure by steaming is due to softening of the lignin-hemicellulose matrix. As water is removed from the matrix, hydrogen bonds re-form between the matrix polymers. Together with the temperature decrease this leads the amorphous fraction to return to the glassy state where the elastic deformation of the microfibrils and the matrix are "frozen".

The effect on the mechanical properties of steaming and dry-heating under conditions that eliminate "springback" are shown in Table 3.2. The colour change is considerably reduced by steaming compared to heat-treatment. The increased hardness from 7 to 25 MPa at a compression set of 60% is not affected by the steam treatment according to Inoue (1993). The specific gravity is increased from 0.36 to 0.90.

Table 3.2 The effect of heat or steam treatment on change of MOE, MOR (cryptomeria japonica), and colour at conditions that eliminate "springback" (Inoue et al., 1991).

Treatment	Temp.°C	Time	ΔMOE	ΔMOR	ΔL Colour
Heating	180	20hr	-9%	-39%	-28%
	200	5hr	-1%	-34%	-29%
Steaming	180	8min	-3%	-0.1%	-13%
	200	1min	-9%	-5.1%	-11%

3.3.1.4 Hygrothermal treatment in a closed system

Recently a "new" treatment was developed for the fixation of the compressive deformation (Inoue, 1994). The wood is softened, compressed, and fixed in one step in a closed system with subsequent cooling in the compressed state. The treatment is using the moisture inherent in the wood to create a steam pressure. The wood is compressed in a hot-press equipped with a sealing to prevent the moisture from escaping.

The basic idea is closely related to the Staypak method mentioned above (Seborg et al., 1945). However, the Staypak method only prevents the moisture from evaporating by using thin specimens with large horizontal dimensions and thus trapping the moisture. Eventually all the moisture will be lost.

Inoue (1994) compared the recovery of set from specimens treated in a closed system with specimens treated in an open system (without sealing) under otherwise identical conditions. The recovery of set of sugi (*cryptomeria japonica*) was minimized already at 170°C after 8 minutes in the closed system while no effect was observed in the open system. The closed system is superior to compression in a traditional hot-press without sealing.

3.3.1.5 Surface compression

Surface densification of maple panels was accomplished, using moisture and heat and high compression load in a continuous belt press. The press was developed by Lam H-Nard Division Hoover Ball and Bearing C., Michigan. The process is described by Tarkow et al. (1968). The surface is rapidly heated at temperatures as high as 260°C, immediately pressed at pressures above 7 MPa and finally quickly cooled in the press. The heart of the process is a pair of endless, special alloy belts, between which the wood panel is sandwiched. Moving at linear speeds up to 7.5 meters per minute the panel is subjected to heat from a heated pair of shoes, the thickness is reduced between a second pair of shoes and finally cooled from a pair of water cooled shoes. The process is shown in Figure 3.7.

The process is happening so fast that only the surface is plasticized sufficiently to improve the density. The surface properties are greatly improved. Specific gravities above 1.0 have been obtained near the surface. The abrasion resistance was increased more than 15 times. It was found that the recovery of the surface depends on the pressing conditions.

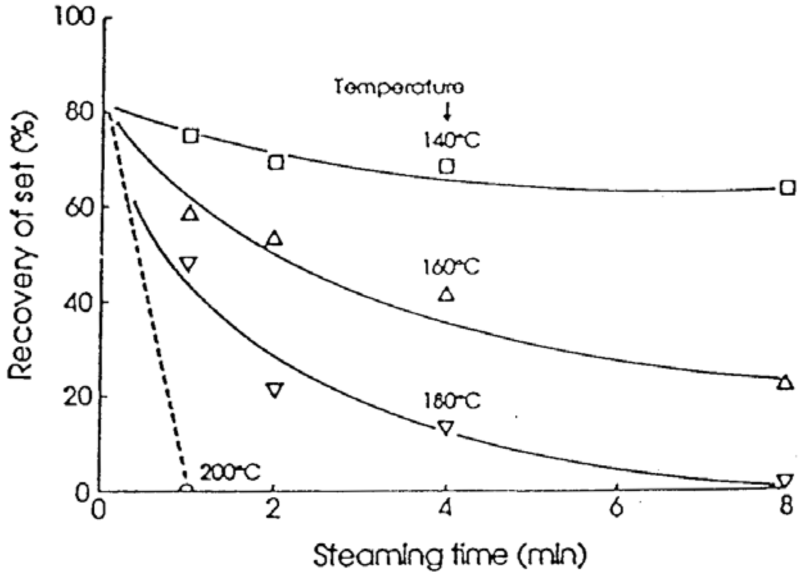

Figure 3.6 Influence of steam pressure and time on the recovery of set for sugi (Inoue et al., 1993).

Legend:
A Panel
B Heated shoes
C Water-cooled shoes
D Separation-Belts (special alloy)

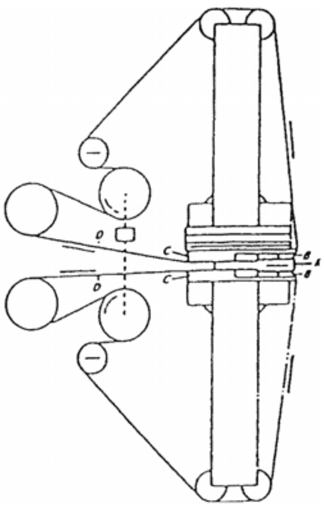

Figure 3.7 Roller belt press for continuously densifying the surface region of wood (Tarkow et al., 1968).

The equipment for surface densifying is rather expensive and also has to be robust. Tarkow et al. (1968) suggest, that better properties with less robust equipment can be obtained when plasticizing with thermosetting resins.

Inoue et al., (1990) suggest a technique for compressing the surface layer of sugi. Narrow grooves 2 mm wide and 5 mm deep are cut across the grain at intervals of 150 mm. The wood is impregnated with water taking advantage of the water penetration in the longitudinal direction. In the water soaked condition the wood is irradiated by microwaves followed by compression and drying under restraint.
The surface properties are greatly improved. The hardness increases by 40-50% compared to untreated wood. The abrasion resistance is improved by 120-150%.
A similar process for surface densification of wood by continuous hot-pressing between rollers was also suggested by Onishi et al. (1984, in japanese). They studied roll-pressing spruce, spruce treated with polypropylene (PP) film and spruce/birch plywood glued simultaneously using PP film. Impact bending properties of PP-spruce were generally improved as was density, hardness, abrasion resistance, MOR and work to rupture.

3.3.2 Chemical treatment

3.3.2.1 Acetylation

Acetylation of the wood prevents water molecules from penetrating the cell wall by bulking the cell wall and substituting the hygroscopic hydroxyl groups with hydrophobic acetyl groups. The acetylation treatment for dimensional stabilisation has been reviewed in several references (e.g. Rowell, 1984).

The use of acetylation as a method for eliminating “springback” was investigated by Inoue et al., (1992). Acetylation was carried out according to the procedure by Rowell et al., (1986). Acetylated wood specimens were compressed in radial direction in a wet state. Inoue (1992) concluded that the acetylation is effective in preventing the re-softening by moisture at room temperature. However, the recovery of set reaches 90% in additional boiling despite the acetyl content. Thus, perfect fixation cannot be achieved by acetylation.

3.3.2.2 Phenol-formaldehyde, “Compreg”

Impregnating wood with a fibre-penetrating polymer followed by drying under conditions that do not set the resin then compressing and curing gives a highly dimensional stable compressed wood.

The most well known and most investigated fibre penetrating resin is phenol-formaldehyde. In the United States it was marketed under the trade name “Compreg” (Stamm et al.,1941 & 1955). The product has improved mechanical properties and in addition eliminates the “springback” effect. A resin treated laminated compressed wood known as “Kunstharzschichtholz” was introduced in Germany for commercial production some years before.

“Compreg” is compressed under pressures of 7 MPa or less to a specific gravity of 1.2 to 1.35 at app. 150°C. Phenol-formaldehyde is a thermosetting resin. Fortunately the wood is compressed faster than the resin cures.

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“Compreg” is difficult to make from solid wood, because of treating difficulties, including drying without premature curing of the resin. Therefore practically all “Compreg” was made from thin veneers. When the resin content is above 30% the veneer can be laminated without use of additional bonding resin if the plies are compressed to a specific gravity of 1.3 or more (Stamm, 1941 & 1955). Additional resin has to be used when the specific gravity is less than 1.3, the resin content is less than 30%, or the veneers are cross-laminated.

When producing “Compreg” of thin veneers the moisture content may be 4% or less. When using thicker veneers the moisture content has to be below 2% to avoid face checking. Face checking can also appear if “Compreg” is compressed to a specific gravity of more than 1.35.

Two types of “Compreg” have been commercialised based on the following:

1. Water soluble phenol-formaldehyde
2. Phenol-formaldehyde dissolved in alcohol

Water soluble phenol-formaldehyde is a highly fibre-penetrating polymer that gives the highest dimensional stability. While dissolved in alcohol, phenol-formaldehyde increases the impact strength considerably.

“Springback” is almost eliminated in both cases (less than 3%), but the dimensional stability in the case of dissolving in alcohol is very poor (app. 14% swelling in water). The swelling rate of water soluble phenol-formaldehyde treated compressed wood is extremely slow but the final equilibrium dimensional changes are still more than 10% (Findley et al. 1946).

Most of the strength properties are improved in proportion to the increased density.

“Compreg” looks varnished or lacquered and has an easily renewable finish, because the whole wood structure is treated. The same woodworking tools as for “Staypak” can be used.

The major drawback is the discoloration and the cost for which reasons “Compreg” has found limited commercial use. It was used for military purposes during World War II. The known uses were antenna masts and the hub section of the wooden aeroplanes propellers on the British Mosquito bomber. Since the war it has been used for picker sticks, shuttles, and bobbins in textile industry, for knife handles etc.

Inoue et al., (1991) followed up on the work of Stamm and others and impregnated sugi with a water soluble phenol-formaldehyde of low molecular weight to increase the fibre penetrating ability. The impregnated specimens were irradiated by microwaves, followed by pressing in radial direction in a hot-press at 130°C and curing for 1 hr. The results showed a significant effect of the concentration of the resin mixture and compression set, on abrasion resistance and hardness. A decrease in abrasion resistance and hardness at low resin concentration was observed. This may be due to the fact that penetration and the subsequent swelling are increased at low concentrations and therefore the plasticization of the cell wall is increased.

3.3.2.3 Melamine-formaldehyde

Inoue et al., (1993) studied the process of impregnating sugi with increasing concentrations of a low molecular weight melamine formaldehyde. The procedure was identical to the phenol-formaldehyde impregnation process.

A dimensional stability of 45% was obtained for the highest concentrations. This shows that the cell walls were not completely penetrated. The hardness increased in proportion to the melamine concentration. At a compression set of 54% and a melamine concentration of 25% the hardness increased 3 times compared to compressed untreated wood (Inoue et al., 1993).

Inoue et al. (1991,1992, 1993) investigated the influence of resin concentration and compression set on springback of low-molecular weight melamine-formaldehyde and phenol-formaldehyde. It was found that the resin concentration has a significant influence on the recovery of set.

Resent research (Inoue 1991, 1993) on melamine-formaldehyde has prompted world wide interest in the process. A project running in parrallel with the present study is dealing with low molecular melamine treatment of beech (Nielsen, 1995). A main disadvantage is the presence of formaldehyde, which may limit the industrial application in the future, due to environmental concerns.

3.3.2.4 Formaldehyde

Formaldehyde treatment is well known. It is a very effective treatment for dimensional stabilization of wood components, because of the formation of crosslinks between the wood components (Rowell, 1984). The recovery of set consequently decreases rapidly with increasing treating time of formaldehyde (Inoue et al., 1992). It should be noted that by vapour phase formaldehyde treatment for only five minutes, the compressive deformation is almost completely fixed even in the case of boiling (Inoue et al., 1992). The weight percent gain needed is only about 1 percent. However, formaldehyde treatment, however, is not relevant in Denmark, due to environmental restrictions.

3.4 Hygrothermal properties of wood

The chemical composition of wood appears very complicated. Parts of the polymers are amorphous (hemicellulose and lignin); other parts are semi-crystalline (cellulose); some are linear (cellulose and hemicellulose); other parts are cross-linked (lignin) etc. If possible this complexity will in the following be disregarded, calling only on those aspects of the structure which directly influence the hygrothermal properties.

Because of their complex structure wood polymers have only for the last four decades been characterised with respect to typical polymeric properties.

It is intended to outline the physical and chemical factors which limit plasticity in wood polymers and review the consequence of hygrothermal plasticization of solid wood, cf. Section 3.4.1. Thermal degradation of wood and wood polymers are reviewed in Section 3.4.2 and the effect of hygrothermal treatment on wood stability is treated in Section 3.4.3.

3.4.1 Wood softening

The following section starts with an introduction to the polymeric background of wood softening, hereunder the central role of glass-transition and the influence of plasticizers. This supports the literature survey on hygrothermal softening of wood presented at the end of the section.

3.4.1.1 Polymeric background

The softening behaviour of amorphous polymers is characterised by the glass transition temperature, T_g, also known as the softening temperature. At the glass-transition temperature, the material softens and many properties especially the stiffness (elastic modulus) changes drastically, cf. Figure 3.8.

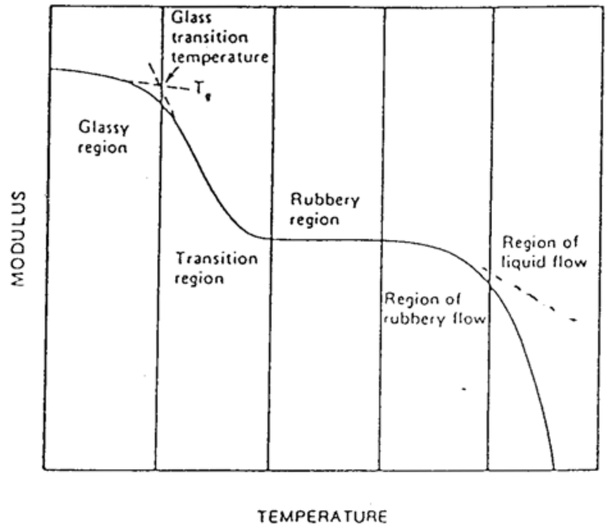


Figure 3.8 The viscoelastic behaviour of amorphous polymers, showing transition from glassy- to rubbery region indicated by the glass transition temperature, Irvine 1985.

At temperatures below the glass transition temperature the polymers are stiff and glassy (high modulus). In the transition region the material softens and the stiffness decreases. At higher temperatures the material exhibits rubber-like elasticity as a result of entanglements.

The length of the rubbery "plateau" in the stiffness-temperature curve is dependent upon the number of entanglements per molecule, and hence upon the molecular weight. If the material is *not* cross-linked, and provided thermal degradation does not occur, further increase in temperature will eventually result in rubbery flow. If cross-linking is present, such flow can not occur, unless primary bonds are broken.

In order to understand the molecular basis for the glass-transition, the various molecular motions occurring in an amorphous polymer may be broken into four categories:

1. translational motion of entire molecules, which permits flow;
2. cooperative wriggling and jumping of segments of molecules, permitting flexing and uncoiling;
3. motions of a few atoms along the main chain or of sidegroups on the main chains;
4. vibrations of atoms about equilibrium positions.

The motions are listed in order of decreasing activation energy. The glass-transition temperature is thought to be at that temperature where there is only sufficient energy available for motions 3 and 4.

Several different theories of the mechanism of the glass-transition temperature exist. A generally accepted model is the free volume theory (e.g. Andrews 1966, Kaelble 1971, Aklonis et al., 1972). When motions or vibrations of segments or atoms (motions 3 and 4) become thermally activated, it is due to thermal expansion which increases the amount of free volume (the volume not occupied by molecules). This permits small relative movements of side-groups, or of short segments of the chain, at "loose sites" in the structure. Consequently the stiffness drops dramatically.

Factors affecting softening (or T_g) at the molecular level can be summarised as follows
(Rosen, 1982):

1. Free volume (for the chains to move)
2. The attractive forces between the molecules
3. The internal mobility of the chains, that is their freedom to rotate around bonds
4. The "stiffness" of the chains. Chains that have difficulty coiling and folding will have a higher T_g.
5. The chain length until a molecular weight of app. 500 is reached after which no changes in T_g is noted.

The softening behaviour of wood polymers most likely depends on a combination of the above-mentioned five factors. The numbers in the following refer to these factors.

Softening of *Cellulose* is severely limited due to the crystalline nature and the strong secondary forces between the molecules (factor 2). The transition temperature of the amorphous parts of semi-crystalline polymers is generally found to be almost independent of the crystallinity (Rosen, 1982), i.e the effect of the interface between amorphous regions and crystallites can be disregarded. Crystalline cellulose has a T_g higher than its degradation temperature because of extremely strong secondary bonding between chains.

In *lignin* the softening and thus the molecular movements is hindered both by structural complexity and the possibility of intermolecular secondary bonding (factor 2). Lignin is a branched and highly crosslinked high-molecular polymer with stiff and bulky groups such as phenyl residues. Cross-linking restricts chain mobility (factor 3 and 4). The structure forms a very rigid network and flow is unlikely to occur in lignin, unless numerous primary bonds are first broken.

Hemicelluloses are structurally heterogeneous, and a high concentration of hydroxyl groups offers opportunity for both inter- and intra-molecular bonding (factor 2). The hemicelluloses have an open amorphous structure due to many side-groups with little possibility of cross-linking. The hemicelluloses therefore offer a high internal mobility (factor 3) and the glass-transition temperature can be expected to be lower than for cellulose and lignin.

The main limitations to softening of *solid wood* thus stem from two sources:

1. The crystallinity of cellulose
2. The branched and crosslinked structure of lignin with very high molecular weight.

A fact that adds to the complexity of the softening behaviour of *solid wood* is the existence of chemical bonds between the main components, such as in lignin-carbohydrate complexes (Section 2.1). This clarify why wet wood and dry wood act differently with respect to softening, as seen in the following (cf. P.36).

3.4.1.2 Plasticizers

Plasticizers are substances which, when added to polymers, increase softness and flexibility. This effect may be explained in terms of an increase of the free volume of the system. The most important criterion of a plasticizer to function in connection with polymers is the hydrogen bonding ability (Rosen, 1982). For a plasticizer of general structure R-OH, the free volume generated will depend upon the size and nature of the group R.

Moisture acts as plasticizer for wood polymers. By forming secondary bonds to the polar groups in the polymer molecules and spreading them apart, the moisture reduces the secondary bonding between the polymer chains and provides more room for the polymer molecules to move around. The moisture thus increases the free volume of the system and the wood becomes more easily deformed (Birkinshaw, 1993).

Various equations for predicting the influence of plasticizers in connection with polymers have been proposed in the literature. Birkinshaw (1993) has reviewed the available theory of plasticizer action on polymers with respect to wood.

The time temperature superposition principle (TTSP) is very useful for predicting long-term (e.g. mechanical-) responses from short term of polymers data (Aklonis et al., 1972). TTSP states that a property measured over a short period of time at a higher temperature is equivalent to the property measured over a long time at a lower temperature. This time-temperature correspondence is modelled by the Willams-Landel and Ferry (WLF) approach based on the idea of increased system free volume. The shift factor, a_T, is the ratio between time, t_T, required to reach a particular response at temperature T and time, t_{T0}, required to reach the same response at the reference temperature T_0. If the polymer's glass-transition temperature is chosen as the reference temperature, then the shift factors is given by,

$$\log(a_T) = \log\left(\frac{t_T}{t_{T_0}}\right) = \frac{-C_1 \cdot (T - T_0)}{C_2 + T - T_0} \qquad 3.3$$

where C_1 and C_2 are constants. If T_0 is taken as T_g to T_g then the constants become "universal" values: C_1=17.4 and C_2=51.6.

The WLF-equation is only valid in the temperature range T_g to T_g+100°C (Young et al., 1991). The constants may vary somewhat from polymer to polymer, but it is often quite safe to assume the universal values within this temperature range.

The master curve produced by superimposing data at different temperatures is a very useful way of representing the mechanical behaviour of a polymer. The WLF equation is also useful in predicting the mechanical behaviour of a polymer outside the range of temperature and frequency for which experimental data are available. The response can be from any mechanical behaviour.

The advantage of the WLF free volume approach is that it leads to simple predictive equations for the effect of plasticizers on T_g. However, the equation does not take into account specific molecular interaction. This is a serious drawback for systems of high polarity such as wood/water. A model that incorporates a chemical interaction parameter is Kwei's equation:

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2 \qquad 3.4$$

where polymer and plasticizing agent are designated as components 1 and 2 respectively and W represents the weight fraction present. k is an adjustable free volume parameter and q an adjustable parameter taking account of specific molecular interactions. Kelley et al. (1987) calculated values for k and q from results obtained with lignin and hemicelluloses at various moisture contents, cf. Table 3.3.

Table 3.3 Best fit values of k and q based on experimental results, (Kelley et al., 1987).

Polymer:	k	q
Lignin	10	585
Hemicellulose	13	355

For reference temperatures below T_g, the shift factor is related to the absolute temperature (T) by an activation energy (ΔH) through the Arrhenius equation (Aklonis et al., 1983), where R is the gas constant.

$$\Delta H = 2.030\frac{R\log(a_T)}{\left(\frac{1}{T}\right)-\left(\frac{1}{T_g}\right)} \qquad 3.5$$

A number of other equations is available to predict the glass transition temperature of plasticizer polymer systems. The equation of Kaelble (1971) uses terms from a polymer solution theory related to molecular interactions. For detailed information see Kaelble (1971) and Birkinshaw (1993).

3.4.1.3 Hygrothermal softening of wood

The term softening or plasticization carries no immediate quantitative meaning. It is therefore important to identify parameters which reflect the softening behaviour. The glass transition temperature can be determined by all methods whose resultant values are coupled to the molecular movements identified at T_g.

A number of methods exist such as nuclear magnetic resonance (NMR), dielectrical measurements, dynamic-mechanical analysis (DMA), measuring of long-term mechanical properties (relaxation and retardation, creep), differential scanning calorimetry (DSC), and specific volume expansion. These methods will not be discussed in this review.

Most of the previous research has been devoted to the prediction of the transition behaviour with paper and pulp in mind (e.g. Hess et al., 1953; Goring, 1963; Becker et al., 1977; Back et al., 1982). Table 3.4 summarises the thermal transitions reported for wood polymers. Main emphasis is on whole wood. However some of the most important results from pulp and paper are included. From that aspect the survey may not be complete but represents what the author consider of importance.

The disagreement between researchers data, results, in part, from the use of different experimental methods and different rates of measurements (frequency), and, in part, from difference in the samples e.g. species, direction, size etc.

Although the overall response of wood softening is partly a function of the interaction between the cell wall components, the importance of the softening behaviour of the individual components is indisputable. It is therefore useful to consider the behaviour of the constituents separately. From Table 3.4 it is clearly seen that cellulose, hemicellulose and lignin behave differently with respect to hygrothermal plasticization.

Lignin: Lignin, the main cementing substance of the cell wall, has potentially the greatest effect on overall plasticity. As indicated in Table 3.4, the hygrothermal plasticization of wood is to a large extent a function of the lignin response as proposed by Goring (1963), Sakata et al. (1975), and Birkinshaw (1993).

It is considered that the replacement of hydrogen bonding within the lignin by lignin/water bonds is the main mechanism of plasticization in solid wood (Goring, 1963, Sakata et al., 1975). As reported in Table 3.4 the glass transition temperature is located in the range from 60° το 90°C for native lignin *(in-situ)*. In general caution is required in specifying precise T_g values for lignin as shown by Rials et al. (1984). In addition to the experimental and material variables identified in the foregoing, lignin is extremely sensitive to thermal history.

Several researchers have demonstrated that the viscoelastic properties of water-saturated wood follow a WLF-type of behaviour, indicating that the lignin behaves as a normal amorphous polymeric material under these circumstances (Goring, 1963; Salmén 1984; Irvine, 1985; Olsson et al., 1992; Samarasinghe et al., 1992). However, the shift factor is reported to be more limited in its range of temperature applicability than is usual with simple organic polymers. Salmén (1992) and others suggest the WLF-equation to be valid up to 130°C for water-soaked wood. Kelley et al., (1987) found similar results when adding ethyl formamide as a plasticizer.

Salmén (1984) and Olsson et al. (1992), used the WLF equation to calculate an activation energy of 450 kJmole^{-1} for the glass transition temperature of saturated *in-situ* lignin. Olsson et al. (1992) also found that hardwood lignins soften at a lower temperature than softwood lignins. They suggest that the difference is caused by the difference in degree of cross-linking of the lignin within the wood. This supports the statement of Sjöström (1983) that hardwood lignins are less cross-linked than softwood lignins.

Table 3.4 Experimental measurements used to estimate glass transition of wood polymers (cellulose=C, hemicellulose=H, lignin=L).

Reference	Method	T_g (dry), °C			T_g(wet), °C			Form
		C	H	L	C	H	L	
Goring, 1963[1]	"Powder collapse"	>230	167-217	134-235	>220	54-142	77-128	sulphite pulp, periodate lignin, etc
Höglund et al., 1976	DMA (torsional modulus)						90	Whole wood
Young, 1978	DMA (torsional pendulum)	>230		154				Kraft paper
Irvine, 1984	DTA						60-90	Whole wood
Blechschmidt et al., 1986	DMA (Resonance frequency)						115-145[3]	Whole wood
Kelley et al., 1987	DMTA, DSC[2]					-10	60	Whole wood
Salmén, 1984	DMA						72	Whole wood
Östberg et al., 1990	DSC						59	Whole wood
Olsson et al., 1992	DMA						70	Whole wood

[1] The variation in glass-transition temperatures is primarily due to different isolation methods and secondly due to difference in wood species.

[2] The same results from both methods.

[3] The specimens were initially conditioned at 100% RH, corresponding to a moisture content of app. 30%.

Based on the data presented in Table 3.3 and equation 3.4, Figure 3.9 shows the glass-transition temperature of lignin as a function of moisture content. The figure includes data from Irvine (1984). The main reduction in T_g occurs at the low moisture contents until it gradually reaches a constant level. The constant level is reached when the maximum moisture uptake of lignin is exceeded (Figure 2.8).

The equation of Kwei on lignin *in-situ* depends on knowledge of the dry glass transition temperature of lignin which cannot be found in the literature. The softening of dry lignin *in-situ* is restricted due to bonds between the main components in the wood. The values found in the literature on dry lignin are always on extracted and thus modified lignin.

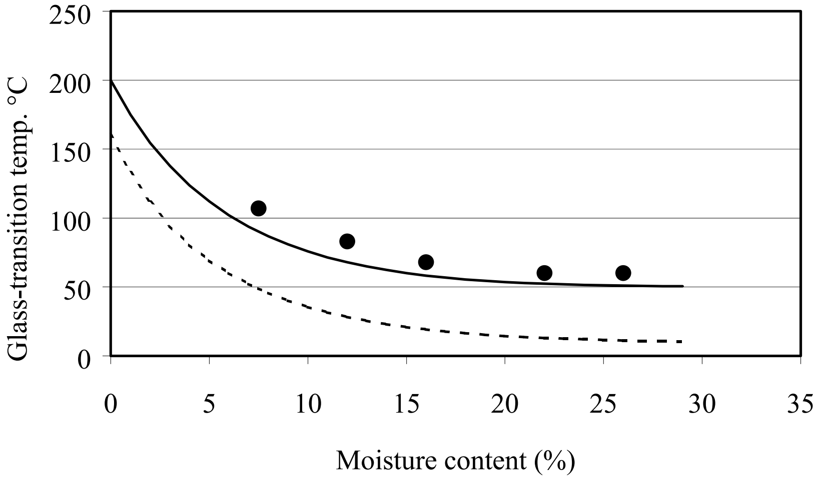


Figure 3.9 Influence of water on T_g of lignin and hemicellulose (dotted line) using the approach of Kwei. Circles refer to measurements of Irvine (1984) on lignin. The value of T_g of water is 136°C taken from Back et al. (1982).

Hemicellulose: Plasticization by water is sufficient to bring softening temperatures close to room temperature, c.f. Figure 3.9. No data of T_g for dry hemicellulose *in-situ* are available. Irvine (1984) suggests a temperature of about 160°C with the reservation that it could be closer to 180°C.

Evidence has been presented for primary bonding between hemicellulose and lignin (Section 2). However, the clear separation of the softening events suggests little interaction.

Cellulose: The potential for hygrothermal plasticization of the crystal region is severely limited. Polymer-polymer strength interaction exceeds the polymer-water interaction at all temperatures below the thermal decomposition temperature of cellulose.

Dry solid wood: Shiraishi (1992), states that no thermal softening can be identified similar to that of the individual components. *Dry wood* does not show thermal softening until it is heated to a much higher temperature.

This suggests that the interaction between the main components is of great importance. Goring (1963) found an insignificant softening of dry wood at temperatures above 200°C. Chow et al. (1971) reported similar results although he found that softening of wood started around 180°C and reached the maximum rate of softening at 380°C. This implies that the softening behaviour of dry wood is mainly governed by semi-crystalline cellulose (microfibrils), as proposed by Shiraishi (1992). The thermal behaviour of lignin and hemicellulose is restricted by the interaction due to secondary intermolecular bonding with cellulose.

Wet solid wood: Hygrothermal plasticization of wet solid wood is mainly governed by the lignin response. In the wet state lignin will soften independently of crystalline cellulose.

Olsson et al. (1992) used measurements of T_g on *wet wood* as a tool for lignin structure studies. In the experimental range 10°C to 100°C they found that only lignin is exceeding T_g. This supports that in the wet state there is little interaction between the main components of wood.

Literature references frequently indicate that the transition of solid wood is manifested as an abrupt softening of the lignin either at a single temperature or over a relatively narrow temperature range (e.g. Salmén 1992). Irvine (1985), on the contrary, suggests that the glass transition is occurring over a large temperature range. Based on the time-temperature correspondence and the WLF equation (Eq. 3.3), he suggests that the transition is spanning an interval from 100°C to 170 °C.

Olsson at al. (1997) summarises the influence of moisture and temperature as shown in the schematic drawing in Figure 3.10.

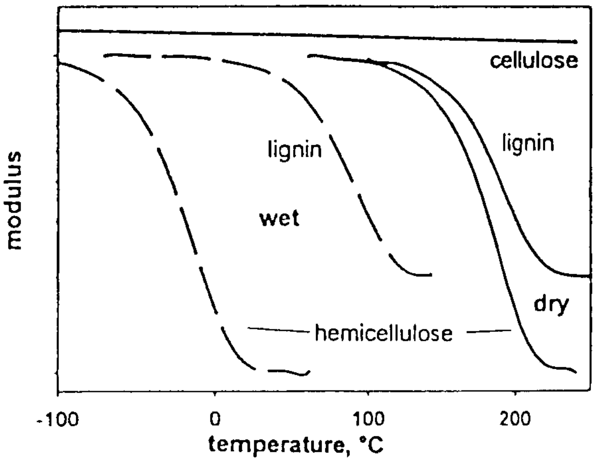


Figure 3.10 Schematic drawing of the modulus as a function of temperature for the wood polymers. Solid lines representing dry polymers and broken lines representing wet polymers (Olsson et al. 1997).

3.4.2 Thermal degradation of wood and its components

Heating wood at elevated temperatures involves thermal degradation. Not only the temperature causes changes in the wood substance. There are additional factors which influence thermal degradation processes, e.g. time of treatment, atmosphere, pressure, water content and state of distribution. A detailed description of the influence of these parameters on the thermal degradation requires an extensive chemical background. However, the subject is vital in order to understand the underlying mechanisms of dimensional stability and elimination of springback and it will therefore be introduced. The review is merely considering thermal degradation up to 200°C which is the upper temperature limit for the present research.

The review will not go into analysing- and extraction methods, but merely emphasize the conclusions. These methods are adequately covered in Fengel et al. (1984). However, it should be kept in mind that the analysis is strongly influenced for instance by the isolation method of the individual components, the conditions of heating (rate and environment), the sample size etc. The figures presented are therefore mainly showing general trends.

Solid wood: A "simple" illustration of the effect of heat treatment on *solid wood* is provided in Figure 3.11 by Hirai et al.. (1972). The thermal degradation is characterised by the residual weight of hinoki *(cypress)* after heat treatment at various temperatures versus heating time. At temperatures above 200°C the degradation or weight loss is dramatically increased. Coinciding with these data Kosik et al. (1969) found that thermal treatment of beech resulted in a weight loss of 8.1% at 150°C and of 9.8 % at 200°C with a heating rate of 5°C per minute. At first sight these observations might seem simple, nevertheless, the results involves considerable differences between the individual components.

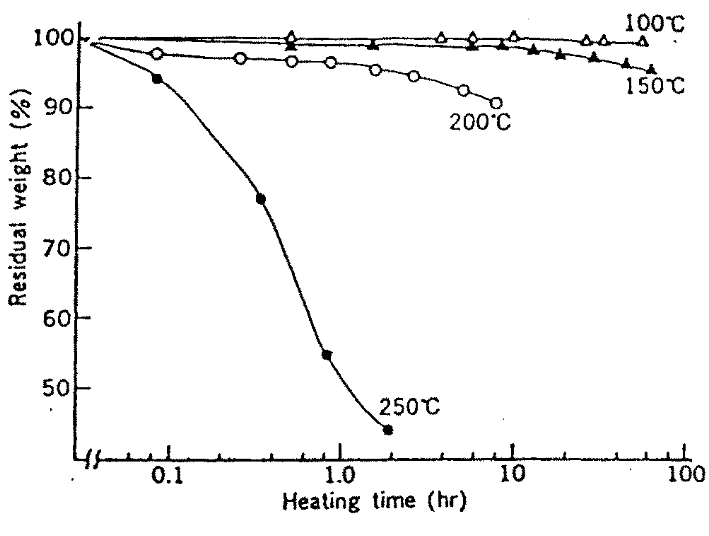


Figure 3.11 Residual weight of hinoki by thermal degradation during heat treatment (Hirai et al., 1972).

The kinetics of thermal degradation of the *cell wall components* was examined and reviewed by Fengel et al. (1984).

The degradation at the temperatures involved (<200°C) is considered a result of mainly hydrolysis, oxidation, and mild pyrolysis of the components (Zavarin, 1984). Other thermal reactions such as dehydration and gasification are identified in wood at elevated temperatures. Severe pyrolysis of wood begins at temperatures above 270°C and gasification at temperatures of more than 500°C.

Thermal degradation reactions of wood are very complex and do not involve simple, single reactions, but a series of reactions that occur at different rates. In fact, Wise et al. (1952) identified more than 200 different breakdown compounds from the distillate of wood heated at high temperatures.

Chemical analysis of wood after thermal treatment at various temperatures shows relatively good stability of the components up to 100°C (Figure 3.12). At higher temperatures the content of polysaccharides decreases, polyoses reacting obviously more sensitively than cellulose. This suggests that the hemicelluloses are degraded most rapidly, followed by the cellulose and finally the lignin. Furthermore, the rate of degradation of the individual components increases with increasing temperature.

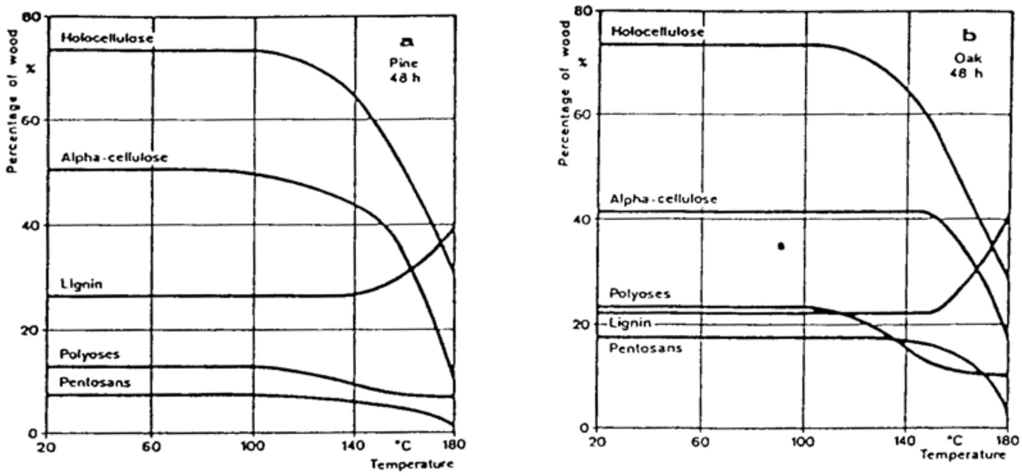


Figure 3.12 Variation of the composition of pine wood (a) and oak wood (b) after heating at 48 hours, as evaluated by wood analysis (adapted from Fengel et al., 1984).

Cellulose: The crystalline nature of cellulose is unchanged up to a certain temperature, which may be as high as 200°C depending on the conditions involved, according to Levanova et al. (1976). They concluded that the amorphous regions in cellulose grow with increasing temperature and time of heating. A completely amorphous state is reached beyond 270°C (Taniguchi et al., 1966).

On the contrary Raffael et al. (1971) observed an increase of crystallinity in thermally treated cellulose up to temperatures of 120-160°C followed by a decrease. The temperature at which the maximum value was reached depended on the water content of the cellulose sample. The crystallinity of cellulose is increased by steaming at high temperatures according to Tanahashi et al. (1989).

Hemicellulose: The hemicelluloses are degraded most rapidly. Sandermann (1964) found that during heat-treatment of beech with continuously increasing temperature the loss of pentosans was 8% at 170°C and 100% at 350°C, while the acetyl content was reduced from 4.6 % at the beginning to 0% at the end. For the 0-acetyl compound a first order reaction in the range 182-210°C with an activation energy of 160 kJ/mole was attributed to the hydrolysis of the acetyl group. Ramiah et al. (1967) determined the beginning of degradation of birch xylan to be at 117°C with a first order activation energy of 193 kJ/mole.

According to studies of Domburg, (1966) the decomposition of hardwood xylan begins near 200°C depending on the conditions involved. The decomposition was distinguished as a rupture of the glycosidic linkages as well as some C-C bonds of the pyranose rings.

The final products of thermal degradation of hemicelluloses under non-hydrolytical conditions are methanol, acetic acid, and volatile heterocyclic compounds (furan, γ-valerolactone), (Fengel, 1984). After a thermal treatment of 4-O-methylglucuronoxylan from beech wood at 180°C Kosik et al. (1968) detected acetaldehyde, methylacetate, propylaldehyde and methylketone in addition to acetic acid, methanol and furfural.

Lignin: Though lignin is seen to be the thermally most stable component of wood, various changes were observed even at temperatures below 200C°. Sergeva et al., (1960) found no change in lignin up to 155°C. Heating at 175°C caused a lignin condensation which increased with the heating temperature up to 240°C.

An infrared spectroscopic study of various lignin samples isolated from spruce and cypress, and heated in the range of 20° to 250°C gave evidence of a cleavage of hydrogen bonds at 60°C to 80°C. A change in the spectroscopic bands representing the aromatic skeletal vibration was found between 100°C and 180°C.

The thermal stability of probable linkages between lignin and polysaccharides was investigated by Kosikova et al. (1978). Splitting of ether linkages occurred at temperatures above 200°C, and was influenced by the methoxyl groups at the aromatic body, and by the hydroxyl group in para-position to the benzyl ether bond. Both reduced the thermal stability of the aryl ethers.

Structural changes: Degradation of the wood polymers will naturally change the cell wall structure. A hygrothermal treatment applied to beech wood and birch loosened the cell wall structure mainly at the interface between the S_1 and S_2 layers even at temperatures of 120°C to 160°C (Gromov et al., 1972). A disappearance of warts at the lumen side of the vessels in heated beech wood was observed by Kollmann (1967).

After cooling a heated wood sample the plasticity of the amorphous components, particular in the compound middle lamellae (lignin), is maintained until a temperature of about 60°C is reached (Necesany, 1965). Below this temperature, corresponding to the glass transition temperature of lignin, the components consolidate again.

3.4.2.1 Hygrothermal degradation

The presence of water highly effects the degradation reactions, by promoting the hydrolysis process. Attempts to analyse data from steam treated wood were made by Stamm (1959), Skaar (1976) and Hsu et al. (1988). The influence on the degradation reactions is here even more complicated than for dry heat. Stamm (1959) found that the degradation of wood is at least ten times faster under steaming conditions than when subjected to dry heat. Similar results were found by Skaar (1976). In addition, Skaar (1976) observed that the degradation rate increases rapidly with increasing temperature.

Table 3.5 Yield and composition of water-insoluble and water-soluble fractions of steamed wood at 180°C. Percentages based on equivalent oven-dry weight of original, Hsu et al. *, (1988).*

Species	Aspen			Lodgepole pine		
Treating time (min.)	0	2	4	1	2	4
Water-insolubles %	98.0	92.6	83.2	94.9	90.8	85.2
Klason lignin %	20.7	19.6	20.0	27.8	28.4	29.0
Acid soluble lignin %	3.4	1.9	1.6			
Cellulose %	43.7	40.1	42.5	38.7	37.5	37.3
Xylan %	18.5	16.3	11.1	5.5	5.6	4.5
Mannan %				9.2	8.6	6.7
Galactan %				2.0	1.9	1.3
Water solubles %	2.1	7.4	16.8	5.1	9.2	14.8
Xylose %	0	0.1	0.4			
Arabinose %				0.36	0.8	1.3

From chemical analysis (Table 3.5) Hsu et al. (1988) observed a time dependent degradation of carbohydrate polymers as a result of steam treatment. The major change was a solubilization of hemicelluloses and it did not appear to involve neither lignin nor cellulose. The steam treatment was so mild that the total content of lignin and cellulose based on the oven-dry weight of the original wood, did not decrease significantly within the duration of steam-treatment.

The results of the chemical analysis show that the total content of water insoluble xylan, mannan, and galactan of lodgepole pine and the xylan content of aspen decreased with increasing steam-treatment times. Hsu et al. (1988) conclude that the partial hydrolysis of hemicelluloses increases the compressibility of wood, reduces the tendency for stresses to be built-up during compression and lowers the springback of the compressed wood.

3.4.3 The effect of temperature on dimensional stability

An improved dimensional stability of wood is observed after heat treatment (Tiemann, 1920; Stamm et al., 1937; Stamm, 1964; Schneider, 1973; Skaar, 1976; Burmester, 1973; Suematsu, 1980; Giebeler, 1983; Hillis, 1984; Hsu et al., 1988). The effect was found to depend on the time of treatment and on treating conditions (e.g. temperature, moisture content and distribution, the presence of oxygen, sample size etc.).

It is believed that the observed dimensional stability is the consequence of thermal degradation of the wood polymers. It is explained by the decomposition of hygroscopic hemicelluloses and other carbohydrates followed by condensation or polymerization of the resulting furan-type compounds (Seborg et al., 1953). The polymerization products are considered less hygroscopic.

At the beginning, dimensional stabilization with heat was believed to be a result of a cross-linking reaction between two adjacent cellulose chains, with the formation of ether linkages (Seborg et al., 1937). This was disproved by showing that swelling in pyridine and an 18 % aqueous solution of sodium hydroxide is not reduced as it is for water. If ether linkages were formed, swelling in all three media should be reduced (Seborg et al. 1953). Back (1967) suggests that acetal linkages are formed between hemicelluloses and cellulose.

Most researchers (Burmester, 1973; Giebeler, 1983; Hillis, 1984; Inoue, 1992) have accepted the interpretation of Seborg et al. (1953, 1967). However, considering the complex degradation reactions described in Section 3.4.2, one might expect the explanation to be even more complicated.

As early as 1920, Tiemann showed that high-temperature kiln drying reduces the hygroscopicity and subsequent shrinkage and swelling of lumber. Based on the work of Tiemann (1920), Stamm et al. (1937, 1946), introduced a method for dimensional stabilization by using heat alone. The product was known as "Staybwood" (cf. the Staypak method described in Section 3.3.1).

The dimensional stability was accompanied by a *weight loss* (Stamm, 1937). This weight loss was found to be proportional to the square of the reduction in swelling, (Stamm, 1959). The proportional constant was found to vary depending on whether the heating is carried out in the presence or absence of air. This means that heating without oxygen causes less reduced strength properties when achieving a certain improvement of the dimensional stability than in the presence of oxygen.

"Staybwood" was heated beneath the surface of molten metal. The heating is thus carried out under relatively non-oxidative conditions. The time of heating at different temperatures required to give three different levels of dimensional stabilization is plotted in Figure 3.13, Stamm (1959).

Due to the degradation of hygroscopic hemicellulose the *hygroscopicity* of the wood is greatly influenced by the thermal treatment. Figure 3.14 shows isotherms at 20°C (adsorption) for untreated and heat treated wood (Kollmann et al., 1975). Coinciding with this, Suematsu (1980) found that drying at temperatures from 100°C to 180°C results in a reduction of equilibrium moisture content of 3%. There is only a slight decrease of equilibrium moisture content in beech at temperatures between 130°C and 180°C (Schneider, 1973)

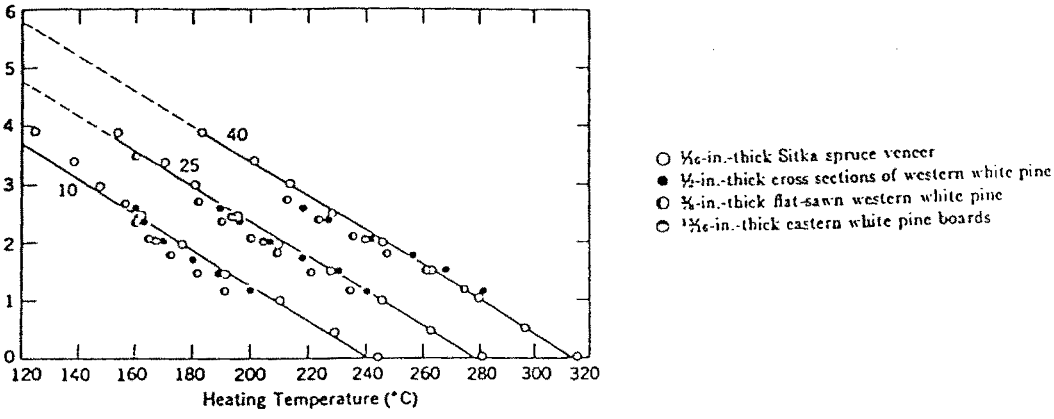


Figure 3.13 Temperature time combinations required to give three different reductions in swelling and shrinking of wood (Staybwood) heated under non-oxidative conditions. Figures on the graphs indicate the ASE value, (Stamm, 1959).

As hemicellulose has an important cohesive function in the cell wall, heating of wood is accompanied by a significant loss of strength properties. Table 3.6 shows that the strength losses become excessively high in attaining a reduction of swelling and shrinkage of 40 percent. Abrasion resistance is the most severely affected property. Stamm (1964) states that the commercial uses of "Staybwood" are limited by the significant strength losses. Another severe disadvantage is that the wood darkens as it is heated. In fact, the degree of colour change was found to correlate with the improvement in dimensional stability.

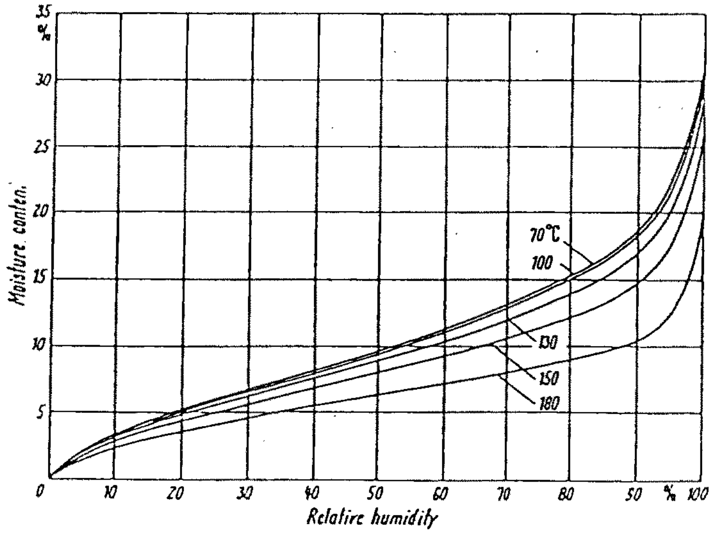


Figure 3.14 Adsorption at 20°C for heat treated wood. Labels indicate treating temperatures (Kollmann et al., 1975).

During the seventies Burmester (1973) improved the heating process. The heating was carried out under steam pressure at 140°C for 15 hours. The technique is known as FWD (Feuchte-Wärme-Druck). Burmester reports that a dimensional stability of 60% of beech can be achieved without an inconvenient decrease of strength. The loss of substance was less than for the heat treatment of dry wood using the "Staybwood" method.

Giebeler (1983) reproduced the work of Burmester (1973). Giebeler tested the dimensional stability of specimens treated in an inert gas atmosphere at 8-10 bar. Reduction in swelling and shrinkage of 50-80% was obtained, depending on species without a decrease in mechanical properties. Treating time was still very long making of little use for industrial purposes.

Hsu et al. (1988) increased dimensional stability of fibreboards by pre-steaming the fibres before compressing them into fibreboards. Using a steam pressure of 1.55 MPa (180°C) for 4 minutes reduced the thickness swelling of the boards by one-third.

Table 3.6 Weight and strength losses accompanying reduction in swelling and shrinking, by the Staybwood method, (Stamm et al. 1946).

Temp. °C	Weight loss (%)	MOR loss (%)	Hardness loss (%)	Toughness loss (%)	ASE (%)	Abrasion loss (%)
210	0.5	2	5	4	10	40
245	3	5	12	20	25	80
280	8	17	21	40	40	92

3.5 Compressive deformation of wood perpendicular to the grain

This section presents a discussion of the fundamentals of compression of wood perpendicular to the grain. The compressive stress-strain behaviour, creep behaviour and stress-relaxation are discussed in relation to the influence of hygrothermal treatment.

3.5.1 Short-term compressive behaviour

Compressive stress-strain curves for a number of woods, including beech loaded in tangential direction are shown in Figure 3.15. At low strain values (less than 0.02) the behaviour is linear elastic. Beyond the linear elastic regime, the stress strain curve shows a slowly increasing stress plateau extending the strains between 0.02 and 0.7 depending on the density of the wood. At the end of the plateau the stress rises steeply up to high strain levels. It should be noted that as the density increases the modulus and plateau stress increases.

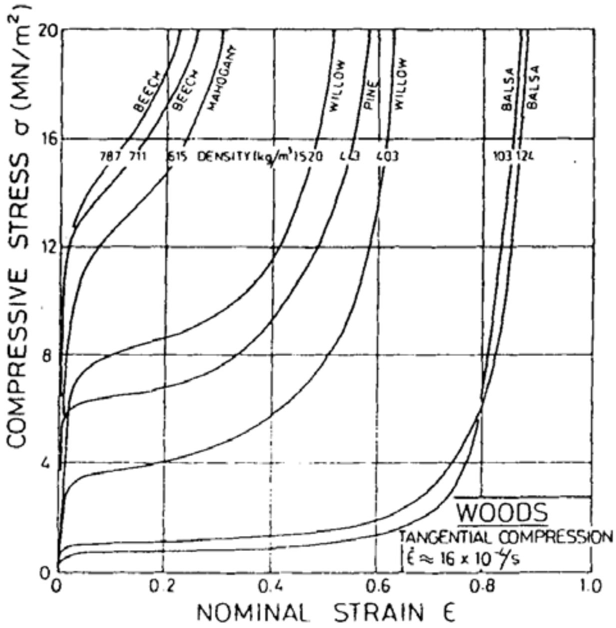


Figure 3.15 Compressive deformation in tangential direction for several species including beech. The curves for radial loading are similar in principle (Gibson et al., 1988).

Compression curves of balsa (low density) in transverse directions are compared in Figure 3.16.

Insight into the mechanism of deformation is obtained by observing the cells directly in a deformation stage mounted in a scanning electron microscope (Easterling et al., 1982).

Compression in tangential direction (Fig. 3.16a), causes uniform bending of the cell walls in the linear elastic region, and then cell collapse by plastic yielding at the stress plateau.

Compression in radial direction is shown in Figure 3.16b. In the beginning the bending of the cells is uniform just like for tangential loading. However, the plastic collapse of the cells is non-uniform, starting at the surface of the loading platen and propagating inward along the length of the specimens. Finally the cell walls crush and the stress rises steeply.

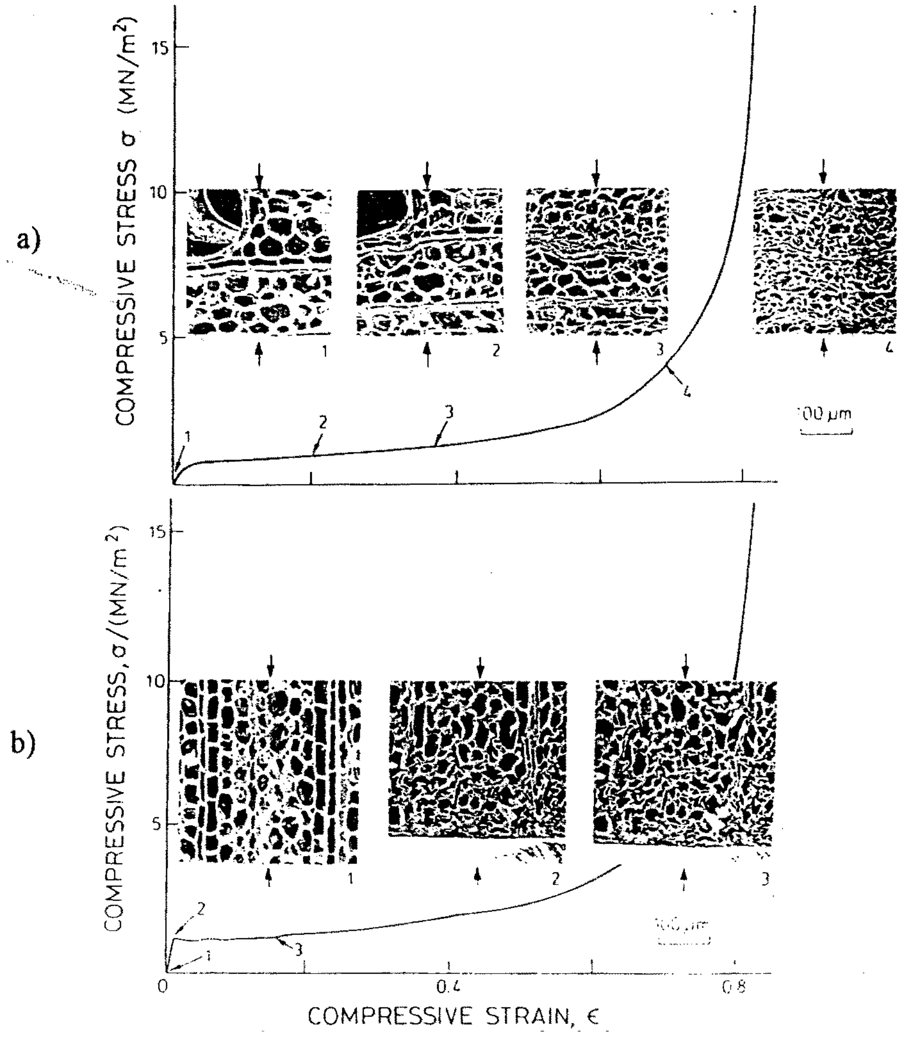


Figure 3.16 Compressive stress-strain curves for balsa: a) tangential direction, b) radial direction (Easterling et al., 1982).

Influence of hygrothermal treatment on the compressive behaviour:
Compressive tests in radial direction for different hardwoods were carried out by Liu et al. (1993) (the paper is in Japanese, however, the results were discussed by Gril et al., 1994). The wood was compressed under three different conditions: Air-dry condition at 20°C (A), wet condition at 20°C (H) and wet condition at 100°C (HT). The tangential deformation was either free or restricted. Figure 3.17 shows stress strain relationships obtained in water at 100°C in the case of *acer rufinerve*.

In general, a marked decrease of the radial yield stress σ_y and the initial elastic modulus E was observed from airdry (A) to wet (H) and to hot and wet (HT), by typical ratios 10:6:2 for σ_y and 10:5:1 for E (for most species). As expected, in the case of lateral restriction, it results in higher strain levels. However, the difference was slight, showing that most of the radial compressive strain is absorbed by internal buckling of the cell walls.

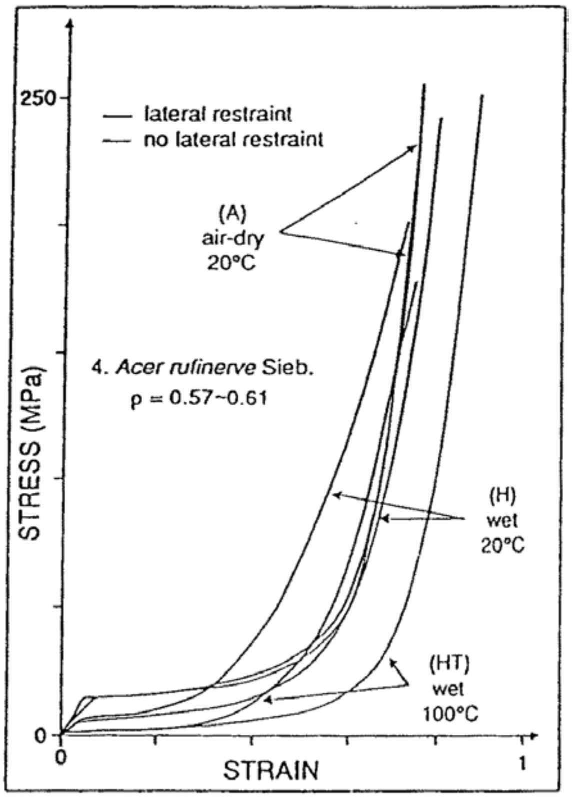


Figure 3.17 Stress strain relationships obtained in water at 100°C in the case of acer rufinerve. The thick lines correspond to lateral restriction, the thin line to lateral freedom (Gril et al. 1994).

As observed in the foregoing stress strain diagrams, three distinct regions may be identified; that is the elastic region, the stress plateau (the wood structure is densified) and the densification region (the cell wall is compressed). The following describes these regions with respect to hygrothermal treatment considering first the case of monotonous loading and then the case of increasing loading cycles.

Linear elastic behaviour: When wood is compressed in the radial direction the cell walls start to bend. At very small strains (<0.02) the stress strain relationship can be assumed to be linear.

Compression in tangential direction results in a non-linear relationship even at small strains (cf. Fig. 3.16a). This is due to the deformation of the cells when compressing in tangential direction.

The elastic deformation depends merely on the cell wall conditions and density of the wood. Since lignin is primarily responsible for the rigidity of the cell wall, the softening conditions of the lignin will highly effect the elastic modulus.

The radial modulus has roughly the same dependency on density as the tangential modulus, but is usually a little larger, the difference increasing with decreasing density. The rays act as reinforcing plates when the loading is radial. They have a higher density, and therefore the modulus is higher, than for the rest of the wood. In beech with a high ratio of ray cells this is particularly significant.

Stress plateau: The cells start to collapse which is recognised as the plateau of the compressive stress-strain curve. The origin of this behaviour is both elastic buckling and plastic collapse of cell walls (Gibson et al., 1988). The end of the plateau is where all the lumens are finally squeezed out of the structure.

In wood, plasticity refers to one of the following two situations (Gril et al. 1994):

1. A residual strain remains after unloading, but is almost completely recovered through hygrothermal treatment.
2. The residual strain corresponds to irreversible structural changes and thus is truly permanent.

An empirical model proposed by Liu et al. (1993) states that the stress strain diagrams can be expressed by the following model,

$$\varepsilon < \varepsilon_y \Rightarrow \sigma = E\varepsilon$$

$$\varepsilon > \varepsilon_y \Rightarrow \frac{\sigma}{\sigma_y} = 1 + C\left(\frac{\varepsilon_d}{\varepsilon_d - (\varepsilon - \varepsilon_y)} - 1\right) \qquad 3.6$$

$$\varepsilon_d = 1 - K\left(\frac{\rho}{\rho_s}\right)$$

where σ is the stress, ε is the strain, σ_y is the yield stress, $\varepsilon_y = \sigma_y/E$ the yield strain, E the elastic modulus, ρ the density of whole wood, and ρ_s the density of the cell wall, and ε_d is the strain at which all the lumen space is just squeezed. C indicates the extent of the increase in stress with strain above the yield point. k is related to Poissons ratio in large deformations and accounts for the lateral deformation: K=1 in the case of lateral restriction and k<1 in the free case. k decreases with increasing density. Detailed information on the identified parameters can be found in Liu (1993).

It was concluded that values calculated from the model proposed by Liu et al. (1993) correspond well with experimental values shown in Figure 3.18. The model is based on actual knowledge of the stress strain relationship through the C and K parameter, and does not take into account the aspect of hygrothermal softening.

***Densification of wood and the cell wall**:* At large compressive strains the opposing walls of the cells crush together and the cell wall material itself is compressed. When this happens the stress rises as shown in the final regime in the stress strain diagram. The strain is changed only slightly.

In the case of densification of wood as a whole the boundary between the plateau and densification of the cell wall seems to be the maximum strain that can be obtained without any damage of the cell wall. One might anticipate that the limiting strain (or maximum compression degree) would simply be equal to the porosity, because this is the strain at which all pore space disappear. The maximum compression set, $C_{s,max}$, is given by,

$$C_{s,\,max} = \left(1 - k \cdot \left(\frac{\rho}{\rho_s}\right)\right) 100\ (\%) \qquad 3.7$$

where, ρ, is the wood density and ρ_s is the cell wall density, k is a constant depending on the species taking into account that in reality, according to Gibson et al. (1988), cell walls lock together at a smaller strain than where all pore space is squeezed out.

According to Liu et al. (1993) the maximum strain level reached in the experiment, corresponding to the complete densification of the cellular structure, does not depend much on the hygrothermal treatment.

Increasing loading cycles

Wet and hot wood behaves differently from dry wood when subjected to repeated loading cycles. Figure 3.18 shows results of loading cycles of increasing load level for Japanese Cypress in wet and dry state.

At normal indoor conditions the curves show apparent plasticity. Evidence that the plasticity is only apparent is given in the curve at 100°C in water soaked condition (wet), where almost complete recovery was observed whatever maximum stress level had been reached. However, subsequent loadings never follow the previous path. Instead a new plateau is observed, for a much lower yield stress, followed by the start of a typical densification curve. Eventually, the highest previous stress and strain are reached again simultaneously, so that the original curve corresponding to monotonous loading is reached exactly where it had been left previously.

Wet and hot wood behaves differently. As the cell wall is being softened, other types of deformation processes become involved. Wet wood reflects to a large extent the properties of lignin as indicated in Section 3.4.1.

Gril et al. (1994) consequently suggest that the deformation mechanisms of wet and hot wood are more or less those of elastomeric honeycombs, and that they can be analysed following the method proposed by Gibson et al. (1988). However, elastomers typically show insignificant damage after unloading, and subsequent loading will therefore lead to the exact same shape. This is not the case for wet wood.

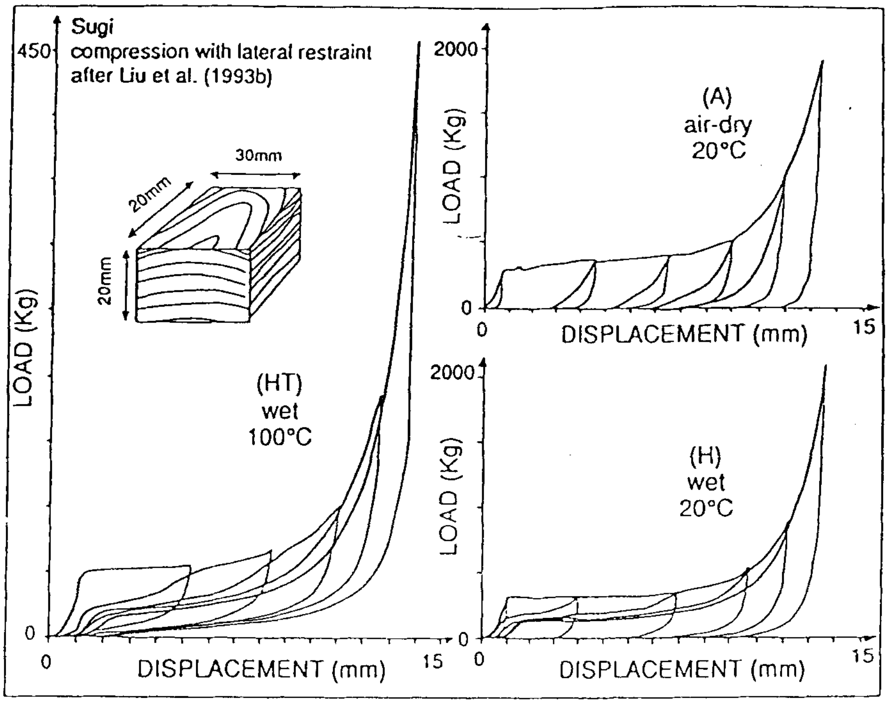


Figure 3.18 Radial compression of sugi in dry respective wet state under increasing loading Cycles (Gril et al.,1994).

As an interpretation of the damage part of the deformation (non-recoverable), Gril et al. (1994) suggests that the portions of wood of lowest density are crushed first (earlywood), then followed by the next in terms of density. When a portion has been crushed to a certain level, it is damaged, and it will thus behave differently during subsequent loading. Careful observations of the microstructure suggests that some of the damage results from local stress concentration (formation of plastic hinges) in the cell wall not far from cell corners, at the maximum moment in the warped elements of the cell wall, as exemplified in Figure 3.19.

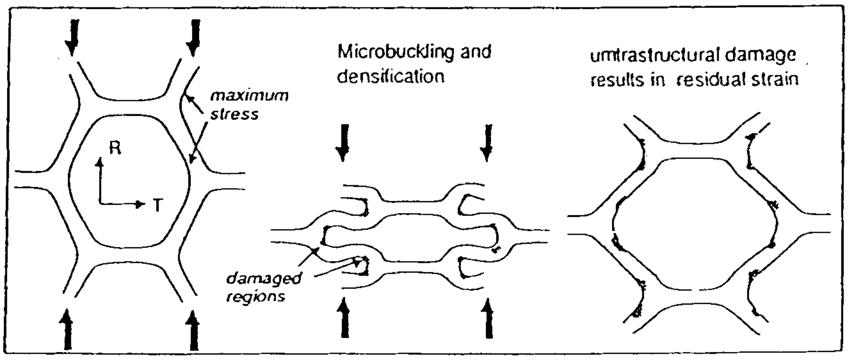


Figure 3.19 Location of damage during wood compression in the radial direction, Gril et al. (1994).

3.5.2 Long-term compressive behaviour

A viscoelastic material such as wood has a time dependent mechanical behaviour, which manifests itself in the phenomena of creep and stress-relaxation.

Creep

The creep behaviour of wood has been extensively treated in numerous references. Hoffmeyer (1990) reviewed the literature in this area. None of the references are treating the special case of the combination of high temperature and moisture content.

When the load is kept constant for a period of time the increase in deformation over the initial elastic deformation is called *creep*. The total deformation (strain) consists of three components:

1. Elastic deformation, recoverable
2. Delayed elastic deformation, time dependent and recoverable
3. Viscous deformation, permanent (irrecoverable).

The total time dependent strain (creep component) may be expressed as the sum of the three contributions and can be expressed by,

$$\varepsilon(t) = \frac{\sigma}{E(t)} \qquad 3.8$$

where E(t) is the time dependent modulus of elasticity.

As long as the normalised creep function stays independent of the stress level, the material is said to be linear. In other words, there is a linear relationship between stress and resultant strain and the theory of linear viscoelasticity can be applied. The stress levels used in the present study exceed in most cases the limit of linearity. Thus the theory of linear viscoelasticity is not applicable.

Different modes of creep behaviour are illustrated in Figure 3.20. The figure presents the effect of different stress levels. Similar figures could be presented for different moisture levels or for different temperature levels.

At high stress levels (or moisture- and heat levels) creep may cause failure. The resultant creep curve will be as curve 3 in Figure 3.20.

The primary creep is characterised by a rapidly decreasing rate of strain. Secondary creep is characterised by a slow and almost constant creep rate. Tertiary creep is characterised by an increasing strain rate.

The model most frequently applied to describe primary and secondary creep is the power function (Clouser, 1959).

It is expected that the parameters under the conditions investigated in the present study will greatly increase the creep response.

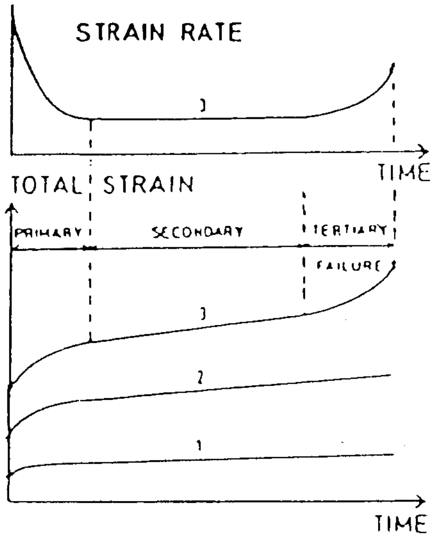


Figure 3.20 Creep curves for constant stresses $\sigma_1<\sigma_2<\sigma_3$ *or for one stress level at different temperatures* $T_1<T_2<T_3$ *or moisture content levels* $\omega_1<\omega_2<\omega_3$ (Nielsen, 1972).

Stress-relaxation:

The fact that the load necessary to maintain a constant deformation decreases with time is called *stress-relaxation*.

The deformation mechanisms involved in stress-relaxation are similar to those of creep. It can be expected that moisture and heat accelerates stress relaxation. Only a few researchers have reported on the influence of hygrothermal treatment. Norimoto et al. (1994, in Japanese) found that accelerated stress-relaxation was obtained by steaming wood. The normalised relaxation was found to be almost independent of the stress level and the internal stresses could be almost eliminated.

Stress relaxation is useful for quantifying the process of hot-pressing solid wood. It can be mentioned that the stress in hot-pressing will decrease with time. When removed from the press, the wood will springback unless internal stresses have been eliminated. Experiments of this kind can be used to estimate the time to minimise springback.

The mechano-sorptive effect may have an advantageous influence on stress relaxation, that is if the moisture content is changed during compression, the compressing time necessary to eliminate internal stresses may be decreased.

3.6 Summary

Four stages in making compressed wood have been identified:

1. Softening
2. Compression
3. Setting
4. Fixation of compressed state

Hygrothermal treatment highly influences the mechanical behaviour during compression. The phenomena of softening and degradation will occur depending on the conditions (temperature, moisture, steam, time). The present study is focused on steam treatment as a plasticizer and a method of eliminating springback.

Softening temperatures of wood polymers and degradation temperatures are outlined in Table 3.7.

Table 3.7 Outline of softening and degradation temperatures of wood components.

	T_g , °C		Severe degradation starts at, °C	
	Dry	Wet	Dry	Wet
Cellulose	>230	>220	>200	>200
Hemicellulose	160-220	< 25	>160	>160
Lignin	>150	60-90	>160	>160

The glass transition temperature is changed dramatically when moisture is present as seen in Table 3.7. However, the temperature at which severe degradation occurs is found to be independent of moisture. The rate of degradation is increased more than ten times in the case of steam treatment compared to dry-heat treatment.

Interactions between dry wood components are believed to restrict softening. Under softened conditions where the secondary bondings are reduced the wood components will soften separately. The mechanical response of softened wood simply reflects to a large extent the thermoplastic lignin. This softening of lignin results in a major reduction of the elastic modulus of the wood.

Several researchers have proposed that the fixation by steam of the compressed wood is due to softening of the lignin-hemicellulose matrix.

The following four chapters 4-7 present the results of a series of experiments designed to shed additional light on the four stages of compressing wood.

The main aims of the various experiments are summarised below.

Experiment 1.

With the aim of investigating the influence of hygrothermal treatment on the compressive behaviour of wood, four types of mechanical tests are carried out. The mechanical response from short-term static tests, creep tests, stress-relaxation, dynamic modulus under severe steam conditions investigates the influence of the combined effect of the parameters temperature, steam pressure, compression pressure, moisture content and time.

When using pressurised steam (temperature above 100°C) it should be expected that T_g is exceeded according to Table 3.7, thus the mechanical response from the above-mentioned tests should be expected to reflect the rubbery plateau.

Applying the principle of time-temperature superposition and the WLF equation on the data from the mechanical tests should be useful in order to get a better understanding of the relationship between time and steam temperature.

Experiment 2

Different species act differently to the process of densification, which mainly can be addressed to the variations in structure and chemical composition (cf. Chapter 2). How beech will perform with respect to densification has not been investigated. Beech is a high density species and has a lower lignin content compared to most softwoods. It will be intensively investigated in experiment 3 and 4.

A minor experiment will be carried out to investigate the relationship between hygrothermal recovery and compression set of beech to clarify if this difference is reflected in the compressive behaviour.

Experiment 3

Different methods for minimising springback can be found in the literature. Many of these treatments are not of relevance due to environmental concern. Some “new” treatments are dealing with hygrothermal methods. Experiment 3 is focused on steam and heat treatments of beech. The aim is to permanently fix the structure without harming the physical and mechanical properties.

Experiment 4

The aim is to characterise compressed, steam treated wood with respect to its physical and mechanical properties. An important experimental effort is to investigate the dimensional stability.

It is believed that combining the results from mechanical tests with an examination of the parameters needed to eliminate springback and knowledge of the obtained properties will enable optimisation of the technique of densifying wood. The models taken from the theory of thermoplastic polymers might be useful tools for this optimisation.

4. Experiment 1 : The influence of steam on the mechanical response

Various mechanical tests were carried out in order to study the influence of hygrothermal treatment on the compressive behaviour of wood. The study focuses on four types of mechanical tests:

- Static tests:
  1. short-term stress-strain relation
  2. stress-relaxation
  3. creep
- Dynamic tests:
  4. Frequency response method.

Below is given an outline of the tests and a description of the material and the equipment involved. The static tests were carried out at Wood Research Institute (WRI), Kyoto University in co-operation with Dr. Inoue and Dr. Morooka. The Dynamic tests were carried out at BKM at the Technical University of Denmark.

A pilot study on the static tests was carried out at WRI in January 1993. The results were presented at the COST 508 meeting in Ireland (1993). Reference is made to Morsing et al. (1994) which contains a short note on the experiments.

4.1 Material

The species used throughout this study is beech (*fagus sylvatica*). The material was sampled from Zealand, Denmark.

4.1.1 Static tests

Small clear straight grained specimens were cut from the same board. The dimensions of the specimens were 40 mm (longitudinal) x 40 mm (tangential) x 20 mm (radial). Two replicas for each test were used.

The oven-dry density of all specimens was assessed prior to the testing by measuring the oven-dry dimensions and weight. Specimens with approximately the same density were selected. The average oven-dry density of the specimens used for short-term tests was 757 kg/m^3 with a standard deviation of 24 kg/m^3. The average oven-dry density of the specimens used for long-term tests was 768 kg/m^3 with a standard deviation of 21 kg/m^3.

In the case of long-term tests conducted at 180°C and 200°C the wet dimensions were app. 70 mm (longitudinal) x 50 mm (tangential) and 20 mm (radial). The initial oven-dry density is not known.

It was attempted to avoid size effects (rate of steam penetration depends on dimensions of specimens). All specimens were cut according to Figure 4.1 prior to testing.

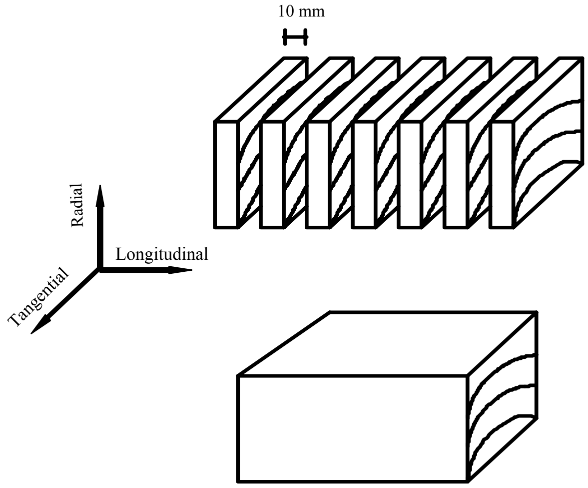


Figure 4.1 Specimen cutting to avoid "size effect".

This enables a quick and equal rate of penetration of the steam into the wood structure in longitudinal direction.

The size effect was previously investigated by Inoue et al. (1993) on sugi wood during steam treatment. They concluded that 10 mm thick slices (in the longitudinal direction) had reached the test temperature within approximately two minutes. It is expected that this time is slightly increased in the case of beech due to the higher density.

Water soaked conditions were obtained by vacuum impregnation using distilled water. Dry specimens were kept at room conditions prior to testing.

4.1.2 Dynamic tests

The fundamental problem of the dynamic tests is to select beam dimensions which at the same time allow uniform steam treatment and produces reliable measurements. In the present dynamic experiment a test set-up was used whereby a cantilever beam is subjected to transverse vibrations.

One difficulty in such a set-up is that the clamped end is under the influence of a compression force. This results in deformation when the wood beam is softened which might influence the results. The problem was examined (Appendix A) and a significant but minor influence on the dynamic response was found. At a compression set of appr. 20% in the clamped end the dynamic modulus was increased less than 10%. This is considered to be unimportant compared to the reduction of modulus of elasticity due to steam pressure.

Wood specimens were cut into small straight grained beams. The preferred dimensions of the beams for tests in fibre direction were 190 mm (L) x 14 mm (R) x 7 mm (T) in dry condition. Only axial specimens allowed reliable measurements (Appendix A).

Both ends of the beams were provided with small metal drawing pins pressed into the wood (see Appendix A).

4.2 Equipment

4.2.1 Static tests

At the Wood Research Institute at Kyoto University a setup which basically consists of a compression test machine built into an autoclave has been developed.

A schematic outline of the overall set-up for static tests is shown in Figure 4.2.

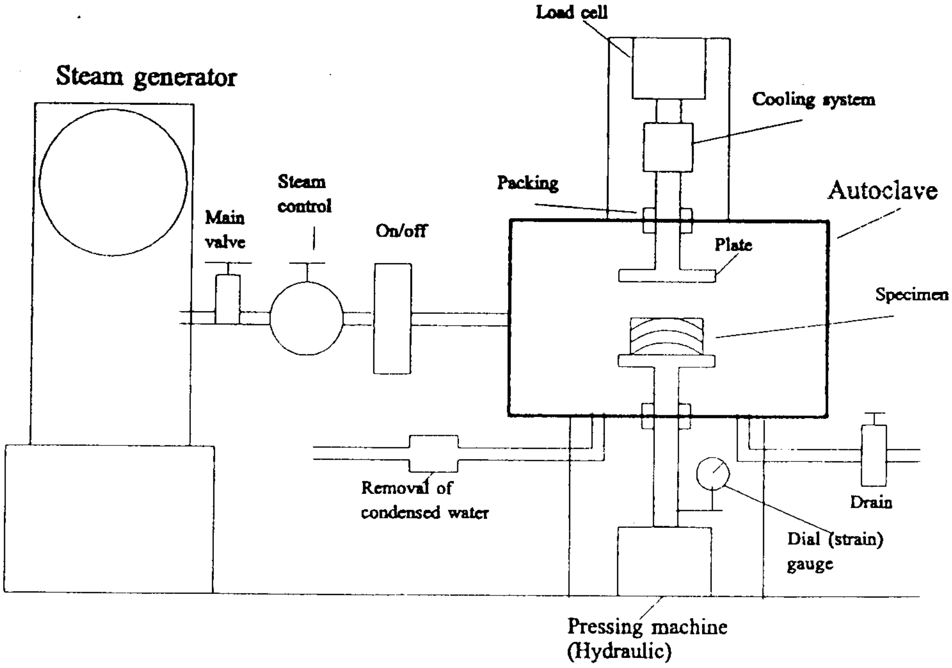


Figure 4.2 Set-up for static tests.

The equipment has the ability of steaming wood during compression. It consists mainly of an autoclave, a steam generator and a hydraulic compression test machine. The connection between the steam generator and the autoclave is equipped with a steam control unit and an on/off switch. These units enables an almost perfect control of the steam pressure inside the autoclave and also makes it possible to reach the desired steam pressure within a few seconds.
The load cell is cooled by cold water to avoid distortions of the compression load. Problems due to friction at the packings during compression seem to have an impact on the results for some tests. It influences the control of the load cell and small fluctuations of the load cell position were identified.

The load cell and the dial gauge is connected to a data-logger. Programs for data logging have been developed by Dr. Morooka.

Preparation of equipment

The set-up was prepared by pre-heating the autoclave at the test temperature. This was done in order to increase the heating rate of the vessel and to avoid an excessive quantity of condensed water. The temperature was measured on a thermometer connected to the inside of the autoclave, and also controlled indirectly by way of the pressure guage. For more detailed information on the equipment and operation, reference is made to WRI.

4.2.2 Dynamic tests

At BKM a set-up which basically consists of a complex modulus apparatus built into an autoclave has been developed. The set-up has the ability of measuring the dynamic Youngs modulus of small wood beams influenced by steam treatment. A schematic outline of the overall set-up for the dynamic tests is shown in Figure 4.3.

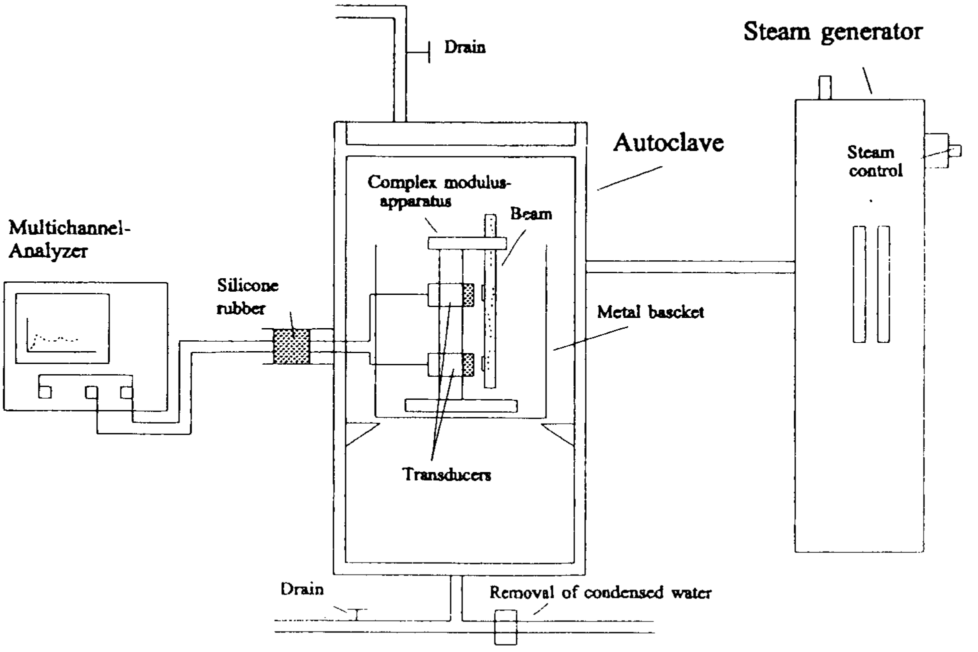


Figure 4.3 Equipment for dynamic tests.

The steam equipment consists of an autoclave and a steam generator. For information on operation, reference is made to separate instruction manuals at BKM.
The steam pressure is controlled by a "pressure-stat" and measured on a pressure gauge.

The equipment for making the dynamic measurements consist mainly of:

1 piece	"Complex Modulus Apparatus", Brüel & Kjær, Type 3930.
2 pieces	"Magnetic Transducers", Brüel & Kjær, Type MM002.
1 piece	"Multichannel Analyzer" including frequency generator, Brüel & Kjær, Type 3550.

For detailed information, see separate instruction manuals for each unit or Appendix A, where the equipment is described with special reference to the application under severe steam conditions.

Saturated steam

Both steaming systems have the ability of providing saturated steam.

A fundamental difference between the systems should be noticed. The equipment in Japan enables a perfect control of the steam pressure inside the autoclave and makes it possible to reach the steam pressure within a few seconds. The same precise control of the steam pressure is not possible in the autoclave located at BKM. The equipment was originally built for other purposes and the vessel of the autoclave has a very large volume compared to the effect of the steam generator. The steam pressure is consequently reached within app. 2 minutes depending on the pressure. Compared to the static tests a time shift between the experimental data must be expected.

Constructing a smaller vessel was out of the economic range of the present project.

4.3 Methods

This section presents an outline of methods used for the various mechanical tests.

4.3.1 Static tests

Static tests were carried out to assess the influence of hygrothermal treatment on the short-term strength as well as on the viscoelastic properties. The specimens were compressed and steam treated inside an autoclave at steam pressures ranging from 1.37 MPa to 1.55 MPa (corresponding to 140°C and 200°C respectively).

Short term tests

Small wood blocks were steamed at elevated steam temperatures during compression. The influence of hygrothermal treatment on the stress strain relationship was studied. Three types of experiments were carried out in accordance with Table 4.1. The compression rate was 20 mm/min. The relationship between stress, strain and time was recorded on a data-logger for further analysis.

The material and equipment were prepared as described in Sections 4.1 and 4.2.

Table 4.1 Experimental set-up for short-term tests. All specimens were in water saturated condition and compressed in radial direction.

Type of test	Temperature, °C	Time, min	No. of specimens[1]
1	140, 160, 180, 200	5	8
2	160, 180	0, 2, 10, 20	16
3	180	2, 10	4

[1] Two replica for each treatment

Type 1:The effect of steam temperature on the stress-strain relationship.

- A total of 8 specimens were impregnated with distilled water until water saturation.
- They were placed in the autoclave and pre-heated at the test temperature for 5 minutes prior to compression. This pre-heating time is estimated to be sufficient to reach an even temperature distribution inside the specimen.
- The specimens were compressed in the radial direction at temperatures ranging from 140°C to 200°C.

Type 2: *The effect of steaming duration on the stress-strain relationship.*

- A total of 16 specimens were impregnated with distilled water until water saturated (wet) and placed in the autoclave.
- The steam was introduced into the autoclave at two levels of steam pressures (160°C and 180°C).
- The specimens were compressed in radial direction after preheating at 4 different periods of time (0, 2, 10, 20 min.) at 160°C or 180°C.

Long-term tests
The influence of hygrothermal treatment on the viscoelastic properties was investigated. Two types of tests were carried out: stress-relaxation and creep.

Stress relaxation
The main aim was to study the influence of steam temperature on stress-relaxation perpendicular to the grain. Another aim was to examine the influence of the initial moisture condition (wet or dry) of the specimens. The specimens were compressed in radial direction.

The principle of a stress-relaxation test is to apply an initial load to reach a certain deformation (strain) and keep the deformation at a constant level during the test. The following procedure was adapted:

1. The specimens were impregnated with distilled water until water saturation using a vacuum technique. Specimens for testing in dry condition were equilibrated at room conditions.

2. Having prepared the equipment as previously described in Section 4.2, the load on the gauge was zero-adjusted before compressing and steaming. A "blank" test was conducted to adjust for the steam pressure applied to the load cell. The data-logger was prepared by loading the programs and provide the input: initial area and thickness.

3. The initial load was determined from the stress-strain diagrams found in the short-term tests and was set to correspond to a compression set of maximum 0.02. Compensation for the steam pressure applied to the load cell was carried out when setting the load.

4. The specimens were placed in the autoclave and water was added to avoid pre-drying of the wet specimens.

5. All specimens were preheated by steaming inside the autoclave at the test temperature for three minutes. The steam pressure was reached within a few seconds.

6. The specimens were subsequently compressed inside the autoclave in the radial direction at 4 levels of steam temperature. The hydraulic press was placed in a neutral position and turned off to keep the deformation constant.

7. The stress relaxation versus time was recorded for a period of 20 minutes on a data-logger.

Parameters involved in this study are outlined in Table 4.2.

Table 4.2 Parameters involved in the stress-relaxation and creep test. All specimens were compressed in radial direction.

Temp, °C	Time, min	Initial condition	No. of specimens
140	20	Wet	2
160	20	Wet/dry	2
180	20	Wet/dry	2
200	15	Wet	2

Creep

The main aim was to study the influence of steam temperature on the creep response in the radial direction. Additionally, the influence of the initial moisture condition (saturated or room climate) of the specimens on the creep response was examined.

The principle of a creep test is to apply a constant stress and subsequently record the creep response (increasing strain) versus time. Apart from this basic difference in principle the procedure is essentially identical to the procedure for the stress-relaxation tests. Preparation of the test is identical to the procedure described in the stages 1-5 above.

6. Following stages 1-5, the specimens were compressed inside the autoclave in the radial direction at 4 levels of steam temperature. The hydraulic press was switched on throughout the test to keep the load at a constant level.

7. For constant stress the creep response versus time was recorded for 20 minutes on a data-logger.

The parameters investigated are identified in Table 4.2. Specimens kept initially in dry condition were only tested at 160°C.

4.3.2 Dynamic test

This section outlines the procedure adopted in the dynamic tests. The method is an innovation, and it is therefore described in detail. In the present approach longitudinal dynamic mechanical properties are measured during steam treatment utilising a resonance frequency method. Attempts to measure radial dynamic properties were not successful.

The arrangement of the equipment, demonstrated in Figure 4.3, was developed at the Department of Structural Engineering and Materials. A Complex Modulus Apparatus was positioned inside an autoclave that provided water saturated steam conditions up to 200°C.

For details on a particular unit, the manual for that unit can be consulted or reference is made to Appendix A where application under the special conditions of the present study is outlined.

The method applied is well known in principle. Dynamic mechanical properties were measured using a cantilever beam method as illustrated in Figure 4.4. The beam is excited by an electromagnetic transducer at one end, while the vibration is detected at the other end.

The following step by step procedure was carried out:

1. Initially all specimens were vacuum impregnated with distilled water until water saturated. Dimensions and weight in water saturated condition were reported.

2. Prior to testing the specimens were pre-heated for a short period of time, using microwaves. The pre-heating was done to minimise the heating time before an even temperature distribution in the wood beam was reached.

3. Having prepared the sample as described in Section 4.1 and mounted small magnetic drawing pins at both ends, the specimen was clamped at one end in the Complex Modulus Apparatus. The beam was excited into vibration using a variable periodic force. *One end* was influenced by a magnetic field, transduced from a Multi-channel analyser equipped with a frequency generator (Type 3550; Brüel & Kjær), producing simultaneous oscillations within a range of frequencies. At the *other end* the amplitudes of the vibrations were registered by the analyser for all frequencies within the frequency range. The amplitude of the vibrations was varied within the linear range. The resonance frequency is identified on the instrument monitor and identified by moving a cursor line to the frequency peak, see Figure 4.5.

4. The steam was introduced and the resonance frequency of the water saturated wood beam was measured as a function of the duration of steam-treatment. Resonance frequencies at the time the final steam pressure was reached were reported. Measurements after 1, 3, 5, 7, 10, 12, 15 minutes were carried out. The steam pressure was reached within app. 2 minutes, depending on the desired steam pressure.

5. The resonance frequency and damping ratio were measured at the following steam temperatures: 120, 130, 140, 150, 160, 170, 180, 190, 200 °C. 4 replicas for each temperature were used. For each measurement 3 resonance frequencies (mode 1, 2 and 3) including damping ratio were reported.

6. The dynamic Youngs modulus was calculated from Equation A1 (cf. App. A.). Correction for the weight of the drawing pins was considered to be superfluous, since all specimens were treated the same way and since the discussion is primarily based on relative values.

7. Weight and dimensions were recorded after treatment.

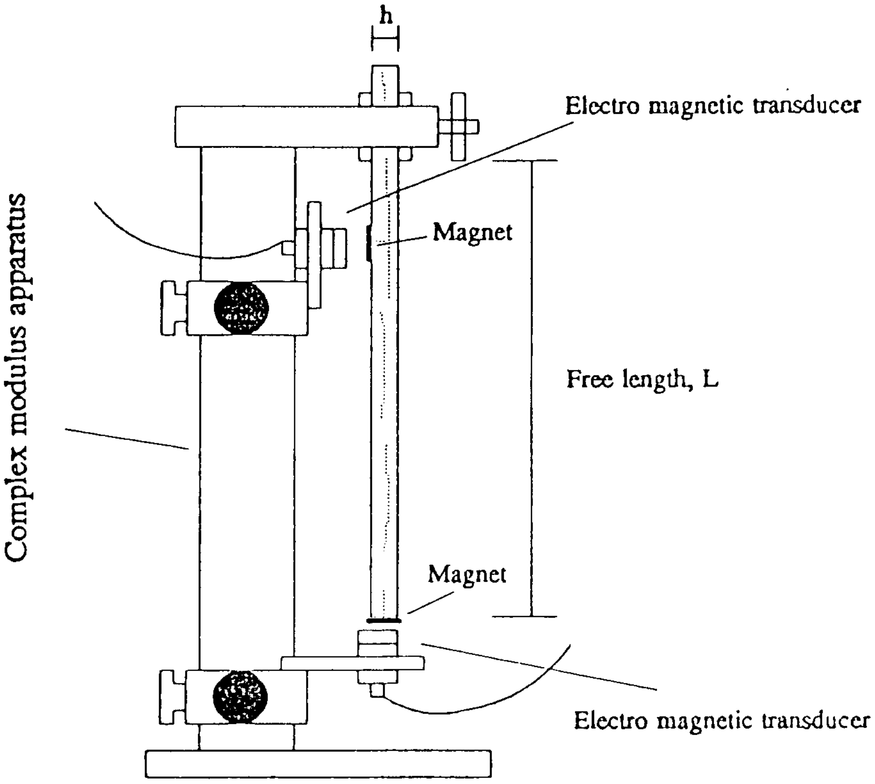
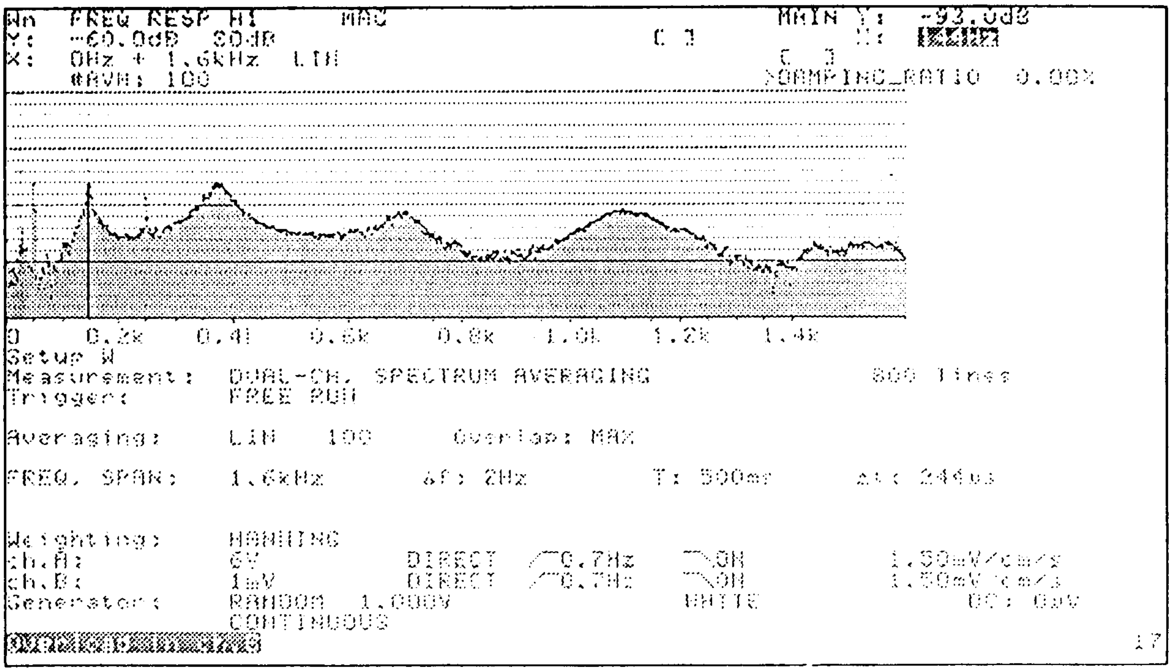


Figure 4.4 The test set-up in the Complex Modulus Apparatus.



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Wn  FREQ RESP H1       MAG                            MAIN Y:   -93.0dB
Y:  -60.0dB  30dB                     [ ]                   X:
X:  0Hz + 1.6kHz  LIN                                 [ ]
    #AVN: 100                                         >DAMPING_RATIO   0.00%

0    0.2k    0.4k    0.6k    0.8k    1.0k    1.2k    1.4k
Setup W
Measurement:   DUAL-CH. SPECTRUM AVERAGING                  800 lines
Trigger:       FREE RUN

Averaging:     LIN   100      Overlap: MAX

FREQ. SPAN:    1.6kHz       Δf: 2Hz          T: 500ms       Δt: 244us


Weighting:     HANNING
ch.A:          6V           DIRECT   ⁄‾0.7Hz   ‾\ON         1.50mV/cm/s
ch.B:          1mV          DIRECT   ⁄‾0.7Hz   ‾\ON         1.50mV/cm/s
Generator:     RANDOM  1.000V                  WHITE            DC: 0mV
               CONTINUOUS
                                                                         17
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Figure 4.5 Measured frequencies from an oscillating wood beam (Figure 3.24). The frequency peaks indicate resonance.

4.4 Results and discussion

In the following the results from the static and dynamic tests are presented. The results from each experiment are discussed individually. Finally a comparison of the different tests is carried out in a concluding section taking into account the theoretical background presented in Section 3.2.

4.4.1 Static tests

This part presents the results from the static tests: short-term tests, stress relaxation and creep tests on beech subjected to steam treatment at elevated steam temperatures.

4.4.1.1 Short-term tests

The purpose of the experiment was to examine the influence of steam on the compressive behaviour perpendicular to the grain of water-saturated beech. This was done by determining stress-strain relationships during steam treatment. The effect of steam temperature and time on stress-strain diagrams are presented and discussed as is the importance of the initial moisture conditions of the specimens.

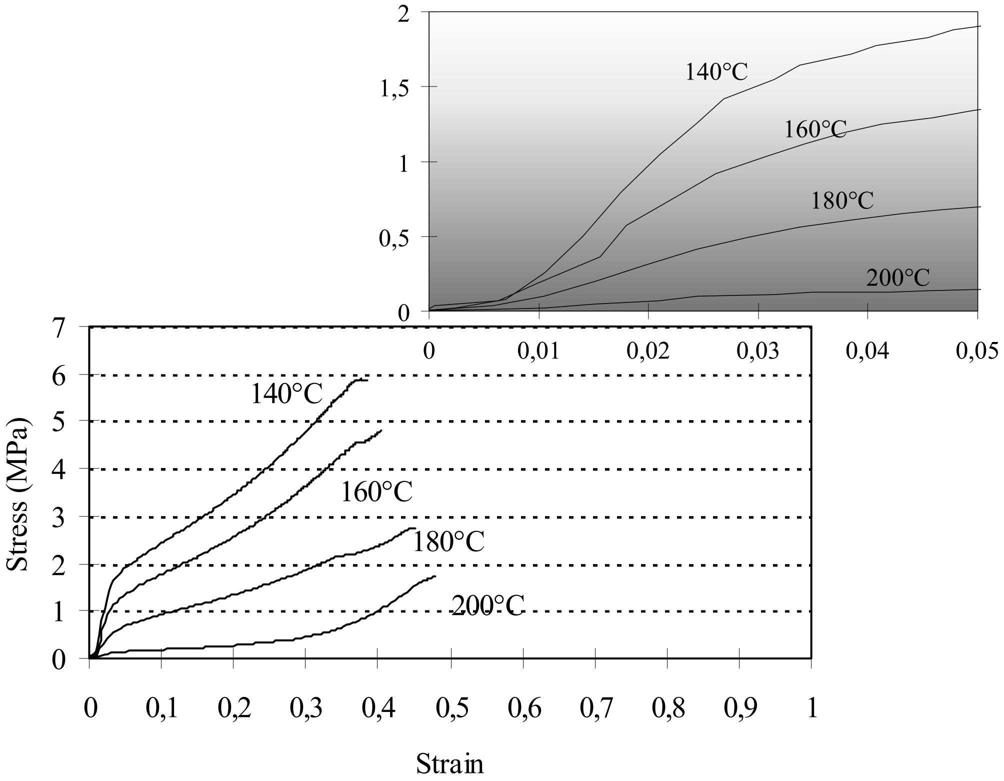


Figure 4.6 Stress-strain diagrams showing the effect of steam temperature.

The effect of steam temperature

Compression stress-strain curves at different steam temperatures for beech loaded in the radial direction, are shown in Figure 4.6. The level of the curves decreases gradually in the temperature range investigated.

The general observations are as follows:

Elastic behaviour: At small strains (less than 0.02) Youngs modulus is decreasing as the steam temperature is increased (Figures 4.6 and 4.7).

The Youngs modulus is evaluated by fitting a straight line to the elastic region of the stress-strain diagram and determine the inclination. The upper concave part of the curve at very small strains is omitted. This is caused by the test method applied where the deflection is measured as the displacement of the cylinder, which may present a problem, e.g. when the compression planes of the wood specimens or the testing machine are not parallel.

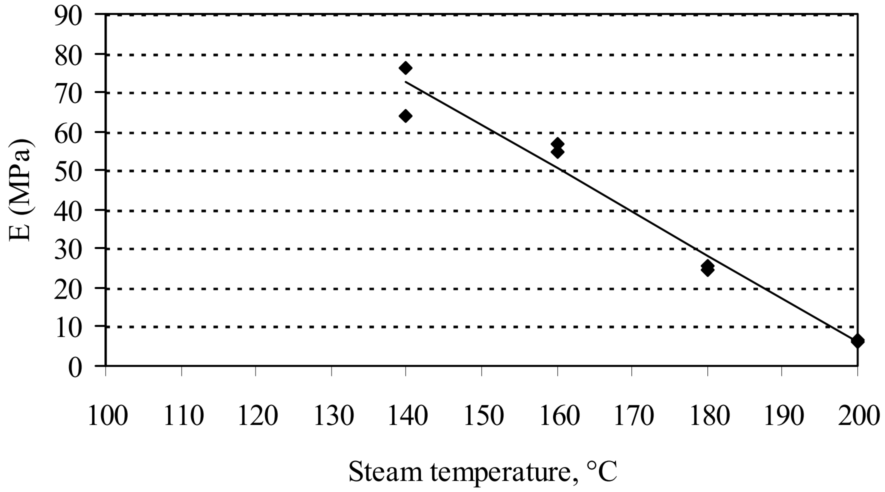


Figure 4.7 The change of static Youngs modulus, E, as influenced by steam temperature.

Plastic plateau or cell collapse: The yield stress (or yield strain) can be found as the interception point of the straight line in the elastic region and a fitted straight line of the plastic plateau.

A characteristic of the diagrams in Figure 4.6 is that the yield stress decreases dramatically at elevated steam temperature. The yield stress versus steam temperature is illustrated in Figure 4.8.

The yield strain (app. 0.02) seems unaffected of steam temperature while even large visco-elastic deformation without damaging becomes possible at higher steam temperatures.

All the curves in Figure 4.6 show a stress plateau in the strain range of app. 0.02 to 0.3, due to cell wall collapse, c.f. Section 3.5. The slope of the curves in this plateau, is gradually decreasing as the steam temperature is raised.

The work of straining may be used as an indicator of the softening condition of the wood specimens (Höglund et al. 1988). If wood samples are strained to the same degree, the work of deformation is proportional to the area under the curves. The work carried out at a nominal strain of 0.2 or 20% degree of compression is shown in Figure 4.9. The area (the work of straining) decreases with increasing steam temperature.

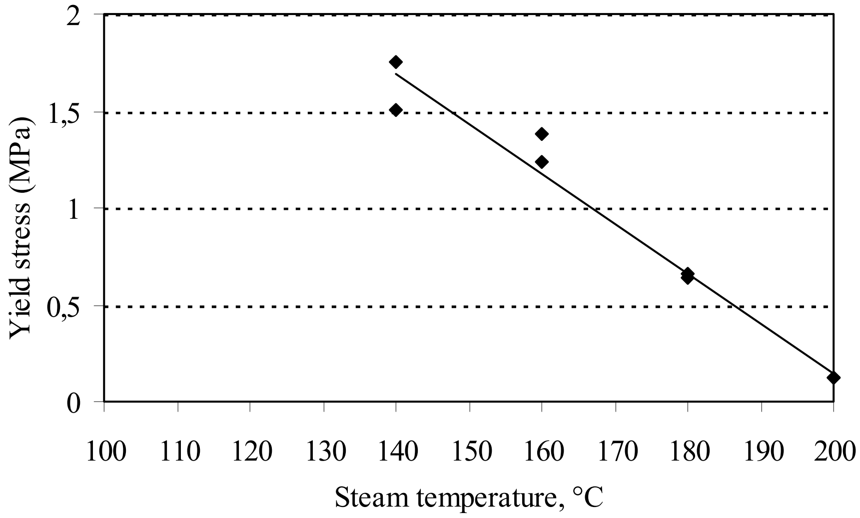


Figure 4.8 The change in yield stress as influenced by steam temperature.

Linear regression analysis was applied to the data shown in Figures 4.7-4.9. Table 4.3 summarises the result from the analysis. Coefficients of determination in the range of 0.96 and 0.98 suggest that regression models relating the dependent parameter (Youngs modulus, yield stress, work of straining) to steam temperature are significant within the temperature range investigated. A linear relationship between the mechanical response and the steam pressure is to be expected. The steam temperatures investigated are above the softening temperature of lignin (Section 3.4.1). Consequently the response consequently reflects the rubbery region of a thermoplastic polymer (Figure 3.8). However, the decrease of the properties examined is more than would be expected from mere softening. Degradation is thought to contribute to the dramatic reduction.

Table 4.3 Regression of selected mechanical properties against steam temperature, T.

Property (Y)	Reg. Line	R
Youngs modulus	Y= – 1.11 T + 228	0.96
Yield stress	Y= – 0.026 T + 5.32	0.97
Work of straining	Y= – 0.072 T + 1.48	0.98

In all cases there is a good agreement between the selected property and the softening behaviour. Thus, all the parameters are suitable as indicators of softening. Work of straining, however, is preferable since it includes the elastic and the plastic plateau. Thus, it expresses the amount of energy applied to reach a specific degree of compression.

Densification: At large compressive strains the opposing walls of the cells crush together and the cell wall itself is compressed. The theoretical limiting strain for beech is 0.5 for a density of app. 750 kg/m^3, cf. Section 3.5 and Eq. 3.7. In reality, the cell walls lock together at a slightly smaller strain than that as illustrated in Figure 4.6 (c.f. Figure 3.19 or Section 7.3.1 where this phenomena is treated in more detail). In Figure 4.6 a steep rise in stress as the strain limit is exceeded is seen at a steam temperature of 200°C. This indicates that the strain limit is decreased as the temperature increases.

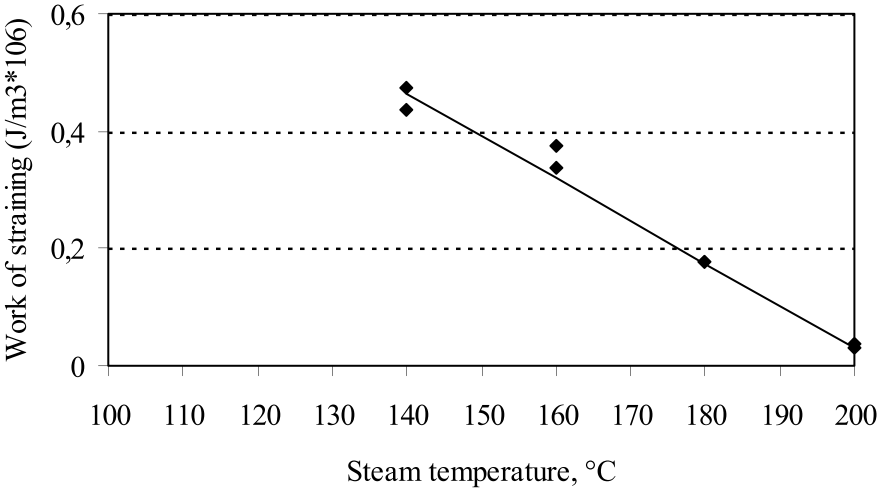


*Figure 4.9 Quantifying the softening degree at different steam temperatures by measuring the work of straining (J/m^3*10^6) in a stress-strain diagram and plotting against steam temperature.*

The effect of time

The effect of duration of steam treatment before compression is illustrated in Figure 4.10 and 4.11 at 160°C and 180°C respectively. The general trends are similar to the temperature effect on the stress-strain diagrams shown in Figure 4.6. The level of the curves decreases gradually as duration of treatment increases.

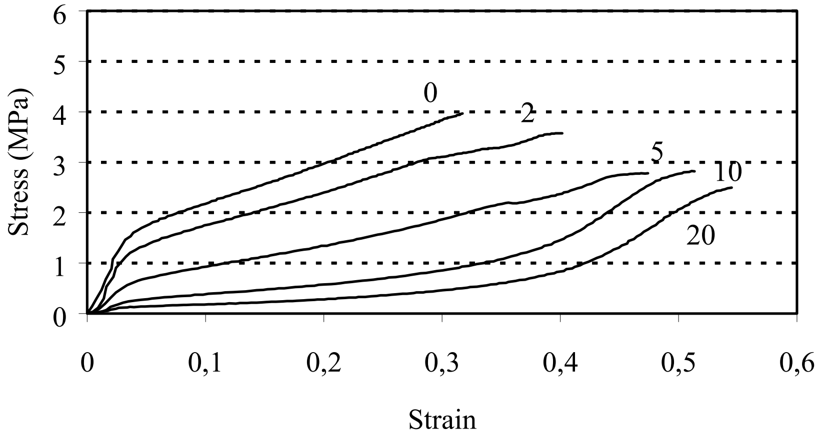


Figure 4.10 The effect of the duration of steam treatment on the stress-strain curves at 160°C. The numbers indicate duration (in minutes) of steaming before starting the compression test.

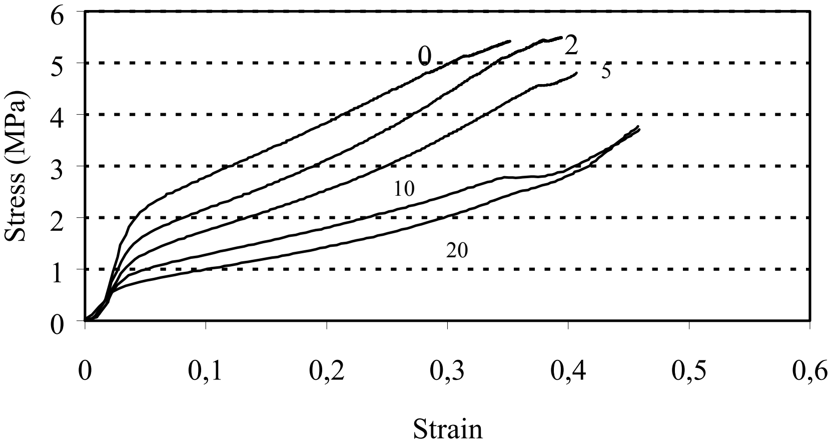


Figure 4.11 The effect of the duration of steam treatment on the stress-strain curves at 180°C. The numbers indicates duration (in minutes) of steaming before starting the compression test.

Elastic behaviour: A dramatic reduction of the elastic region is observed as duration of steam treatment increases as shown in Figure 4.12. Youngs modulus is determined as described previously.

The curves flatten as time increases, most significantly at 180°C. A similar trend would probably be noticed if the time prior to compression testing were increased in Figure 4.7 which shows the effect of steam temperature. A reason for this flattening may be that all secondary bonds are broken and optimum softening is being reached (max. free volume). However, the curves approach a level that is lower than would be expected from softening (breaking of secondary bonds). This is most likely due to degradation mechanisms (breaking of primary bonds) occurring in the material.

Stress plateau: Both yield stress and stress plateau decreases dramatically as time of steaming increases. The yield stress is determined as previously described and illustrated as a function of time in Figure 4.13. The general trend is similar to that of the Youngs moduli.

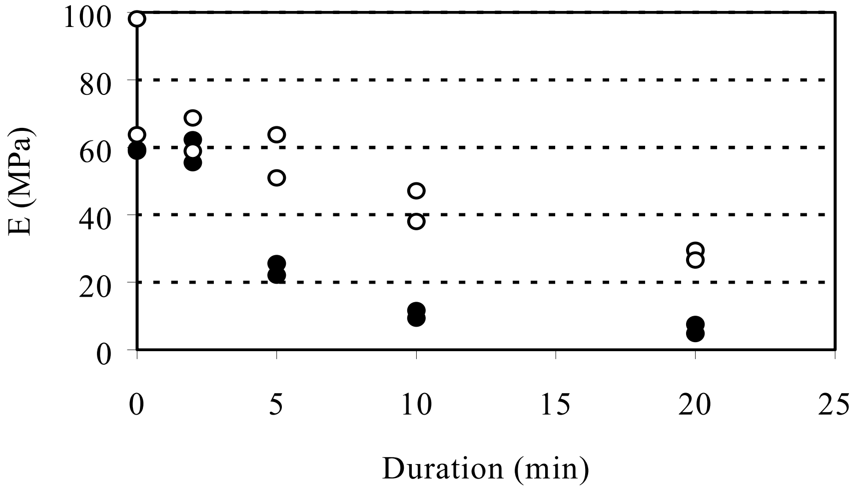


Figure 4.12 The change of static Youngs modulus versus duration of steam treatment at ○=160 °C and ●=180 °C.

The relative reduction in stress level of the plastic region is more significant at 180°C than at 160°C. The reduction of the yield stress level from 0 minute to 20 minutes of steaming prior to compression is 65% at 160°C and almost 90% at 180°C, when the wood is strained 0.1. The main reason is probably an increase of the degradation rate of the cell wall polymers rather than an increase of the system "free volume" as explained above.

The work of straining at different duration of steam treatment is shown in Figure 4.14. The work was calculated at a nominal strain of 0.2 as the area under the stress strain curve. The tendency corresponds with the foregoing.

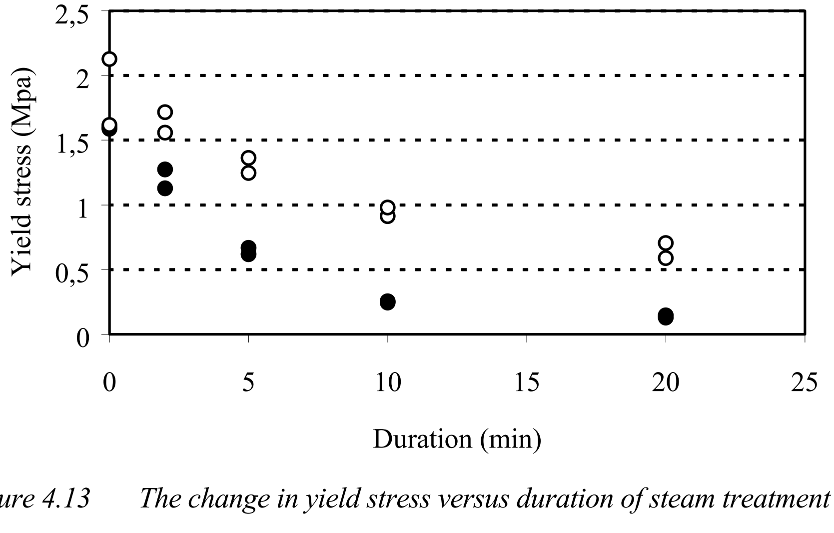


Figure 4.13 The change in yield stress versus duration of steam treatment at ○=160 °C and ●=180 °C.

Densification: The steep rise of stresses at the end of the plastic region is most significant for more than 5 minutes of steam treatment at 180 °C. As time increases the cell wall becomes more flexible which enables larger deformation before cell wall densification.

Modification of the empirical model of Liu (Eq. 3.6) taking into account the change by steam temperature of the parameters involved is achievable. Yield stress can be identified in Table 4.3 as a function of steam temperature and the yield strain seems to be unaffected by steam temperature (ε_y =0.02 as seen in Figure 3.10). The limiting strain ε_d (maximum compression set) seems to change slightly with steam temperature which influences the k and C value. The relationship is not detectable from Figure 4.6. Assuming a constant ε_d, however, results in values of k=1.07 and ε_d =0.5 (calculated according to Section 7.3.1). Using these parameters the model can be modified using the following expression in the plastic region,

$$\frac{\sigma - \sigma_y}{\sigma_y} = C\left(\frac{\varepsilon - 0,48}{\varepsilon + 0,52}\right)$$

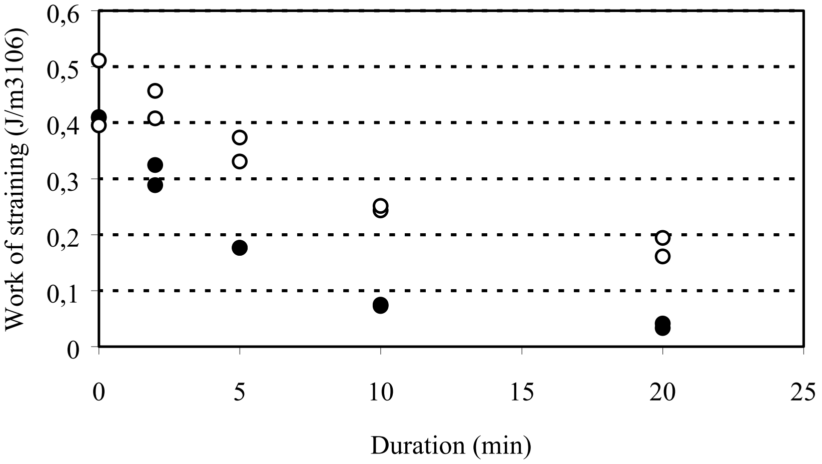


*Figure 4.14 The change in work of straining (J/m^3*10^6) versus duration of steam treatment at ○=160 °C and ●=180 °C.*

4.4.1.2 Stress-relaxation

The purpose of the experiment was to investigate the visco-elastic properties of beech at high steam temperatures.

The initial load was determined from the stress strain diagrams obtained in the short-term tests. The intention was to conduct the stress-relaxation test within the linear visco-elastic region and then employ normalised stress and relaxation modulus as indicators of plasticization. In order to achieve this it was necessary to increase the area of the cross section of the specimens compressed at the temperatures 180°C and 200°C.

The initial deformation and the accomplishment of keeping the strain constant during the relaxation test at the different temperatures is shown in Figure 4.15. The figure shows that the strain changes during the test. According to the short-term tests the yield strain is exceeded (app. ε=0.02) at all temperatures after a short time. The effect on the tests is significant. Another problem recognised in the figure is the "small" fluctuations of the strain that suggest problems with the compression cylinder.

Consequently, conclusions should be made with great caution. Analysis of the data becomes very complicated and the figures only express general trends.

Figure 4.16 shows stress relaxation versus time at four different steam temperatures. The different initial stress levels are illustrated. The curves at 180°C and 200°C

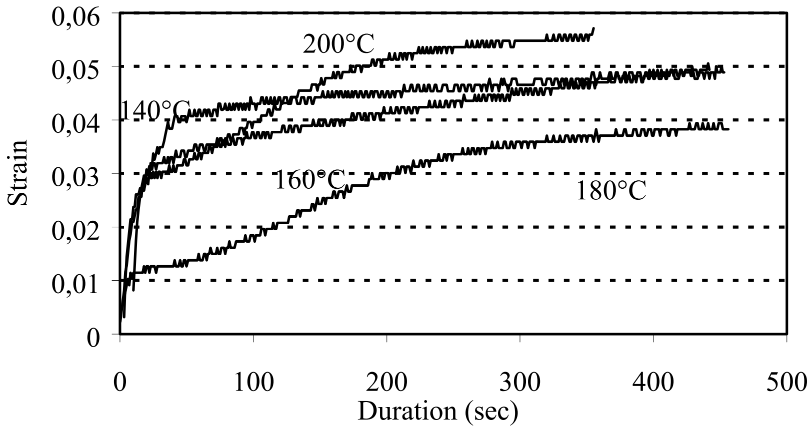


Figure 4.15 Strain versus time for stress-relaxation tests at different steam temperatures .

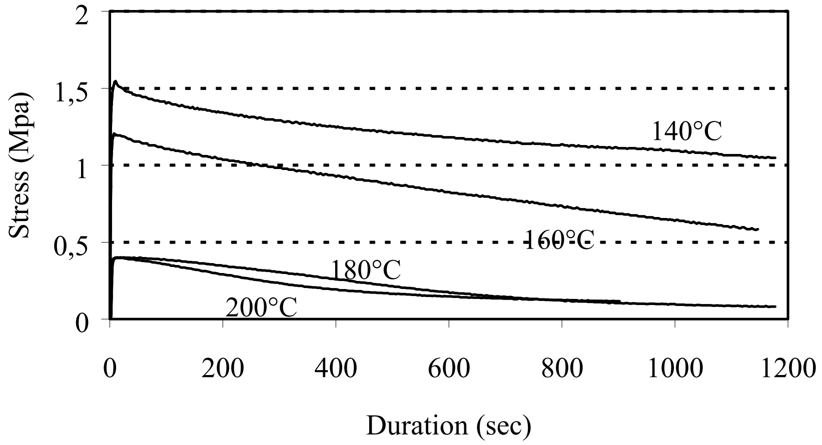


Figure 4.16 Stress relaxation at different steam temperatures.

show downward concave parts in the beginning of the test probably due to the increasing strain illustrated in Figure 4.15.

Calculation of normalised stress becomes meaningless due to the increasing strain. Maximum stress will change with the change in strain. Figure 4.17 shows the relaxation modulus $\sigma(t)/\varepsilon(t)$ with the reservation that the strain is varying during the test. The modulus is normalised according to the value after a period of 30 seconds to minimise difficulties in the beginning of the test.

Figure 4.17 clearly shows that an accelerated stress-relaxation can be identified. The relaxation of stress increases dramatically with increasing steam temperature. The main reduction takes place in the beginning of the experiment after which the relaxation modulus gradually flattens. This phenomenon is particular significant at the highest temperatures within the time scale of the experiment.

From the figure it is seen that the stress is relaxed almost completely after approximately 10 minutes of steaming at 200°C. When stresses are relieved springback must be expected to be completely eliminated.

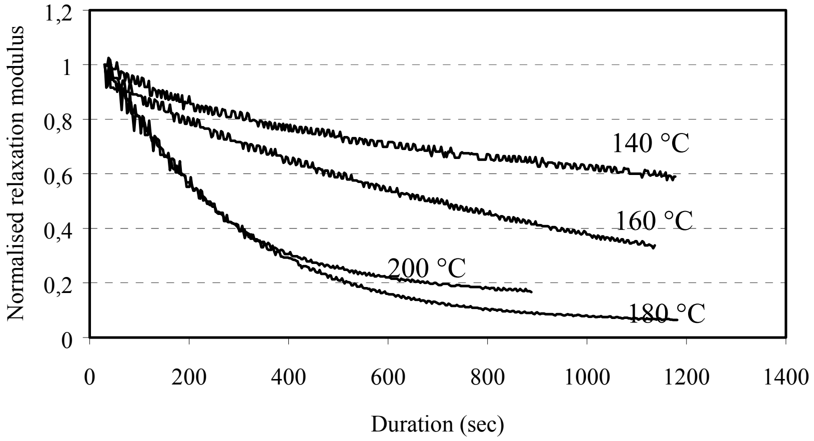


Figure 4.17 Normalised relaxation modulus at different steam temperatures.

4..4.1.3 Creep test

The influence of high steam pressure on the creep behaviour of wet beech was investigated.

The intention was to run the tests within the linear viscoelastic region in the beginning of the test and evaluate the use of creep modulus and normalised creep as indicators of softening and degradation.

The load necessary for a linear-elastic response was determined from the short-term tests. However, it was realised that the size of specimens combined with the problems affecting the load cell would make it impossible to stay within the viscoelastic range during the whole test.

The creep response versus time is shown in Figure 4.18. The initial stress and the success of keeping the stress constant during the creep test at the different temperatures are shown in Figure 4.19.

From Figure 4.18 combined with Figure 4.19 the following conclusions are drawn:

- The stress during the creep tests was almost constant. Thus, the problems identified in the stress relaxation tests do not have the same influence on the results of the creep tests.

- The curves at 160°C, 180°C and 200° shows typical tertiary creep response (cf. Figure 3.20). After exceeding the plateau of constant strain the deformation increases dramatically. This is due to collapse and subsequent damage of cell walls. A comparison of the diagrams of the short-term tests carried out after different periods of time with these results confirms the observations.

- The curves at 160°C, 180°C and 200° progress differently from the 140°C curve. This is because the yield of strain is exceeded already at the beginning of the test (ε>0.02).

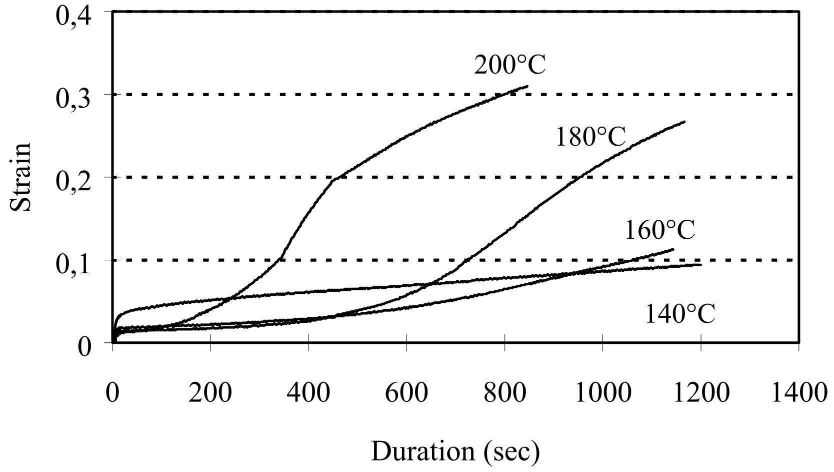


Figure 4.18 The creep response at different steam temperatures.

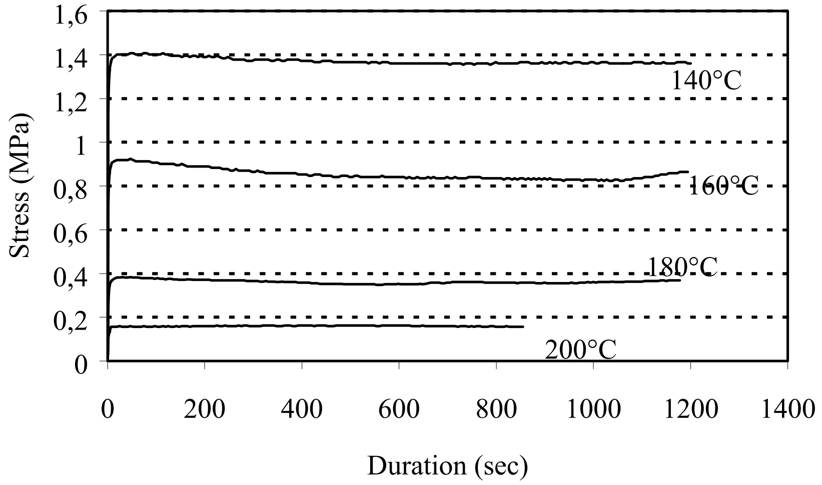


Figure 4.19 The stress during the creep tests at different steam temperatures.

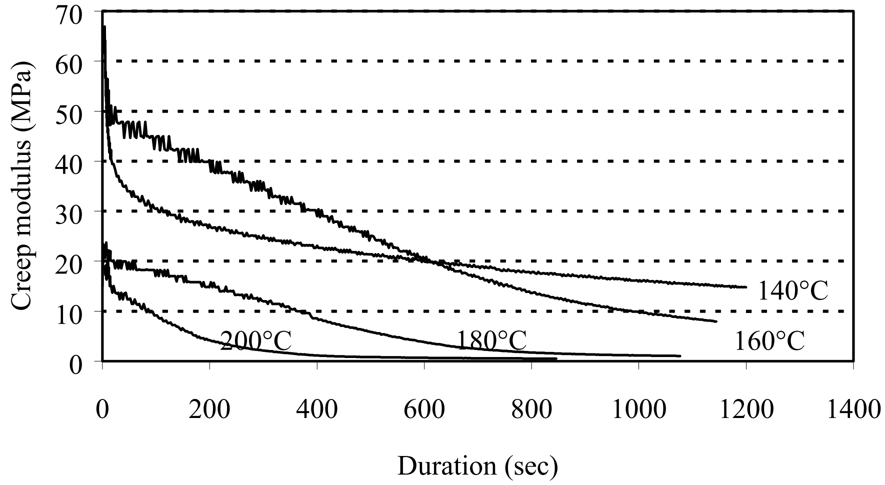


Figure 4.20 Creep modulus versus time for different steam temperatures.

The time dependency of the creep modulus was determined by calculating σ(t)/ε(t). Figure 4.20 and Fig.4.21 shows the reduction in creep modulus versus time at four levels of steam temperature.In Figure 4.21 the creep modulus was normalised by the value at 30 seconds to minimise problems arising from the equipment. Analogous with stress relaxation tests the main change in creep response takes place in the beginning of the experiment.

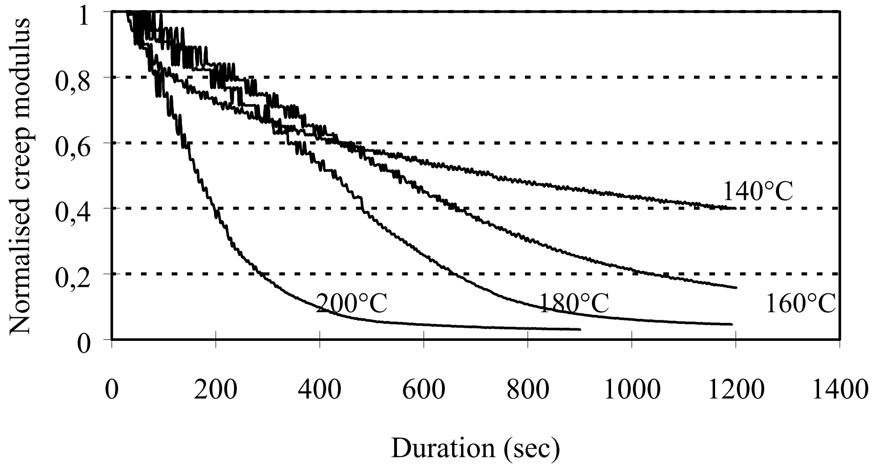


Figure 4.21 The normalised creep modulus at four different steam temperatures.

The creep modulus at 120 sec. (total 300sec. incl. preheating) displayed in Figure 4.21 corresponds well with the Youngs modulus obtained in short-term tests after five minutes (300 sec.) in Figure 4.7. Except at 140°C where the yield strain is exceeded of the creep curve and a drastic decrease in creep modulus therefore is observed.

Dynamic tests

The main aim of this experiment was to determine the storage modulus (E_{dyn}) as a function of steam temperature.

A Complex Modulus Apparatus was placed inside an autoclave. The resonance frequency measured at a certain steam temperature is proportional to the rigidity/softness of the specimen. Consequently, substantial decreases in frequency indicate a distinct softening/degradation of the wood. The storage modulus was calculated from Equation A.1 (cf. Appendix A), where the modulus is expressed by the resonance frequency.

Whilst there are many experimental advantages using this resonance frequency method, including the ability of controlling moisture and temperature, a number of both theoretical and practical difficulties exist. Designing specimen dimensions and sample clamping is a major practical problem as temperature and moisture induces dimensional changes, which must be accommodated without compromising the assumptions made in the mechanical analysis. Furthermore, the storage modulus is frequency dependent, which further complicates the analysis.

The results of the present study proved reproducible which indicates a satisfactory solution of the problems (cf. Appendix A).

Absolute values of storage moduli, should be compared with each other with caution, because of the compressibility of the clamping and because of the frequency dependency. Attempts to measure the damping ratio (loss factor) were not successful probably for the same reason. Discussions can be based on trends only.

The effect of temperature

The storage modulus was calculated based on an average of 4 specimens for each treatment. Figure 4.22 shows the effect of steam temperature on the storage modulus after 10 minutes of steaming. A large reduction of the modulus is observed with increasing temperature.

The effect of time

The effect of steaming time at different steam temperatures on the storage modulus is illustrated in Figure 4.23. The main reduction takes place in the beginning of the test until the curves gradually levels off.

The tendency is quite similar to the results found in the short-term tests. After approximately 8-10 minutes at 180°C, an almost constant level is reached. The diagrams at each temperature show identical shapes. This indicates that the time-temperature super-positions principle (cf. Section 3.4.1) is a reasonable approach, (see next section 4.5).

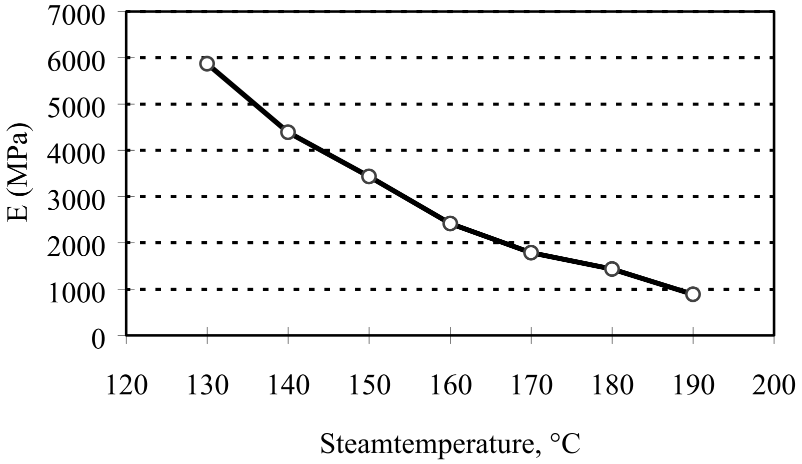


Figure 4.22 The storage modulus versus steam temperature after 10 minutes of steaming (the small numbers indicates standard deviation).

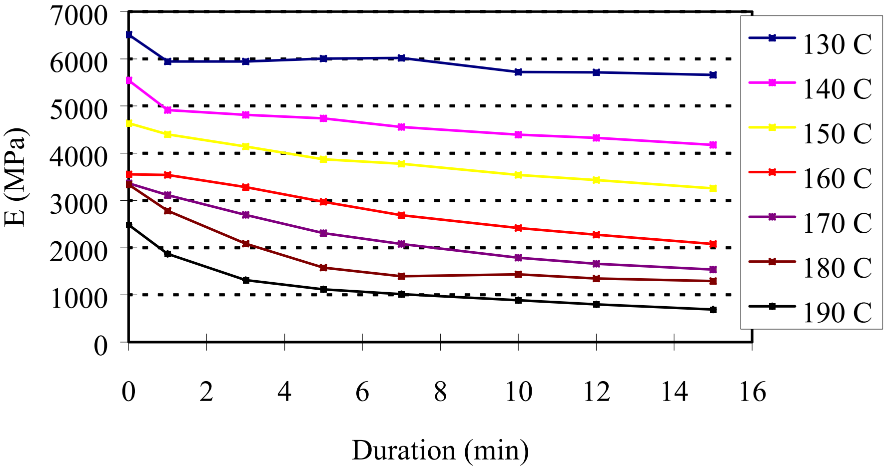


Figure 4.23 The storage modulus versus duration of steam treatment at different steam temperatures.

4..5 Concluding remarks

In the experimental work presented in the previous sections, four types of mechanical tests were carried out to study the compressive behaviour of beech at high steam temperatures; that is short-term tests, stress-relaxation, creep-tests, and dynamic mechanical tests using a resonance frequency method.

This kind of experiments under the conditions studied has not previously been presented in the literature. Since the methods applied in the present study are innovations, the experiments have been accompanied by a number of difficulties. However, some general trends were identified as will be summarised in the following.

In the range of temperatures considered here, the wood material is expected to have exceeded its glass-transition temperature and thus exists in a rubber-like state during the tests. Hence, the dramatic reduction of modulus of elasticity is considered to be attributed to structural differences caused by degradation of the wood structure.

Thus the steam treatment has two types of effect on wood: temporary effects that exist only as long as steam is maintained (softening), and permanent effects that result from thermal degradation of the cell wall components. The first effect is explained by the free volume theory, while the second effect is a very complex process consisting of a number of different degradation mechanisms.

All the mechanical tests applied to the wood in the present study show good agreement between property and softening/degradation behaviour.

Attempts to measure dynamic mechanical properties in the radial direction were not successful. However, Salmén (1992) showed that the softening behaviour along and across the grain is characterised by almost identical softening temperatures. This indicates identical softening behaviour at least in the elastic region.

Some general trends can be deducted from the experiments.

- All experiments showed a gradually reduced elastic modulus that levels off.

- In the linear-elastic region a constant level of the storage modulus is reached after 8-10 minutes in the dynamic tests. This corresponds with the results from the short-term tests where a constant level is reached after app. 10 minutes at 180°C.

- The creep modulus and relaxation modulus found in long-term tests reached constant levels after a little longer time than 10 min.. However, difficulties in those tests made the analysis very complex.

- The curves of Youngs modulus or storage modulus in each separate test at different temperatures, appear to be different sections of one continuous curve. This indicates that the time-temperature superposition principle is applicable.

Time-temperature superposition principle (TTSP)

The following describes the TTSP applied to the modulus data found in the dynamic tests.

A shift in a temperature curve along the time axis is carried out, corresponding to dividing every value of the abscissa by a constant factor. This constant factor, which brings a curve at a particular temperature into alignment with the one at a reference temperature, is known as the *temperature shift factor* a_t, (cf. Section 3.4.1). The logarithm of the experimentally determined temperature shift factor is plotted as a function of temperature in Figure 4.24. The reference temperature is 160 °C.

The master curve represents the mechanical response at 160°C. Multiplication by the appropriate value of a_t establishes the master curve at any other temperature and can thus be used to predict response at that temperature over the entire time scale. The master curve is illustrated in Figure 4.25 where all data at temperatures from 150°C to 190°C are shifted to the reference temperature.

There are two additional aspects that enhance the applicability of the time-temperature superposition concept.

Firstly, the same temperature shift factors apply to a particular polymer regardless of the nature of the mechanical response; that is, the shift factors as determined in dynamic tests are applicable to the prediction of the time-temperature behaviour in creep- or short-term tests. The shift factor at 180° is a_t=0.18 as shown in Figure 4.24 (log (a_t) = -0.75). A similar shift factor is found in the short-term test in Figure 4.12. The time to reach a modulus of 22 MPa at 160° (reference temperature) is app. 23 min. At 180°C the same response is reached after only 5 min. The shift factor is then a_t=0.22.

Secondly the shift factors can be expressed by the WLF-equation previously mentioned in Section 3.4.1. However, when the glass transition is excessively exceeded one might anticipate that the WLF equation is not applicable. Salmén (1992) showed that the WLF equation is only valid up to 130°C, which is 30-70°C above the glass-transition temperature of saturated lignin. The WLF equation is based on the free volume theory. However, at elevated temperatures other mechanisms start to dominate the behaviour (degradation). Attempts to calculate the constants C_1 and C_2 of the WLF- equation based on the shift factors presented in Figure 4.24, confirmed these findings. The constants were found to depend on temperature, and are only valid within the temperature and time range investigated.

In the case where the WLF-equation cannot be used empirically other approaches must be developed. Another means is to evaluate the mechanical properties for the range of conditions of service expected and display them graphically for the prediction of the response (Figure 4.24 and 4.25).

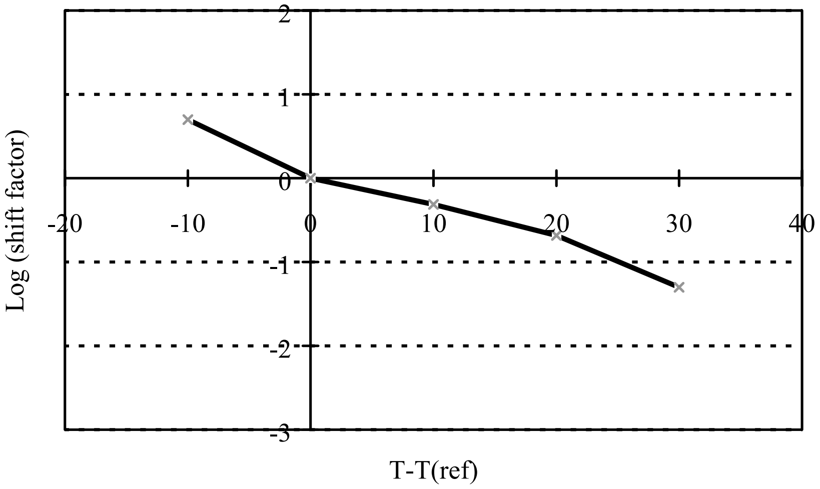


Figure 4.24 Experimentally determined shift factors from the data illustrated in Figure 4.23.

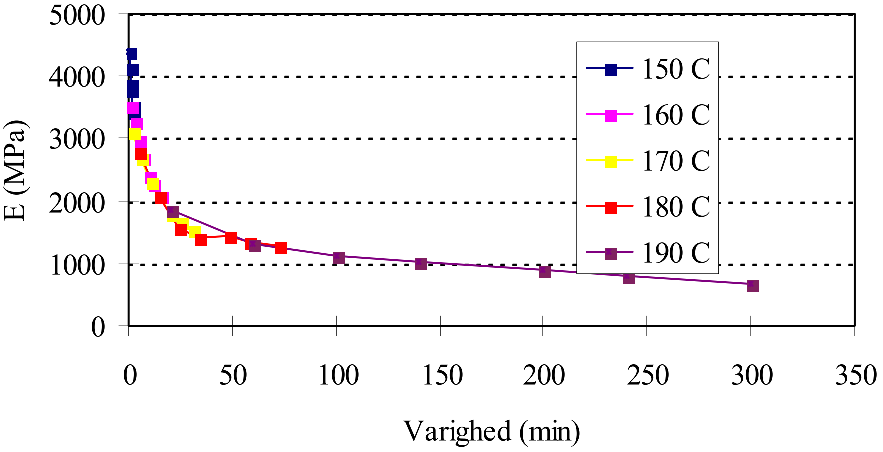


Figure 4.25 The master curve at 160℃.

5. Experiment 2 - Hygrothermal recovery

A remarkable feature of wood compression is the existence of a rheological memory. The effect of this rheological memory manifests itself in an exceptional swelling, often referred to as springback, when the compressed wood is subjected to moisture and/or heat. A minor experiment was carried out to investigate the relationship between compression set and recovery of set of beech.

5.1 Materials and method

A total of 32 beech specimens of dimensions 20mm (R) x 20mm (L) x 30mm (T) were cut from the same wood block. Initial oven-dry dimensions and weight were recorded.

The specimens were conditioned at 90% relative humidity corresponding to a moisture content of approximately 20%. They were placed in a hot-press (Garver) and compressed in radial direction at 120°C for 1 hour. The compression set was varied from 10% to 60%.

Five replicas were used for each compression set. The compressed specimens were oven-dried for 24 hours. Dimensions and weight were recorded.

Recovery of set was provoked by hygrothermal treatment. The specimens were impregnated with distilled water until saturated and boiled for 60 minutes. The recovered thickness in oven-dry condition was recorded.

Compression set and recovery of set were calculated from Equation 3.1 and Equation 3.2 respectively.

5.2 Results and discussion

The recovery of set versus compression set is shown in Figure 5.1. The compression set is seen to have no influence on the recovery of set, which corresponds with the findings of Inoue (1992) and Stamm (1948). However, there was an insignificant deviation at a compression set of 10%. The reason for this is unclear, but similar results were found for Danish spruce (unpublished data).

Since the results correspond well with those of Inoue (1992), no further investigations were carried out. It is expected that the parameters time and temperature also have an influence on the recovery of set as that found for Sugi (Inoue 1992).

Apparently the recovery of set depends mainly on the softening conditions of the matrix and not on the compression set. Hence, compression pressure is considered to have minor influence on the recovery of set and will only be examined in the succeeding experiments when considered of importance.

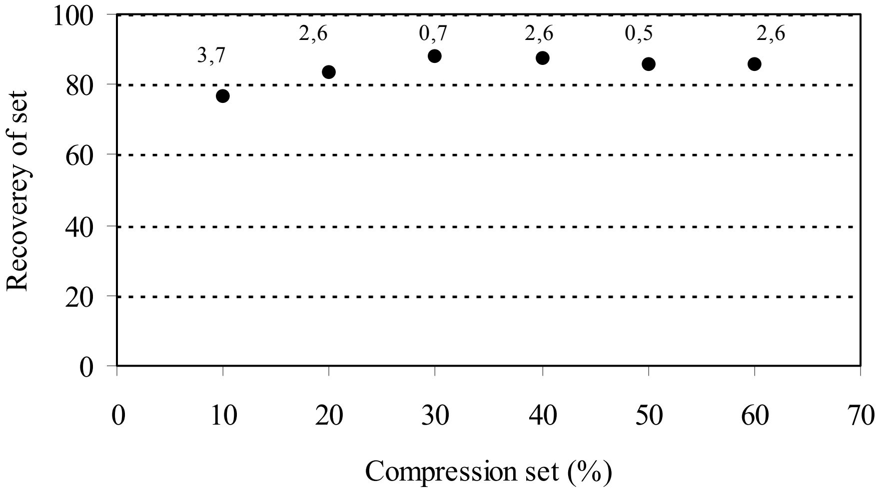


Figure 5.1 Recovery of set versus compression set for solid beech. The numbers above the markers indicate standard deviation of the measurements.

6. Experiment 3 - Fixation of compressive deformation of beech by hygrothermal treatment

The purpose of the experimental work reported in this section is to examine methods to minimise springback of compressed wood. Methods for permanently fixing the compressive deformation are reviewed in Section 3.3. The most efficient methods are formaldehyde treatment or steam treatment in the deformed state. Formaldehyde treatment, however, is out of relevance due to environmental concerns. Main emphasis is therefore placed on hygrothermal treatments.

The section includes four experiments dealing with heat treatment in the wet or in the dry state:

1. Heat treatment in a hot-press
2. Steam treatment in an autoclave at high steam pressures
3. Heat treatment in an oven
4. Hygrothermal treatment in a closed system.

It is believed that comparing wet and dry heating methods will help explaning the underlying mechanism of eliminating springback.

The four methods are assessing the combined influence on the recovery of set of the parameters temperature/steam pressure, duration, moisture content and compression set (see Table 6.1).

Table 6.1 Hygrothermal treatments examined and the parameters involved.

Treatment:	M.C[1]	Temperature °C	Duration of treatment	Compression set
1. Hot-press	12%, FSP[2], saturated	120, 160,200	1 hour	30%
2. Steam treatment in autoclave	-	140,160,180,190, 200	up to 20 min.	30%
3. Heat treatment in oven	-	140,160,180,190,200	up to 30 hours	30%
4. Steam treatment in closed system	12%, FSP	160, 200	5, 15 min	10, 30%

[1] M.C: Moisture Content

[2] FSP: Fiber Saturation Point

6.1 Preparation of compressed beech and method

6.1.1 Heat-treatment in hot-press

The experimental procedure applied when the wood is heat treated in a traditional hot-press is described. The influence of initial moisture content and temperature in a hot-press is examined.

54 specimens were cut from the same board to the dimensions 20mm (R) x 20mm (L) and 30mm (T). The oven-dry dimensions and weight were recorded.

The specimens were subdivided into three groups, and conditioned at three levels of relative humidity. The first group at 65% RH in a humidity chamber, the second group in a desiccator above distilled water, and the third was impregnated with distilled water until saturated. Hence, three levels of moisture content were obtained: app. 12%, close to fiber saturation point and saturated.

Prior to treatment half of the specimens were irradiated using microwaves for 30 seconds. All specimens were then compressed in the radial direction for one hour in a hot-press, at three levels of hot-press temperature (120°C, 160°, 200°). They were then oven-dried (at 103°C) and weight and dimensions were recorded. A distance bar was used to secure a compression set of app. 30%. Three replicas for each treatment were used.

The recovery of each specimen was provoked by hygrothermal treatment. A cycle swelling test was carried out where the specimens were repeatedly dried and soaked in water. The specimens were carefully dried to avoid cracking of the wood structure. The following procedure was followed:

- The specimens were *soaked* with distilled water by vacuum impregnation (vacuumed for 2 hours and soaked for 24 hours). Radial dimension and weight in water saturated condition were recorded.

- The specimens were *dried* for 2 days by conditioning at 65% RH. Then slowly heated at 40°C, 60°C and 80°C for 24 hours at each temperature level. Finally, they were dried at 103°C for 20 hours and the oven-dried radial thickness and weight recorded.

- The wetting and drying cycling procedure was repeated six times. After wetting the 6th time the specimens were boiled in distilled water for 30 minutes and then dried using the same procedure. The recovery of set was calculated from Equation 3.2.

6.1.2 Steam treatment

To determine the effect of steam treatment on recovery of set the following experimental procedure was followed.

A total of 59 specimens of dimensions 20mm (R) x 20mm (L) and 30mm (T) were oven-dried and radial dimension and weight recorded. Three replicas for each treatment was used.

The specimens were conditioned at 70% RH prior to treatment and then pre-heated using microwaves (700W) for 30 seconds before compression.

The specimens were compressed in the radial direction in a hot-press (Garver) at 120°C for 1 hour until dry. A compression set of app. 30% was obtained. A distance bar between the hot-plates secured approximately the same compression set for all specimens. The oven-dry radial dimension and weight after compression were recorded.

The compressed specimens were steam treated in an autoclave (cf. Figure 4.2) under restraint, that is between two stainless steel plates bolted together. The treatment was carried out for various periods of time ranging from 0 min (control) to 20 minutes. The steam pressure corresponded with the temperatures 140°, 160°, 180°, 190° and 200°C. Finally the specimens were oven-dried and the radial thickness and weight recorded.

Additional specimens for the steam treatment had to be included because none of the adopted combinations of time and temperature eliminated springback. These specimens were treated at 190°C for up to 15 minutes. Five replicas were used.

A recovery test as reported in Section 6.1.1 was carried out.

6.1.3 Heat treatment in oven

The specimens were prepared and compressed as described for the steam treatment (Section 6.1.2).

A total of 49 specimens were compressed in the radial direction. After compression and in an oven-dried condition, the specimens were vacuum treated in small airtight plastic bags for two hours to reduce oxygen concentration in the system.

The specimens were heat treated in a traditional oven at 140°C, 160°C, 180°C, 190°C and 200°C for various periods of time ranging from 0 (control) to 30 hours. Vacuum remained inside the plastic bags after treatment. Finally a cycle recovery test for all specimens was carried out as described in Section 6.1.1.

6.1.4 Hygrothermal treatment in a closed system

Because of the work of Dr. Inoue at WRI at Kyoto University the author became interested in the closed system hygrothermal treatment (cf. Section 3.3.1). The necessary equipment was established at BKM. The set-up consisted of a hot-press equipped with a sealing of a Viton O-ring and a cooling system. Figure 6.1 shows schematically the overall set-up of the apparatus.

A screening experiment was carried out to assess the interaction between the involved parameters on the recovery of set after the hygrothermal treatment.

32 samples were cut from the same board. The dimensions were 20mm (radial) x 20mm (longitudinal) and 30mm (tangential).

The specimens were divided into two sub-groups consisting of 16 specimens each and conditioned at 65% and 90% relative humidity respectively. Each of the 32 specimens were cut into two smaller specimens. The first specimen was used for a recovery test and the second specimen was used for determination of initial moisture content and density. Weight and dimensions of all samples including the match samples were recorded prior to treatment. The dimensions after cutting were 10mm x 20mm x 30 mm (RxLxT) for the recovery tests and 8mm x 20mm x 30mm (RxLxT) for the moisture- and density tests.

The specimens were compressed in the "closed" hot-press between two thin stainless steel plates. They were subjected to compression in the radial direction.

The moisture inside the wood is vaporised by increasing the temperature and reducing the volume of the system by compressing. The moisture is trapped inside the O-ring sealing resulting in steam development. The Viton O-ring (diameter=10mm), is heat proof up to 250°C, and located inside an aluminium ring to make the system pressure proof. The aluminium ring also functioned as a distance bar between the hot-plates indicating the final thickness of the specimens. The thickness was 8 or 6 mm depending on the degree of compression.

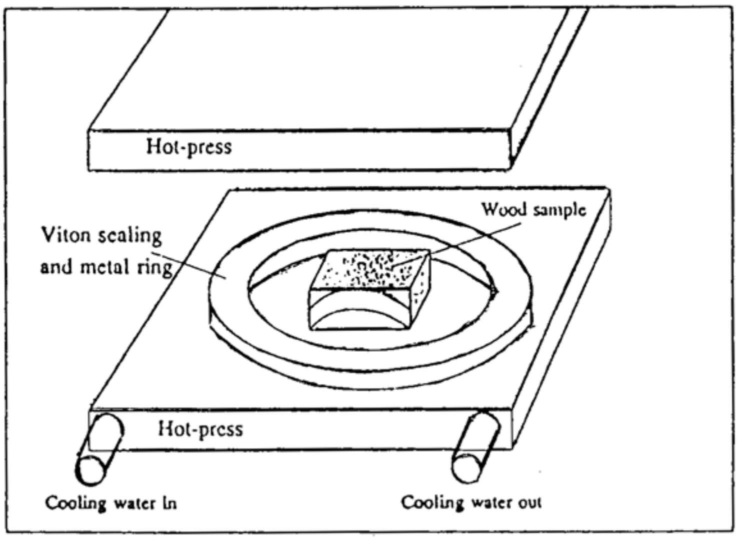


Figure 6.1 Schematic drawing of the closed system apparatus.

The influence of four different parameters on the recovery of set was investigated:
- Compression set (C_S)
- Hot-press temperature
- Initial moisture content
- Duration of treatment.

The experimental set-up is presented in Table 6.2. After treatment the specimens were cooled in the press to a temperature of less than 80°C by having cold water running through the press platens (app. 5°C). The time of cooling varied from 2 to 4 minutes depending on the hot-press temperature.

Recovery of set was determined by impregnating all specimens with water and boiling them for 30 minutes. All specimens, including matched specimens, were finally oven-dried and dimensions and weight recorded. The compression set and recovery of set were calculated using the expressions defined in Equations 3.1 and 3.2.

The experiment was carried out as a complete 2^4-factor experiment for statistical analysis. The parameters were investigated at two levels as indicated in Table 6.2. The response variable was recovery of set.

Table 6.2 Experimental set-up, closed system, showing the levels of the parameters involved: hot-press temperature, compression set, duration of pressing and initial moisture content.

		Compression set =10%		Compression set =30%	
		5 min	15 min	5 min	15 min
160 °C	ω=12%	•	•	•	•
	ω=20%	•	•	•	•
200, C	ω=12%	•	•	•	•
	ω=20%	•	•	•	•

6.2 Results and discussion

6.2.1 Heat treatment in a hot-press

The following presents the results from the heat treatment in a traditional hot-press. The specimens were compressed at three different moisture levels and at three different hot-press temperatures. The three moisture levels obtained were: ω=11.6% ± 0.2, ω=25.5% ± 1.0, ω=114% ± 5.

Table 6.3 shows the response from the recovery test after the first wetting and drying cycle. A statistical variance analysis was applied using the GLM procedure of SAS. The analysis showed that all 2-factor interactions had significant influence on the recovery of set.

Table 6.3 The recovery of set (%) for specimens heat-treated in a hot-press at three different moisture levels (12%, fiber saturation point (FSP),water saturated (SAT)) and at three different hot-press temperatures..

	Micro-waves: Yes			Micro-waves: No		
	12%	FSP	SAT	12%	FSP	SAT
120°C	0.96	0.85	0.68	0.86	0.73	0.71
160°C	0.78	0.77	0.59	0.72	0.62	0.64
200°C	0.08	0.07	0.03	0.11	0.07	0.08

The results from the wetting, drying and boiling procedures are presented in Figures 6.2-6.3.

The following conclusions are made:

- The hot-press temperature has a significant influence on recovery of set, as seen in Figure 6.2. When the hot-press temperature increases the recovery of set decreases dramatically. There is an important gap between 160°C and 200°C, illustrating the increasing degradation rate at temperatures above 160°C (cf. Section 3.4.2).

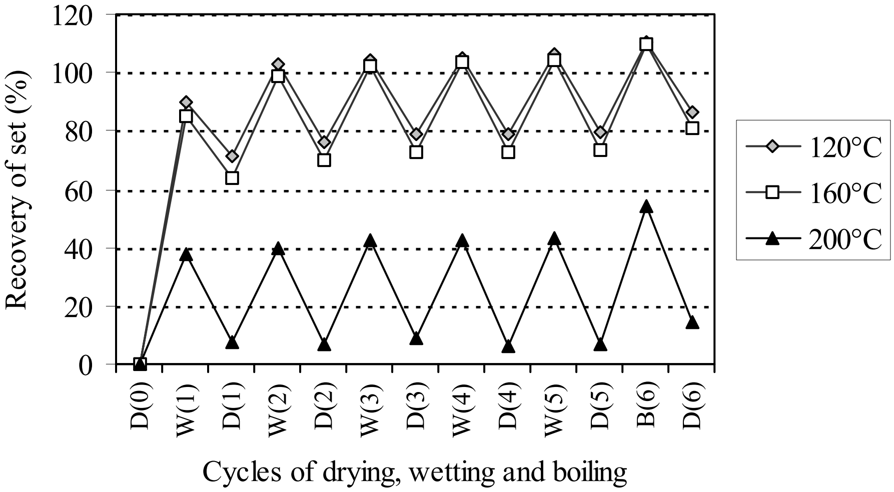


Figure 6.2 The recovery of set versus hot-press temperature in saturated condition.

- The moisture content has a significant influence on recovery of set, that is when moisture content increases, the recovery of set decreases. However, the influence is much less than the effect of hot-press temperature. The influence decreases with increasing hot-press temperature and number of cycles, as shown in Figure 6.3.

- Micro-waves have a negative effect on recovery of set at low moisture contents, due to pre-drying of the specimens before compression. At high moisture contents there is a "positive" but small effect on the recovery of set, particularly at 200°C.

- The recovery of set of the compressed wood was almost eliminated when the wood was initially saturated, preheated by micro-waves and compressed at 200°C for 1 hour (cf. Figure 6.3).

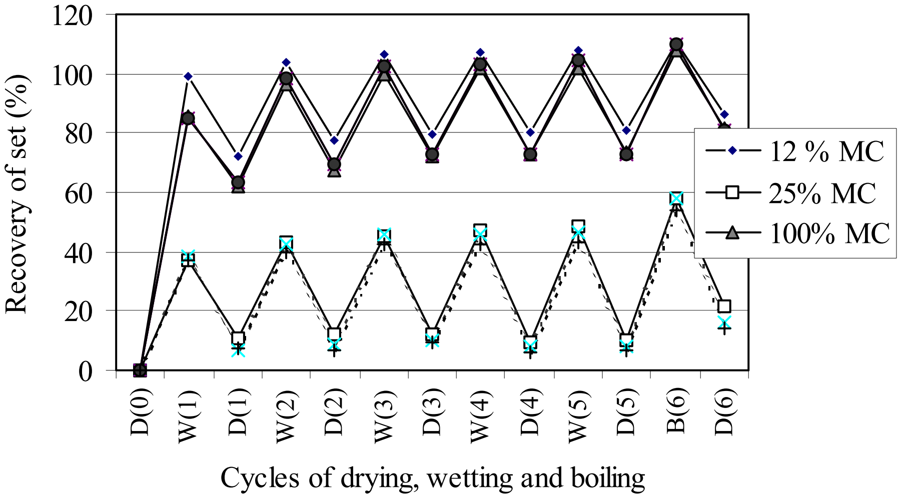


Figure 6.3 The recovery of set versus m.c. at 160°C (solid) and 200°C (dotted lines).

6.2.2 Steam treatment and heat treatment

The following is a presentation and discussion of the results from steam treated and heat treated wood specimens exposed to hygrothermal recovery. The specimens were treated as described in Section 6.1.2 and Section 6.1.3. The two methods are treated in this section in order to compare the results.

The effect of temperature

The outcome of the cycling test at different temperatures is plotted in Figure 6.4 for the steam treatment and in Figure 6.5 for the heat treatment. The treating time was 5 minutes for the steam treated wood and 20 hours for heat treated wood.

Both figures include data from untreated compressed specimens. The untreated specimens recovered more than 90% after the first wetting and drying cycle; after six cycles including boiling the specimens recovered almost 100%.

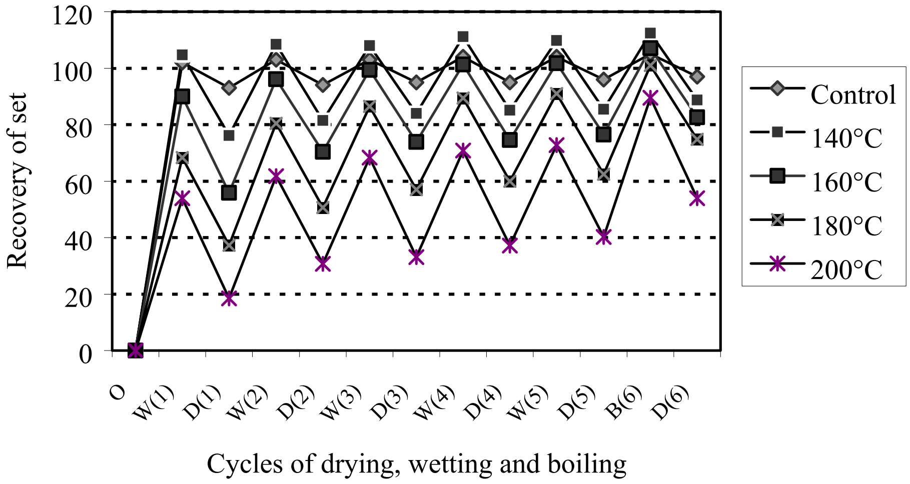


Figure 6.4 The effect of drying (D), wetting (W) and boiling (B) cycles on the recovery of set for compressed specimens treated with steam for 5 minutes.

The specimens that were steam treated at 180°C recovered almost 40% after the first cycle and almost 55% after boiling. The corresponding heat-treated specimens recovered 20% after the first cycle and increased to 30% recovery after boiling. Boiling the specimens increased the recovery of set, because of increased softening of the matrix.

There is a significant difference between the recovery of set at 160°C and 180°C, particularly for the heat treated wood (Figure 6.5). This corresponds with the fact that rate of thermal degradation increases dramatically above 160°C, which support that thermal degradation contributes in the process of permanently fixing compressed wood (Section 3.4.2).

A significant characteristic of the steam treated compressed wood (Figure 6.4) is that the dimensional changes are increased with increasing remaining compression set (or density). For

the highest steam temperatures the compression set after the cycling tests is the largest. Therefore excessive dimensional changes occur (due to the highest density).
In the case of heat treated wood there is a tendency that the dimensional changes are reduced with increasing temperature (Figure 6.5). The dimensional stability of compressed wood is treated in Section 7.

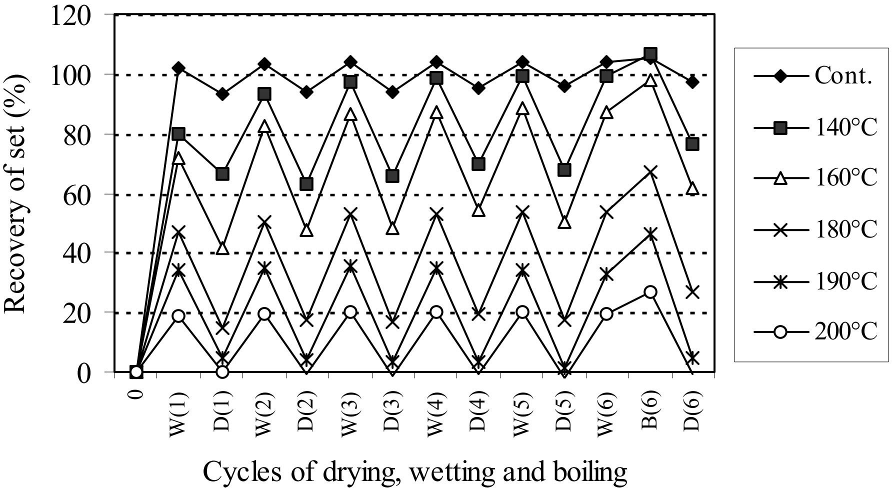


Figure 6.5 The effect of drying (D), wetting (W) and boiling (B) cycles on the recovery of set for compressed specimens heat treated for 20 hours.

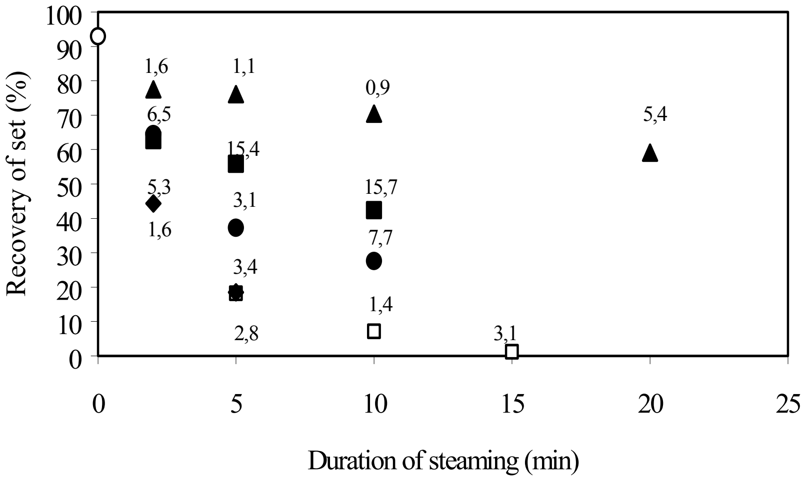
The effect of time

Recovery of set versus time of treatment of steam treated and heat treated specimens is plotted in Figure 6.6. The recovery of set is based on the first wetting and drying cycle. The numbers above the markers indicate the standard deviation of the measurements.

The large standard deviations identified on the measurements of the steam treated wood might be due to variations in density. Using weight of the specimens as an evidence of density (almost the same dimensions) indicates that a high initial weight results in a higher recovery of set for the same treatment

As anticipated, the recovery of set as illustrated in Figure 6.6 decreases with increasing time. The results show clearly, that steam treatment dramatically reduces the treating time to achieve predetermined recovery of set compared to heat treatment.

Additional specimens for the steam treatment had to be included because none of the adopted



combinations of time and temperature eliminated springback. It would be expected that the diagram at 190°C would be above the diagram at 200°C.

Figure 6.6 Recovery of compression set after the first wetting and drying cycle versus time for steam treated wood (above) and heat treated wood (below). The steam/heat temperature was in accordance with the following: ○= control, ▲=140°C, ■= 160°C, ● = 180°C, ▼=190°C, □=200°C. Numbers above the markers show the standard deviation on the measurements.

Nevertheless, this is not the situation, which might be due to problems of controlling the time parameter in the autoclave (see Section 4.2, Equipment).

Almost no recovery of set was observed at 190°C after 15 minutes for the steam- treatment while a similar result was obtained at 190°C after 20 hours for the heat- treatment (recovery of set less than 5%). Based on these results and the results of Inoue (Figure 3.5) it may be concluded that a more tough treatment is needed to eliminate springback of beech compared to sugi. This is surprising, since it is generally believed that hardwood lignin is softening more easily than softwood lignin. However, it might be due to a lower content of lignin in hardwood and that the mechanisms of permanent fixation is a degradation phenomena. Primary bonds in lignin might be broken more easily in softwood than in hardwood resulting in a slight flow of lignin (Section 3.4.2).

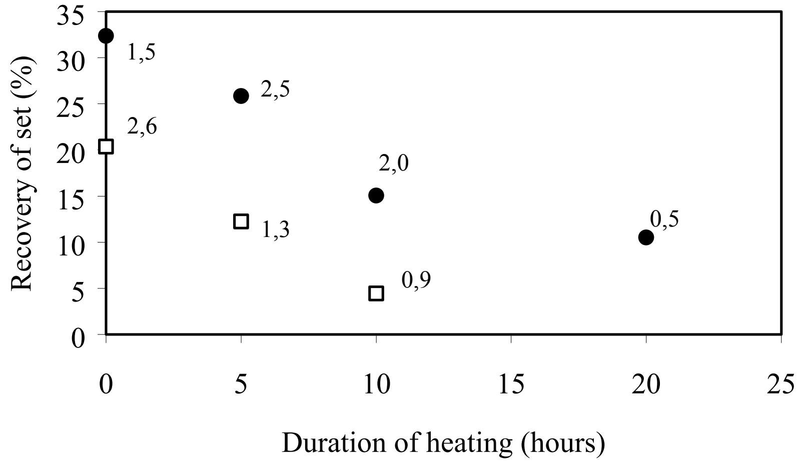


Figure 6.7 and 6.8 show the effect of cycles of drying, wetting, and boiling on the recovery of set as a function of steaming time. The compressed specimens were steam-treated at 140°C and 180°C respectively for various periods of time. It is seen clearly that the decrease in recovery with increasing steaming time is most significant for the specimens treated at 180°C.

Figure 6.9 shows the effect of drying, wetting and boiling for heat treated specimens at 180°C for various length of time. Trends coinciding with those of steam treated wood are identified in the figure. Heating for 5hr, 10hr, 20hr and 30hr reduces recovery of set after boiling to app. 55%, 45%, 30% and 20% respectively. Another important characteristic is that the dimensional changes decrease as the treating time increases.

It is obvious that time and temperature have similar effects on the recovery of set. Increasing time or temperature lowers the recovery of set. An important conclusion is that springback can be completely eliminated.

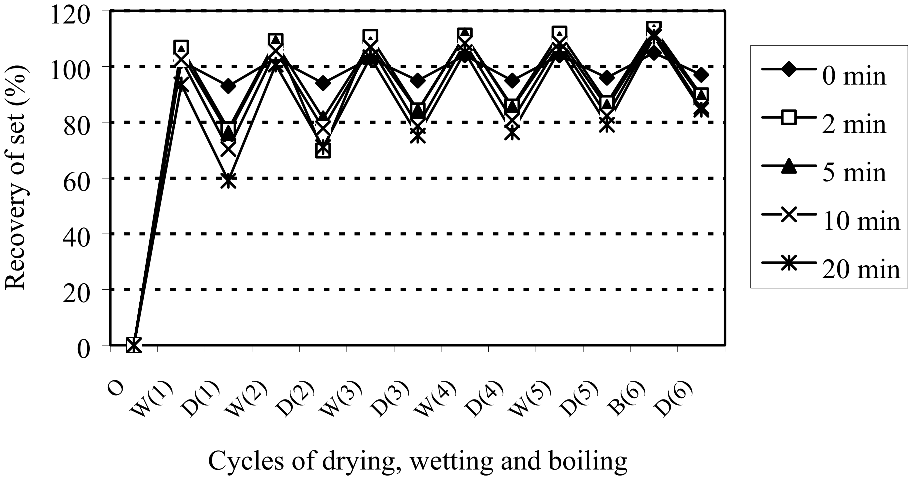


Figure 6.7 The effect of drying (D), wetting (W) and boiling (B) cycles on the recovery of set for compressed specimens treated with steam at 140 °C for various periods of time.

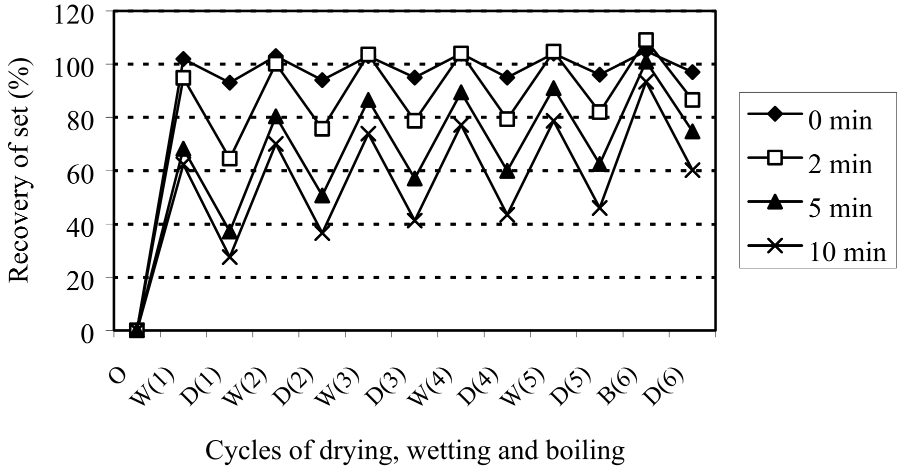


Figure 6.8 The effect of drying (D), wetting (W) and boiling (B) cycles on the recovery of set for compressed specimens treated with steam at 180 °C for various periods of time.

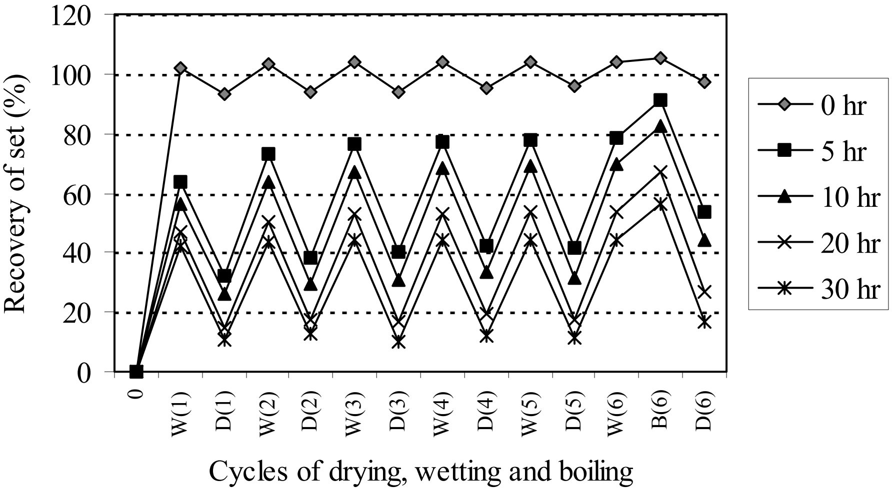


Figure 6.9 The effect of drying (D), wetting (W) and boiling (B) cycles on the recovery of set for compressed specimens heat-treated at 180 °C for various length of time.

6.2.3 Hygrothermal treatment in a "closed system"

Beech specimens were compressed in the radial direction and heated in a closed system in a hot-press (Section 6.1.4). The initial moisture content, temperature and degree of compression affect the developed steam pressure in the closed system. It should, therefore, be expected from Section 6.2.2 that these parameters along with the duration of the treatment would have significant influence on the recovery of set. Table 6.4 shows the response from each treatment. Apparently, increasing the temperature, pressing at a higher moisture content, increasing the compression degree and treating for a longer time all reduce springback.

The GLM procedure in SAS was used for a statistical variance analysis. From the analysis it can be concluded that all 3-factor interactions have a significant influence on the recovery of set. Using the linear model proposed by SAS-GLM a coefficient of determination of $r^2=0.99$ is obtained. The chosen parameters determine the response almost perfectly.

It is important to cool the wood samples in the press. This has two main reasons: Firstly, lignin is thermoplastic and will allow the wood to springback if insufficiently treated. Secondly, and most importantly, if the steam pressure is released immediately the cell wall will collapse because of pressure differences between the interior and the exterior of the wood.

A comparison of data from a "closed" system with data from an "open" system (without sealing), treated under otherwise identical conditions, revealed a very large difference between the two systems.

Table 6.4 Recovery of set (%) using the closed system.

		C_s=10%		C_s=30%	
		5 min	15 min	5 min	15 min
160°C	ω=12%	78	74	83	79
	ω=20%	71	65	53	61
200°C	ω=12%	76	38	72	6
	ω=20%	61	9	17	<1

Compressing at 160°C and 200°C in an open system for 15 minutes at a high moisture content resulted in a recovery of set of 0.79 and 0.72 respectively. Under similar conditions the recovery of set was 0.61 and <0.01 respectively for the closed system.

This strongly suggests that the moisture inside the wood contributed to the fixation of the compressive deformation. Investigation of the effect of time shows that recovery of set of compressed beech is eliminated at 190°C for any treating time beyond 10 minutes.

The closed system can provide a complete fixation of the compressed state in a short time, due to no limiting size effect from steam penetration of the specimens. The equipment is simple, at least on a laboratory scale. Furthermore, the treatment is uniform because the steam is created inside the wood. The steam pressure, however, develops inhomogeneously, starting at the heating-platens.

6.3 Conclusion

The subject of the experiments presented in Section 6. is to devise methods to eliminate springback. Four separate hygrothermal treatments were applied to wood and the recovery of set determined. The parameters involved (moisture content, temperature, time, compression pressure) to eliminate springback for the individual treatments were assessed. It is concluded that an almost complete fixation of the deformation in compressed *beech* can be accomplished using the following treatments:

- *Compressing saturated wood in a hot-press at 200°C for 1 hour.*
- *Steaming compressed wood in an autoclave at 190°C corresponding to 1.55 MPa for 15 min.*
- *Heating compressed wood in an oven at 190°C for 20 hours.*
- *Compressing wood in a "closed" hot-press at 190°C for 10 minutes. The moisture inherent in the wood is used to create the steam pressure.*

The results are comparable because identical dimensions of the specimens were used in all four investigations.

6.3.1 Mechanism of eliminating springback

Inoue (1993) and others suggest that the reduced springback from *steam-treatment* is due to softening of the thermoplastic matrix (lignin and hemicellulose).

This corresponds poorly with the fact that the temperature needed for permanent fixation is far beyond the softening point of lignin for saturated wood (between 60-90°C). Since the softening of the matrix is connected to breaking of secondary hydrogen bonds and this process is reversible, the theory is inadequate for explaining permanent deformation.

It is suggested that softening is accompanied by a permanent change in cell wall structure (degradation). It is anticipated that a breakdown of the cross-links within the microfibrils and between the cell-wall polymers occur. The breakdown of primary bonds probably allow a slight flow of lignin (Section 3.4.1). This hypothesis is confirmed by the fact that the temperature needed to eliminate springback seems to be above 160°C for both dry heat treatment and steam treatment (unaffected of presence of moisture). This corresponds well with degradation temperatures of lignin and hemicellulose shown in Table 3.7. It is mainly a matter of time above that specific temperature before springback is eliminated. Furthermore springback of steam treated wood is eliminated without an accompanying improvement of the dimensional stability, this rejects that degradation (hydrolysis) of hemicellulose contributes to the elimination of springback.

On the contrary elimination of springback for the *heat treated* wood is a result of thermal degradation of the hygroscopic components in the cell wall (especially the hemicellulose). Flow of lignin is unlikely to occur in dry wood (Section 3.4.1). Another aspect contributing to the elimination of springback is macrostructural changes of the wood cells. Microbuckling and damage of the structure will make the cell wall unable to springback completely (Section 3.5 and Appendix B showing micrographs of the beech structure).

Comparing the results from the treatments of beech with similar data obtained on sugi (Inoue et al., 1991) the conditions to eliminate springback of beech are clearly more severe than for *sugi*. The general opinion is that hardwood lignin is more easily softened than softwood lignin (Salmén 1992). This surprising result may be due to more easy breakdown of cross-links in softwood lignin, or the lower lignin content in hardwood, or more likely, due to macro-structural differences. Beech has a large amount of ray cells in the radial direction and a more inhomogenous structure which restricts a uniform compressibility. Beech also has a higher density this increase the necessary duration of heating for eliminating springback.

7. Experiment 4 - Properties of densified beech

With the aim of clarifying some of the basic properties of compressed beech an experimental study was carried out focused on dimensional stability and hardness.

Hygrothermal treatment greatly reduces springback as shown in Section 6. However, hygrothermal treatment also results in thermal degradation of the structure which influences the properties. The primary scope of experiment 4 is to assess the influence of compression set and thermal treatment (heat or steam) on the density, the sorption, the dimensional stability and the hardness of beech.

During the planning of the research a number of other properties were also considered such as: strength properties, colour change, abrasive properties, toughness etc. These properties, although important for some purposes, are not part of the experimental study reported here.

7.1 Materials and preparation of samples

Materials

Six types of material were prepared for the investigation. Not all of the six types of material were used for each test:

1. Non treated wood (reference)
2. Heat treated wood (non-compressed)
3. Steam treated wood (non-compressed).
4. Compressed wood (varying the compression set).
5. Compressed heat treated wood (fixed compression set of 30%).
6. Compressed steam treated wood (fixed compression set of 30%).

All specimens were cut from beech (*fagus sylvatica*) into clear straight grained samples. The dimensions varied depending on the type of test. Reference is made to the above mentioned numbers:

Density:

2,3 Samples, app. 10 mm (L) x 30 mm (T) x 30 mm (R) were used for the density tests of *compressed heat or steam treated wood (non-compressed)*.

4 Samples, app. 20 mm (L) x 30 mm (T) x 20 mm (L), were used for density tests of compressed wood.

Sorption and dimensional stability:

1 Samples, approximately 30 x 30 x 10 mm (RxTxL), were cut from *untreated wood (reference)*.

4,5,6 Small segments, approximately 14 x 7 x 7 mm (RxTxL), were cut from c*ompressed beech and compressed heat- or steam treated beech*.

The treated samples were cut from the specimens used for the hardness tests.

Hardness

1,4,5,6 For all hardness tests the dimensions were 50 mm (L) x 50 mm (T) x 20 mm (R).

Preparation of samples
The material mentioned above (2-6) was prepared as follows:

Compression:
The material for making compressed wood (4,5,6) was initially saturated with distilled water by vacuum impregnation (1 hour of vacuum, 2 hours soaking) and then irradiated by microwaves for 30 seconds prior to compression.

The specimens were compressed radially in a hot-press (Garver) at 120°C for 1 hour. A distance bar was used to guarantee a specific compression set. Subsequently, the specimens were dried in the press and held in the compressed state.

Two types of compressed wood were produced. The first (4) where the compression set varied (C_s=10,20,30,40,50%) and a second (5,6) where the compression set was fixed at 30% used for the heat- or steam treatment.

Heat and steam treatment:
Non-compressed (2,3) as well as compressed wood (5,6) were treated as follows.

Heat: The specimens were vacuum treated in airtight plastic bags for two hours in order to reduce oxygen concentration in the system. They were then heated in a traditional oven. The temperature range of the treatment was 140°C - 200°C. The specimens were treated for various duration of time spanning an interval from 5 hours to 30 hours, depending on the type of test.

Steam: The steam treatment was carried out in an autoclave with the ability to produce saturated steam at pressures up to 15 atm corresponding to app. 200°C, (Section 4.2, Equipment). The compressed specimens (5,6) were fitted between stainless steel plates, and then steamed under restraint. The steam pressures applied corresponded to 120°C (2bar), 140°C (3.6bar), 160°C (6.3bar), 180°C (10bar), 190°C (13bar) and 200°C (15bar) depending on the type of test. Duration of steaming varied from 2 min up to 60 min. Most frequently a 10 minutes treatment was used. In the following the treatment is expressed by the steam temperature in °C.

7.2 Test methods

7.2.1 Density

Compressing wood results in an increased density proportional to the compression set. Since the density is the single most important property of wood this effect is the main idea of producing compressed wood. This part of the research is aimed at studying the density of compressed wood. The density of three types of material were examined: compressed wood (varying compression set), heat treated wood, and steam treated wood. The material was prepared as described in Section 7.1.

The total number of specimens were 145, covering the following material:

Compressed wood:	45 specimens, including five replicates for each compression set (0, 10, 20, 30 ,40, 50, 60%).

Heat treated compressed wood: 55 specimens, including five replicates for each treatment (see below).
Steam treated compressed wood: 45 specimens, including five replicates for each treatment (see below).

The heat treatment was carried out at: 140°C, 160°C, 180°C, 190°C, 200°C for 20 hours. The specimens were heat treated for various durations of time (5, 10, 20, 30 hours) at 180°C and 190°C.

The steam treatment was carried out at 120°C, 140°C, 160°C, 170°C, 180°C, 190°C and 200°C for 10 minutes. Two levels of duration of treatment (10, 30min) were used at 180°C and 190°C

The initial dimensions and weight in oven-dry condition before treatment were assessed as was the oven-dry dimensions and weight after compression, heating or steaming. The weight loss was calculated based on oven-dry conditions and the change of oven-dry density was expressed as follows,

$$\Delta\rho = \frac{\rho_{treated} - \rho_{untreated}}{\rho_{untreated}} \cdot 100(\%) \qquad 7.1$$

where ρ is the oven-dried density (weight/volume in oven-dried condition) before treatment (untreated) and after treatment (treated).

7.2.2 Sorption and dimensional stability

The material was prepared as described in Section 7.1. The samples were cut from the specimens used for the hardness tests. The sorption ability and dimensional stability of four types of material were examined: reference, compressed wood (varying compression set), heat treated and compressed wood, and steam treated and compressed wood.

The total number of specimens were 441, covering the four types of material:
Reference material: 21 specimens, including 3 replicas.
Compressed wood: 140 specimens, including 4 replicas.
Heat treated compressed wood: 140 specimens, including 4 replicas.
Steam treated compressed wood: 140 specimens, including 4 replicas.

The temperature levels of the heat- and steam treatment are outlined in the next section (hardness test).

All specimens were dried in an oven at 103°C for two days, and the dry weight measured along with the dimensions. The specimens were placed in weighing glasses placed in desiccators containing various saturated salt solutions to maintain specific relative humidities. The desiccators were placed in a bath with the ability of keeping the temperature constant at 22.8±0.5°C. Each glass was weighed at regular intervals, until the change of moisture content over a two week period was less than 0.1 %. When such defined equilibrium was reached the weight as well as the dimensions were recorded.

The types of salt used to obtain seven different relative humidities are identified in Table 7.1, together with the corresponding values of relative humidity.

Table 7.1 Types of salt used to obtain seven different relative humidities.

Salt type	$MgCl_2$	K_2CO_3	$NaNO_2$	NaCl	KCl	KNO_3	K_2SO_4
RH (%)	33	44	65	75	86	94	97

The moisture content was calculated based on the oven-dry weight (Section 2.2). From these calculations adsorption isotherms for each treatment were produced.

The moisture exclusion efficiency (MEE) was calculated from Equation 2.3 to express the reduced moisture uptake. The anti-swelling-efficiency (ASE) and the volumetric swelling at the different relative humidities were determined from Equation 2.1 and Equation 2.2. respectively. The swelling of treated wood was compared with the swelling of the reference material at each moisture level at a constant temperature of 22.8°C.

7.2.3 Hardness test

The specimens were prepared as described in Section 7.1. The hardness of four types of material was examined: reference, compressed wood (varying compression set), heat treated and compressed wood, and steam treated and compressed wood.

The total number of specimens were 116, covering the following material:

Reference material:	5 specimens, non-compressed
Compressed wood:	25 specimens, including five replicas.
Heat treated compressed wood:	50 specimens, including five replicas.
Steam treated compressed wood:	36 specimens, including three replicas.

The heat treatment was carried out at: 140°C, 160°C, 180°C, 190°C, 200°C for 20 hours. The specimens were heat treated for various length of time (5, 10, 20, 30 hours) at 180°C and 190°C. The steam treatment was carried out at 140°C, 160°C and 200°C for 10 minutes. At 180° duration varied from 5 min to 60 minutes. The specimens were weighed and dimensions measured prior to the compression test.

A Brinell hardness test was conducted on all specimens in radial direction according to the standard. A 9.4 mm steel ball was embedded into the surface of the wood to a depth of 2.4 mm in a Instron compression machine. The head speed was 1mm/min. Prior to testing the specimens were conditioned at 65% RH and dimensions and weight recorded. The hardness, H_B, was determined from:

$$H_B = \frac{P}{\frac{1}{2}\pi D\left(D - \sqrt{D^2 - d^2}\right)} \; (\mathrm{N/mm^2}) \qquad 7.2$$

where P is the force in Newton, D is the diameter of the steel ball and d is the diameter of the impression. The hardness was evaluated based on the average of three replicas (steam) or five replicas (heat).

7.3 Results and discussion

7.3.1 Weight and density

The aim of the experiment was to examine the influence of compression set and hygrothermal treatment on the density of wood. In addition, the thermal degradation of wood demonstrated by the weight loss due to hygrothermal treatment is treated. Reference is made to Section 3.4.2 for the discussion of thermal degradation.

Weight and density were studied, as described in Section 7.2.1, and calculated based on oven-dried dimensions and weight before and after treatment.

Compression set

As expected, the compression of wood results in increased density, depending on the compression degree. Figure 7.1 shows the increase in density with increasing compression set. A linear relationship is observed until a compression set of 50% is reached. The density increases from app. 700kg/m^3 to app. 900 kg/m^3 corresponding to app. 30% at a compression set of 30%. Regression analysis was applied to the results in the linear range (below 50%) and leads to the following:

$$\rho = 7.97 \cdot C_s + 679 \quad (\mathrm{kg/m^3})$$

The coefficient of correlation is 0.99 and the standard error of estimate is 11 kg/m^3. The regression line is included in Figure 7.1. The average standard deviation on individual measurements is 23 kg/m^3, with little difference between measurements.

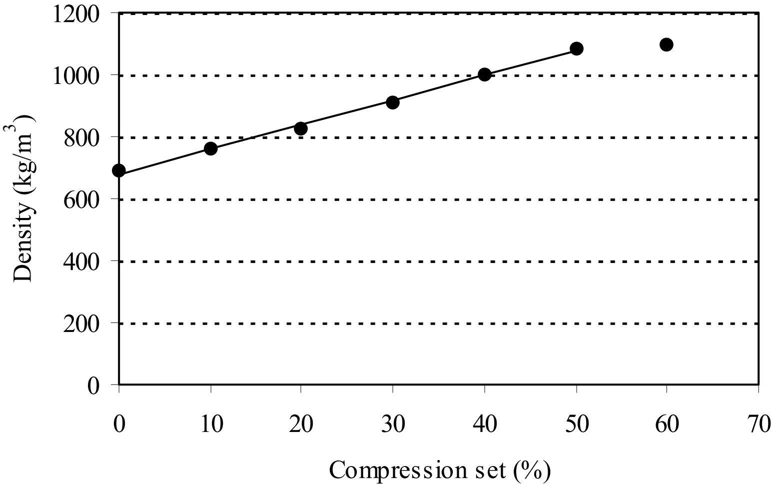


Figure 7.1 Density versus compression set of beech. The numbers below the markers indicate standard deviation of the measurements.

The theoretical maximum compression degree, corresponding to the degree where all pore space is eliminated, is (the initial density is app. 700kg/m^3 according to the figure): $C_{s,max}=1-700/1500\approx0.55$. This matches the fact that the relationship is linear below a compression set of 50% and little effect above this point on the overall density is noticed. The wood cell wall is damaged before this compression set is achieved.

The results presented in Figure 7.1 are different from the results of Inoue et al. (1991) on sugi (softwood), which showed a parabolic relationship between compression set and density. This substantiates the proposal of Gril et al. (1994) that the parts of wood of lowest density are crushed first, then followed by the next in terms of density (Section 3.5). In sugi a big difference between earlywood density (lowest density) and latewood density exists. Furthermore, the earlywood represents the largest volume of cell wall. In beech there is only a small difference in density and proportion of earlywood and latewood. Accordingly, a linear influence of compression set on density is expected.

Heat and steam treatment

Figure 7.2 and Figure 7.3 show the effect of heating- respectively steaming temperature on the weight and the density of compressed wood (C_S=30%). The duration of treatment was 20 hours and 10 minutes respectively.

The weight- and density loss below 160°C is limited in both cases. This implies that thermal degradation of the wood components commence around 160°C and that the degradation rate increases with increasing temperature as stated in Section 3.4.2.

However, the findings in Figure 7.2 are slightly different from those of Hirai (1972) on dry heat treatment of *hinoki*, see Section 3.4.2. This difference can be attributed to the time scale of the present experiment.

Above 160°C a dramatic weight loss and a moderate loss of density is observed as the temperature increases. From this it can be concluded that the weight loss is accompanied by a volume change resulting in a lower decrease in density than would be expected from the loss of weight.

As displayed in the figures he presence of water highly effects the degradation rate. The same quantity of degradation can be reached within much shorter time when moisture is present. After 10 minutes of steaming the weight loss is actually higher than after 20 hours of heat treatment.

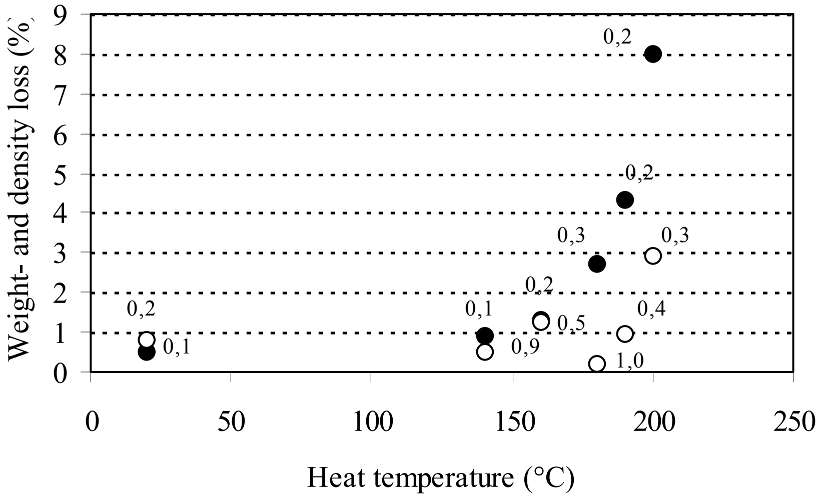


Figure 7.2 Weight loss (%) and density loss (%) of compressed wood as a function of heat temperature after 20 hours treatment. The numbers indicate standard deviation of the measurements. (○) shows density loss and (●) shows weight loss.

The large weight loss observed for steam treated wood may be due to extraction of mainly decomposition products. The hemicellulose is decomposed as a result of hydrolysis (Section 3.4.3). Some of the decomposition products are "washed" out instead of polymerising into less hygroscopic polymers, as in the case of heat treated wood.

The reference samples for the heat treated wood show a significant weight loss due to leaching of extractives during soaking in water. The value of this weight should be subtracted from the values in Figure 7.2. The steam treated samples were extracted in distilled water prior to treatment such that the same weight loss is not observed.

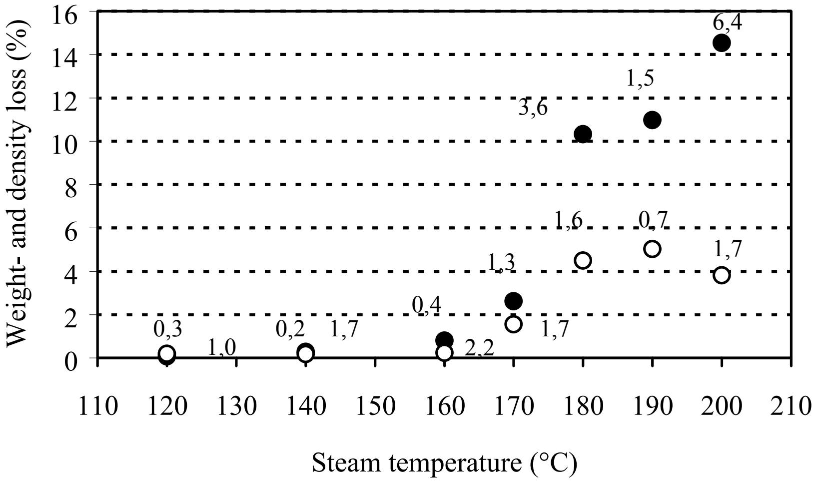


Figure 7.3 *Weight loss (%) and density loss (%) of compressed wood as a function of steam temperature after 10 minutes treatment. The numbers indicate standard deviation of the measurements. (○) shows density loss and (●) shows weight loss.*

The thermal degradation as a function of duration of heat treatment is illustrated in Figure 7.4.

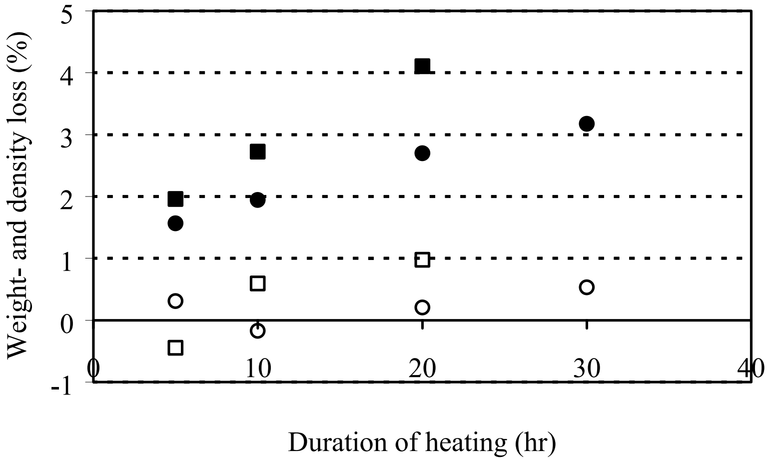


Figure 7.4 *Weight- and density loss of compressed beech by heat treatment at two different temperatures as a function of duration:*
180°C: Weight (●); 190°C: Weight (■)
Density (○) Density (□)

The rate of degradation is significantly increased from 180°C to 190°C. The density of the wood is not severely lowered during the treatments. Parallel data from steam treatment do not show a similar increase in degradation. When steam treatment is reduced from 10 minutes to 30 minutes at 180°C, then the quantity of degradation is increased less than 1%.

7.3.2 Sorption and dimensional stability

As stated in Section 3.4.3 an improved dimensional stability of wood is achieved by hygrothermal treatment. The effect depends on temperature, presence of oxygen, moisture and duration of treatment.

Only limited effort on investigating the dimensional stability of compressed wood is found in the literature. Investigators mainly deal with the springback effect incorporated in the structure during compression (cf. definitions in Eq. 2.1 and Eq. 3.2). The dimensional stability is correlated with the density (cf. Figure 7.5). This complicates investigations on the subject.

In the present study several attempts to study dimensional stability of compressed wood have been carried out. In section 6. cycle tests of compressed wood treated at different steam- or heat temperatures were presented. The first half cycle expresses the dimensional changes from dry to water saturated condition. From the figures presented in Section 6. (Figures 6.4-6.5) it is clear that a reduced dimensional stability compared to untreated wood is obtained.

Figure 6.4 shows the swelling in radial direction for heat treated specimens. Under conditions where springback is eliminated the swelling was approximately 35% based on the reduced volume. This is in agreement with what would be expected from the increase in density. A swelling of 35% is expected from Figure 7.5. The regression is not valid outside the experimental range. The estimated swelling should be taken with caution.

Attempts to carry out traditional ASE test (Section 3.4.3) on non-compressed steam treated wood do not clarify the problem. Whereas the specimens showed significantly improved dimensional stability, the data were not reliable due to checking caused by the steam treatment. The dimensional changes may have been internal rather than external and therefore this experiment was excluded.

In addition two types of tests, sorption tests (MEE) and ASE tests as a function of relative humidity were carried out. For these test the outcome was less complicated to analyse.

7.3.2.1 Sorption

The idea of this experiment was to use adsorption isotherms to reveal any significant change of the moisture uptake in the cell wall of compressed beech caused by compression set, heat- or steam treatment. An adsorption isotherm represents the moisture uptake at different relative humidities. The experiment was carried out as described in Section 7.2.2. Results are given in Table 7.2 and illustrated in Figures 7.6 - 7.7. Moisture exclusion efficiency (MEE) was calculated from Equation 2.3.

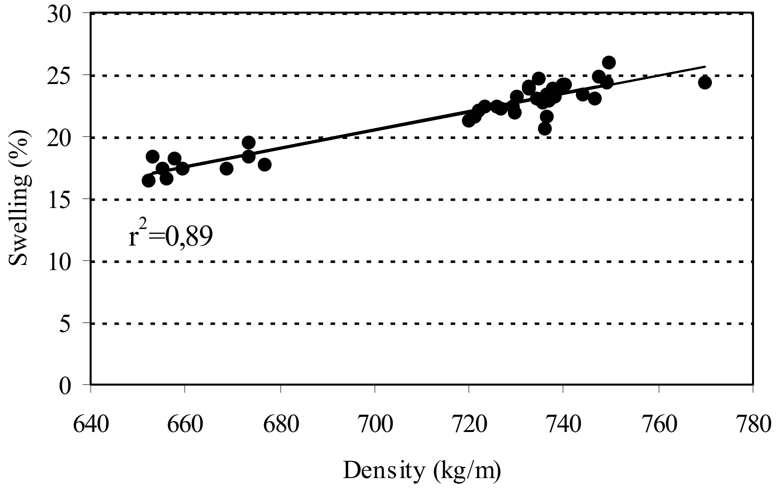


Figure 7.5 Swelling in water versus density. An increased density increases swelling in water according to the regression equation shown in the figure.

Compression set

Figure 7.6 shows adsorption isotherms for compressed wood at different compression sets. No difference of moisture uptake between the compression sets are observed. However, a slight reduction in moisture uptake compared to the reference is noticed (see also MEE in Table 7.2). MEE is seen to depend on the climatic conditions (relative humidity). The MEE value is almost constant up to 97% RH where a loss is observed for all compression sets. This loss of MEE may be the result of springback at very high relative humidities, thus more and more sorption sites become accessible.

Even at very high relative humidities a certain reduction of moisture uptake is seen. This can partly be attributed to the thermal history of the samples. The samples originate from the specimens used for the hardness testing as mentioned in Section 7.2.3. They were hot-pressed at 120°C and then oven-dried overnight. The reference samples were not hot-pressed. Moisture uptake is extremely sensitive to the thermal history and part of the remaining MEE may be explained by this difference in treatment. The residual MEE is because springback is not completed and fewer sorption sites compared to the reference are accessible.

The time to reach equilibrium increases with increasing compression set, due to the more dense structure. Obviously this also reduces the rate of swelling and shrinkage. However, the final dimensional changes cannot be expected to be reduced significantly.

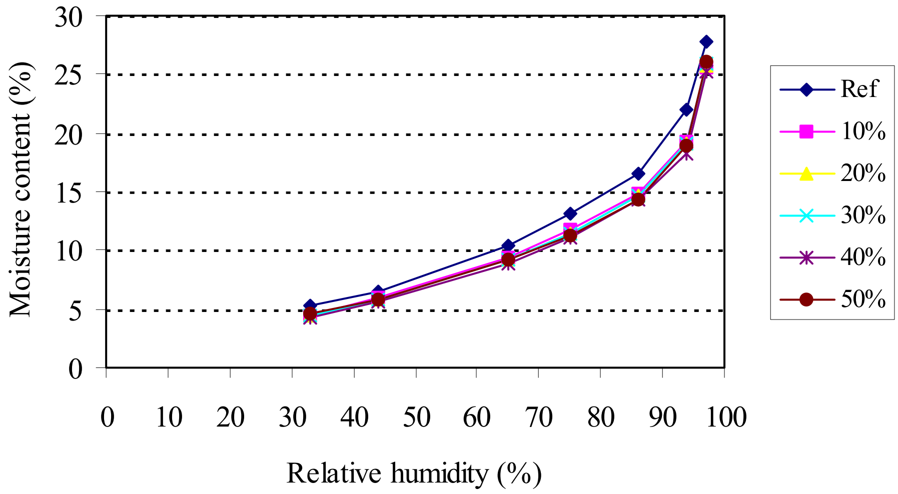


Figure 7.6 Adsorption isotherms for non-treated compressed wood at different compression sets.

Heat- and steam treatment

Adsorption isotherms for compressed heat- and steam treated wood are illustrated in Figure 7.7 and Figure 7.8 respectively. The samples were compressed to a compression set of 30%. The isotherms represent the effect of temperature on the moisture sorption. The duration of heating was 20 hours and the duration of steam treatment was 10 minutes. Table 7.2 shows the influence of treatment on the moisture uptake expressed as the moisture exclusion efficiency (MEE). MEE is calculated based on the non-treated and non-compressed reference samples.

The tendency is clear: as the temperature increases the moisture uptake decreases. However, taking a closer look on the data, some interesting conclusions can be drawn:

- The MEE-value is seen to decline as the relative humidity increases for both heat- and steam treated samples. This indicates that there is a strong dependency of relative humidity on MEE (Table 7.2).

- A significant reduction of sorption is observed for heat treated wood at 180°C and for steam treated wood at 160°C. Below these temperatures no detectable difference of MEE between the compressed wood (30%), and the treated samples can be identified (Table 7.2).

- Considering the MEE at 180°C and 200°C for both heat- and steam treated samples and comparing the values with the MEE values for compressed wood (30%), (see Figure 7.7) there appears to be no change of the hygroscopic nature of steam treated wood at very high relative humidities (97% RH). On the contrary the heat treated wood maintains a high value of MEE even at the highest relative humidities. Applying MEE as an expression for dimensional stability a significant improvement for heat treated samples is expected even at high moisture contents. For steam treated samples the improvement is only significant below 97% relative humidity, in addition it is of a lower magnitude.

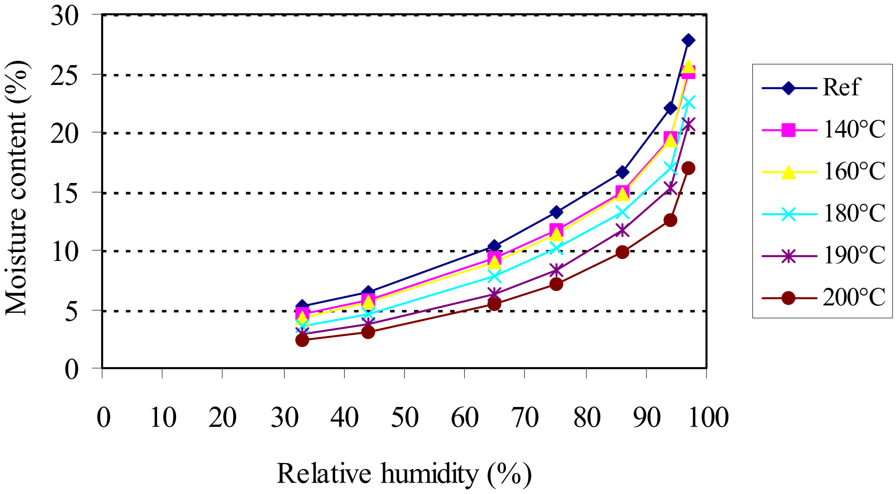


Figure 7.7 Adsorption isotherms for compressed wood heat treated at different temperatures.

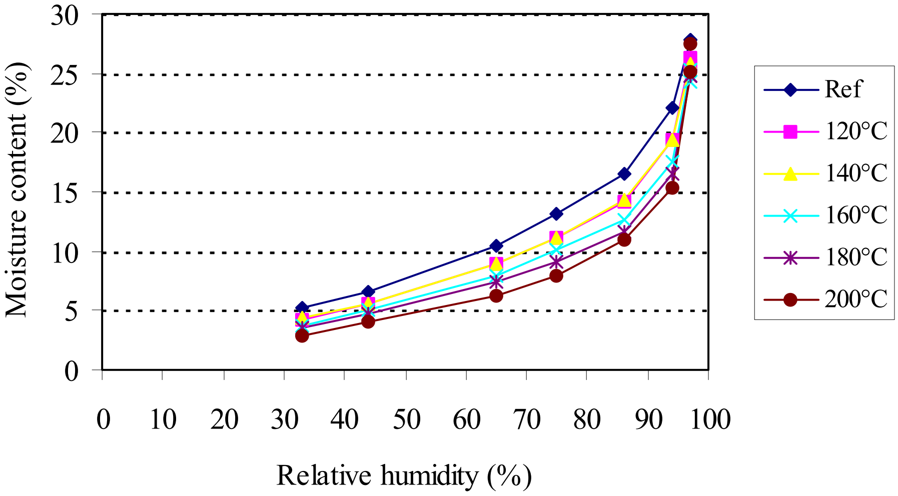


Figure 7.8 Adsorption isotherms for compressed wood steam treated at different temperatures.

Table 7.2 *Equilibrium moisture content as a function of relative humidities for compressed wood, heat treated compressed wood and steam treated compressed wood. The table includes MEE values for all treatments at the relative humidities involved.*

Relative humidity			33%	44%	65%	75%	86%	94%	97%
Ref. (normal wood)			5.2	6.5	10.4	13.2	16.6	22	27.8
Compressed	10%	ω	4.5	5.9	9.4	11.7	14.9	19.3	25.6
		MEE	14	9	10	11	10	12	8
	20%	ω	4.4	5.8	9.2	11.5	14.7	19.1	25.7
		MEE	15	11	12	13	11	13	8
	30%	ω	4.5	5.8	9.2	11.4	14.6	19.0	26.0
		MEE	14	11	12	14	12	14	6
	40%	ω	4.3	5.7	8.9	11.0	14.4	18.3	25.3
		MEE	17	12	14	17	13	17	10
	50%	ω	4.5	5.8	9.1	11.3	14.3	18.9	26.1
		MEE	14	11	13	14	14	14	6
Heat	140°C	ω	4.5	5.8	9.3	11.7	14.9	19.5	25.1
		MEE	14	11	11	11	10	11	10
	160°C	ω	4.3	5.6	9.0	11.3	14.7	19.3	25.6
		MEE	17	14	14	14	11	12	8
	180°C	ω	3.5	4.6	7.9	10.2	13.2	17.0	22.6
		MEE	33	29	24	23	20	23	19
	190°C	ω	2.8	3.7	6.3	8.3	11.7	15.3	20.7
		MEE	46	43	39	37	30	30	26
	200°C	ω	2.3	3.1	5.5	7.2	9.9	12.5	16.9
		MEE	56	52	47	45	40	43	39
Steam	120°C	ω	4.2	5.6	8.9	11.2	14.2	19.4	25.6
		MEE	19	14	14	15	14	12	8
	140°C	ω	4.3	5.6	9.0	11.2	14.3	19.3	25.3
		MEE	17	14	14	15	14	12	9
	160°C	ω	3.7	5.1	7.9	10.1	12.6	17.5	24.3
		MEE	29	22	24	23	26	20	13
	180°C	ω	3.6	4.8	7.5	9.1	11.7	16.	24.8
		MEE	31	26	28	31	30	27	11
	200°C	ω	2.9	4	6.3	7.9	10.9	15.3	25.1

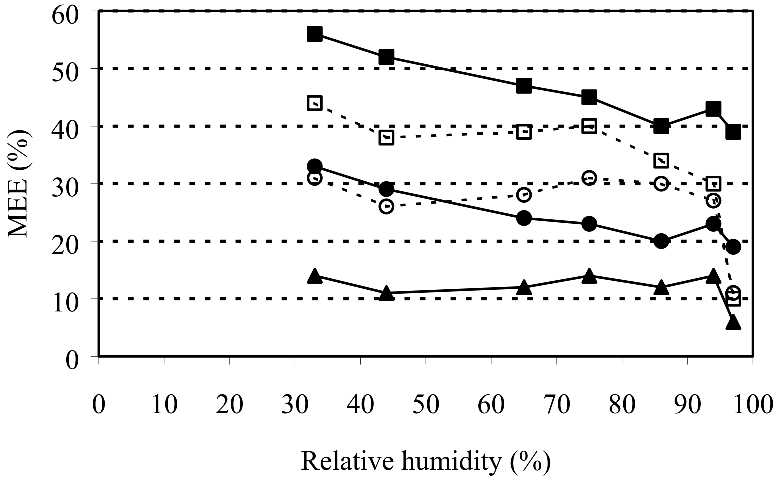


Figure 7.9 MEE (moisture exclusion efficiency) for compressed wood, C_s=30%, (▲), heat treated wood (solid line) at 180°C (●) and 200°C (■), and steam treated wood (dotted line) at 180°C (O) and 200°C (V).

7.3.2.2 Dimensional stability (ASE)

The dimensional stability of compressed wood, compressed heat treated wood and compressed steam treated wood was investigated by measuring dimensions in oven-dried condition and in swollen condition at different relative humidities, as presented in Section 7.2.2 The samples were identical to the samples used for the sorption tests. The ASE value was calculated from Eq. 2.1 and Eq. 2.2, based on the swelling of non-treated and non-compressed reference samples. The results are shown in Figures 7.10-7.12.

Compression set

Figure 7.10 illustrates ASE values for compressed wood as a function of compression set. The compression set is seen to have excessive influence on the dimensional changes. As the compression set increases the dimensional changes increase dramatically as a result of the higher density. When exposed to high relative humidity, they not only swell to a high degree but even tend to loose their compression set as a result of springback. A dramatic reduction in ASE is therefore observed. The decline at very high relative humidities corresponds well with the tendency presented for the sorption isotherms mentioned above.

Heat and steam treatment

ASE-values for compressed heat- or steam treated wood are presented in Figure 7.11 and Figure 7.12 respectively. The diagrams represent the effect of temperature on the dimensional stability. A significantly improved dimensional stability is recognised in both figures at the highest temperatures, although a strong dependency of the relative humidity is observed. The data at 160°C for the steam treated wood have been disregarded.

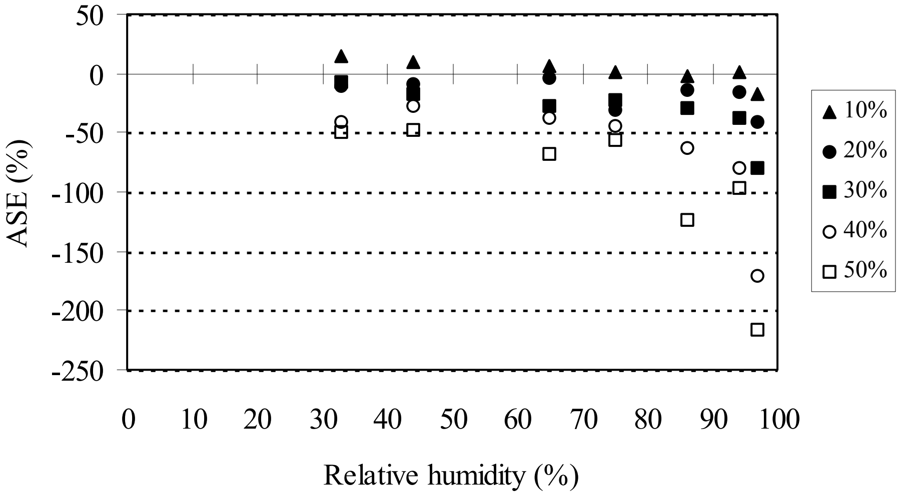


Figure 7.10 Dimensional stability (ASE) of non-treated compressed wood as a function of relative humidity at different compression sets.

The dimensional stability of heat treated samples is very high at 180°C and 200°C especially at the lowest relative humidities (Figure 7.11). At 200°C the dimensional stability of the compressed specimens is improved by 40% compared to non-treated and non-compressed wood at 65% RH. This value drops to app. 20% at 97% RH. Springback is almost completely eliminated under such conditions. At a compression set of 30% the density increases app. 30% (Figure 6.9). This corresponds with an increase of swelling of app. 60% (Figure 7.5). The dimensional stability is therefore seen to have been improved if compared to normal wood of a corresponding density.

A similar argument can be used in the case of steam treated wood (Figure 7.12). The dimensional stability of steam treated compressed wood is moderately improved at 180°C and 200°C compared to non-treated reference specimens. At 200°C a reduction of the dimensional changes of app. 20% compared to the reference samples is observed for the lower relative humidities.

Compared to the compressed specimens a highly improved dimensional stability is identified. Even at the highest relative humidities the stability is improved compared to compressed wood.

When exposed to high relative humidity, the specimens treated at temperatures at 160°C or below, for both treatments, tend to loose their compression set as a result of springback in the direction of compression. Accordingly, a dramatic reduction of ASE is observed.

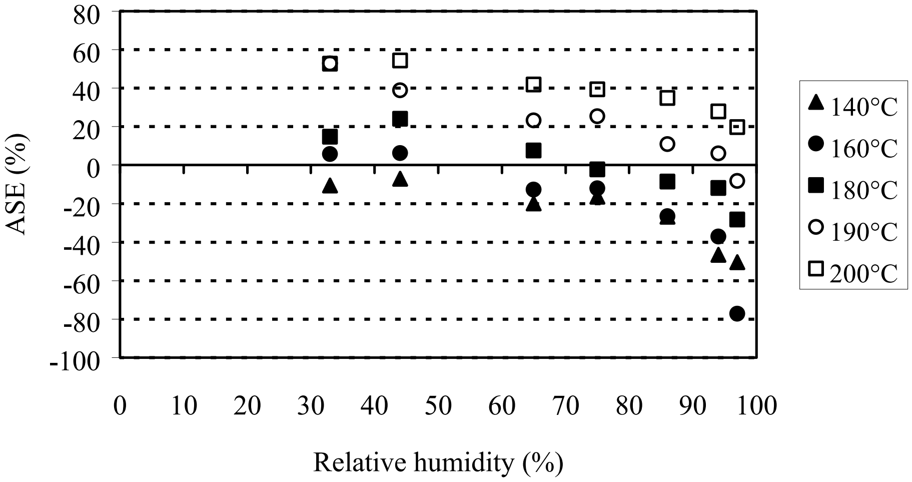


Figure 7.11 Dimensional stability (ASE) as a function of relative humidity for compressed heat treated wood at different temperatures

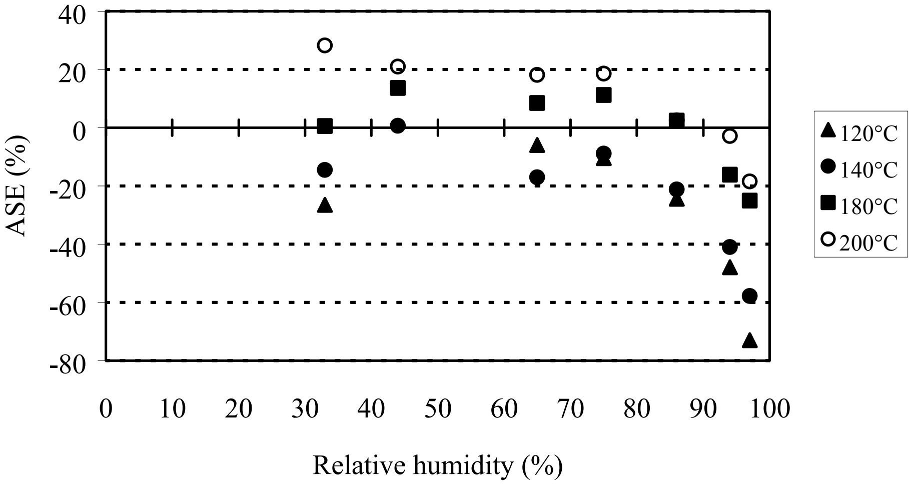


Figure 7.12 Dimensional stability (ASE) as a function of relative humidity for compressed steam treated wood at different temperatures.

The steam treatment applied to the compressed wood did not involve heating to temperatures sufficiently high for long enough periods of time to give dimensional stability as that of the heat treated wood.

The results from the sorption tests and the ASE tests combined with the springback results presented in Section 6., confirm that elimination of springback by heat- or steam treatment is the result of two different mechanisms (cf. Section 6.2). In the case of heat treatment the dimensional stability incorporated in the cell wall, as the result of thermal degradation particularly of hemicellulose, is considered to help locking the compressed state. In the case of steam treatment flow of lignin due to breaking of primary bonds and resetting in the compressed state is considered to be the main mechanism.

7.3.3 Hardness

For an anisotropic, heterogeneous material the hardness value is questionable. Already in 1881, Nördlinger pointed out that no "absolute" but only a "relative" hardness value is reasonable. The methods for measuring hardness dates back more than 100 years old, but the conclusion is definitely still valid. In this section the figures show absolute hardness values in order to evaluate the proportion of the hardness. However, the values should be taken with caution and the discussion is based on relative hardness values.

Several methods for testing hardness have been proposed (e.g. Janka, 1906; Brinell, 1900; Pallay, 1937). A discussion of these methods is outside the scope of the present study. The most universally accepted method is the Brinell hardness test, which has been applied in the present analysis. The hardness was measured by compressing a steel ball 1/4 of the diameter into the wood surface (Section 7.2.3).

A number of factors influence the hardness of wood: density, thermal degradation, moisture content etc. The effect on the hardness of compressed beech of compression set, heat temperature, duration of treatment, and steam temperature is investigated. The hardness of the surface of wood is tested as a indicator of the mechanical properties.

Compression set

As shown in Figure 6.9 the compression set is proportional to the density, hence it should be expected that hardness increases with increasing compression set. The effect of compression set of beech on the hardness is illustrated in Figure 7.13. At a compression set of 30% the hardness is increased almost 50%.

In early attempts to measure hardness Ylinen (1943) found that in practice a linear relationship between Brinell hardness and density is applicable to the whole range of densities of commercial timbers. In the case of compressed wood where the cell walls start to crush and the wood is damaged a parabolic relationship is observed. Cell walls touch before all pore-volume is eliminated. A non-linear relationship is identified when this takes place.

Heat- and steam treatment

The density is effected by thermal treatment and a significant influence on the hardness is expected.

The initial oven-dry density of the heat treated wood was 649 kg/m^3 with a standard deviation of 14 kg/m^3, and in case of steam treated specimens a dry-density of 644 kg/m^3 with a standard deviation of 12 kg/m^3 was measured.

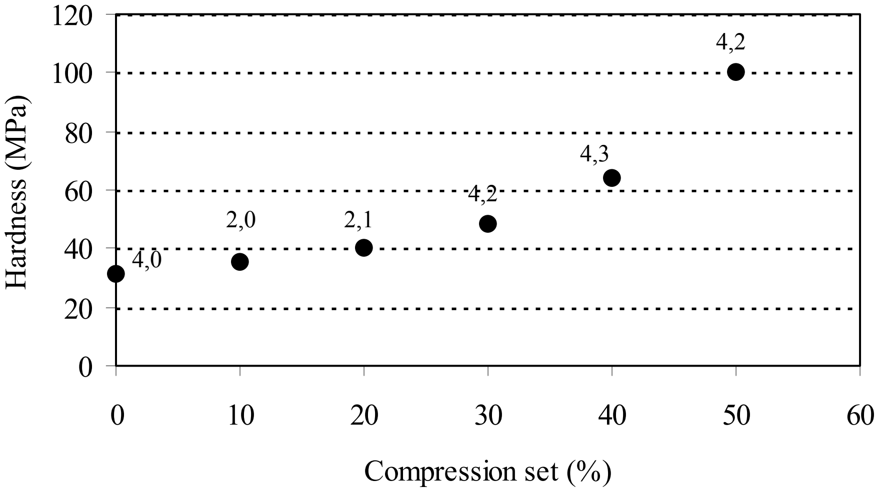


Figure 7.13 Hardness of compressed wood versus compression set. The numbers show standard deviation.

Figures 7.14 - 7.15 show the effect on hardness when heating compressed wood as a function of temperature and duration of treatment respectively. A decline of the curves is observed as the temperature or time increases. The decrease of hardness is only slight as would be expected from the moderate loss of density shown in Section 7.3.1.

After 20 hours of heat treatment at 190°C a loss of hardness of approximately 20% is noticed. The loss is believed to be caused by the degradation of the matrix (hemicellulose and lignin) (Section 3.4.2). After five hours at the same temperature the reduction of Brinell hardness is less than 5%.

The effect of steam temperature and duration of steaming is shown in Figure 7.16 and 7.17 respectively. Parallel to the heat treated samples only a modest loss in hardness is expected within the time/temperature range investigated.

Surprisingly the figures show a slight increase in hardness as the temperature is increased (Figure 7.16). This might be due to a reorganisation of the matrix. The relative quantity of lignin is increased as only holocellulose is degraded in the beginning, (Section 3.4.2). In addition, an increase of crystallinity is reported for steam treated wood.

This explanation is confirmed by Figure 7.17 where the hardness as a function of duration of treatment at 180°C is shown. After 10 minutes of steaming the hardness starts to drop and after 60 minutes treatment a 50% reduction compared to untreated compressed wood is observed. Unpublished data on the change of modulus of elasticity (MOE) due to steam treatments show that MOE is increased after short steaming times. This can also be explained by an increase of the relative amount of lignin in wood before lignin starts its thermal degrading.

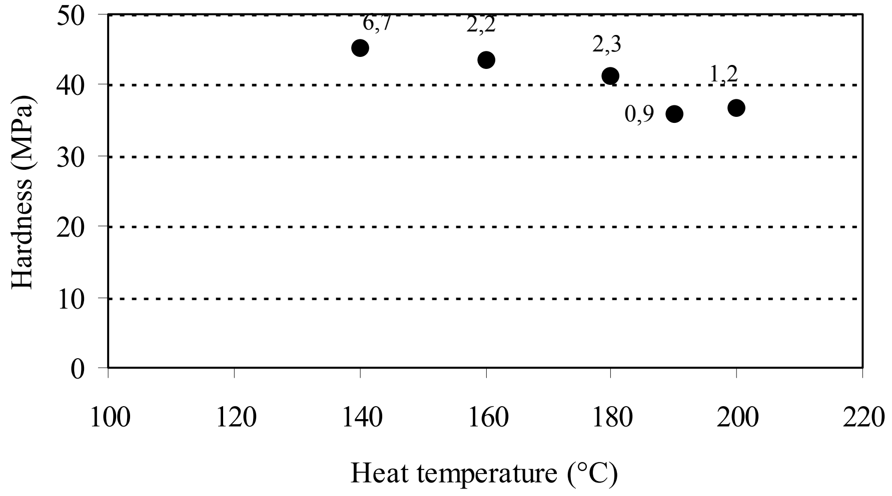


Figure 7.14 Hardness of compressed heat treated wood as a function of temperature. The numbers above the markers show the standard deviation on the measurements.

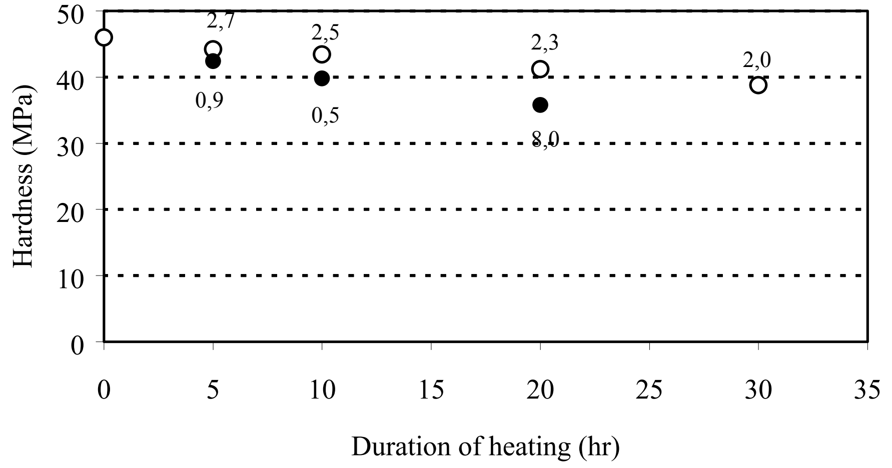


Figure 7.15 Hardness of compressed heat treated wood as a function of duration of treatment at 180℃ (○) and 190℃ (●). The numbers above the markers show the standard deviation of the measurements.

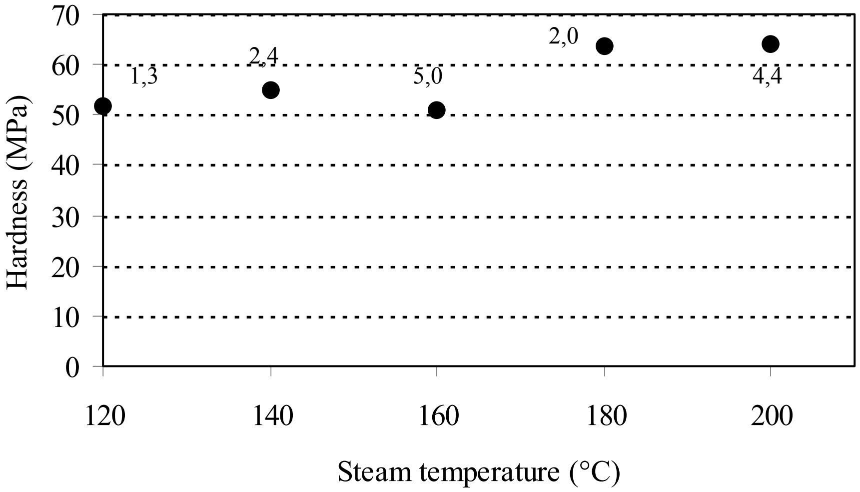


Figure 7.16 Hardness of compressed steam treated wood as a function of steam temperature.

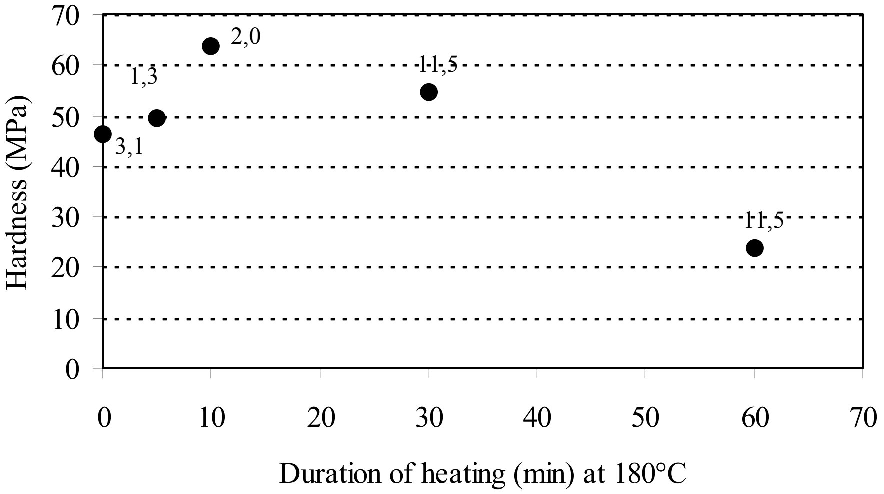


Figure 7.17 Hardness of compressed steam treated wood as a function of duration of treat-ment at 180°C.

7.4 Concluding remarks

An experimental study was carried out with the aim of characterising compressed wood with respect to its physical and mechanical properties.

Compressing wood results in an increase of density proportional to the compression set. Since the density is the single most important property of wood and many of its other properties are correlated to density, this effect is the main idea of producing compressed wood.

In order to avoid springback of the compressed wood such hygrothermal treatments have to be applied which influence the properties. Two types of thermal treatments were carried out: heating in an oven and steam treatment in an autoclave. Thermal degradation of the wood is shown to commence at about 160°C in both cases. This is indicated by the weight loss. This weight loss is only slight at short treating times and has only a moderate influence on the density, as the loss is accompanied by a change of volume.

The steam treatment applied to the wood did not involve heating to temperatures sufficiently high for long enough periods of time to give dimensional stability of the same order as that of the heat treated wood. However, at relative humidities below 97% the final equilibrium moisture content and the dimensional changes were significantly reduced compared to untreated wood. When compared to untreated compressed wood an extensive effect of steam treatment was observed, even at high relative humidities.

The hardness is of great importance when producing flooring. The hardness of the surface was found to be increased 50% when beech was compressed to 30% of its original radial thickness.

Steaming the compressed wood at a compression degree of 30% slightly improved the hardness within the range of time and temperature investigated. This was explained by an increased content of lignin and a reorganisation of the matrix resulting in an increased degree of crystallinity of the cellulose.

Heating wood resulted in a slight decrease of hardness as the time or temperature increased. This was explained by degradation of the matrix including both hemicellulose and lignin due to the long treating times compared to steam treatment.

Remaining problems

Although the compressed thermally treated wood is seen to have improved those properties considered of importance in the present study (dimensional stability and hardness), some serious problems are accompanied with the treatments.

The most serious technical problem due to the thermal treatment is most likely the *colour change*. All treatments resulted in a darkening of the wood. The degree of colour change depends on the temperature and the duration of treatment. *Beech* has shown to be more discoloured than most other species. For the most severe treatments an almost "burned" look was observed. This colour change is a result of degradation of the matrix.

The discoloration in the "closed system" (Section 6.2.3) gives some indications that less and more uniform darkening can be obtained compared to the methods described in this section. However, it is not possible to completely eliminate the discoloration as the effect on the stability is closely related to the chemical reaction which causes the colour change.

Checking of the wood as a result of the steam treatment is another problem of essential importance. This problem is most significant for solid wood. For the compressed wood used in the present study no severe checks were observed in a light microscope. This may be due to the dimensions used for the experiments.

In particular heat treatment is accompanied by a loss of *strength properties* (MOR, abrasion resistance). This has limited the commercial use of compressed heat treated wood.

For steam treated wood the thermal degradation is less severe. This is due to the fact that the short treating times and the loss in strength properties are of much lower magnitude.

8. Optimisation of the process of densifying wood

The following example presents a method to optimise the process of making compressed wood. The method is based on the knowledge obtained in Chapter 3-7. The main aim is to determine the parameters compression pressure, steam pressure/temperature and time during the process of making compressed wood to eliminate springback, maximise softening conditions and dimensional stability. The parameters involved are defined based on some ficticious requirements.

Requirements:
1. No springback
2. Treating time max. 20 minutes
3. Hardness improved 50%
4. Dimensional stability improved

Re: 1 and 2.
The "master curve" and shift factors presented in Figure 4.24 and Figure 4.25 can be used for the prediction of the parameters time and temperature (based on the time-temperature superpositions principle) to eliminate springback. In Section 6. it was shown that complete elimination of springback was achieved at 190°C after 15 minutes which corresponds with a storage modulus of 600 MPa (Figure 4.23). At 160°C this level is reached after app. 300 minutes (18000 sec) cf. Figure 4.25. The logarithmic shift factor is then determined from,

$\log(a_T) = \log(t_T/t_{To}) = \log(900/18000) = -1.30$

A corresponding temperature of 188°C is obtained from Figure 4.24.

Re: 3.
An improved hardness of 50% coincides with a compression set of app. 30% (Figure 7.13). The compression load is then determined from Figure 4.6. A compression set of 30% corresponds to a compression load of app. 1 MPa (app. 10 kg/cm^2) at 185°C.

Re: 4.
The dimensional stability after 20 minutes of steam-treatment at 185°C is significantly improved (app. 20% compared to untreated non-compressed wood) at relative humidities below 97%, (cf. Figure 7.12).

In order to satisfy the requirements the parameters needed can be summarised as follows:
Temperature: 185°C
Duration of steam treatment: 20 minutes
Compression set: 30 %
Compression load: 1 MPa

9. Conclusion

The main objective of the present work is the investigation of the combined effect of temperature, steam pressure, time and moisture content on compression of beech perpendicular to the grain. A better understanding and control of those parameters has been achieved by investigating.

- The influence of steam on the mechanical response during static tests and dynamic tests inside an autoclave.

- The hygrothermal recovery of densified beech.

- The elimination of springback of compressed beech using different hygrothermal treatments.

- The properties of densified beech.

The conclusions of the static- and dynamic tests can be summarised as follows:

- The mechanical tests all showed good agreement between the property investigated and the condition of the hygrothermal treatment. Such tests are useful in quantifying the phenomena of softening and degradation of wood.

- The elastic modulus, yield stress and work of strain are dramatically and gradually reduced as the steam temperature is increased.

- Stress-relaxation is dramatically increased as the steam temperature is increased. The elimination of springback corresponded with the state where no internal stresses were left in the material.

- The results from the mechanical tests indicate that the well known principle from polymer technology of time-temperature-superposition (TTSP) can be applied to the data. However, it is found that the WLF-equation cannot be used, since degradation mechanisms at the high steam-temperatures investigated dominate the behaviour.

- Instead of using the WLF equation it is proposed to evaluate the mechanical properties for the range of conditions of service expected and display them graphically (master-curve and shift factors). This can then be used for the prediction of a particular mechanical response.

- TTSP was used in order to compare the influence of hygrothermal treatment on modulus of elasticity in the longitudinal direction (dynamic test) and the creep modulus in radial direction (static test). The shift factor found in the dynamic tests was matching the shift factor found in the static test. It is concluded that the influence of steam treatment on the softening and degradation behaviour in longitudinal direction is matching the influence in radial direction.

Elimination of springback is of particular importance when making densified wood. Four separate hygrothermal treatments were applied to the wood. It is concluded that springback can be completely eliminated by one of the following procedures:

1. ***Heat-treatment in a hot-press:*** *Compressing water saturated wood in a hot-press at 200°C for 1 hour.*

2. ***Steam-treatment in autoclave:*** *Steam treating compressed wood in an autoclave at 190°C corresponding to 13atm. for 15 minutes.*

3. ***Heat-treatment in an oven:*** *Heating compressed wood in an oven at 190°C for 20 hours.*

4. ***Hygrothermal treatment in a closed system:*** *Compressing wood in a "closed" hot-press at 190°C for 10 minutes. The moisture inherent in the wood is used to create the steam pressure.*

- As can be seen from the results the steam treatment greatly reduces the time of treatment to eliminate springback compared to traditional heat treatment.

- It is assumed that the elimination of springback for ***steam-treated*** wood is the result of a break-down of the cross-links responsible for the memory effect in wood. This breakdown of primary bonds results in a slight flow of lignin and formation of bonds in new positions. This assumptions is confirmed by the fact that springback of steam-treated wood is eliminated without an accompanying strong improvement of the dimensional stability. This rules out the possibility of severe degradation (hydrolysis) of hemicellulose.

- Elimination of springback for the ***heat-treated*** wood is the result of a thermal degradation of the hygroscopic components in the cell wall especially the hemicellulose.

In the present study the hardness and dimensional stability of the products are considered of prime importance. The following conclusions were obtained:

- The ***steam-treatment*** applied did not result in ***dimensional stability*** at the same level as did ***heat-treatment***. However, at relative humidities below 97% the final equilibrium moisture content and the dimensional changes were greatly reduced compared to untreated wood. When compared to untreated compressed wood a significant effect of the treatments were observed, even at high relative humidities.

- When beech is subjected to a degree of compression of 30% the ***hardness*** was found to be increased 50%. The ***steam-treatment*** applied in order to eliminate springback slightly improved the hardness. This is explained by a change of chemical composition involving an increased relative amount of lignin and a reorganisation of the matrix resulting in a increased crystallinity.

- The ***hardness*** of ***heat-treated*** wood was moderately reduced, due to thermal degradation resulting in chemical changes of the matrix.

It is concluded that the hardness and dimensional stability of wood can be greatly improved by compressing wood and applying a hygrothermal treatment. However, such an improvement is not possible without an accompanying discoloration of the surface. For most of the severe treatments a dark brownish colour is observed.

Based on the combined knowledge from the experiments carried out in the present work, it can be concluded that TTSP is a useful tool for the optimisation of the method of densification of beech

Future work

It is hoped that the knowledge obtained can form the basis for further work in the field of densification of wood. Experimental work is still needed in order to implement the process industrially.

- The mechanical tests carried out in the present work are new methods, which can be improved technically. In order to compare the dynamic and the static tests more effectively, a dynamic method measuring the dynamic modulus at a specific frequency and in the transversal direction is needed.

- For specific structural uses the mechanical properties of compressed wood should be examined extensively. As an example it can be mentioned that the creep behaviour in service is expected to be altered by the thermal degradation.

- Another aspect in the case of structural uses is the biological degradation. The chemical alteration of the structure suggests that heat or steam treated wood will to some extent be protected against biological degradation.

- Future work should focus on specific end-uses of the product and include considerations on economical aspects of the treatment.

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Appendix A. Frequency response method

The resonance frequency method and the application of this method to the present study is summarised in the following. The information is partly taken from the manuals for the specific units involved (from Brüel & Kjær). This appendix supplements Section 3.3.2 Equipment-dynamic tests.

The appendix is organised in four subsections:

A1. Theoretical background
A2. Complex Modulus Apparatus
A3. The Electromagnetic transducers
A4. The Multichannel analyzer

A1. Theoretical background

This section deals with the theoretical background for the resonance frequency method. The dynamic E-modulus and the internal damping is introduced. For further details reference is made to Trudsø (1978), Pickett (1945).

For a solid material subjected to dynamic conditions the, internal and external friction exert a resistance to the exciting force. The friction is generally assumed proportional to velocity (viscous friction), and in the steady state causes a phase shift between stress and strain. This is expressed as a complex modulus of elasticity (or dynamic modulus, E^*):

$$E^* = E'(1 + jd)$$

where E' is the real part of the elastic modulus, d is the loss factor, which is defined as,

$$d = tg\delta$$

where δ is the phase shift between stress and strain caused by friction.

The resonance frequency method

In this method a bar shaped sample is clamped at one, or both ends, and excited into vibration with a variable periodic force. The amplitude of the vibration is plotted as a function of the frequency. From such a curve, at a resonance peak, the loss factor is calculated as:

$$d = \frac{\Delta f_n}{f_n}$$

where Δf_n is the bandwidth at the half power points (3dB points) and f_n is the resonance frequency. The index n is the order of resonance or mode number.

The real part, E', of the modulus of elasticity can be found from the resonance frequency and the mechanical dimensions of the bar as,

$$E_{dyn} = 48\pi^2\rho\left(\frac{l^2 f_n}{h k_n^{\ 2}}\right)^2 \qquad \text{A.1}$$

where,
l is the free length of the beam,
h is the thickness in the vibrational plane,
k_n depends on the boundary conditions of the beam and the mode number n.

In the present study a bar clamped at one end was used, and k_n is given as:
k_n^2 =3.52 for n=1
k_n^2 =22 for n=2
k_n^2 =61.7 for n=3
k_n^2 =121 for n=4

A2. Complex modulus apparatus

The Complex Modulus apparatus consists basically of two electromagnetic transducers (see next section) and a special test jig which provides firm clamping of the samples and precise mounting of the transducers with respect to the sample (Figure 3.25).

The clamping arrangement for the sample bars is located at the top of the apparatus. It is very difficult to devise a satisfactory clamping as steam temperature induced dimensional change must be accommodated without compromising the conditions assumed in the mechanical analysis. The following precautions were taken:

- The samples were pre-heated, and then tightly clamped using a spring in the clamping arrangement that follows the dimensional changes.

- The pick-up transducer was located below the sample bar to avoid distortions of the signal (Figure 3.25). The exciting transducer was located near the clamping arrangement.

- The dimensions of the samples were chosen as the maximum thickness allowed in the manual, considering the high degree of softening that is obtained at high steam pressures. A free length of 190 mm was found to give a stable measuring procedure.

The effect on the resonance frequency of the special arrangements used in the Complex Modulus Apparatus were experimentally verified. The high degree of compression in the clamping increases the resonance frequency less than 10%. The steam pressure has the opposite effect of. Furthermore, placing the pick-up transducer below the sample bar did not effect the resonance frequency.

A3. The Transducers, Type MM002, used under steam conditions

Introduction

Two magnetic transducers, type MM002 from Brüel & Kjær, were used for the dynamic tests. The magnetic transducer is a variable reluctance (moving-iron) device, which can be used as a velocity sensitive vibration pick-up or an electro-magnetic vibration exciter. An iron disc has to be fastened to the wood specimen to complete the magnetic circuit. When using the transducers under steam conditions the magnetic discs have to be mechanically fastened, because no glue can withstand the combination of high temperature and steam. In this case small magnetic drawing pins were nailed into the wood specimen.

Characteristics:
Sensitivity: The sensitivity of the transducer is 1.5mV/cm/sec, when the mean distance between the housing of the transducer and a special high-μ discs delivered from B & K is 2 mm. The sensitivity changes with the attraction between the transducer and the disc. The static force acting on the disc decreases rapidly when the distance increases. If other magnetic discs are used (in this case drawing pins) then the attraction force is changed and thus the sensitivity is changed.

Important! The change in the sensitivity of the transducer influences only the magnitude of dB signal and not the resonance frequency or damping of the signal. However, for other purposes this matter can have great importance.

Internal impedance: 1800 Ω in series with 400mH. The internal impedance is increased slightly at high temperatures and under the influence of steam. Table A1 shows the relationship as found by measuring the impedance with an ohm-meter during increasing steam pressure.

Table A1 The relationship between internal impedance and steam pressure.

Room-conditions	1.8 kΩ
2 bar	2.0 kΩ
4 bar	2.4 kΩ
10 bar	3.2 kΩ

Environment: The transducers can withstand temperature variations in the range from very low temperatures up to 250°C. Ambient pressure and humidity (e.g. steam) have practically no influence on the open circuit sensitivity of the transducer.

Transducer set-up: The transducer set-up can be stored on a floppy disk and down loaded to the multi-channel analyzer, see Hansen (1994), prior to testing.

Note: Brüel & Kjær recommended to make a hole in the transducer to avoid collapse of the transducer kit. However, this was not practiced. The transducer was instead filled with a polymer (Polyurethane compound). This caused a disconnection after some time of use and the transducers were destroyed. Finally the transducers were used as they are delivered from B & K. Accordingly, many of the problems were eliminated. However, after some time of use, disconnections may occur at very high temperatures.

A.4 Multi-channel analyzer

The multi-channel apparatus consists primarily of two sections, one generates mechanical vibrations and the other senses these vibrations. The exciting transducer is connected to the "direct input" in channel A and the frequency generator module, while the pick-up transducer is connected to the "direct input" in channel B.

The frequency generator is producing simultaneous oscillations within a range of frequencies. The amplitudes of the vibrations are registered by the analyzer for all frequencies within the frequency range. The resonance frequency is seen on the instrument screen and identified by moving a cursor line to the frequency tip. The loss factor and the resonance frequency identified can be read on the instrument screen.

The set-up of the multi-channel analyzer is shown in Figure 3.25. The experimental set-up can be down-loaded from a floppy disk. For instructions on how to operate the instrument reference is made to the manual.

Appendix B. Light-microscopy study of compressed beech

Insight in to the macrostructure of compressed beech and recovered beech is given in a light microscope.

The specimen used was treated in the closed system, (Section 3.5) at 190°C for 10 minutes. The compression set was 30%. The density was 1150 kg/m^3 before recovery. Springback under these conditions is almost eliminated.

Procedure

Compressed beech: The specimen was sliced to a small section perpendicular to the grain directly in a Reichert microtome (25µm). The cutting is difficult due to the non-softened state and a very hard structure from compressing. The sections cracked very easily. The drawback is that some damage of the structure may have occurred from the cutting.

Recovered beech: After soaking the specimen for 24 hours in demineralised water the specimens were sliced as above.

Results:

The macrostructure of compressed beech is shown in Figure B.1 and of recovered beech it is shown in Figure B.2.

It is seen that opposing cell walls are locked together and that lumen almost disappears due to cell wall collapse and buckling of the cell walls, cf. Figure B.1. Deformed ray cells can be identified.

From Figure B2, it is clearly seen that the cell wall is slightly recovering after immersion into water. However, the lumen structure is more open, however, compared to the macrostructure of original beech. The differences are clearly seen in Figure 2.1.

Figure B.1 Compressed beech, C_s=30%.in dry state, magnification 100 X.

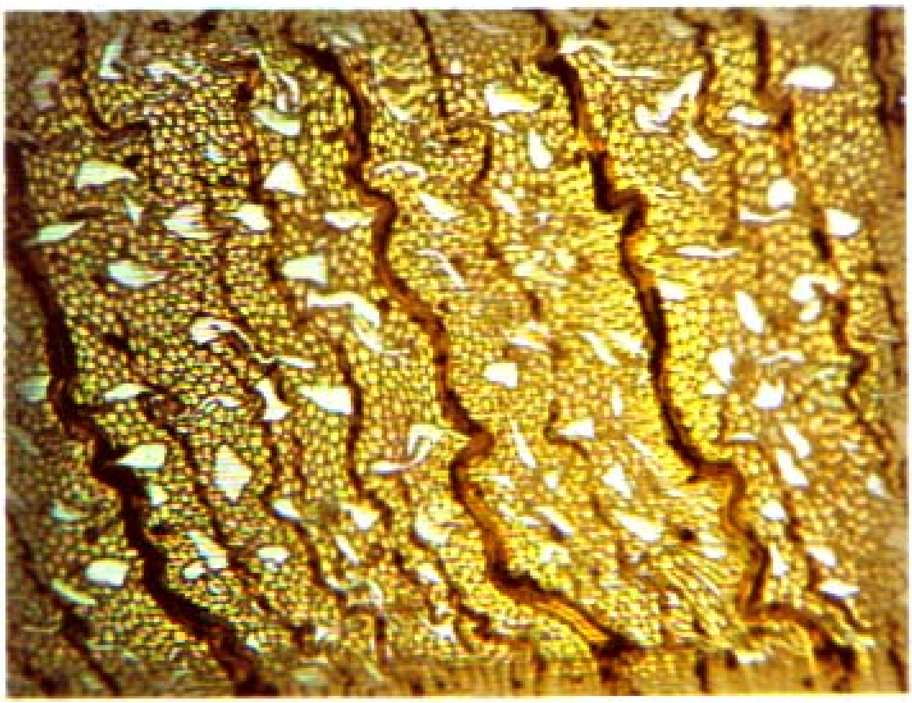

Figure B.2 Compressed beech after recovery test in water, magnification 100 X.