Technological improvement of Portuguese pinewood by chemical modification

Dissertation
In Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy (PhD)
of the Faculty of Forest Sciences and Forest Ecology
Georg-August-University Göttingen

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born in Salto, Portugal
Göttingen, 2013

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Date of Oral Examination: 26th of August, 2013

Keywords: Chemical modification, creep, durability, DMDHEU, *Limnorids*, Maritime pine, mechanical properties, mechano-sorptive creep, melamine, physical properties, Silane, TEOS, *Teredinids*, wax

ABSTRACT

Wood has a long tradition as a structural and building material in Portugal. In the last decade, the European trend to improve physical properties of wood by chemical modification allowed extending its performance on durability and improve its performances in properties relating to moisture, in general.

The objective of the ***Technological improvement of Portuguese pinewood by chemical modification*** was to study Maritime pine (*Pinus pinaster* Ait.) wood characteristics and the impact of the chemical modification at large range on resistance to marine organisms, physical and mechanical properties. Four modification methods were tested: 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), N-methylol melamine (MMF), tetra-alkoxysilane (TEOS) and wax.

This work comprises *two* parts: a preliminary and a main-study. In *the former*, a large variety of material properties was studied - physical and mechanical properties, and their interactions. Particular attention was taken on the marine organisms, where the role of hardness, shape of specimens as well as the toxicity of chemicals were investigated.

In the *second part* of the work, a study on the subject of creep was carried out. Types and levels of the modification together with stress levels, different environmental conditions and mechano-sorptive effect were evaluated.

Although stiffness appeared to be statistically unaffected, significant differences in other properties occured. The anti-swell-efficiency and stiffness stabilization increased, on the one hand. On the other hand, the impact bending strength and the equilibrium moisture content appeared to be significantly reduced in the cell wall modification (with DMDHEU and MMF resins) where a close inter-connection between the latter variables was observed.

Under high stress level or under the mechano-sorptive effect, the creep was lower for both modifications with cell wall reaction (with DMDHEU and MMF) than for unmodified wood. For both types of resin, relative creep reduced significantly, despite different changes took place in

the equilibrium moisture content, stiffness stabilization or strength. The anti-creep efficiency has shown a close correlation between the equilibrium moisture content reduction, anti-swelling efficiency and stiffness stabilization effciency. The lumen fill modification with TEOS solution had no effect in creep as well as in the equilibrium moisture content and stiffness stabilization efficiency.

In the marine trials, the main conclusions were the unimportant role of the hardness and the specimens shape against the attack of marine borers (*Limnorids* and *Teredinids*). Modified wood with lumen fill (with TEOS and wax) has no effect on the resistance to both marine borers. Modified wood with condensation resins (DMDHEU and MMF) were unaffected by *Limnorids* attacks. But, to prevent the attacks of Teredinids over 3 years of exposition, only DMDHEU resin was effective with a required minimum level of modification.

The use of modified wood as building material is well known in non-loaded bearing components, where applications in moist rooms, wall claddings or garden furniture are the main applications. This study supports the possible extension of its application for structural purposes, mainly if the design is governed by the *serviceability limit state*, deformation. Therefore, the brittleness behaviour, mainly in the cell wall modification with DMDHEU resin, and design properties for mechanical connections must be determined in order to extend the use of modified wood as load bearing components where often the *ultimate limit state* govern the design of structural components.

Schlüsselwörter: Chemische Modifizierung, DMDHEU, Dauerhaftigkeit, Kriechen, Limnorids, See-Kiefer, mechanische Eigenschaften, mechano-sorptives Kriechen, Melamin, Modifikation, physikalische Eigenschaften, Silan, TEOS, Teredinids, Wachs

ZUSAMMENFASSUNG

Das Ziel der Arbeit „**The *Technological improvement of Portuguese pinewood by chemical modification***" bestand darin, die Charakteristiken des Holzes der See-Kiefer (*Pinus pinaster* Ait.) und den Einfluss der chemischen Modifizierung hinsichtlich des Widerstandes gegen Meeres organismen, sowie ihrer physikalischen und mechanischen Eigenschaften zu untersuchen. Vier Modifizierungstypen wurden getestet: 1,3-Dimethylol-4,5-dihydroxyethylen-Harnstoff (DMDHEU), N-Methylol-Melamine (MMF), Tetra-alkoxysilane (TEOS) und Wachs.

Diese Arbeit besteht aus zwei Teilen: eine vorläufige und eine Haupt-Studie. In ersterer wurde eine Vielzahl von Materialeigenschaften untersucht - physikalische und mechanische Eigenschaften und ihre Wechselwirkungen. Besonderes Augenmerk wurde auf die Resistenz gegenüber Meeresorganismen gelegt, wobei die Rolle der Härte, der Form der Proben sowie der Toxizität der Chemikalien untersucht wurde.

Im zweiten Teil der Arbeit wurde eine ausführliche Studie zum Thema Kriechen durchgeführt. Art und Grad der Modifizierung wurden in Abhängigkeit von der Belastung, von verschiedenen Umgebungsbedingungen und vom mechano-sorptiven Effekt evaluiert.

Obwohl die Steifigkeit nicht signifikant verschieden war, traten Unterschiede in den anderen Eigenschaften auf. Einerseits waren die Anti-Quellungs-Effizienz und Steifigkeit-Stabilisierung erhöht. Andererseits waren die Bruchschlagarbeit und die Gleichgewichtsfeuchte signifikant durch Zellwand-Modifizierung (DMDHEU und MMF-Harz) reduziert, wobei eine enge Wechselbeziehung zwischen letzteren Variablen beobachtet wurde.

Unter hohem Belastungsgrad oder unter dem Einfluss des mechano-sorptiven Effekts war für das modifizierte Holz mit Zellwandreaktion (DMDHEU and MMF) das Ausmaß des Kriechens geringer als das des unmodifiziertem Holzes. Für beide Arten von Harz, wurde das relative Kriechen deutlich verringert, trotz unterschiedlicher Veränderungen in der Ausgleichsfeuchte, Steifigkeit Stabilisierung und Festigkeit. Die Anti-Kriech-Effizienz zeigte eine enge Korrelation mit der Abnahme der Gleichgewichtsfeuchte, der Anti-Quell-Effizienz und der Steifigkeits-

Stabilisationseffizienz. Die lumen-füllende Modifizierung mit TEOS-Lösung hatte weder einen Einfluss auf den Kriech-Faktor noch auf die Gleichgewichtsfeuchte und die Steifigkeits-Stabilisationseffizienz.

Bei den Meerwasseruntersuchungen waren die wichtigsten Schlussfolgerungen, dass die Härte und die Form der Proben keinen Einfluss auf die Resistenz gegenüber einem Befall durch die Meerwasser-Bohrschädlinge (Limnoriden und Terediniden) haben. Lumen-füllende Modifizierungen (TEOS und Wachs) hatten keine Wirkung hinsichtlich der Resistenz gegen Meerwasser-Bohrschädlinge. Hölzer, die mit Kondensationsharzen (DMDHEU und MMF) modifiziert waren, waren von einem Befall mit Limnoriden nicht betroffen. Aber nur DMDHEU mit einem Minimum an Modifizierung war geeignet, um einen Befall durch Terediniden über eine Expositionsdauer von 3 Jahren zu verhindern.

Die Verwendung von modifiziertem Holz als Baumaterial für nicht-tragende Bauteile wie Anwendungen in Feuchträumen, Wandfassaden oder Gartenmöbeln ist bekannt. Diese Untersuchung unterstützt die Ausweitung seiner Anwendung für tragende Bauteile, besonders wenn das Design durch die Möglichkeit von Deformation bestimmt wird, die seine Funktionsfähigkeit einschränkt. Deshalb müssen das Versprödungsverhalten, insbesondere bei der Zellwand-Modifizierung mit DMDHEU, und die Designmöglichkeiten für mechanische Verbindungen bestimmt werden, um die Anwendungsmöglichkeiten des modifizierten Holzes als tragende Komponente auszuweiten, bei denen oft der Grenzzustand der Tragfähigkeit das Design der strukturellen Komponenten bestimmt.

Palavras chave: Cera, DMDHEU, durabilidade, fluência, mecânico-sortivo, melamina, modificação química, *Limnorids*, Pinheiro Bravo, propriedades físicas, propriedades mecânicas, resina, TEOS, *Teredinids*

RESUMO

Este trabalho apresenta o ***Melhoramento Tecnológico da Madeira de Pinheiro Bravo com Recurso à Modificação Química***. O conhecimento das propriedades da *Madeira*, enquanto material de construção tradicional, e das suas potencialidades, é essencial para a optimização e exploração de um recurso natural excedentário em Portugal. Extrair a máxima potencialidade de um recurso passa por uma incorporação de valor acrescentado com vista a obter produtos de boa qualidade, principalmente de forma sustentada. *Se por um lado* temos o material de construção *madeira* com elevada variabilidade nas suas propriedades intrínsecas, com os defeitos naturais a agravar, *por outro lado* os consumidores têm especificações com padrões de qualidade crescentes na sua utilização. Neste sentido, os recentes desenvolvimentos da modificação, térmica e principalmente química, da madeira macia abre novos caminhos. Em *primeiro lugar*, rentabiliza a exploração das florestas em todos os países Europeus e acrescenta “mais valor” ao produto daí extraído. Em *segundo lugar*, poupa ao sacrifício as florestas tropicais, que têm estado sobre forte pressão da opinião pública, substituindo os seus produtos por outros com idênticas performances.

Neste trabalho são *abordadas* propriedades físicas e de durabilidade face a fungos e insectos, adquiridas pela madeira modificada, já avaliadas por outros autores. A maior homogeneidade de resultados nas propriedades físicas e mecânicas são *confirmadas* para a madeira Portuguesa quimicamente modificada. Adicionalmente, verificou-se a flência com uma redução significativa da deformação e na durabilidade face aos agentes marinhos, principalmente nos tratamentos à base de resina (DMDHEU e MMF). A fluência e a resistência aos gentes marinhos foram a principal novidade apresentada por este estudo.

O *objectivo* principal do trabalho visou o conhecimento e o aumento das potencialidades da madeira de Pinheiro Bravo da espécie *Pinus pinaster* Ait. sujeita a modificação química bem como a influência da modificação na utilização final da madeira.

O Pinheiro Bravo é a principal espécie de madeira macia em Portugal, correspondendo a cerca de 30% da área florestal nacional e a maior fornecedora de matéria-prima para a indústria da

serração, aglomerados e papeleira. Provenientes da região norte do país (Cabeceiras de Basto, Portugal) foram seleccionados 4m^3 de pranchas de madeira com 5cm de espessura e 220cm de comprimento e enviadas para Göttingen, Alemanha. Tanto quanto possível a madeira do *cerne* foi evitada pela sua dificuldade em ser impregnada (EN 350-2). *Quatro* modificações químicas foram usadas: 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), N-methylol melamine formaldehyde (MMF), tetra-alkoxysilane (TEOS) e dois tipos de cera (Amido e Lenhite). O trabalho foi desenvolvido em duas instituições de ensino superior de dois países Europeus e também pode ser dividido em *duas partes*.

A *1.ª parte do trabalho* comportou a preparação de três conjuntos de provetes. O *primeiro* conjunto para exposição em mar aberto e o *segundo* para caracterização das propriedades físicas e mecânicas de referência da espécie de madeira de Pinheiro Bravo. O *terceiro* conjunto de amostras preparadas foi usado na 2.ª parte do trabalho para avaliação do comportamento da Madeira em fluência. As tarefas de preparação e avaliação das propriedades de referência foram desenvolvidas nas instalações do *Departamento Wood Biology and wood Technology* da *Georg-August Universität School of Science* (Göttingen, Alemanha).

Nas propriedades características da espécie da Madeira de Pinheiro Bravo, várias conclusões podem ser extraídas. O melhoramento significativo das propriedades relacionadas com o comportamento da Madeira face a humidade: Redução do teor em água de equilíbrio, dimuição da retracção e inchação para os tratamentos à base de resina (DMDHEU e MMF) e o não-efeito do material depositado no lúmen das células da madeira modificada com TEOS e cera. A não alteração estatística do módulo de elasticidade em todos os tratamentos usados. A redução da resistência e da capacidade de absorção de energia (fragilidade) em diferentes extensões só para os tratamentos à base de resina. Alterações não significativas foram verificadas para as propriedades mecânicas dos tratamentos com preenchimento do lúmen com TEOS e Cera.

Com base na informação gerada na 1.ª parte do trabalho e ao fim do 1.º ano de trabalho foi feita uma análise dos objectivos traçados inicialmente e delineou-se a *2.ª parte do trabalho*. O acompanhamento do material exposto em mar aberto e a avaliação do comportamento mecânico de longa duração (*fluência*) foram eleitos para finalizar o trabalho. Estas duas últimas tarefas desenvolvidas em Portugal, respectivamente no porto de Leixões (Leça da Palmeira, Portugal) e nas instalações do *Instituto Superior de Engenharia do Porto* do *Instituto Politécnico do Porto* (Porto, Portugal). O comportamento em fluência teve ênfase nas variáveis: Tipo e nível de modificação, tensão instalada, humidade ambiente variada e constante (interior e saturada). A condição de humidade variada visou o estudo do efeito mecanico-sorptivo em fluência. Para o efeito desenvolveram-se dois *setups* para ensaiar as principais conclusões da *2.ª parte do trabalho* podem ser assim resumidas:

- Foi encontrada uma estreita ligação entre as alterações introduzidas pelos tratamentos à base de resina (DMDHEU e MMF) no teor de humidade de equilíbrio, estabilidade dimensional e eficiência ou estabilidade da rigidez em ambientes húmidos. O bom comportamento em fluência para os tratamentos com resinas pode ser associado ou correlacionado com os bons resultados da estabilidade dimensional. Os tratamentos com o preenchimento do lúmen não apresentaram qualquer efeito no comportamento em fluência.

Para os quatro processos de modificação química da madeira proveniente da parte do borne do tronco do Pinheiro Bravo os resultados têm diferentes expressões e provam que:

- Todos os tratamentos aumentam a densidade.
- A densidade na madeira modificada não poderá ser usada para estimar as propriedades mecânicas e de fluência como é usada para a madeira natural.
- Os tratamentos à base de resina (DMDHEU e MMF) reduzem a deformação por fluência em ambiente interior (sob elevada tensão instalada) e em ambiente com humidade relativa variada (sob o efeito mecânico-sortivo).
- É requerido um nível de modificação mínima para se obter resistência aos agentes marinhos em mar aberto (*Teredinids*). A resina DMDHEU mostrou maior toxicidade para os agentes marinho do que a resina MMF.
- Os tratamentos à base de resina (DMDHEU e MMF) mostraram-se resistentes aos agentes *Limnorids*, independentemente do nível de modificação.
- A forma dos provetes e a dureza do material exposto em mar aberto não mostraram qualquer efeito significativo na resistência aos agentes marinhos (*Limnorids* e *Teredinids*) tanto na madeira natural como na madeira quimicamente modificada.
- Os tratamentos com preenchimento do lúmen (TEOS e Cera) não mostraram qualquer influência no teor de humidade de equilíbrio, no comportamento em fluência e na durabilidade aos agentes marinhos (*Limnorids* e *Teredinids*). Para o tratamento com cera, o ligeiro aumento da resistência não é estatisticamente significativo.

O uso da madeira modificada é conhecido das aplicações com funções não estruturais como os revestimentos de fachadas, zonas húmidas e mobiliário urbano. Este trabalho prova que é possível usar a madeira modificada como material de construção, principalmente em componentes com funções estruturais em que o estado limite de serviço (as deformações, EC 5) seja condicionante. No entanto, o comportamento em ligações mecânicas, as propriedades de resistência bem como o seu comportamento frágil na rotura devem ser determinados e ultrapassados. Assim, o uso da madeira modificada como componente estrutural pode ser alargado e a madeira modificada poderá ser aceite unanimemente como material estrutural entre a comunidade técnico-científica.

PREFACE / acknowledgements

This work has resulted from a partnership between the section of *Wood Biology and Wood Products* of the *Georg-August-Universität* (Göttingen, Germany) and the *Polytechnic of Porto, School of Engineering* (Porto, Portugal). This inter-disciplinary work covers different areas of chemical, biological and structural engineering.

I would like to express my warmest thanks and gratitude:

I would not have been able to do my work without Prof. dr. Holger Militz helping. I am very grateful for the study opportunities that he gave me. He was strict with me, but let me forge my own path and solve my own problems.

I would like to thank the Polytechnic of Porto, *School of Engineering* for their facility to conduct the creep experiments (in the Laboratory of Building Physics and Structures Laboratory of Civil Engineering Department).

Dr. Carsten Mai for his supervision and valuable comments in the preparation of this work.

The staff of the section of *Wood Biology and Wood Products* has been very helpful throughout my various stays in Göttingen. I would like to extend a special thank to all colleagues and laboratory technicians with who I have worked and that gave me so much help over the years: André Klueppel, Andreas Krause, Bernd Bringemeier, , Dieter Varel, Georg Behr, Gunthard Scholz, Petra Heinze, Sabrina Stumpf and Susanne Bollmus…"Thanks" from the *Portuguese guy*.

The Administration of the Leixões Harbour (APDL SA) for providing the sea space for exposition the wood material according to EN 275 (in Leça da Palmeira, Portugal).

The Radiology Department of Vila Nova de Gaia - Espinho Hospital (V. N. Gaia, Portugal) for providing the x-ray of all material exposed in the open sea.

Dra. F. Russell Pinto from the Centre of Marine and Environmental Research of the Oporto University (Porto, Portugal) for identifying the biofouling and marine borers.

Dra. Júlia Carmo (www.carmo.pt, Lisboa, Portugal) for providing CCA treated logs.

I would not have been able to accomplish my work without the support of my *wife*, Patricia Pinto. It's you that took time out from your carreer in order to let me put all my attention on my study. It's you that brought the *Angels* to our lives, our beautiful *son* and *daughter*, João Pedro and Margarida,

thank you very much, indeed.

Portugal - Porto, January 2013

NOTATIONS

Roman upper-case letter

A	Area
ACE	Anti creep efficiency
A_{end}	Cross section Area, perpendicular to the grain
A_r	Radial area
ASE	Anti shrink/swelling efficiency
A_t	Tangential area
A_{tot}	Sum of radial, tangential and cross section areas
A_w	Impact bending strength, capacity to absorb energy
CCA	Chromated copper arsenate
CV	Coefficient of variation, standard deviation divided by mean
BH	Brinell hardness
D	Dimension
DEN	Density
DIN	German Institute for Standardization
DMDHEU	1,3-dimethylol-4,5-dihydroxyethyleneurea
E	Young's modulus, abbreviated form
$E_{t,0}$	Young's modulus on tensile on the longitudinal direction
EC 5	Eurocode V standard, EN 1995:1-1
EMC	Equilibrium moisture content
ΔEMC	Equilibrium moisture content variation between two climates
EN	Europeen norm
FSP	Fibre saturation point
J	Joule, 1N/m
JH	Janka hardness
IBS	Impact bending strength
L	Length, measured in the longitudinal direction
LVDT	Linear variable differential transducer
MME	moisture-excluding efficiency
MC	Moisture content
MME	Moisture exluding efficiency

MFA	Micro-fibril angle
MMF	Methylated melamine formaldehyde resin
MOE	Modulus of elasticity
MOE_{dyn}	Mod. of elasticity determined dynamically
$MOE_{st,3pb}$	Mod. of elasticity determined statically with three points bending
$MOE_{st,4pb}$	Mod. of elasticity determined statically with four points bending
MOR	Modulus of rupture
MPa	Mega Pascal, unit of stress, similar to Nmm^{-2}
MSE	Mechano-sorptive effect
MTE	Methyl triethoxy silane
N	Newton
NP	Portuguese norm
P	Pound force, load, dead weight
PFM	Power function model
PSU	Practical salinity unit
PTEO	Propyl triethoxy silane
$P\delta$	Effect of the eccentricity of load
R	Length, measured in the radial direction
R^2	Coefficient of determination in a correlation
RH	Relative humidity
RTL	Radial, tangential and longitudinal dimensions
S	Swelling coefficient
SL	Stress level
SLS	Service limit state
SSE	Stiffness stabilization efficiency
SWOT	Analyzes of strengths, weaknesses, opportunities and threats
T	Length, measured in the tangential direction
TEOS	Tetra-alkoxysilane
ULS	Ultimate limit state
V	Volume
WA	Amid wax modification
WL	Lignite wax / Montan wax modification
WML	Work maximum load
WPG	Weight percent gain

NOTATIONS

Roman lower-case letter

3pb	Three points bending (two support and one loaded point)
4pb	Four points bending (two support and two loaded points)
b	With
ctrl	Unmodified wood or control pine
d	Diameter of the lasting indentation in the Brinell hardness
dJ	Creep compliance
dyn	Dynamic
f	Eigen-frequency
$f_{c,o}$	Compression strength parallel to the fibre
$f_{c,o,k}$	Characteristic values of compression strength parallel to the fibre
$f_{c,9o}$	Compression strength perpendicular to the fibre
$f_{m,o}$	Bending strength
$f_{m,o,k}$	Characteristic values of bending strengths
$f_{t,o}$	Tensile strength parallel to the fibre
$f_{t,o,k}$	Characteristic values of tensile strengths parallel to the fibre
$f_{v,o}$	Shear strength parallel to the fibre
$f_{v,o,k}$	Characteristic values of shear strengths parallel to the fibre
h	Height
k_c	Creep factor
kg	Kilogramme mass (9.81N)
k_{def}	Deformation factor
kN	Kilo Newton
l	Length
m_i	Weight at moisture content i
min	Time in minutes
mm	Dimension in millimeters
mm^2	Area in square millimeters
m_o	Weight at oven-dry state
n	Number of specimens
n.a.	Neutral axis of the cross section
p	Level for significance

r	Coefficient of correlation
s	Time in seconds
stat	Static
stdv	Standard deviation
t	Time
u	Unmodified, natural or untreated wood
u_{fin}	Final strain
u_{inst}	Instantaneous or linear strain according to EC 5
x	Axis direction, horizontal
y	Axis direction, vertical

NOTATIONS

Greek upper and lower-case letter

Δ	Denotes difference in general
ϕ	Relative creep (creep strain ε_{time} divided by elastic strain ε_{inst})
ε_i	Swelling strain
ε_{inst}	Linear strain (instantaneous strain after 60 s)
ε_c	Creep strain
ε_{irr}	Creep strain, non-recoverable
ε_{lon}	Swelling / shrinkage strain in the longitudinal direction
ε_{ms}	Creep strain under mechano-sorptive effect
ε_{rad}	Swelling / shrinkage strain in the radial direction
ε_{rec}	Creep strain, recoverable strain
ε_s	Free swelling / shrinkage strain
ε_{tan}	Swelling / shrinkage strain in the tangential direction
ε_{time}	Time-dependent strain
ε_{vol}	Volumetric swelling / shrinkage strain
β	Creep parameter of the Power Function Model
δ	Strain or strain
ρ	Density (kg.m^{-3})
η	Material viscosity
ρ_k	Density, characteristic values
σ	Stress

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1 INTRODUCTION

Compared to other resources used by human beings, wood together with stone, are the most used and durables, if wood is used in appropriate way. However, as an engineering material, wood has the *disadvantage* of the non-homogeneous properties with a large variability in the tree (both, radial and vertical positions), between trees and between stands. Also, whereas demand in wood products is expected to increase, production forest world-wide is under pressures and tends are to decrease raw material availability to the wood-processing industry.

The building industry needs to replace tropical hardwoods under severe restrictions, high prices and poor public image. Deeper knowledge about wood properties and how to use efficiently the material are the key issues for optimization and promote the wood as raw material.

Many of the problems with wood *in service* are attributable to the dimensional stability when subjected variying humidity conditions. Modification of wood, in particular with chemicals, will create new wood materials with high benefit / added value and satisfying customer needs in relation with other competing materials (i.e. for concrete and alloys).

In view of the increased use of modified wood as a building material, the aim of this study was to evaluate and compare the effects of chemical modification concerning to some properties of the Portuguese pinewood. Physical and mechanical properties with the main topic in the creep performance (focused in the stress level and mechano-sorptive effect) were evaluated as well as marine behaviour in the salt water contact (sea trials, hazard class 5 according to EN NP 335-2).

Different lines were undertaken in this work carry a better understanding of the pinewood performances:

- Material properties assessment.
- Structural performances.
- Marine resistance.

From the set of chemical modifications, the best or the most appropriate modification features to apply in the softwood was set out. The wise way to turn softwood Pine, with low commercial value in a new material, where new added value was incorporated, is the chemical addition, followed the latest tendency in Europe and world wide. This type of chemicals modified wood will be showing its performances in high hazard (class 5, EN NP 335-2) and structural behaviour in outdoor components, e.g. such applications are nowdays restricted to hardwood species with high commercial value (tropical hardwoods, usually) or other construction materials (plastics, concrete and steel).

In structures and buildings the wood-moisture interaction has a decisive effect on the behaviour of a wood component. When wood is used in loaded condition, long-term deformation occurs, especially in horizontal members. In moisture changing, wood tends to creep and display the MSE with amplified deformation. Time dependend behaviour in wooden structures can lead to serviceability problems (caused by excessive deformation), or to safety problems (caused by strength losses with consequently reduced load-bearing capacity as well as creep rupture and creep buckling). Some of the risks mentioned above can be reduced by components made of chemical modified wood; *It was one of the initial assumptions*.

Chemical modified wood has good performance on the durability, in general to fungus and termites (Militz et al. 2011; Scholz et al. 2010b). In outdoor conditions, it has good UV stabilization and cracks less than unmodified wood. Then, combined with dimensional stability makes it a good opportunity for solid wood to solve the most shortcomings in structural proposes.

The term *modification wood* applies to the application of a process / modification that alters the material properties such that during the lifetime of a product no loss of the enhanced performance of the wood should occur (Hill 2006). The modified wood should itself *be non-toxic* under service conditions and, furthermore, there should *be no release* of any toxic substances during service, or at end of life following disposal or recycling of the modified wood. If the modification is intended for improved resistance to biological deterioration, then the mode of action should be non-biocidal.

Different authors have used the term *chemical modification* with different meanings. Rowell (2005) defined chemical modification as a chemical reaction between some reactive part of wood and a simple single chemical reagent, with or without catalyst, to form a *covalent bond* between both. In that way, all simple chemical modification, which do not form *covalent bonds*, monomer impregnations that polymerize in situ but do not bond with the cell wall, polymer inclusions, coatings, heat modification, etc. will be excluded.

Hill (2006) presented a wider definition where the term *modified wood* involves the action of a chemical, biological or physical agent upon the material, resulting in a desired property enhancement during the service life of *modified wood*. From the literature and in the course of this work will be possible to check that, when some properties are improved, often others have deteriorated in different extend. The definition of chemical modification given by Hill (2006) will be followed. Two types of chemical modification with different active principles were used:

Cell wall reaction with resin based modification (DMDHEU and MMF); And lumen fill with TEOS and wax.

The mitigation about properties and performances should be done accordingly with integrating them in existing *design procedures* or by omitting modified wood from certain applications. For modified wood, the reference properties (physichal properties, MOE and MOR) are well established. Therefore, it is crucial to gain knowledge about how modified wood can be used in construction applications by taking the enhanced properties and the shortcomings / risks into account. The long-term performance *creep* and marine disposal resistance are the main topic of this work. Motivated by the reported positive effect of resin based and lumen fill modifications on hardness and reference physical properties, this study examined the influence of chemical impregnations on marine apllications and mechanical behaviour of Portuguese pinewood (*Pinus pinaster* Ait.).

1.1 Portuguese wood species and applications

The Portuguese forests, together with the reality of the European market, carried a strong competition with the forest resources from the different countries in the Northern Europe. The use of wood, on the construction industry in Portugal, faces strong competition with other building materials, as concrete, stone, steel, plastics, etc....

In Portugal the forest area covers 35% of the national territory, 3.1E6ha (app.). Maritime pine (*Pinus pinaster* Ait.), Blue Gum (*Eucalyptus globulus* Labill) and Cork (*Quercus suber* L.) are the most abundant species. The cork industry as well as furniture, paper, sawmill, carpentry, flooring, panels, etc..., provide 9% of employments, 10% of exportations and 4% of importations (IFN5 Report 2010).

Table 1 shows the wood species distribution in the Portuguese territory. In the Center and North of the country high expression of Maritime pine and Blue Gum species taking part and in the South mainland the Cork oak species takes place. These are the three most representative wood species, taking 75% of the forest area and also the largest economic interest.

In the total of the National Forest, Maritime Pine species has a significant commercial production, about $5.6m^{3}\cdot ha^{-1}\cdot year^{-1}$ according to Cruz and Souza (1999). It is the only sustainable natural source of wood supply to the construction industry. However, this wood has generally poor quality and low added value, due mainly:

- Tradition and culture, in terms of applications and end-use non-sustainable;

- Failure of the Portuguese industry to respond adequately to the requests, providing consistently material inappropriate to the requirements;
- Strong internal competition (demand) by pulp and paper industries, boards and other wood products (e.g. pallets);
- Increasing coniferous importation from others European countries, especially from the North.

Table 1. Species distribution in the Portuguese forest according DGRF (2010)

Wood species	Forest area [%]	Area [ha · 1E3]
Maritime pine, *Pinus pinaster* Ait.	27.0	885.0
Other conifers	5.0	155.0
Holmoak, *Quercus ilex*	13.0	413.0
Oaks, *Quercus acutissima, pyrenaica*	5.0	150.0
Chestnut, *Castanea sativa* Mill.	1.0	30.0
BlueGum, *Eucalyptus globulus* Labill	23.0	739.0
Cork Oak, *Quercus suber* L.	23.0	716.0
Other Dicotyledons	3.1	82.5

Portugal is the European country with the highest private forest area. The Portuguese wood-based industry has been facing some problems in the last years, arising particularly from the primary sector of activity. Low profitability, the rural-to-urban movements, poor management of ends forest lands and fires in the summer are the main causes to these problems.

Blue Gum wood has similar occupancy than pine species in the national territory, mostly of *Eucalyptus globulus* Labill species, is recent in Portugal, mid of 20th century, and coincides with the origin and growth of the paper industry.

In the last decades in Portugal, different studies have been undertaken, for untreated pinewood (Cruz et al. 1998; Cruz and Machado 2005), Blue Gum wood species (Santos 2009), modified wood with heat (Esteves 2006; Santos 2000) and furfurylated wood (Esteves et al. 2009), that follow the European and world trend.

1.2 Background

At the end of late twentieth century the demand of wood has increased (i.e. sawn wood and wood products). Wood is a promising material for the XXI century, to contribute positively to the environmental conservation and climate stability (Carvalho 1997). As a renewable material and a carbon sink (natural pickup of the main greenhouse gas, carbon dioxide), wood has a strong acceptance in the public opinion. In addition, wood requires *low energy* for being processed into finished products, have a good thermal performance and still have a low ratio strength-density for structural purposes (Cruz and Machado 2005). Moreover, nowadays the reuse and recycling are additional benefits as compared with others construction materials. However in the latter competition, important *shortcomings* of wood are its limited natural resistance to decay, flammability, short renovation intervals and low UV-stability when used in way inappropriately.

1.2.1 Maritime pine, the wood species and wood features

Pinus pinaster Ait. is an important softwood species of wood from Southern Europe, Portugal. It is naturally spread in the Mediterranean regions of France, Corsica, Spain, Italy and Sicily (subspecies *pinaster*) and in the Atlantic regions of Portugal, Spain and France (subspecies *atlantica*). In the last decades, this wood species was introduced with success into South Africa, New Zealand and Australia. In Portugal, it is the most important wood species with an occupation area above 775E3ha (Carvalho 1997).

Pinus pinaster Ait. is an evergreen wood species with 25 up to 40m height in adult tree. The crown is usually pyramidal / cone at young ages and round in adult trees. Well adapted to very temperate maritime climates, this wood species has characteristics of a pioneer species. It registers higher growth rates in low/medium altitudes (between sea level and 1.100m) in sites with 11-15°C as an average annual temperature and with high humidity and precipitation. In relation to *edaphic* conditions (physical and chemical conditions of the soil), it is a very tolerant species with preferences for light and sandy soils, and growing very well on acidic and poor soils (Alves 1982). The main natural enemies of the Maritime pine wood are: Fire, some fungi, wood beetle and the relation with water and sun as well as UV-stabilization (Cruz and Machado 2005).

Maritime pine wood is pale-yellow in the sapwood and reddish-brown in the heartwood part of the stem. The latter is clear distinct and in the transverse section the growth rings are clearly visible (EN NP 350-2). Some trees have straight-grained wood while others present spiral grain. The wood is *resinous* with a rather coarse and uneven texture, and a stripe figure (tangential section) due to the growth rings. The annual rings may present a widely variable thickness but are usually wider in the centre near the pith and thinner at the periphery. The width of the latewood tends to be constant (Carvalho 1997; Cruz et al. 1998). Growth rings show a clear contrast between early wood and latewood, mainly due to the dark thick-walled latewood cells. The *pith* is more or less circular with a considerable volume.

Maritime pine wood is classified as light or moderately heavy and moderately strong in a mechanical point of view (EN NP 4305). The main physical and mechanical properties are summarized in the Table 2.

Table 2. Average of the physical and mechanical properties of Maritime pinewood (EN NP 4305)

	Properties	Units
Physical		
	Density [kgm^{-3}] (at MC 12%)	530-600
	Total volumetric shrinkage [%]	14.0
	Total tangential shrinkage [%]	8.5
	Total radial shrinkage [%]	5.0
	Volumetric shrinkage coefficient [%]	0.6
	Fibre saturation point [%]	30.0
Mechanical		[Nmm^{-2}]
	Compression strength parallel to the grain	53.0
	Shearing strength	10.0
	Static bending strength	96.0
	Cleavage: Rupture force	4.0
	Tensile strength parallel to the grain	87.0
	Tensile strength perpendicular to the grain	3.0

The Portuguese pine wood (Maritime pine, as a commercial name) is a coniferous/resinous softwood easy to cut, although has a tendency to warp when logs with numerous knots were sawn (Carvalho 1997). Drying of wood is easy, often shows the risk of resin exudation as well as splits, dead, burned and unsound knots.

Pine has a nodes volume percentage ranging from 0.07% in the basis up to 1.95% in the top of the tree trunk, whereas the knots core range 28 up to 83% of the radius of the stem base and 70% of the height, respectively (Pinto 2004).

The sapwood is easy to impregnate by *hot* and *cold* immersion processes or using pressure. The heartwood is hard to impregnate (EN NP 350-2).

The *glueability* of the wood is easy and sustainable with adhesives vinyl or urea based, and has shown high performances in connections with metals parts, with nails and dowels (Branco and Cruz 2009).

Sapwood is clearly distinct from the heartwood part of the stem (classified as “g” according to EN NP 350-2). The shape of the stem has normally regular with defined contour.

According Knapic and Pereira (2005) heartwood starts to grow from the age of the 21 years old. However, according Pinto et al. (2004) heartwood starts to grow from the 13th years old, with a rate conversion soft/heartwood about 0.5 and 0.7 rings per year for trees aged below and above 55 years, respectively.

The heartwood of *Pinus pinaster* can follow the profile of the stem or present a maximum at 3.8m of height (Esteves 2001; Pinto et al. 2004; Knapic and Pereira 2005).

The tree rings are distinct and can range from thin (with 1mm) up to large width (with 9mm). Texture is moderately uneven or unequal, grain is coarse and the appearance is listed, designed by the growth layers and texture. The grain is normally right, but also can be coiled/spiralled (Carvalho 1997).

The pinewood has two types of resin channels, longitudinal and transversal. In the wood cross-section is possible to observe macroscopically, or with a magnifying glass (1:10), longitudinal channels that appear as small dots in the latewood. Although these channels may occur in the early-wood in the layers close to the pith (Carvalho 1997). In the lengthwise sectioning, channels appear as lines with a dark hue parallel to the grain. The channels are typically solitary, although groups of two can appeared.

1.3 Natural durability and degradation of Portuguese pine

From Roman historian, Pliny, the natural durability of certain wood species, in special the difference between sap- and heartwood, is well know in general to fungus, insects and marine borers (Zabel and Morell 1992). The natural durability of wood, set to its intrinsic resistance to destructive organisms, has high inter- and intra-specific variability, being always higher in heart- than in the sapwood part of the stem. It is commonly known that sapwood has low natural durability against fungi and insects, which is “classifications” only refer to the heartwood durability (Nunes and Valente 2007).

The European standard EN350-2 ranks the durability of wood to several xylophagous organisms on a scale with five levels for *fungus*, two for *coleopterans* and has three levels for *termites* and *marine borers*. According EN 350-2 the Portuguese softwood species (Maritime pine) has low up to medium durability to fungus and is susceptible to termite attack. The heartwood is hard to impregnate and the sapwood part of the stem is easy. If not adequately dried or else treated immediately after felling, sapwood will be attacked / colonised by blue staining fungi (Cruz et al. 1998).

Scots pine (*Pinus sylvestris*) is the most widely-used wood species in chemical and heat modifications. As EN 350 suggested similar features for both species of Pine, the Portuguese Maritime pine is expected to behave comparable to others softwood species like Scots pine in European countries and Southern yellow pine in USA.

Esteves and Pereira (2009) suggested that heat modification of Portuguese pinewood improved wood durability, increased the resistance to rot, except in contact with soil, and no significant effect was found to weathering, insects and termites. Surini et al. (2012) confirmed no improvement in durability against termites. Nunes et al. (2004) conducted tests of resistance to termites *Reticulitermes grassei* with Portuguese pine heat modified with oil bath (German method, Oil Heat Treatment) and concluded that the mortality of termites and mass loss were slightly higher in control specimens, although the differences were not significant.

1.4 Potential and limitations for industrial uses in solid wood products

Maritime pine wood is used as raw material in sawmill, plywood, particle board, fibre board, pulp and paper industries. In Portugal, the wood-based sector represents 9% of the total industrial Gross Values, 4% is coming from the pulp paper industry and 5% from the other wood-based industries. Sawmills consume around 70% of the produced Maritime pine (wood sawn). This wood species represents 88% of the volume of raw material consumed in these industries (CESE 1996).

Considering its strength, workability and easy treatability with preservatives, Maritime pine has the potential to be used in several products, including outdoors use.

It is currently used in structural components for roofs and floors, stair frames, prefabricated wood buildings or joinery and furniture. It has also been used in foundations, transmission poles, railway sleepers, scaffolding, fences and others elements to be applied in open environment or in ground contact. Although products for building construction have been the traditional end products of the sawmill industry, in the last 25years, the pallets industry has become the main production item in volume.

The wood has good workability if it is well seasoned and has few defects. It is readily easy to work with machinery and hand tools and allows a good finishing. It holds mechanical fasteners well, glues easily and can be given a good finish. Drying can be carried out rather easily, either by air-drying or by kiln drying. This wood species is sensitive to sap staining and mould growth, thereby it must be dried rapidly, though avoiding seasoning checks and distortion (EN NP 4305).

When compared with others pines, like Scots pine, Maritime pine wood is normally more resinous and when produced under conditions favourable to rapid growth is generally coarser, knottier and has a large proportion of sapwood (DSIR 1960).

For structural uses, knots, pith and associated juvenile wood are amongst the worst defects. Being a fast-growing species, Maritime pine is very sensitive to climatic changes which are very common in the moderate seasons of Southern Europe, with large and thin grown rings in raining and dry years. This increases wood heterogeneity especially concerning growth rings widths and anatomic element dimensions. Also, the stands of this wood species are frequently close to the sea, thereby exposed to frequent winds which increase the quantity of resin pockets, stem excentricity and reaction wood. Therefore, it is very important to make a careful selection of this wood, in accordance with the intended use. In Portugal, the structural wood of Maritime pine is classified according to visual grading into two main grades: Grade E (structures) is suitable for general purposes; Grade EE (special for structures) is the higher strength grade. This classification is based on the Portuguese standard EN NP 4305 (2001) and it is compatible with the Eurocode V (EN 1995:1-1).

1.5 Aims

The multidisciplinary research carried out in this work focuses on the interaction between characterization properties of material and its biological performance. The *overall* aim was to increase the knowledge on Maritime pine behaviour through the study of the ***Technological Improvement of Portuguese Pinewood by Chemical Modification***. The study was performed by a comparative analysis.

This work support the role of wood in building applications in order to enable wood to compete with others conctruction materials such as metals, plastics, concrete or stone. It is crucial to provide wood with well-defined and predictable engineering properties. The chemical modification, for instance, moves in to overcome many *drawbacks* to the use of softwood. High-value was added in to the material able to be use in high hazard environment (3 up to 5), set aside for tropical hardwoods. Characterization, understanding and modelling the physical and mechanical behaviour of wood were the main topics as well.

As *specific* aims, this study was to evaluate the main references properties (physical and mechanical). Special focus to the bending creep behaviour as well as the durability against marine borers were given. To pursuit those goals, this work can be set in two parts.

- In the *first part*, a large variety of material properties were studied, physical and mechanical properties, and their interactions. A particular attention on the biological marine resistance was taken. The role of hardness, shape of specimens as well as the chemical effect on the marine resistance were taken into account. The marine part of the research is an extension of the project running at the *Wood Biology and Wood Products* department of the Georg-August-Universität (Göttingen, Germany). The project nº 22004407 was supported financially by the Agency for Renewable Resources, *Fachagentur Nachwachsende Rohstoff*. The preparations of specimens, modifications and determination of some reference mechanical properties were performed in Germany. Afterwards, creep tests and the marine exposition running in temperate waters (open sea at Leixões Harbour, Porto) were performed in Portugal.

The standard EN 275 (1992) suggests the X-ray technique to assess the level of destruction on the wood marine exposed. To see if some suggestion could result to the standard, the non-destructive testing techniques for wood damage evaluation by marine borers was considered. However, the delay of signs of attack over the first twelve months of exposure in the open sea led to drop this line of the study and drove to a new topic.

- In the *second part* of the work, a creep study was carried out. Types of principle active and levels of modification together with stress levels under different environments were evaluated.

Four chemical modifications were chosen: 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), N-methylol melamine (MMF), tetra-alkoxysilane (TEOS) and wax. A total of 1350 specimens in different physical and mechanical properties and 299 specimens in the creep experiments were studied.

As summary the *Technological improvement of Portuguese pinewood by chemical modification* was studied in different ways. Marine resistance, physical and mechanical properties were the main research conducted (creep included). However, all experimental work is focused in a single softwood species with wide growth in Portugal, Maritime pine (*Pinus pinaster* Ait.). The work was carried out at *Wood Biology and Wood Products* department of the *Georg-August-Universität* (Göttingen, Germany) and in *Polytechnic of Porto, School of Engineering* (Porto, Portugal).

1.6 Outline

This work is based on the experimental work and is presented in five sections. One overview to the presented work with a condensed idea of the Portuguese forest *in general* and Portuguese pinewood *in particular* is made in the chapter 1 INTRODUCTION. A background survey about relevant research on the chemical modification (DMDHEU, MMF, TEOS and wax) applied in others soft wood species is presented in the chapter 2 LITERATURE. All features of wood material and methodology followed in this specific work research is presented in the chapter 3 MATERIALS AND METHODS.

Partials results are presented progressively. Discussions are made on the running text of the chapter 4 RESULTS AND DISCUSSION, set at different topics (Physical properties; Mechanical properties;Creep behaviour with Stress level (SL) effect and Mechano-sorptive effect as well as the Performance of wood against to marine borers). General conclusions, references consulted and new ways to explore in further researches are presented in the chapter 5 CONCLUDING REMARKS.

1.7 Original features

The starting point for this work was the good relationship with the moisture and the hardness increasing in the modified wood. Both arguments would be the *touchstone* to meet the improvements on the long-term mechanical properties and marine borer performances.

The systematic comparison between *un*- and modified wood will make a contributes with various new findings to the scientific field of wood research.

- Mechanical and physical properties in flawless specimens of Portuguese pinewood.
- Primary creep behaviour at indoor conditions under different stress levels.
- The mechano-sorptive behaviour under non-symmetrical moistening.
- The contributions of shape of specimens to the marine borers resistance, in open sea field.
- The contributions of hardness to the marine borers resistance.
- The effect of chemical toxicity in the marine borers resistance.

The correlations between properties of wood found in the literature are reported for unmodified and modified wood.

Reference properties of Portuguese pinewood led to fit new performances in different new trials. Then, moderate and significant correlations between mechanical properties of wood material and creep were confirmed for unmodified pinewood as well as similar correlations were *expected* for modified wood. Bending creep tests were carried out, according ENV 1156 and EN NP 408. Small scale 1:10 specimens was used where the homogeneous modification at the cross section was considered. This approach will support other results with structural size 1:1 where uneven modification on the cross section was found. Furthermore, this study deals the compliance creep curves and quantified the distribution of different types of curves between un- and modified wood. The primary and visco-elastic creep (under the mechano-sorptive behaviour) had never been done for these modifications and species.

For the Portuguese pinewood chemically modified, all the results are original as well as its marine borers performance in open sea field with temperate waters (Leixões, Portugal).

2 LITERATURE

Kollmann and Cotê (1968) is the most known and complete one of reference for unmodified wood. However, recent history took new challenges in the wood research: Pressure over deforestation and environmental restrictions in using toxic chemicals led to the demand for eco-efficient modification in the chemical wood industry, where Rowell (1983) and Hill (2006) are the main references.

2.1 The components of the wood material and material properties

The source of strength in solid wood is the wood fibre. The chemical components of wood that are responsible for mechanical properties can be viewed from three levels: *Macroscopic* (cellular), *microscopic* (cell wall) and *molecular* (polymeric). The cell and the cell wall structure, as well as the micro-morphology of the cell wall have been described by e.g. Kollmann and Cotê (1968), Bodig and Jayne (1982), Dinwoodie (1989) and Rowell et al. (2005). The cell wall polymers and their reactive hydroxyl groups are responsible for most physical and chemical properties of wood.

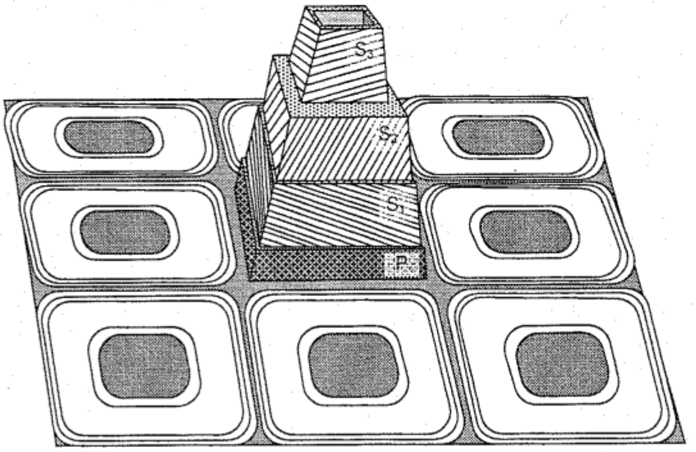


Figure 1. Sketch of the layers of a wooden cell wall (Epmeier 2006)

As a natural polymer composite, wood is mainly constituted of *two* macromolecular components, *lignin* (26-34%) and *carbohydrates* (65-75%). The carbohydrates can be divided into cellulose (40-45%) and hemicellulose (25-35%). In addition, extractives are present (0-7,5%) (Kollmann and Côté 1968; Dinwoodie 1989). Lignin, cellulose and hemicelluloses are distributed throughout the cell wall. Most of the wood *carbohydrate* is in the massive secondary walls, particularly in the S_2 layer, for Maritime pine 80% (app.). Most of the *lignin* is located in the secondary cell wall. The remaining portion of lignin can be found as bounding agent in the middle lamella and in the cell corners, cementing together the individual cells in wood (Kollmann and Côté 1968; Dinwoodie 1989; Rowell et al. 2005).

The mechanical properties change with modification of chemical environment in the cell wall matrix, e.g. with water addition. It deals with stress/strain relationship and is simply a function of the chemical bond strength. At the *molecular* level, strength is related to both covalent and hydrogen intra-polymer bonds. At *microscopic* level, strength is related to both covalent and hydrogen inter-polymer bonds and cell wall layer bonds. At the *macroscopic* level, strength is related to fibre-to-fibre bonding with the middle lamella acting as adhesive. Below proportional stress/strain limit, individual cells (macroscopic) and individual cell wall layers (microscopic) are distorting, hydrogen bonds between adjacent microfibrils (microscopic) are breaking and reforming, while hydrogen bonds and within individual polymer chains (molecular) are breaking, sliding and reforming. Beyond proportional *limit,* covalent *bond rupture* and permanent *distortion* at all three structural levels occur (Winandy and Rowell 2005).

It is generally accepted that crystalline cellulose is one of the responsables for tensile strength in the wood fibre because of its high degree of polymerization and linear orientation. The crystalline cellulose forms the *fibre* constituent, whereas the amorphous cellulose, hemicelluloses and lignin form the *matrix* for the crystalline cellulose and increase the packing density of the cell wall. The proportions of fibre and matrix are roughly 35:65 (Dinwoodie 1989). Lignin does not only hold fibres together, but also holds cellulose molecules together within the fibre cell wall. The physical and chemical properties of cellulose, hemicelluloses and lignin have a large contribution in the chemistry of strength.

Cellulose is a glucan polymer consisting of linear chains of sugar units. It is insoluble in most solvents and is difficult to isolate from wood. About 60 up to 75% of the cellulose in wood is crystalline native cellulose (Dinwoodie 1989; Rowell et al. 2005). The hydroxyl groups, in the crystalline region, are responsible for intermolecular bonding, whereas the hydroxyl groups in the amorphous region result in hydrogen bonding to water molecules. The crystalline cellulose influences reactivity by controlling the access of reagents or enzymes to functional groups and chemical bonds within the crystalline regions. They also interfere with the changes in geometry, which are required for the transition states of various reactions. The amorphous regions of the cellulose are not subject to these restrictions (Wiedenhoeft and Miller 2005).

Hemicelluloses are mixtures of polysaccharides of which some are branched. Hemicelluloses have a much low molecular weight than cellulose and they are soluble in *alkali* and hydrolysed by *acids*. Lignin is a poly-phenolic substance consisting of an irregular array of phenyl propane units (Kollmann and Côté 1968). Lignin is highly branched. It can be isolated by several methods.

The lumens in wood can be regarded as a bulk storage reservoir for chemical reactants, which can be used to modify the cell wall polymers (Rowell 2005).

Cellulose is an unbranched, rigid chain, linear polymer composed of sugar units. The greater the length of the polymeric chain, the greater is the tensile strength of the unit cell, thus the greater the strength of the wood. Hemicelluloses consist of various elementary sugar units. They have linear chain backbones that are highly branched and have a low degree of polymerisation than cellulose. Lignin is a hydrophobic poly-phenolic substance that surrounds and encrusts the carbohydrate complexes (Kollmann and Côté 1968).

Lignin seems to be responsible for part of the stiffness of wood and it is most chemically complex polymer of the wood structure. It consists of highly organised three-dimensional phenolic polymers and the last hydrophilic component of the wood cell. Lignin has the important function of protecting the hydrophilic amorphous cellulose and the hemicelluloses from water, which are mechanically weak when wet. Wood strength is due in part to lignin’s ability to limit the access of water to the carbohydrate components (Kollmann and Côté 1968; Wiedenhoeft and Miller 2005).

2.2 Modification of wood

It is generally accepted that, the *wood modification* have been developed to achieve high durability and high dimension stability of wood. The biological decay (face to attacks by bacteria, fungi, termites and marine borers) vary between the wood species. Despite many standard procedures have been established, for assessing the durability in general and the marine performance in particular, the problem is still quite complex. Normally, different variables are involved: Extractives content, hardness and the constitution of wood by itself. The hydroxyl groups play a role in to the degradation process. Inactivation of those groups reduces the moisture sorption and thus inhibits decay process for which moisture is needed.

Modification performed by *heat* or *impregnation*, with an appropriate agent and a subsequent *in situ* reaction, aims enhancing various wood properties such as durability, moisture sorption, dimensional stability, strength and hardness (Rowell 1983; Kumar 1994; Hill 2006). In addition, it imparts stability towards UV-radiation, improvement of weathering performance and flammability reduction (Xie et al. 2005; Wang et al. 2007).

The possibility to turn fast-growing softwood into wood material able to replace tropical hard wood species with similar high performances (dimension stability and natural durability) is one of the main goal of the modified wood (van Acker and Jones 2002).

Chemical modification of wood will change the wood material and help to overcome one or more of its shortcomings (Hill 2006). It can be *defined* as application of a process (with heat or any chemical) to promote any action between some reactive part of a wood component and a chemical reagent, use or not catalyst that forms a covalent bond between two wood components or can alters the properties of the wood material.

The most abundant reactive chemical sites in wood are the *hydroxyl groups* on cellulose, hemicelluloses and lignin (Rowell 1996). A chemical *modification aims* at the improvement of wood properties, often with regard to decay resistance, by altering the basic chemistry of the cell wall components. The hydroxyl groups take the main contribution, as they are responsible for dimensional movement and biological degradation. Inactivation of those groups reduces the moisture sorption and thus inhibits microbial decay for which moisture is needed. A suitable modifying agent should penetrate the cell wall and react with the available hydroxyl groups in the cell wall polymer, forming stable covalent bonds (Kumar 1994).

Theoretically, any type of chemical modification can be assigned to a combination of the principles at *cellular* level and at *molecular* level. Figure 2 shows the modification models at *cellular* level.

- *Modification of cell* wall with no deposit of chemical in lumen, as shows in Figure 2a;
- *Deposit* of chemical on the surface of the lumen, cell wall is not modified, Figure 2b;
- *Partial or total filling* of the lumen, the cell wall is not modified, Figure 2c.

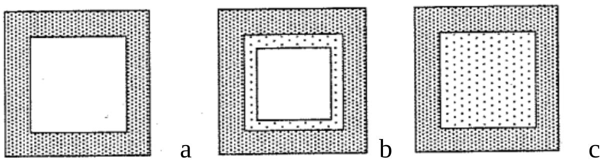


Figure 2. Model of chemical modification of wood at *cellular* level as suggested by Norimoto et al. (1992), cross section of a single wood cell, cell wall and lumen

Figure 3 shows the modifications model at *molecular* level. In the Figure 3a the *chain* indicated by (a) refers to the crystalline core of a cellulose micro-fibril, but be understood in a wider definition (Norimoto et al. 1992). The *hydroxyl group* is illustrated by the letter (b). Neighbouring chains are linked to each other by water-reactive zone (c) as *hydrogen bond*.

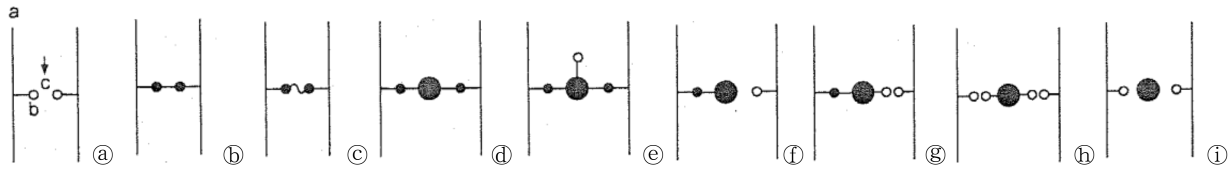


Figure 3. Model of chemical modification of wood at *molecular* level as suggested by Norimoto et al. (1992); Hydroxyl group accessible for hydrogen bonding (o- empty circle); Hydroxyl group with hydrogen substituted by covalent bond (• small filled circles); Strong molecular binding (–); Bulking effect by large molecules (● large filled circle); Weak hydrogen bonding (oo)

The initial model in Figure 3a can be modified according to eight patterns (b up to i). In patterns a and b, *cross-linking* occurs without the bulking effect by using molecules of low molecular weight that link on two sides with hydroxyl groups. In pattern c and d, both *cross-linking* and *bulking effect* occur. The remaining four cases show the *bulking effect* without cross-linking (e, f, g and h). In pattern e and f, the reactant establishes a stable bond on one side. In patterns h and i, the bulking agent does not establish any stable linkage with the constituents.

2.3 Modification methods used in this study

Table 3 shows the methods of modification / treatments used and their classification according to the model above (in Figure 2 and Figure 3). Based on the initial model (Figure 3a), *cross-linking* (Figure 3b and c) and *bulking effect* (Figure 3f, g, h and i), two main reactions take place, independently of each other or in combination (Figure 3d and e). Cross-linking is the establishing of a molecular bond between two adjacent surfaces. *Bulking effect* is the filling of cavities in the cell wall as well as in the cell wall lumen, in some cases along with replacing the water molecules by larger molecules. As a result of bulking, the bonded adduct occupies space within the cell wall/lumen, and consequently less volume is available for water. Bulking modification tend to reduce the swelling and shrinkage of the wood. They might have a beneficial effect on the long-term sorption behaviour.

Table 3. Classification of the modification according the model suggested by Norimoto et al. (1992)

Modification	Active principle	Types	Assignments
Unmodified wood	---	Figure 3a)	0, *ctrl*
1,3-dimethylol-4,5-dihydroxyethyleneurea	Cell wall reaction	Figure 2a) and Figure 3d) f)	DMDHEU
Methylated melamine formaldehyde	Cell wall reaction	Figure 2a) and Figure 3i)	MMF
Tetra-alkoxysilane	Lumen fill	Figure 2b) and Figure 3i)	TEOS
Wax	Lumen fill	Figure 2c) and Figure 3i)	W

All modification methods chosen for this work are being newly investigated in the basic physical properties as well as in marine performances with the Portuguese pinewood species (*Pinus Pinaster* Ait.).

2.3.1 1,3-dimethylol-4,5-dihydroxy ethylene urea resin (DMDHEU)

Dimethylol-dihydroxy-ethylene urea (DMDHEU) is a compound containing N-methylol (Krause et al. 2004; Xie 2006). It is extensively used in textile industry as durable press coatings (Petersen 1983). DMDHEU has been used to improve wood properties since the 80s (Rowell 1983). Nicholas and Williams (1987) have revealed that pine modified with 10-20% of DMDHEU aqueous solutions and $AlCl_3$ or tartaric acid as a catalyst achieves a 60% of ASE. Militz (1993) with DMDHEU modified Beech wood and several catalysts has shown that acid (citric or tartaric) catalyst improves resin curing and the curing temperature of 100ºC is needed.

DMDHEU is one of the most studied methods of chemical modification for wood as thermosetting resin. It is known for its strong reduction in the shrinking / swelling effect and EMC, thereby reducing the hydrophilic nature of wood and biological durability (Krause 2006; Pfeffer 2011; Bollmus 2011). Its dimensional stability was partly induced by the permanent swelling (bulking effect).

From the literature and in a point of view of durability, it is well known the high performance of modified wood against to termites (Schaffert et al. 2006; Militz et al. 2011), to different fungus (Videlov 1989; Sudiyanni et al. 1996; Yusuf 1996; Dieste et al. 2008b; Mai et al. 2010; Pfeffer and Militz 2010; Pfeffer et al. 2012b), weathering (Xie et al. 2007a; Xie et al. 2008; Dieste et al. 2009; Pfeffer et al. 2012a) and marine borers, *in situ* and in the laboratory conditions (Borges et al. 2005; Klüppel et al. 2010). Wood specimens modified with DMDHEU 1,3M after 9months outside exposure have shown a surface discolouration caused by mould and staining fungi while there were no signs of decay and the fungal penetration into the wood tissue was significantly reduced (Pfeffer et al. 2012b).

It is also pointed out that stiffness did not change significantly. However, bending strength decreased significantly with the curing temperature and embrittlement effect took place (Nicholas and Williams 1987; Evans and Schmalzl 1989; Rowell 1996; Xie et al. 2007b; Mai et al. 2007; Dieste et al. 2008a; Bollmus et al. 2010).

For solid wood, the tendency towards deformation (bow, crook and twist) under varying moisture conditions is reduced. These features make DMDHEU modification attractive for application on high-value panels and joinery products.

2.3.2 Methylated melamine formaldehyde resin (MMF)

Melamine resin has several advantageous properties, such as hardness, scratch resistance, low inflammability and UV-resistance (Hagstrand 1999 in Epmeier 2006). Melamine-impregnated papers mimicking the optical appearance of wood are used for the production of highly wear-resistant laminate flooring.

Melamine is added to urea-formaldehyde resins in the modification wood, to enhance the resistances of glue bonds to hydrolysis, i.e, improves the resistance of products to humidity, water and weather (Dunky 1998 in Gindl et al. 2003). Melamine-based adhesives are colourless and therefore preferred to brownish phenolic resins in the production of glue-laminated beams, when visible glue-lines are not intended.

MMF is a thermosetting resin. According to the classification in Table 3, modification with MMF leads to bulk-effect without cross-linking. The cell wall itself can be entailed in two possible ways depending on resin average molecular weight: Modified (and more or less swollen) with or without resin deposit in the lumen, or modified with resin deposit in the lumen. The mechanisms of stabilization of the wooden cell wall and biological protection have been described as physical bulking and blocking of hydroxyls by the cured resin according to Rapp et al. (2000). Deka et al. (2002) reported that the wood is *fully bulked* at weight gain levels of about 30%.

The effect of this modification on physical and mechanical properties of wood is roughly similar to the effect of other resins, DMDHEU, phenol and formaldehyde (Norimoto et al. 1992; Rowell et al. 2005). However, unexpected results appear sometimes, with EMC higher than the unmodified wood (Epmeier et al. 2004).

In the zero-span tensile strength, veneers did not show any loss in Mai et al. (2007). Transverse compression strength increased significantly (Gindl et al. 2003), enhanced hardness (Gindl et al. 2004; Krause et al. 2004), the MOE did not change (Krause 2006) and decreased MOR significantly, specially owing to the embrittlement effect for high concentration (Rowell 1996). In general, enhance the homogeneity of wood properties and significantly reduce MSE on bending creep (Epmeier and Kliger 2005).

2.3.3 Tetra-alkoxy silane (TEOS)

Silanes are known as modification agents in the plastics, textile, building and paper industries. They are used for hydrophobation of ceramics, scratch resistant surfaces, soil proofing and antigraffiti coatings or as adhesion promoters between organic and inorganic materials (Donath 2004; Pfeffer 2011).

In general, silanes have a high potential for wood modification because of their high diversity of chemicals. Different types of silanes were investigated in earlier studies. A review of different silicones and silicone compounds, which has been used for wood modification, was done by Mai and Militz (2004a; 2004b). Silane systems such as ethoxy groups containing TEOS and alky-functional groups containing MTES and PTEO silane systems, amino-functional siloxanes were tested. Depending on the siloxane system, different properties of modified wood are influenced, such as flammability or fire retardance, bulking, scratch resistant on the surfaces, durability against to brown and white rot and water uptake (Saka et al. 1992; Ogiso and Saka 1993; Goethals and Stevens 1994; Donath 2004). Modified specimens with silica incorporation in the cell wall showed a significant resistance against termite *Reticulitermes speratus* attack when compared to unmodified Spruce wood (Donath 2004). However, the active profile of silanes can be described as having a low impact on properties such as EMC and dimensional stability as well as no reduction of cracks formation during weathering (Donath et al. 2006; Donath et al. 2007).

Wood specimens modified with TEOS after 9months outside exposure has shown a surface discolouration caused by *mould* and *staining* fungi while there were no significant signs of decay after 24months without ground contact (Pfeffer et al. 2012a; Pfeffer et al. 2012b).

2.3.4 Wax (WA, WL)

Pure wax has been used as bonding agent for colorants, conservation processes such as mummification or ship building, with the main role as water repellents due to their hydrophobic properties and to improve the hardness. In the wood impregnation with wax, sapwood part of the Pine is easy to impregnate with liquid wax, hot melted, via the radial surface where the ray tracheids are important conductors (Scholz et al. 2010d).

The presence of wax in the wood cavities (lumen) causes a density increase, enhances the mechanical properties slightly, mainly MOR and IBS, as well as decrease the uptake of water (Evans et al. 2009; Scholz et al. 2009; Scholz et al. 2010a; Scholz et al. 2010b; Scholz et al. 2010c).

Scholz et al. (2010b) with Scots pine sapwood wax-impregnated found good performances (durable classification) against three termite species in laboratory and Mediterranean field conditions.

Evans et al. (2009) and Scholz et al. (2009) had suggested that modified wood with wax could be suited for outdoor uses (hazard class 3). Weathering results after two years outside exposure showed less and smaller cracks than *native controls* and these cracks are situated on the wax wood surface compared to unmodified wood. Similar behaviour was observed with blue-stain fungi. In general, neither the wax hydrophobation effect nor the physical presence of the congealed wax deposits could impede blue stain fungal growth on the wood surface (Scholz et al. 2011).

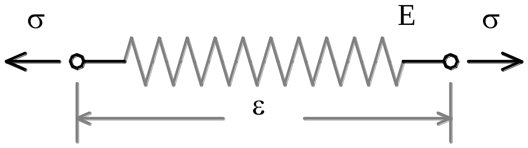
2.4 Creep

2.4.1 The phenomenon

The wood material under a permanent load has a deformation that does not reach immediately a stable point. When the load is removed, there is a recovery that is not immediately complete, but is approaching to the initial condition as time depending. This behaviour is typical of the visco-elastic nature of wood material. What was said earlier is true only for low stress level, under the proportionality limits.

A simplified model is necessary for engineering purposes, in a way to separate in different components, related or not in the model. To understand the real mechanical behaviour of the wood is demanded the combination of several simplified models.

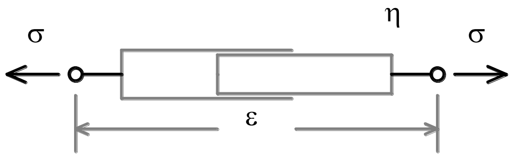
Basic uni-axial models studied by several authors exist, starting at linear elastic behaviour and added successively the concepts of viscous and plastic behaviour. Unidirectional linear elastic behaviour corresponds to the simplest expression of the equation of Hook Law.



$$\sigma_{xyz} = E_{xyz} \, . \, \varepsilon_{xyz}$$

Figure 4. Model with elastic behaviour, σ_{xyz} and ε_{xyz} they are, stress and unitary deformations for each one of the main direction, E_{xyz} means the proportionality constant for the corresponding direction, which conventionally represents E or MOE

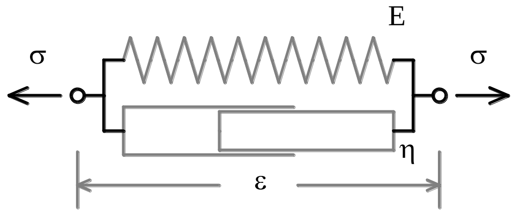
But it may happen that, at applied constant stress, deformation is time dependent, related by a constant η_{xyz}, which means the material viscosity. The physical model is the traditional dashpot. In this model it is clear that the material behaviour to the outside request depends on the speed of the external stimulation.



$$\sigma_{xyz} = \eta_{xyz} \frac{d\varepsilon_{xyz}}{dt}$$

Figure 5. Model with only viscous behaviour, σ_{xyz} and ε_{xyz} they are, stress and unitary strain for each one of the main directions η_{xyz} means the material viscosity for the corresponding direction

The combination of these two models, linear and viscous models (Figure 4 and Figure 5), answers to the behaviour of the wood in creep related to the visco-elastic deformation. It is designated Kelvin-Voigt model, in honour of both researchers who have studied it. This model is represented with a set up comprising a dashpot and a spring *in parallel* in Figure 6. The answer to an exterior solicitation is given by the sum of the elastic spring component and the viscous behaviour of the dashpot (damping effect).

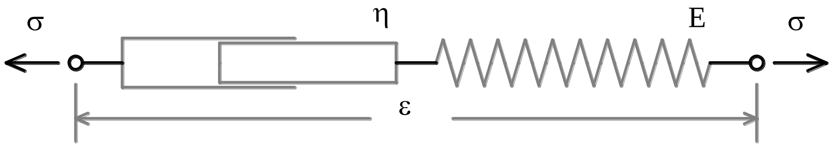


$$\sigma_{(t)} = E \cdot \varepsilon_{(t)} + \eta \cdot \frac{d\varepsilon_{(t)}}{dt}$$

Figure 6. Kelvin-Voigt model for visco-elastic behaviour (Hunt 2004)

The *Kelvin-Voigt* model with damping constant is appropriate to predict the creep behaviour, but does not give a satisfactory answer to represent the stress relaxation (Santos 2009). The Kelvin-Voigt model represents that the deformations are time dependent by the influence of viscosity (η). The latter can be determined experimentally and represent the ratio of increasing of strain of each material.

The *Maxwell* model is another model to represent the material visco-elasticity behaviour. This model corresponds to connect a spring and a dashpot in serie, see Figure 7. Under this model, if the material is put under a constant *strain*, the stress gradually relax. When the material is put under a constant *stress*, the strain has two components: *First*, an elastic component occurs instantaneously, corresponding to the spring and relaxes immediately upon release of the stress; The *second* is a viscous component that grows with time as long as the stress is applied. The Maxwell model predicts that stress decays exponentially with time, which is accurate for most polymers. One limitation of this model is that it does not predict creep accurately. The Maxwell model for creep under constant-stress conditions postulates that strain will increase linearly with time. However, for wood material the strain rate to be decreasing with time (Santos 2009).



$$\frac{d\varepsilon_{(t)}}{dt} = \frac{\sigma_{(t)}}{\eta_{(t)}} + \frac{1}{E} \cdot \frac{d\sigma_{(t)}}{dt}$$

Figure 7. Maxwell model for visco-elastic behaviour (Zhuoping 2005)

From this brief analysis about some models to represent the creep phenomenon, it is unanimous that the most complete is the *Burger* model presented in Figure 8. It allows embrace the full complexity of the actual behaviour of wood (Bodig and Jayne 1982; Lee et al. 2004; Epmeier 2006). A generalized *Burgers* model has one *Maxwell* unit and one or multiple Kelvin units connected in serie.

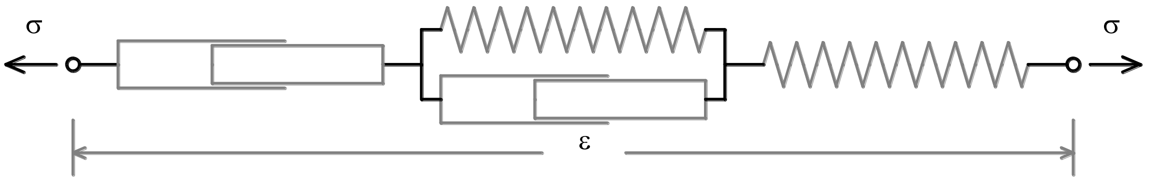


Figure 8. Burger model for visco-plastic, visco-elastic and linear behaviour

Recently Vidal-Sallé and Chassangne (2007) defined models for creep behaviour. However, due to the extreme complexity of the structural phenomenon and anisotropy of wood material (wood variability), they recognized that the model did not include yet the viscous plastic deformation, *not recoverable*. The *Vidal-Sallé* model was developed for applications in finite element code running with ABAQUS Standard® software through UMAT subroutine. While most studies published are seeking for models for forecasting deformation.

Zihui et al. (2006) conducted a study that included the prediction behaviour at unloading period. Although this study has been conducted for industrial materials, fibre composites with epoxy glue, one of the interesting outcome is that deformation forecasting after unloading is much more difficult and results are more scattered than in the loads period.

The *Burgers* model divides the creep strain (ε) of a polymeric material into *three* parts: *Instantaneous* deformation resulting from the Maxwell spring; *Visco-elastic* deformation resulting from Kelvin units; And *Viscous* deformation resulting from the Maxwell dashpot, Figure 9. All these can be presented by the following mathematical equation:

$$\varepsilon_{(t)} = \frac{\sigma_{(t)}}{E_e} + \frac{\sigma}{E_{de}} \cdot \left[1 - e^{-\frac{E_{de}}{\eta_{de}}t}\right] + \frac{\sigma_{(t)}}{\eta_M} t \qquad (1)$$

Where ε(t) is the creep strain, σ is the stress level, t is the time, E_e and E_{de} are the elastic modulus of the springs and η_M and η_{de} are the viscosities of the dashpot. The parameters E_e, E_{de}, η_{de} and η_M can be obtained by fitting experimental data with the mathematical equation and be used for characterization of creep properties. The *first* term is a constant and does not change with time, the *second* term contributes to the early stage of creep, but reaches the maximum quickly; And the *third* and last term determines the long-term creep tend with a constant creep rate.

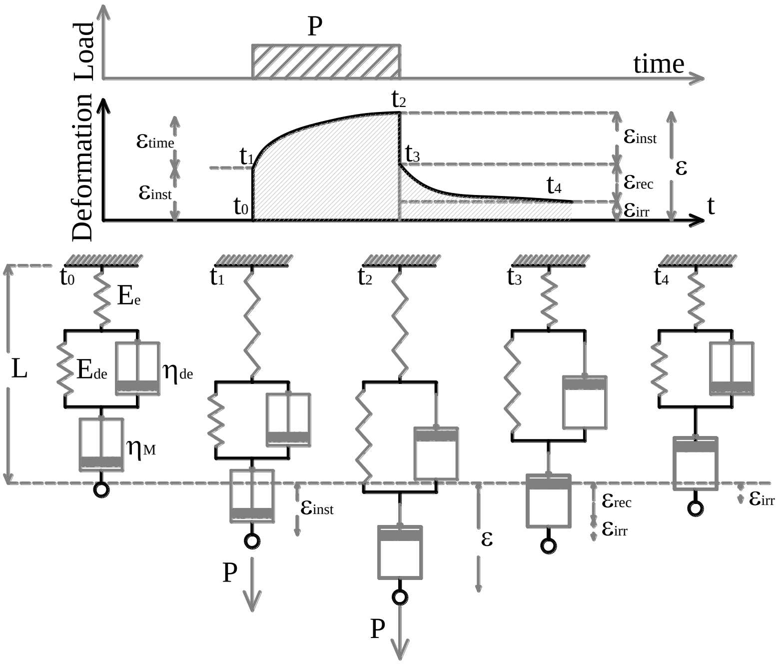


Figure 9. *Burger* model with four-element body diagram of creep behaviour, adapted from Lee et al. (2004) and Morlier (1994): Deformation and its strain components in dependence on load and time, with constant environment

Based on the Burgers model, the creep rate of visco-elastic material can be obtained by taking derivative for eq. (1) as follows:

$$\frac{d\varepsilon_{(t)}}{dt} = \frac{\sigma}{\eta_{de}} \cdot e^{-\frac{E_{de}}{\eta_{de}}t} + \frac{\sigma}{\eta_M} \tag{2}$$

Besides the Burgers model, several empirical models were proposed to simulate creep curves of polymeric material. One of the most commonly used empirical models is the *power function* model PFM (Epmeier 2006; Jiang et al. 2007; Santos 2009; Xu 2009):

$$\varepsilon_{(t)} = \beta_0 + \beta_1 \cdot t^{\beta_2} \tag{3}$$

Where β_0 is the initial strain and can be calculated from the MOE and the size of the specimens for any given load, according to the material behaviour. The *second* term grows with time approaching an asymptotic limit, where $\beta_1 \, . \, t^{\beta 2}$ is the creep strain. The coefficient β_1 describes the *slope* of the relative creep curve dependent on stress and β_2 is the power factor that modifies the influence of time and independent of stress. This PFM is design to fit primary creep and does not include a term that would indicate the possibility of accelerated creep to rupture.

A simpler 2-parameters PFM was also proposed (assigned as relative creep percent) and has been shown to be applicable for the creep modelling (Clouser 1959; Hoyle et al. 1985; Tajvidi et al. 2005).

$$\varepsilon_{(t)} = \beta_1 \cdot t^{\beta_2} \quad (4)$$

Although much works have been done on modelling of creep behaviour of polymeric materials, no study has been reported on modelling of the recovery process, which is important for applications under non-constant stress. Understanding of the recovery process can also advance the modelling and prediction of creep behaviour.

2.4.2 Creep behaviour

Creep study is a classical research problem of wood material rheology. Creep is a phenomenon with time-dependent deformation, in a situation where the intensity of load remains constant over time. Like any other material, wood subjected to stress will respond with instantaneous strain ε_{inst}, which is elastic and fully recoverable. If the stress is maintained for longer, the wood will respond additionally with time-dependent strain ε_{time}, wood creep. This time dependent strain ε_{time} consists of a delayed-elastic component ε_{rec} recoverable and a non-recoverable viscous components ε_{irr}. The time-dependent component is also referred to as the creep component ε_c (Hoffmeyer 1990). The total strain ε thereby consists of three components.

$$\varepsilon = \varepsilon_{inst} + \varepsilon_{time} = \varepsilon_{inst} + (\varepsilon_{rec} + \varepsilon_{irr}) \quad (5)$$

The last equation is valid for a *constant load* under *constant environmental* conditions, such as T and RH. If the load, T or RH is varied, supplementary strain components have to be taken into account. For cycling RH environment, for instance, two more components need to be added to the time-dependent strain (or creep component): The mechano-sorptive strain ε_{ms} and the free swelling-shrinkage strain ε_s. The total strain ε thereby depends of five components, as eq. (6). Both components, ε_{ms} and ε_s, are considered to be fully recoverable and can be quantified individually.

$$\varepsilon = \varepsilon_{inst} + \varepsilon_{rec} + \varepsilon_{irr} + \varepsilon_{ms} + \varepsilon_s \quad (6)$$

In this study, specimens deformation subjected in bending was investigated, i.e. the primary loading direction is along the grain and the free swelling-shrinkage strain could be ignored (Martensson 1994; Martensson 2003). For practical reasons, the components of ε_{rec}, ε_{irr} and ε_{ms} are added up to produce just one component, the creep component ε_c. The creep component is approximately independent of stress level below certain stress limits for unmodified wood, which are dependent on MC, temperature and duration test (Clouser 1959; Hoyle et al. 1985). *Below* these limits, creep decelerates. *Above* these limits, creep is stationary or accelerates. As wood is a cross-linked polymer, stationary creep cannot occur and accelerated creep is a result of a structural change process (van der Put 1989), e.g. crack propagation and fatigue. Consequently, the creep component is always non-linear with time. This non linear behaviour is partly attributed to structural changes induced by factors such as due to the changing RH that results in crystallisation and may lead to the stiffening, producing *repeated stress* a decrease in hysteresis and an *increase in the* MOE (van der Put 1989). The increase in the MOE may be one reason for the phenomenon that the recovery after unloading may be even larger than the initial elastic deformation.

2.4.3 The mechano-sorptive part of the creep (MSE)

MSE is usually investigated by applying a *simultaneous loading* and *changes* of wood moisture content. This procedure allowed accelerating the deformation of a bending horizontal beam. The decision to pursuit the comparative study between un- and modified wood under *assimetric conditions* of moistening was settled in *two* main reasons, both are described as follows:

- The *first* is related to the enhancement of mechanical properties imparted by chemical modification. The cell wall reaction modification (with DMDHEU and MMF resin), that had a good relation with moistening (Pfeffer 2011), have shown significant increasing on the compression strength and decreased in the tensile strength (Bollmus et al. 2010).

- The *second* is a large number of practical applications. Bearing elements working in the so-called semi-open space, condensed water vapour falling on wooden materials and leaking roofs leading to seepage on rafter framing.

The mechano-sorptive phenomena and creep are strongly associated to each other. However, while the expression *creep* implies a time dependency, the MSE is not necessarily time dependent alone but depends on several variables, like: Applied stress, amount of moisture change and parameters of previous hygro-mechanical loading history (Grossman 1976; Mohager 1987; Hoffmeyer and Davidson 1989; Martensson 1994; Morlier 1994; Ying-cheng and Feng-hu 2007). Creep rate and load duration have no significant influence on the MSE part of the creep strain (Navi et al. 2002).

Creep under varying moisture conditions was named MSE by Grossman (1976). Analogous is creep called *visco-elastic* when the results are strictly time-dependent and are obtained from creep tests under constant MC. Hunt and Gril (1998) found some empirical evidence that visco-elastic and MSE can be considered as equivalent.

MSE is usually investigated under applying *standard experimental* set-up of simultaneous loading and change the RH environment, leading to change the wood moisture content. The higher strain in bending creep occurs in the first moistening cycle. It is followed by smaller ones during all subsequent drying periods (Hauska and Bucar 1996; Bengtsson 2001).

In the standard mechano-sorptive creep behaviour, increasing the RH environment (or MC in the wood material) induces increased strain, and even the following decrease in RH or MC cause another change in strain (Norimoto et al. 1992).

Numerous studies in the MSE for unmodified wood have been done but the mechanism is not yet fully understood (Clouser 1959; Schniewind 1967; Schniewind 1968; Boyd 1982; Hoyle et al. 1985; Hoffmeyer and Davidson 1989; Mohager and Toratti 1993; Martensson 1994; Hanhijarvi 1999; Bengtsson 1999; Calvo et al. 2002; Bengtsson and Kliger 2003; Piter et al. 2006). *One reason* is the limited standardisation of the experimental conditions and its parallelism with conditions in service.

2.4.4 Parameters affecting creep

Parameters that affect the creep behaviour of unmodified wood are *time,* the amount and the rate of changing *moisture*, *stress*, dimensions and *wood* features such as knots in the tensile zone and *micro-fibril angle* (MFA) of the S_2 layer of the cell wall. Mean MFA correlates well with the MOE, density (ρ) or ratio of MOE/ρ. As smaller the MFA is, the deformation creep becomes much smaller (Hunt and Grill 1998; Kojima and Yamamoto 2004).

Important parameters for modelling are visco-elasticity and strain in different components. Creep *strain* is depended of external load, time and surround environment. Therefore, it may be considered the creep strain as a dependent variable parameter. On the other hand, the creep is also a measure of the material condition at any time and it is therefore an independent parameter, on which the strain rate is dependent (Hunt 2004).

2.4.5 Modelling creep

Bodig and Jayne (1982) presented some empirical equations to model the creep behaviour: Primary creep (Parabolic, 1/3 law and logarithm); *primary* and *secondary* creep (hyperbolic sine and polynomial); And *primary*, *secondary* and *tertiary* creep with de Lacombe model. Only the latter models include a term that indicates a possible acceleration of creep to rupture.

Bengtsson (1999) give an overview of different approaches of modelling creep in the wood material. Descriptive suggestions such as the anatomical model by Boyd (1982), the slip-plane model by Hoffmeyer and Davidsson (1989) and Hoffmeyer (1990), as well as models by Gril (1988) and van der Put (1989) based on breaking and reformation of hydrogen bonds were presented.

Table 4. The most common empirical equations to model the total strain in creep (Bodig and Jayne 1982)

Model	Equation	Coefficients
Parabolic	$\varepsilon_{(t)} = \beta_0 + \beta_1 \cdot t^{\beta_2}$	β_0, β_1, β_2
1/3 Law	$\varepsilon_{(t)} = \beta_0 \cdot \left[1 + \beta_1 \cdot t^{\frac{1}{3}} \right] \cdot e^{\beta_2 \cdot t}$	β_0, β_1, β_2
Logarithm	$\varepsilon_{(t)} = \beta_0 + \beta_1 \cdot \log(t)$	β_0, β_1
Hyperbolic sine	$\varepsilon_{(t)} = \beta_0 + \beta_1 \cdot \sinh \beta_2 \cdot t^{\beta_3}$	β_0, β_1, β_2, ($\beta_3 = 0.333$)
Polynomial	$\varepsilon_{(t)} = \beta_0 + \beta_1 \cdot t^{\beta_2} + \beta_3 \cdot t^{\beta_4}$	β_0, β_1, β_2, β_3, β_4
de Lacombe	$\varepsilon_{(t)} = \beta_0 + \beta_1 \cdot t^{\frac{1}{\beta_2}} + \beta_3 \cdot t^{\frac{2}{\beta_2}} + \beta_4 \cdot t^{\frac{3}{\beta_2}}$	β_0, β_1, β_2, β_3, β_4

Legend: t – time; Creep coefficients β_i with i=0 to 4.

To estimate the magnitude of the creep component, two different kinds of models can be used: Rheological / mechanical models and empirical / mathematical models. The *formers* are based on spring and dashpot combinations, see Figure 9. The springs represent the elastic components and the dashpot represents the viscous components. The elastic springs of the model correspond to the crystalline cellulosic core of the micro-fibril, whereas the time-dependent dashpots symbolise the visco-elastic and viscous behaviour of the matrix materials: Lignin, hemicelluloses and non-crystalline cellulose (Dinwoodie et al. 1990). A rheological model consists of three components: The elastic, visco-elastic and viscous parts.

Mathematical models, represented by de power functions, do not contain mechanical / physical interpretation of creep behaviour (Gressel 1984), see Table 4. Normally, the first term representing the initial elastic strain and the second (next) term representing the creep strain. All parameters / coefficients have to be determined experimentally.

2.4.6 Prediction creep

In a practical point of view, to predict a long-term strain from the initial elastic strain, a creep factor is recommended (ENV 1156). The *creep factor* (k_c) is the ratio of the increase in strain with time to the initial elastic strain, alternatively defined as *ratio of increase* in creep strain to the instantaneous strain. Introducing the *relative creep* definition by Hoffmeyer (1990) where $\varepsilon / \varepsilon_{inst} = \phi_t$ (creep strain divided by elastic strain), equation (5) can be rewritten as:

$$\varepsilon = \varepsilon_{inst} \cdot (1 + k_c) \tag{7}$$

$$k_c = \frac{\varepsilon - \varepsilon_{inst}}{\varepsilon_{inst}} = \frac{\varepsilon}{\varepsilon_{inst}} - 1 = \phi_t - 1 \tag{8}$$

When it comes to prediction and limitation of deformations in SLS of the wood structures design, the creep factor is also referred to MSE coefficient or k_{def} (Martensson 2003). In EC 5 (EN 1995:1-1), when the final strain u_{fin} of a structural member has to be calculated, k_{def} is the deformation factor for quasi-permanent actions (10years and more). The creep factor k_{def} takes into account, through the parameter of stiffness, the effect of the load and the moisture content in the structure.

$$u_{fin} = u_{inst} \cdot (1 + k_{def}) \tag{9}$$

Where u_{inst} is the initial strain (instantaneous). According EC 5, values of k_{def} are specified for different duration loads and service classes.

3 MATERIALS AND METHODS

Flawless specimens of Maritime pine wood species (*Pinus pinaster* Ait.) from pure sapwood part of the stem were prepared with different sizes, as described in the corresponding section, see Table 6 and Table 7. Wood was chemically modified with four methods: 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), Methylated melamine formaldehyde resin (MMF), Tetra-alkoxysilane (TEOS) and two types of wax (amid and montan). Similar wood features before modification were used, like density and tree-ring width.

3.1 Material properties

For prior determination of any material property, all specimens were conditioned at 21ºC and 65% of RH for at least four weeks. The following material properties were studied:

- Density.
- Dimension stability in terms of anti-shrink / swelling efficiency (ASE).
- Swelling strain (often simply called swelling) for two directions (radial and tangential).
- Equilibrium moisture content at three humidity levels (30, 65 and 87% RH).
- Stiffness stabilization efficiency (SSE) based on the differences in MOE at different. climates for un- and modified wood.
- Bending strength (MOR) measured statically in three-points bending test.
- Tensile strength parallel to the grain.
- Compression strength parallel to the grain.
- Compression strength perpendicular to the grain.
- Impact bending strength by using the charpy pendulum method.
- Superficial hardness according to the Brinell method.
- Depth hardness according to the Janka method.
- Modulus of elasticity (MOE) measured dynamically (MOE_{dyn}) using eigen-frequency.
- Modulus of elasticity (MOE) measured statically in four-points bending test in creep after 60seconds ($MOE_{st,4pb}$).
- Modulus of elasticity (MOE) measured statically in three-points bending test in creep after 60seconds ($MOE_{st,3pb}$).
- Creep factor calculated after 35days (840hours) under three stress levels.
- Creep factor calculated after 42days (1000hours) under two moistening processes.

- Anti-creep efficiency (ACE) based on the differences in creep strain between un- and modified wood specimens.

For comparative purposes, all physical and mechanical properties were studied with small specimens between un- and modified wood with at least 10 specimens per property, type and level of modification methods studied (and curing process, when applied).

3.2 Modification methods

All specimens were dried 24hours at 103°C before any impregnation. Full cell process with a vacuum step of 100mbar for 30min and a subsequent pressure step at 12bar for 2h was used for impregnations.

3.2.1 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU)

Impregnations with aqueous solution of DMDHEU supplied by BASF (Ludwigshafen, Germany) were performed in the following concentrations: 0.8M, 1.3M and 2.3M using 4% (w/w) of magnesium nitrate relative to the mass/mass of DMDHEU solution as catalyst, $Mg(NO_3)_2$.

Afterwards, all specimens impregnated with DMDHEU solution were pre-dried at room temperature for *one week* and followed with curing at *120ºC for 48hours* in an oven. The curing process was abbreviated as *wet curing* because the materials were held in wet conditions during curing (Xie et al. 2005; Krause 2006).

3.2.2 N-methylol-Melamine formaldehyde (MMF)

MMF resin was Madurit MW 840 supplied by INEOS (Frankfurt a. M., Germany). For MMF modification, the original resin/water solution had 75% of concentration. To obtain two levels of concentration, it was diluted with water, 10% and 20% of MMF solution.

After impregnation, all specimens were dried for 48h at room temperature. For resin curing, the wood material was stored *four days* in an oven with 5 steps of temperature increase every day (10°C) until the temperature of 90ºC was reached. The curing process was abbreviated as *oven process* (o) because the material was held in oven conditions during the curing (Krause 2006).

For large specimens and to avoid the cracks appearance, *steam dryer* (s) was used as curing process. Boards were stacked in a steam dryer. Between each board, spacers with 20mm thick were inserted to ensure good air circulation. The *main part* of the reaction process consisted of a temperature phase at 90°C for 36h, which was enclosed by a heating and wet phase as high as possible, app. 90% of RH (Krause 2006). All material cured in this way was used in marine exposition according to EN 275 (in item 3.6).

Concentrations and curing processes (oven and steam dryer used) are hereafter assigned as follow, i1o and i2o or i1s and i2s, respectively.

3.2.3 Tetra ethoxy silane (TEOS)

TEOS with ethanol (1 mol), which was acidified with hydrochloric acid (37%), was added to 1mol silane and stirred at room temperature for 30minutes, assigned T2. To achieve the lowest TEOS concentration (T1), half weight of mass water was added in the latter solution to obtain low concentration. After the impregnation, all specimens were weighed and cured in an oven at 60ºC for 4days, according to Donath et al. (2004).

3.2.4 Wax

Two types of wax were used, a synthetic amid wax (based on oxazolin) and a montan wax extracted from lignite (is an esterified montan acid C_{24}/C_{34}), assigned WA and WL, respectively. Both types of wax have similar densities (app. 0.99 and 1.02 gcm^{-3}) and melting points (78 and 81ºC) respectively for WA and WL.

Following the same procedures for impregnation described in 3.2, wax was impregnated at temperature of 120ºC in liquid state. After the impregnation, the excess of wax was cleaned with a filter-paper. All specimens were weighed and left for several months (three) in the climate room, at 65% of RH.

Table 5 shows a summarized overview about all modifications used: *Resin based*, DMDHEU with three concentrations (0.8M, 1.3M and 2.3M) and MMF with two concentrations and two types of curing, and TEOS and wax as *lumen fill* modification.

Table 5. Abbreviations of modification processes used

Modification\concentration		Low	Medium			High			
Active principle/Curing process		oven		steam	oven		steam	oven	---
Cell wall reaction	DMDHEU	D1(0.8M)	D2(1.3M)			D3(2.3M)			
	MMF		i1o	i1s		i2o	i2s		
Lumen fill	TEOS				T1			T2	
	Amid wax								WA
	Montan wax								WL

3.3 Physical properties

Table 6 shows a summarized overview about specimen sizes and applied standards followed in the experimental work to determine all physical properties.

Table 6. Physical properties, specimen sizes, applied standard and number of specimens (n)

Property	LRT [mm³]	Standard	n (unt)
Density and WPG	200 · 75 · 25	DIN 52 182	70
EMC	25 · 25 · 10	House standard, Dieste et al. (2009)	10
Iso curves	25 · 25 · 10	---	10
ASE	25 · 25 · 10	Hill and Jones (1996)	10
Swelling	25 · 25 · 10	---	10

3.3.1 Density (DEN)

Density was calculated as weight per volume. Dimensions in all directions, radial, tangential and longitudinal, RTL were measured.

Before isotherms curves (and EMC) and ASE were measured, leaching according EN 84 was done to leach out possible *unreacted chemicals*. Between each measurement, all material was left for several months at constant environment in the climate room with the respective RH environment.

3.3.2 Equilibrium moisture content (EMC)

EMC was calculated at three humidity levels (30, 65 and 87%) based on the oven-dry weight (before and after modification, using gravimetric method) and the weight at the specific climate.

$$EMC_i = \frac{m_i - m_0}{m_0} \cdot 100[\%] \tag{10}$$

Where m_i is the weight of the specimen at the respective moisture content (30, 65 and 87%) and m_o is the material oven-dry weight before modification.

3.3.3 Iso-therms curves

Isotherms curves were obtained by calculating two times the EMC, in the dry and wet phases. Different relative humidity environments were used at each phase (Wet and dry, 35%, 50%, 65%, 80% and 90%).

3.3.4 Anti swelling-srinkage efficiency (ASE)

ASE was determined according to Hill and Jones (1996). Specimens were subject to climate cycling between dry state and saturated condition with tap water. At four cycles, the average values were found. Before each climate change, weight and thicknesses in R and T direction were measured. It was calculated by comparison of the volumetric swelling coefficients between un- and modified specimens.

Improvement of the dimensional stability means reduction of the free swelling-shrinkage of a modified unloaded specimen submitted to humidity changes, compared to the swelling-shrinkage of an unmodified wood specimen under the same conditions (Norimoto et al. 1992). The expression of ASE is commonly used to quantify this effect. The swelling-shrinkage coefficient S was determined according to the follow equation, where D_{humid} and D_{dry} represent dimensions measured in *humid* and in *dry* conditions, respectively. To obtain ASE, two ratios of S from modified, S_{modified}, and unmodified wood material, $S_{\text{unmodified}}$, were compared according to the following equations (11) and (12).

$$S\,[\%] = \frac{D_{humid} - D_{dry}}{D_{dry}} \cdot 100 \qquad (11)$$

$$ASE\ [\%] = \frac{S_{unmodified} - S_{modified}}{S_{unmodified}} \cdot 100 \qquad (12)$$

High ASE may be the consequence of the replacement of the water molecules. Altered dimensional stability is also expected to have an impact in all properties relate with moisture, on mechanical and mechano-sorptive properties, in general.

3.3.5 Swelling strain (ε)

The swelling strain (ε) was calculated for both directions, R and T. The RT tree rings direction was clearly oriented perpendicular and parallel to the sawn surface of the specimens. The swelling strain in both directions RT was calculated.

$$\varepsilon_i\ [\%] = \frac{|\,I_{87} - I_{30}\,|}{I_{30}} \cdot 100 \qquad (13)$$

Where I_{87} is the dimension at 87% of RH and I_{30} is the dimension at 30% of RH.

3.3.6 Swelling coefficient (β)

The swelling coefficient β was calculated according to the equation (14) for both directions RT, where ε_i is the swelling strain (at each direction RT) and EMC_{87} and EMC_{30} are the EMC at 87% and 30% of RH, respectively.

$$\beta_i\ [\%] = \frac{\varepsilon_i}{(EMC_{87} - EMC_{30})} \cdot 100 \tag{14}$$

3.4 *Mechanical properties*

Table 7 shows a summarized overview about all mechanical properties, specimen sizes and applied standards followed.

Table 7. Mechanical properties, specimen size, applied standard and number of specimens (n)

Strength properties	Assignments	LTR [mm³]	Standards	n
Parallel compression	$f_{c,o}$	30 · 20 · 20	DIN 52 185	10
Perpendicular compression	$f_{c,90}$	60 · 20 · 20	DIN 52 185	10
Modulus of elasticity	$MOE_{st,3pb}$ $^{1)}$	200 · 10 · 10	DIN 52 186	10
Modulus of rupture	MOR	200 · 10 · 10	DIN 52 186	10
Work maximum load	WML	200 · 10 · 10	DIN 52 186	10
Shear	$f_{v,o}$	20 · 20 · 20	DIN 52 187	20
Tensile parallel to the grain	$f_{t,o}$	300 · 20 · 15	DIN 52 188	20
Impact bending	IBS	150 · 10 · 10	DIN 52 189	20
Modulus of elasticity	$MOE_{st,4pb}$ $^{2)}$	400 · 20 · 20	EN 408	20
Creep, stress level	---	200 · 20 · 10	EN 310	20
Creep, moistening change	---	400 · 20 · 20	ENV 1156	20

Legend: $^{1)}$ bending at 3 points; $^{2)}$ bending at 4 points.

3.4.1 Stiffness and strength (MOE and MOR)

Both tests were conducted in a 10kN ZWICK testing machine (Ulm, Germany) with 1% load accuracy, loaded with a rate of 0.30mm.min^{-1} and the strain at the middle of the specimens length (uniform cross-section) was obtained using an MFA 25 extensometer, gauge length 50mm with 0.5% accuracy. MOR and WML were determined in three points bending (3pb).

3.4.2 Stiffness stabilization efficiency (SSE)

To quantify the SSE of a wood modification process, the SSE ratio, expressed as a percentage, was calculated according to the equation:

$$SSE\ [\%] = \frac{\Delta MOE_{unmodified} - \Delta MOE_{modified}}{\Delta MOE_{unmodified}} \cdot 100 \tag{15}$$

The $\Delta MOE_{modified}$ is the average ΔMOE value for each group (10specimens) of modified specimens and the $\Delta MOE_{unmodified}$ is the average ΔMOE value of the unmodified controls.

The MOE_{st} was assessed in dry conditions with 30% of RH (MOE_{dry}) and wet conditions with 87% of RH (MOE_{humid}). The differences in $MOE_{st,3pb}$ between both climates for all un- and modified wood specimens were used to calculate the SSE.

$$\Delta MOE = MOE_{dry} - MOE_{humid} \tag{16}$$

3.4.3 Modulus of elasticity, dynamically determined (MOE_{dyn})

Dynamic MOE_{dyn} tests were carried out using the *impulse vibration technique*. The specimens were placed on foam rubber to simulate the free-free condition with respect to axial vibration (0.224·l, where l is the specimen's length). A hammer then excited the axial vibration of the specimens. The sound pressure was registered via a microphone connected to a computer-based data acquisition system. The frequency spectrum was established from the sound pressure using *Fast Fourier Transformations* and the eigen-frequency was determined from the appropriate peak. Based on eigen-frequency f [Hz], length l [m] and density ρ [kgm^{-3}], the MOE was calculated as follow.

$$MOE_{dyn} = 4 \ .\ \rho \ .\ f^{2} \ .\ l^{2} \ [kNmm^{-2}] \tag{17}$$

3.4.4 Compressive strength ($f_{c,0}$ and $f_{c,90}$)

Compression tests, parallel and perpendicular to the grain, were conducted in a 100kN ZWICK testing machine (Ulm, Germany) with 1% load accuracy and loaded rate of $0.60mm.min^{-1}$, according to DIN 52 185.

In these properties, since no strain gauges were attached to the specimens, because their small size (Table 7), displacements of the crosshead were recorded and used for the strain calculation. Thus, the absolute strain is not entirely correct, but still useful for *comparatives purposes* between un- and modified specimens.

3.4.5 Tensile strength ($f_{t,o}$)

Tensile test in the grain direction was conducted in a 100kN ZWICK testing machine (Ulm, Germany) with 1% load accuracy and with an elongation rate of 0.25mm.min^{-1}, according to DIN 52 188.

3.4.6 Impact bending strength (IBS)

The IBS was determined using the *Charpy pendulum* according to DIN 52 189. For the energy calculation, the following equation was used, where Q is the energy required to fracture the test piece (J), b and h are the dimensions of the test specimen in the RT directions (mm).

$$A_w[kJ \cdot m^{-2}] = \frac{1000 \cdot Q}{b \cdot h} \tag{18}$$

3.4.7 Brinell hardness (BH)

The BH consisted of a steel ball with a diameter of 10mm(0.39”) pressed with a load of 1000N to the specimen surface during 40s, Figure 10a. On each specimen, four measurements were made, two on the radial surface and two on the tangential surface. The BH was calculated according to eq. (19), where D is the diameter of the indenter and *d* the diameter of the lasting indentation after unloading.

$$BH(N \cdot mm^{-2}) = \frac{2 \cdot F}{\pi \cdot D \cdot (D - \sqrt{D^2 - d^2})} \tag{19}$$

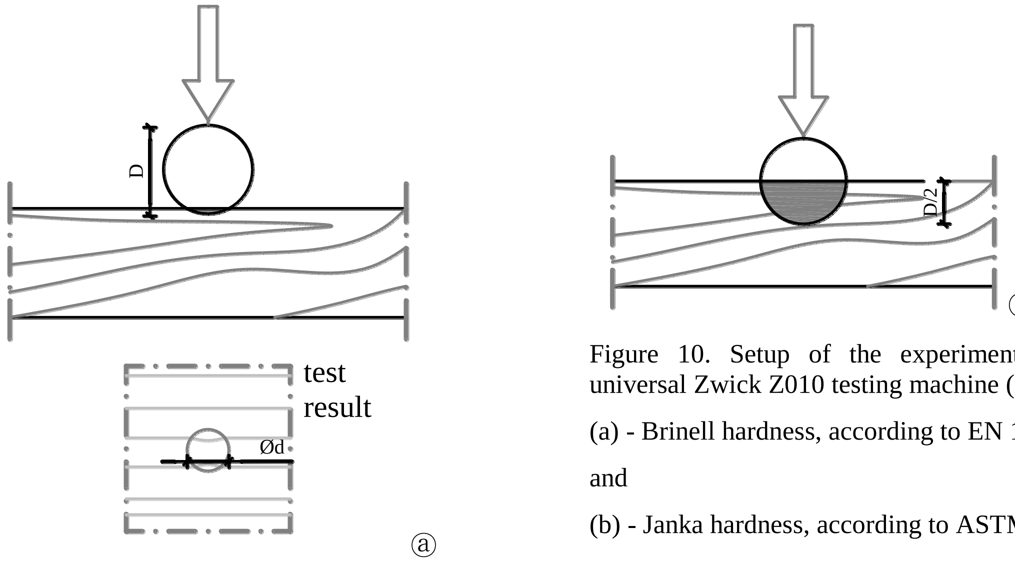


Figure 10. Setup of the experiment performed with a universal Zwick Z010 testing machine (Ulm, Germany)

(a) - Brinell hardness, according to EN 1534

and

(b) - Janka hardness, according to ASTM D143-83

3.4.8 Janka hardness (JH)

The JH test measured the required force to embed an 11.28mm (0.444”) steel ball into the wood, for un- or modified wood, until the half ball's diameter was reached, according Figure 10b.

3.5 Bending creep

3.5.1 Stress level (SL) effect

The standard creep tests were made at three points bending (3pb) under constant load with 160mm span. The load was selected in such way to ensure the bending stresses of: 0.1, 0.2 up to 0.4 of the mean MOR determined at the wood specimens conditioned at EMC, with 65% of RH. Three bending SL, normal or lower, medium and high, were used, respectively with 8, 16 and 35Nmm^{-2}//MPa.

To isolate the effect of the resin deposit (*embrittlement)* by the resin based modification, and neglect the effect of MC in the wood material, two extra experiments were performed to assess the creep in saturated conditions:

- In the *former*, the moistening was in the upper side of the specimen in the compression zone, Figure 11b. A strip of filter paper with 20mm width throughout the length development of the specimen, plus 15mm on each end side, was dipped in two containers with 20mll (app.). To keep the water saturation by capillarity, without needed to clean the impurities in the filter paper, *distilled* water was used. The evaporation losses were compensated by the water replacement every two days. The end tops of the specimens were sealed with paint to avoid moisture absorption longitudinally. The specimens were saturated forty-eight hours before the loading start until reaching 35days/840hours, Figure 11b.
- In the *second*, the test specimens were saturated with *tap* water and wrapped with plastic film to avoid any exchange with air or moisture of the outside environment. Therefore, high MC above the fibre saturation point (FSP) was kept constant until the end of the test was reached.

Two additional wood species, Blue Gum (*Eucalyptus globulus* Labill) and Beech (*Fagus sylvatica* L.) were included with a mean density of 900 and 775.kgm^{-3}, respectively, to access the effect of the duration test in creep, item 4.2.1.1.

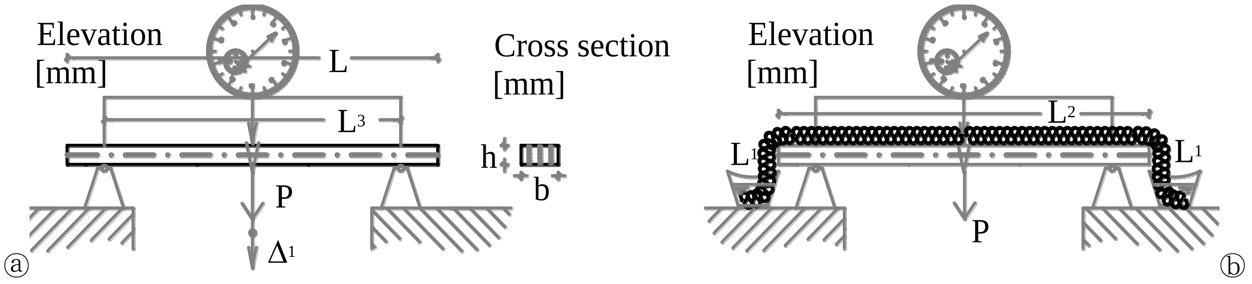


Figure 11. Principle of the load and moistening arrangement for the creep tests in bending with 20.10.200mm^3 RTL specimens, (a) - indoor climate have ($\Delta_1 = \square P L_3^3 / 4 E b h^3$) strain and (b) - saturated condition

3.5.2 Mechano-sorptive effect (MSE)

Specimens were subjected at five moisture cycles with a length-cycle of seven days (1 week) each. The temperature was kept constant at 21ºC (±2ºC) and the RH was between 30 to 35% (±2%). The distance between the loading shoes was in such way to ensure a SL of 12Nmm^{-2} (app.). The strain in the constant moment area was recorded with a specific schedule. The bending strain was measured from the top surface of the specimen at mid-span with 160mm span using lvdt gauges. The same procedure was repeated every week cyclically. Figure 12 shows the load arrangement.

Annual tree-rings (parallel to its faces in the cross section of the Figure 11a and Figure 12b with inner-vertical grey lines) were placed perpendicular to the supports. Specimens were loaded on the radial surface, at the horizontal position, in 4mm width of the steel-ring. Care was taken to minimize the impact loading caused by the weights application. The loads were gently applied in 10seconds (app.).

Data taker DT 515 serie 3 (www.datataker.com, with 9 digital channels with 0.3hz of acquisition dates) coupling with 8 Linear Variable Displacement Transducers LVDT's (www.rdpe.com/ex/dcth.pdf type DCTH400/256 ser.111048) with 0.001mm precision and a thermo-hygrometer (CPC ¼-TH nr. 67226) fed with ±24 tension volts were used over a period of 200,000hours. LVDTs gauges measured the curvature, between the load supports. Dates of temperature, RH and displacements from LVDTs were recorded with a PC-based data logging procedure automatically at 5s of intervals (for the first 4hours) at the beginning of each test/cycle, for the setups showed in Figure 11 and Figure 12a. Then, at each 30minutes until the end of test/cycle was reached.

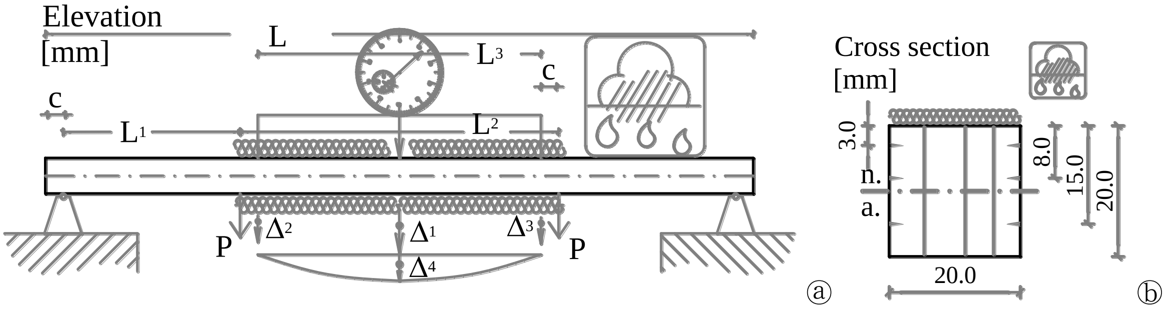


Figure 12. (a) - Load and moistening arrangement for $20 \cdot 20 \cdot 400mm^3$ RTL specimens ($\Delta_4 =$ □ $3 P L_3^2 L_1 / 2 b h^3 E$), (b) - Points of local measurements of moisture content in the cross section at different depths from the radial surface wetted (3, 8 and 15mm). The inner vertical grey-lines are the annual tree-rings

The strain was measured at mid-span from the top of the specimen. From this curvature, the static MOE was calculated at 60seconds after loading began (with three points bending referred as $MOE_{st,3pb}$ in Figure 11a and four points bending referred as $MOE_{st,4pb}$ in Figure 12b).

Two *moistening* processes were applied separately, Figure 12a. In the *first* case, the moistening was carried out on the upper compression stress side and in the *second* one, at the tensioned fibres, where the position of supports and load-shoes (P) were changed.

The moistening was achieved by placing strip filter paper to the radial surface on top of the specimen stretched in the middle part of 180mm (between load shoes, P) and whose ends were dipped into a container to adsorb *distillated* water by capillarity (over 5hours at each cycle). The moistening processes were initiated after seven days/first week of loading and repeated every week until 5 cycles were reached (42days/1000hours). These environmental conditions are similar at Mediterranean climate in *Southern* Europe with moistening variation by a downpour and low or medium RH at the remaining weeks.

The *length of the cycle* was defined with a preliminary evaluation of MC based in the electrical method (Protimeter 2005). Unloaded specimens under similar conditions of moistening as the creep test were used. Afterwards, the MC was measured with a *Protimeter Moisture Measurement System* (Protimeter 2005). Two pins were pressed against to the tangential surface of wood specimens with few millimetres (2-3mm) of penetration. After few seconds, the MC was obtained in 3 depths, according to Figure 12b. The average of both sides of the cross section was taken and showed in Figure 42 of the item 4.2.5.1.

3.5.3 Anti-creep efficiency (ACE)

The ACE is a mean of quantifying the ability of a specific process of wood modification to reduce the MSE in creep (Norimoto et al. 1992). The higher ACE is, the larger the reduction in creep is. The ACE is determined according to the following equations:

$$ACE\ [\%] = \frac{dj_u - dj_t}{dj_u} \cdot 100 \tag{20}$$

$$dj_i\ [\mathrm{MPa}^{-1}] = \frac{2 \cdot b \cdot h^3}{3 \cdot P \cdot L_1 \cdot L_3^2} \cdot (\delta_2 - \delta_1) \tag{21}$$

Where dJ_i is the *creep compliance* with i = u or i = t, dJ_t is the creep compliance for modified wood, dJ_u is the creep compliance of unmodified wood, P is the applied load, δ_2 is the strain after 42days, δ_1 is the strain after 60s of loading, L_3 is the length with pure bending for the determination of MOE, L_1 is the span between support and load and $bh^3/12$ is the moment of inertia of the cross-section (see Figure 12a).

3.5.4 Moisture-excluding efficiency (MEE)

The MEE is the ability of a modification to prevent moisture from entering to the wood, see follow equations. High MEE might be a consequence of the replacement of the water molecules by polymer in the bonding sites of cellulose (Deka and Saikia 2000 in Epmeier 2006). The higher the MEE, the low is the EMC, where MC_{humid} and MC_{dry} represent the MC measured in humid and dry condition, respectively. The humid and the dry conditions refer to notably different moist conditions, e.g. 30% and 87% RH.

$$MEE\ [\%] = \frac{\Delta MC_{unmodified} - \Delta MC_{modified}}{\Delta MC_{unmodified}} \cdot 100 \tag{22}$$

$$\Delta \mathrm{MC}\ \ [\%] = MC_{humid} - MC_{dry} \tag{23}$$

3.6 Marine exposition, set-up

After curing and conditioning in the climate chamber for three weeks, specimens with features indicated in Table 8 and Table 9 were exposed in open sea (Leixões harbour, Portugal, 41º11'N 8º42'W) according to EN 275 standard. All specimens were drilled in the middle with a hole of 20mm of diameter to be hanging on a steel bar of 16mm of diameter protected by a plastic sleeve of 18mm of diameter to avoid contact between wood and steel. Plastic tubes of 25mm of length were used as spacers to avoid contact between adjacent specimens, see Figure 13b and Figure 14.

The exposure arrangement in the open sea field consisted in six structures with two bars accomplish 30 specimens/each (app.). Each structure was suspended from the outside of water level with stainless steel cables 2+2 with 3mm of diameter, see the Figure 13b and c and its legend. Individual and groups of four specimens of each thickness and widths were randomly and alternately placed along the structures. The structures were submerged two meters below the lowest expected tide level for this place.

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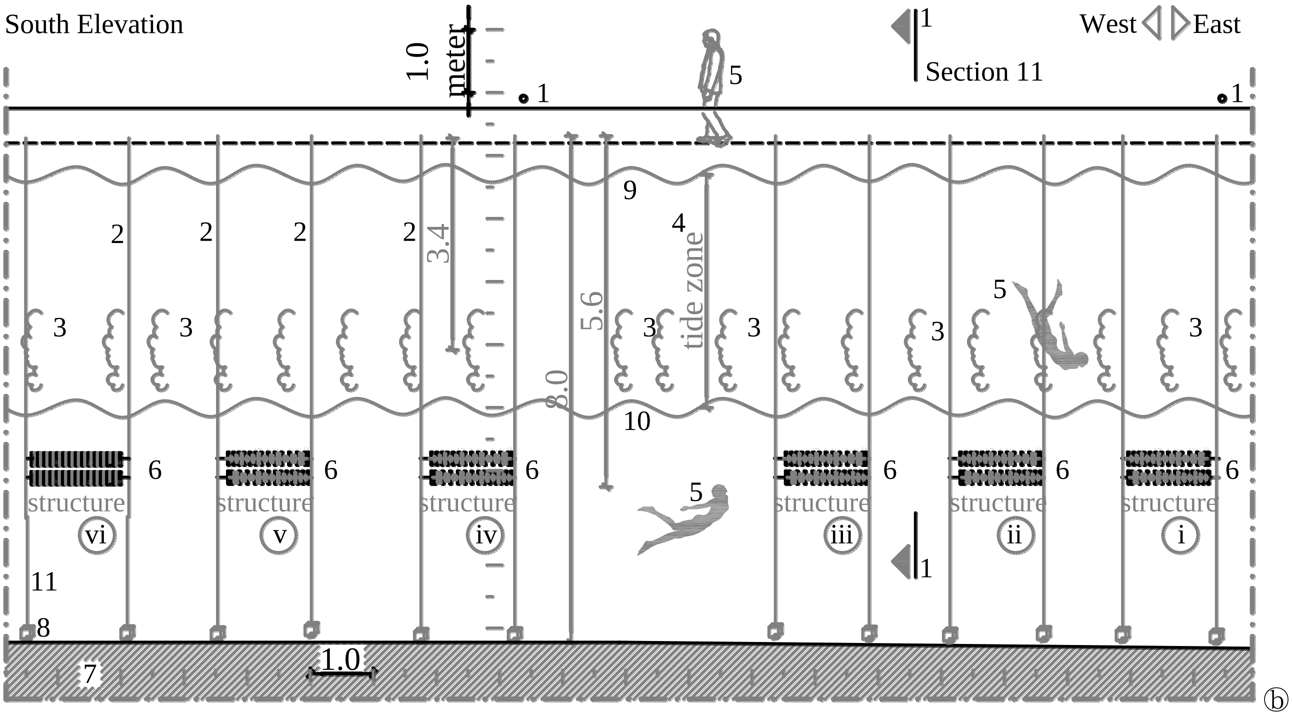


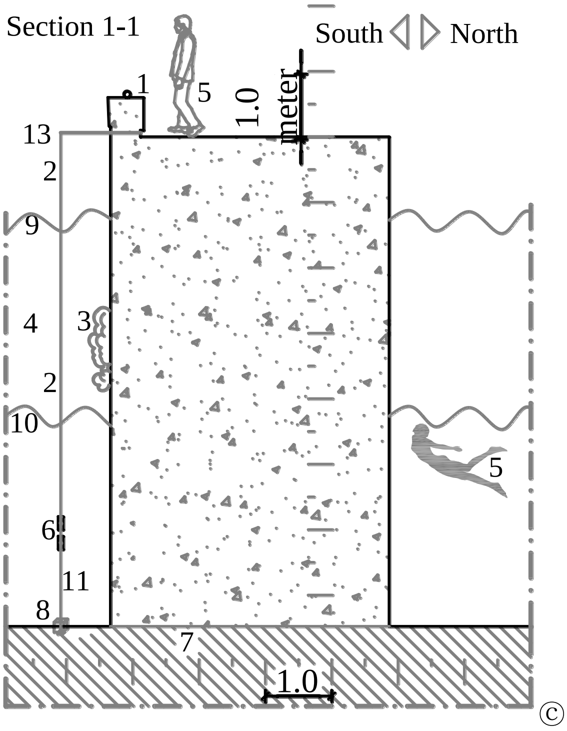


Figure 13. Disposition arrangement *in situ*, Leixões harbour,

(a) - perspective picture from the test site,

(in the previous page)

(b) - elevation and

(c) - section

Legend:

1. Existent steel ring,
2. Stainless steel cable ϕ2x2mm plastic-cover,
3. Mussel, 4. Tide zone, 5. Human scale,
6. Specimens (structures ⓘ up to ⓥ),
7. Level of sand and mud,
8. Concrete weight, 15·15·15 cubic shape,
9. High tide, 10. Low tide, 11. Wire (ϕ3.5mm).

3.6.1 Features of the test site

The harbour, where the test specimens were placed, is located in the mouth of river Leça, Leixões-harbour with temperate waters (Porto, Portugal). During the test period, sea-surface temperature in the area was monitored monthly (www.hidrografico.pt). Maximum sea-surface temperature was observed in August (22.5°C) while the minimum temperature was observed in

January (10°C). The average annual sea-surface temperature at the site was 14.4°C. In the North of Portugal, temperate sea waters has an annual average temperature of 11-12ºC at five meters deep and 14-18.5ºC on the surface. Solids content of 35.5gl^{-1} and an average salinity of the seawater of 30 up to 32.5PSU were found at the site.

3.6.2 Features of the wood exposed

The following features of wood were used to access the influence of chemicals and hardness on the marine borers resistance. To be submitted to modification (Table 5), all wood material of pine had a range of density between 535 up to 580kgm^{-3}.

Table 8 shows the density of the wood specimens at indoor climate for unmodified wood species (*Pinus pinaster* Ait.) and WPG of modified pinewood: DMDHEU, MMF, TEOS and Amid and Lignite wax.

Table 8. Density before and after impregnation, WPG and abbreviations used for un- and modified pinewood at 65%RH (n=10)

Modification	0	D1	D2	D3	i1s	i2s	T1	T2	WA	WL
Concentration	*ctrl*	DMDHEU low, medium and high			MMF low / high		TEOS low / high		Amid / montan	
Density, b. [kgm^{-3}]	574	590	561	545	586	579	550	521	525	514
Density, af. [kgm^{-3}]		652	679	728	631	726	616	649	1063	1098
WPG [%]	---	9	18	34	9	24	13	32	112	110

In addition, for comparative purposes, unmodified wood as Ipê lapacho (*Tabebuia serratifolia*), European Beech (*Fagus sylvatica*) and Blue Gum (*Eucalyptus globulus*) were included in the experiment. According to EN275 (1992) the comparative reference biocide preservative, *acid copper chromium arsenate* (CCA), was used too. CCA wood treated specimens were extracted from two logs with 15cm in diameter and 1.5m long supplied by CARMO *madeiras* company (Lisboa, Portugal). Ten specimens were cut from logs treated in an industrial scale autoclave. In order to analyze the gradient of chemical distribution on the cross-section, three depths were analyzed. Five wood specimens, with dimensions of 5·15·25mm RTL, were extracted, milled and the powder was analyzed to determine the *copper* and *chromium* content. The references copper and chromium content was determined by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectroscopy, Ciros CCD, SPECTRO Analytical Instruments GmbH, Kleve), after decomposition by acid hydrolysis.

Table 9 shows the mean density at 20ºC and 65% of RH for the unmodified references wood species: Ipê, Beech, regional Blue Gum wood species and Maritime pine treated with CCA. Blue Gum and Beech, according to EN 350-2 are hardwood species and have low durability to fungus and are susceptible to termite attack. Ipê was known as a durable species in marine environments (Longwood 1971; Scheffer and Morrell 1998).

Table 9. Density of the unmodified reference wood species, Beech, Ipê, Blue Gum and Maritime pine treated with CCA (n=10)

Assignments	CCA	E	B	P
Wood species	Pine, 12kgm^{-3}	S. Blue Gum	Beech	Ipê
Density [kgm^{-3}]	544	908	780	1018

To access the *effect of specimen size* on marine borers performance, no standard shape reference of specimens was used. According to the next figure, different thicknesses (8, 16, 30 and 50mm) and widths (60, 100, and 160mm) were included. One face of the specimens was not planned to keep the rough surface.

For extracting specimens every 6 months, 15 specimens of each thickness and width were used, resulting in a total of 180 specimens.

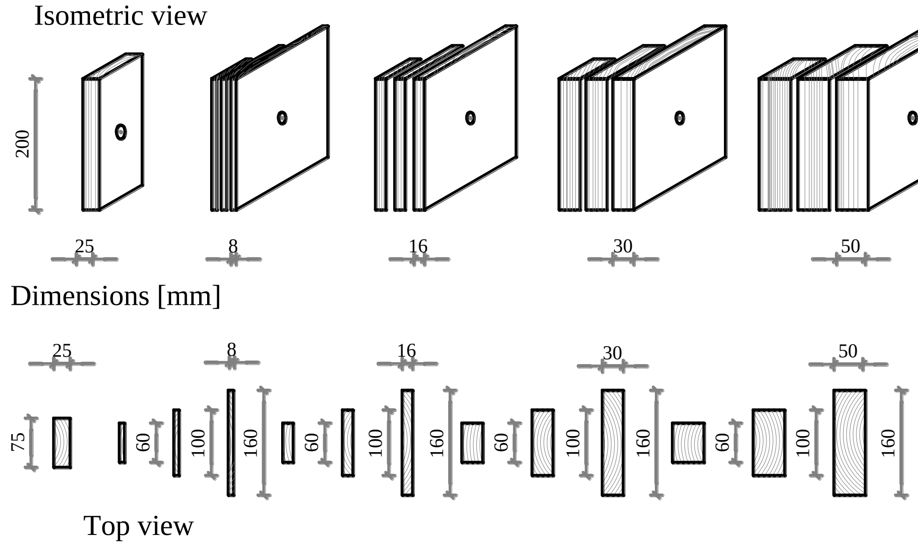


Figure 14. Isometric and top view of the specimen dimensions, 25·75·200mm as recommended by EN 275 and the out standard proposes: Thicknesses (8, 16, 30 and 50mm) and widths (60, 100, and 160mm)

3.6.3 Material inspections

Four inspections were made, after six months and then annually in the spring. At each inspection, the fouling was carefully removed with a scraper from the specimens and therefore they were visually inspected, x-rayed and placed back in to the seawater.

- The *first* inspection took place at October 2009; Three specimens of each modification and unmodified reference wood species were inspected.

- The *second* inspection was carried out in February 2010; Fourty five specimens in total (3 specimens per modification and level and 15 specimens of unmodified pinewood species) were extracted, x-rayed and visually inspected. The low marine borer activity at the 2nd inspection, up to the 12th month - 1st year, postponed the 3rd inspection to the 24th month instead of 18th month.

- The *third* inspection was carried out in March 2011, where all exposed material was extracted, visually inspected and x-rayed and placed back. All material classified as rate 4 were replaced by new specimens.

- The *fourth* inspection took place at the end of the third year, March 2012.

3.6.4 Assessment of test panels

The x-ray was performed in *Centro Hospitalar de Vila Nova de Gaia - Espinho* with fixed equipment Philips (Eindhoven, Netherlands). Images were modified with Philips Software DiagNET 2.2. To optimize images, ampoule was placed at one meter away from the specimens with filter AL-thorax, 60kVp maximum voltage and 10mA maximum current.

The visual analysis of specimens was done with individual photos of both sides of exposed specimens. A digital camara *Canon* EOS 500 - 50mm *Tamron lens* and a *laptop* were used for acquisition and latter analyzes of photos.

Table 10 shows the classification method presented in the EN 275 standard for rating each specimen, x-rayed for *Teredinids* and other mollusks and visually inspected for *Limnorids* and other crustaceans.

Five grades (0 up to 4) were considered in the classification of the marine borers attack. For *Limnorids* and other crustaceans the variable *tunnels* (in Table 10) should be replaced by *galleries* cover the surface and cross-section of the specimens.

Fouling and boring organisms were extracted from the wood and identified under a stereo microscope in the *Centre of Marine and Environmental Research* of Porto University. Boring organisms were classified according to Turner (1966) and Schultz (1969).

Table 10. Rating system for attack by *Teredinids*, according to EN 275 standard

Rating	Classification	Appearance on X-ray (*Teredinids*)
0	No attack	No sign of attack
1	Slight attack	Single or few scattered tunnels covering not more than 15% of the area of the specimen
2	Moderate attack	Tunnels covering not more than 25% of the area of the specimen
3	Severe attack	Tunnels covering between 25% to 50% of the area of the specimen
4	Failure	More than 50% of the area of the specimen cover by tunnels (specimens completely fail or rejected)

3.7 Statistical analysis

All performances (physical and mechanical properties as well as marine resistance) were characterized by the standard deviation through a rectangle, average (–), median (x), upper and low whisker with 5 and 95 percentile, see Figure 19 i.e.. The statistical analyses were done using the ORIGIN 8.5 software and tested with univariate analyses, followed by a t-test with a 95% confidence interval. For comparative purposes, to verify whether a change was significant or not, the level for significance was set at $p<0.05$.

For fitting curves and forecasting data, the ORIGIN 8.5 statistical software was used too. For unconstrained models, the Gauss-Newton method was used as the default algorithm, to find the minimum of a function that is a sum of squares of non-linear function.

4 RESULTS AND DISCUSSIONS

In this chapter, findings obtained in the main three topics will be presented and grouped according to which material that were provided (physical and mechanical properties with creep included as well as marine performances).

4.1 Material properties

4.1.1 Physical properties

Physical properties are features of the analyzed materials and can be determined without any changes of the materials analyzed.

4.1.1.1 Density

Density is one of the most determinants features of unmodified wood species (Kollmann and Cotê 1968). When large cross sections were used in the wood modification, see Figure 14, despite pine wood is easy to impregnate (EN NP 350-2), two problems can arise:

- Chemical gradients into the cross section, mainly due to the curing process, at one hand.
- Wood specimens extracted from different position of the stem have different wood features for impregnation, on the other hand.

Figure 15 shows the correlations between WPG imparted by modification and the original dry density of wood before modification. This analysis was conducted with specimens used for marine expositions according to EN 275, Table 8.

In the cell wall modification (with DMDHEU and MMF resins), the WPG and density correlated significantly, Figure 15a and b, respectively. In DMDHEU resin with low concentration (D1, 0.8M), a moderate correlation was found, R^2. The WPG took 100% of variations, between 6 up to 12%. Both concentrations of MMF resin have shown significant correlation between density and WPG, however a range of 10 up to 50% of WPG was found.

In the lumen fill modification: TEOS has shown low correlation between density and WPG (not significant). Therefore, WPG ranged between 10 up to 40%, Figure 15c. In both types of wax (WA and WL) a range between 75 up to 130% of WPG was found, with no difference between both types of wax, Figure 15d.

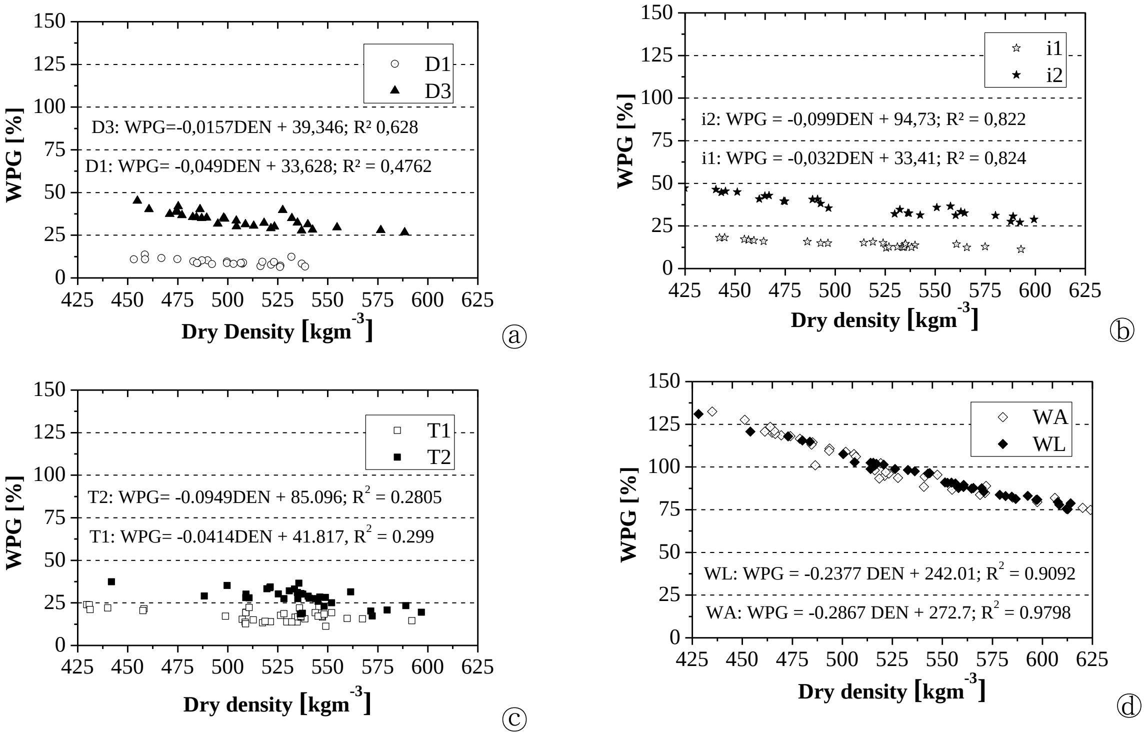


Figure 15. Correlations between WPG and density for all modified wood with, (a) - DMDHEU, (b) - MMF, (c) - TEOS and (d) - wax (n 38). For abbreviations see Table 5

4.1.1.2 Equilibrium moisture content (EMC)

To determine the EMC, two analyzes can be made according to Dieste et al. (2009). The calculation of EMC based on the *oven dry weight* of wood material *after* and *before* modification is presented, respectively in Figure 16a and Figure 16b. The WPG of the *wood material* imparted by the modification will *underestimate* the EMC found, Figure 16a.

Specimens with wax (WA or WL) have shown the EMC approximately the double comparing to the EMC in 87% of RH environment, Figure 16a and Figure 16b, for instance.

Modified specimens with TEOS in dry and indoor conditions (30% and 65% of RH) have shown similar EMC with both concentrations (T1 and T2), with a slight reduction up to 10%. The EMC in wet condition (high RH, 87%) has shown a reduction up to 20%.

Notice that the EMC difference/reduction in the lumen fill modification, of 20% in TEOS and the double (100%) in wax, is roughly similar to WPG imparted by the modification, represented with Star with five nozzle in Figure 16a (✰).

For three concentrations of DMDHEU, modified specimens was shown similar EMC in dry and indoor climates (with 30 and 65% of RH). Pinewood modified with different concentrations of DMDHEU has shown a reduction up to 30% and for high RH a reduction up to 50% was found. Between high and low levels of modification slight difference of EMC (app. 25%) was found.

Both levels of modification with MMF resin in dry condition (30% of RH) shown similar EMC. In wet condition (87% of RH), the EMC were reduced from 20 up to 40%, respectively with the level of modification.

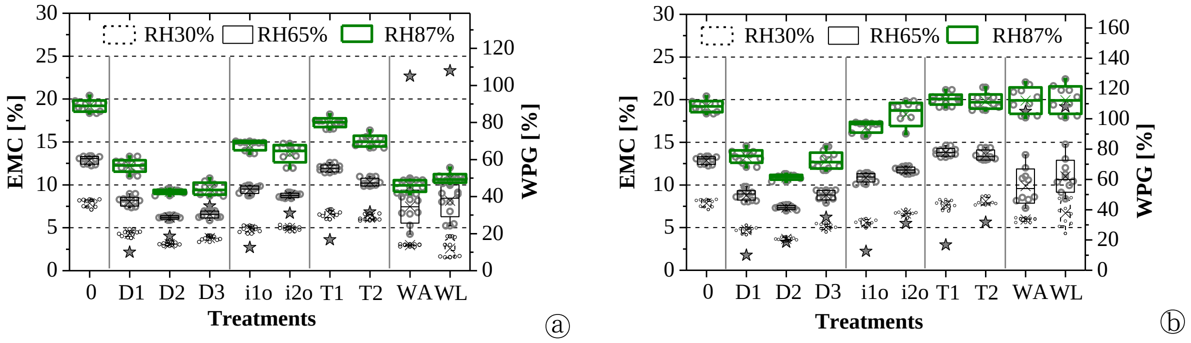


Figure 16. The EMC calculated at three RH environments (30%, 65% and 87%) with (a) - dry weight after modification and with (b) - dry weight before modification, and WPG (☆). For abbreviations see Table 5

Figure 16b shows the EMC according to the *latter* method, when the EMC was calculated with dry mass of wood before modification. In the cell wall modification: MMF resin had a slight effect on the EMC reduction and DMDHEU reduced up to 30%. In the lumen fill modification (TEOS and wax) no effect in the EMC of the wood material was found when calculated on bases of dry weight.

4.1.1.3 Isotherms curves

Figure 17 shows the sorption and desorption isotherms curves for un- and modified pinewood chemically. The compliance curve depends of the RH environment. For un- and modified wood the sorption and desorption isotherms curves were different.

To fit the compliance isotherm curves, several models were described in the literature and are briefly summarized in Papadapoulos et al. (2005) and Bastías and Cloutier (2005). In this analysis, the *Hailwood-Horrobin* model was used according to the equation quoted from Hailwood and Horrobin (1946).

$$EMC = \frac{1.8}{W} \cdot \frac{k_1 \cdot k_2 \cdot RH}{1 + k_1 \cdot k_2 \cdot RH} + \frac{k_2 \cdot RH}{1 - k_2 \cdot RH} \tag{24}$$

Where W is the molecular weight of the dry cell wall in kg per mole of sorption sites, k_1 is the equilibrium constant for the hydrated cell wall with the dry cell wall and dissolved water, and k_2 is the equilibrium moisture constant for dissolved water with the external vapour pressure.

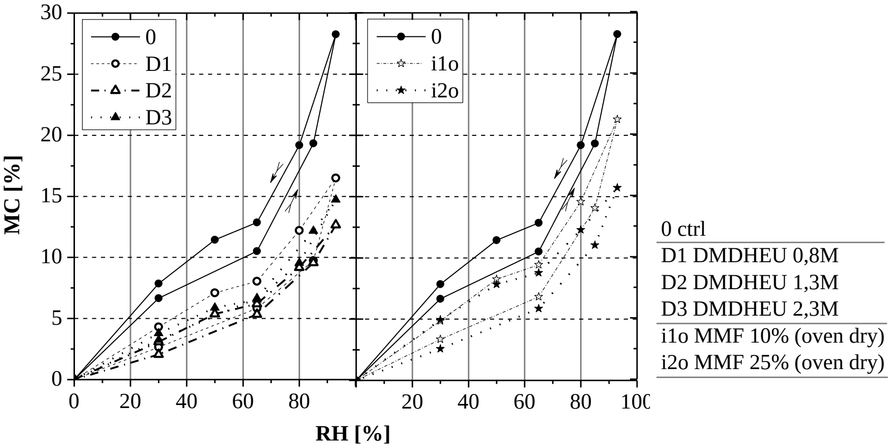


Figure 17. Isotherms curves determined with app. T 21ºC, downward-*desorption* is (↙) and rising-*sorption* is (↗)

Table 11 shows the constants of the Hailwood-Horrobin model (k_1, k_2 and W) calculated using dry mass material and fitting the function from the last equation to experimental data obtained at different environment: 0%, 30%, 50%, 65%, 80% and 93% of RH. All parameters were initialized W=0.28; k_1=5.5; k_2=0.75 as suggested in Papadapoulos et al. (2005).

Table 11. Coefficients of fitting isotherm curves in sorption (So) and desorption (Ds) behaviour for cell wall modification (DMDHEU and MMF resin) according to the equation (24). For abbreviations see Table 5

Modification	0 [*ctrl*]		D1 [9.33]		D2 [18.6]		D3 [34.6]		i1o [14.7]		i2o [38.5]	
and WPG[%]	So	Ds	So	Ds	So	Ds	So	Ds	So	Ds	So	Ds
W	0.40	0.29	0.61	0.37	0.62	0.47	0.59	0.57	0.68	0.35	0.65	0.32
k_1	79633	69	11.2	6.5	2.3	5.3	5.0	54.0	19.2	7.7	5.1	8.1
k_2	0.90	0.84	0.90	0.77	0.85	0.77	0.83	0.85	0.96	0.82	0.90	0.71

Significant differences in the *sorption* and *desorption* behaviour between un- and modified with resin-based are shown. Specimens modified with DMDHEU exhibited the lowest level of hysteresis compared to MMF or unmodified wood (ctrl-0). For both types of resins (DMDHEU and MMF), medium and high level of modification did not show significant differences on the histeresis behaviour. In the DMDHEU with low concentration (D1, 0.8M), significant difference to the unmodified wood was found, but not between concentrations of the same resin.

4.1.1.4 Anti swelling-shrinkage efficiency (ASE)

Figure 18 shows the compliance curve of ASE after four cycles. As higher the ASE is, higher the dimensional stabilizing effect is on the modified wood. An ASE of 60%, for instance, means that a modified wood specimen swells 60% less than an unmodified wood specimen.

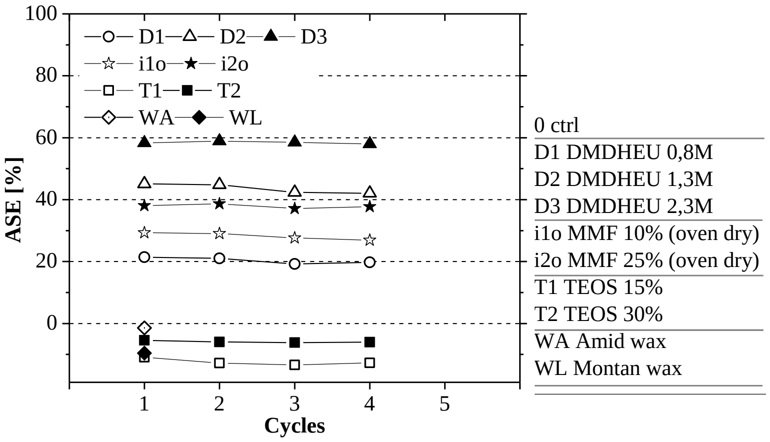


Figure 18. Compliance ASE for four dry and wet cycles

In the cell wall modification with DMDHEU with three concentrations, three ASE values were found. A higher concentration of DMDHEU resin is (D3, 2.3M), higher ASE is, 60%. At low concentration (D1, 0.8M) slight effect was shown, app. 20%. Both concentrations of MMF resin have shown similar ASE, 28 and 38%.

In the lumen fill modification (TEOS and wax) the ASE was negative, roughly -15%. These figures indicated that both modifications probably did not increase swelling effect but instead marginally low values are rather results of natural variability of wood material.

4.1.1.5 Swelling strain (ε)

Figure 19 shows the swelling strain (ε) in the both directions RT, Figure 19a and b respectively. High concentration of DMDHEU (D3, 2.3M) decreased the swelling strain (ε) in both directions RT with significant effect in the T direction. Modified specimens with MMF resin did show significant effect, only in T direction and for high concentration of resin. Lumen fill modification (TEOS and wax) had no effect in swelling strain (ε).

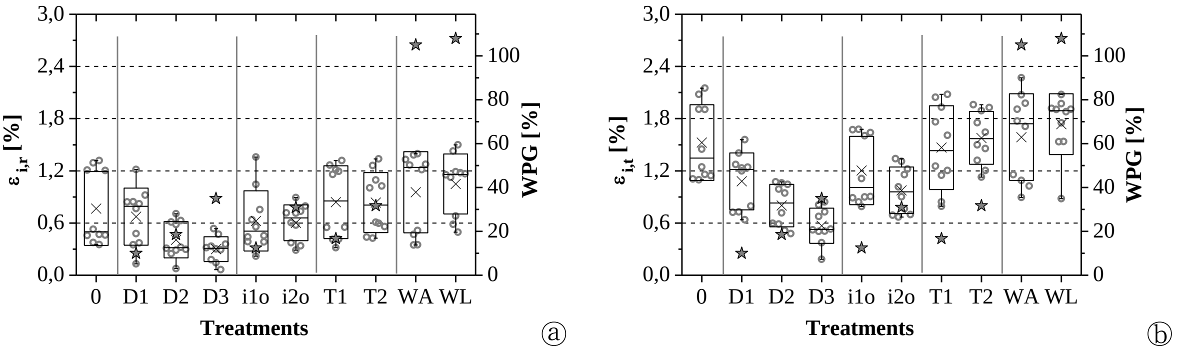


Figure 19. Swelling strain (ε) between 30% and 87% of RH for two directions RT, respectively, (a) - $\varepsilon_{i,r}$ and (b) - $\varepsilon_{i,t}$, and WPG (✰). For abbreviations see Table 5

The Portuguese unmodified pinewood has shown similar results as Ficha M9 (1997), with higher swelling behaviour in the T than in R direction, roughly 1:2 RT. The same tendency (1:2, RT) was kept for resin-based modified wood but with lower extention.

4.1.1.6 Swelling coefficient (β)

Figure 20 shows the swelling coefficients for different modification in both directions, RT. In the cell wall modification (DMDHEU and MMF resin) variable changes took place in swelling coefficient (β). Even though, not all changes were significant in the R direction. In the T direction, *higher* concentration of resin was *required* to reach significant reduction in the swelling coefficient. That means, no significant effect in low and medium concentration levels was found. However, high concentration showed a significant reduction in RT direction. For both directions, lumen fill modification (TEOS and wax) did not show any effect.

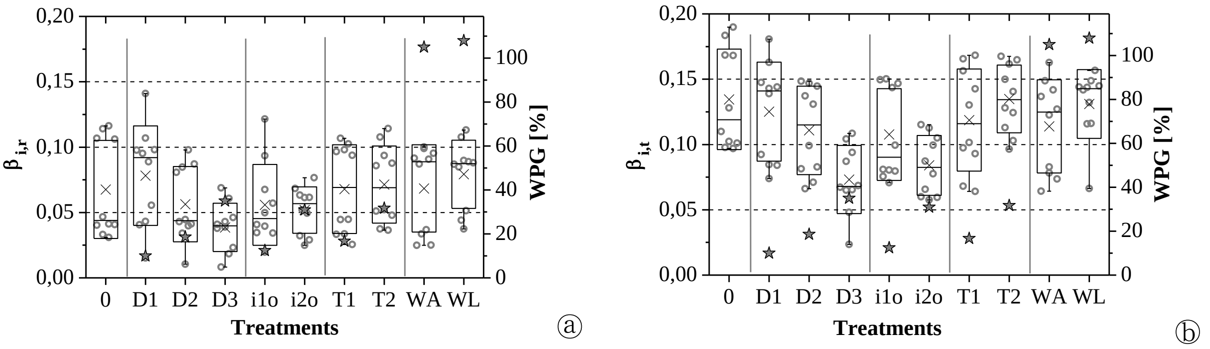


Figure 20. Swelling coefficient (β) for RT directions between dry and wet conditions at (30% and 87% of RH), (a) - $\beta_{i,r}$ and (b) - $\beta_{i,t}$, and WPG (✰). For abbreviations see Table 5

4.1.2 Physical properties, discussion

Wood is a hygroscopic material, which means that the *hydroxyl groups* contained in the cell wall polymers attract and form hydrogen bonds with environmental moisture (Rowell 2005).

In wood modification, the cell wall reaction with resin using acid catalyst, result in cross linking between two hydroxyl groups in the cell wall polymers (Rowell 1996). The less effect of the chemical of MMF resin on the physical properties in comparison to the resin DMDHEU may be explained by the acidic hydrolysis of the polysaccharides as a result of the use of magnesium nitrate as catalyst in DMDHEU solution.

In the lumen filling modification only a delay in the capillary water uptake at wax modification was found by Scholz et al. (2009), whilst all others physical properties remain unaffected.

Wood modification with resin is a way to enhance physical properties in softwood species (Militz 1993; Epmeier et al. 2004; Krause and Militz 2005; Dieste et al. 2009; Bollmus 2011; Pfeffer 2011). Esteves (2006) showed similar improvements with *heat* modification in Portuguese Maritime pine and he shown similar EMC at three RH environments (dry, indoor and wet conditions).

Chemical modification with DMDHEU resin in the Scots pine and European Beech wood species has shown similar EMC reduction, up to 30% (Militz 1993; Pfeffer 2011). Krause et al. (2004) modified Scots pine with DMDHEU (25% of WPG) at indoor conditions have shown similar results, with a reduction up to 20%.

Krause et al. (2004) with Scots pine modified with low concentration of MMF resin, at indoor climate, has shown an EMC reduction up to 15%. Epmeier et al. (2007a) has shown unexpected results for Scots pine modified with MMF resin with a slight increase of the EMC compared to unmodified wood.

The lumen fill modification did not show any effect on the EMC. Donath et al. (2004) with Scots pine modified with TEOS as well as Krause et al. (2004) with wax modified wood at indoor climate did not show any effect on the EMC as well.

Within one modification with resin based, between concentration levels, the EMC did not show significantly different reduction. The similar behaviour was found in other properties, iso-curves fitting values as well as swelling coefficients. This result has *an important meaning* in the chemical modified wood with large cross section where the dimension of wood specimen plays an important role. A gradient of (app.) 50% with uneven chemical distribution in the cross section (great than 50mm) was shown by Homan and Bongers (2004) for acetylation and mentioned by Lande et al. (2004) in the furfurylation process of wood modification. However, homogeneous results obtained in this study, despite different concentrations were used, helped to explain that for achieving the dimensional stability in modified wood no high level of modification is needed.

Krause (2006) with Scots pine modified with DMDHEU and MMF resin found similar results for ASE to this study. Low figures or slight effect for ASE (comparatively to the unmodified wood behaviour) in the lumen fill modification (with wax) were also shown by Weigenand et al. (2005) and mentioned by Santos (2000). However, Donath et al. (2004) with Beech wood modified with TEOS has shown a medium value of ASE, up to 30%. The features of hardwood species and the effect of the deposit material TEOS on the cell lumen, could be a possible explanation for this diference.

Bollmus (2011) with Beech modified with DMDHEU resin has shown a reduction up to 30% and 40%, for RT direction respectively. Nevertheless the wood species used, similar results to this study were shown. Epmeier et al. (2007a) presented a partial increase in the swelling strain of Scots pine modified with low and medium concentration of MMF resin.

Normally, physical properties are used as an attempt to understand the material behaviour and support some changes imparted by the modification in other properties (mechanicals e.g.). Epmeier et al. (2004) and (2007b) suggested no correlation between EMC variation and long-term performances on mechano-sorptive creep effect. Norimoto et al. (1992) agreed in the same line and suggested a new variable, anti-creep efficiency - ACE see item 3.5.3, similar to ASE in the item 3.3.4.

Since there are many variables to influence the EMC (chemical, catalyst, curing temperature, wood species, loading procedures, etc…), it is difficult to compare head-to-head reported results. However, this study point out that *modification* of Portuguese pinewood species can *enhance* its physical properties in the same way than others modified wood species and modification processes (through heat, i.e.).

4.1.3 Physical properties, main conclusions

The chemical modification can turn the wood into an engineered building material. Prospective modification methods are those that provide high dimensional stability, i.e. high ASE leading to a large reduction in the EMC. This, however, seems to be not possible to be achieved with the lumen fill modification methods studied here (TEOS and wax).

All modifications imparted an increased density in different extention, represented by WPG. Except for specimens modified with TEOS, the remaining modification methods (DMDHEU, MMF and wax) have shown significant correlations between WPG and density of wood material.

The cell wall modifications (resin based) were the most effective modification methods to achieve high dimensional stability (ASE), low EMC and low swelling effect. Wood modified with DMDHEU resin was more effective than MMF resin.

The lumen fill modification (TEOS and wax) did not show any effect on dimensional stability, EMC, ASE and swelling.

4.1.4 Mechanical properties

4.1.4.1 Stiffness (MOE)

None of the four modifications used in this work changed the MOE significantly, regardless the active principle of the chemical or level of the wood modification, in Figure 21a. In contrast, the SSE varied substantially, mainly for resin-based modification, in Figure 21b. In the lumen fill modification (TEOS and wax), between both RH environments, no effect was found.

The higher the SSE is, the higher is the stabilization effect of the modified wood. An SSE of 60%, e.g., means that the MOE of the modified wood differs 60% less between two climates than the MOE of the unmodified wood. A negative SSE indicates that the modification made the material more sensitive to moisture changes and the MOE variation (ΔMOE) in the modified wood was higher than in the unmodified ones.

Figure 21 shows the stiffness (MOE) at indoor climate (65% RH) and the SSE observed with WPG respective.

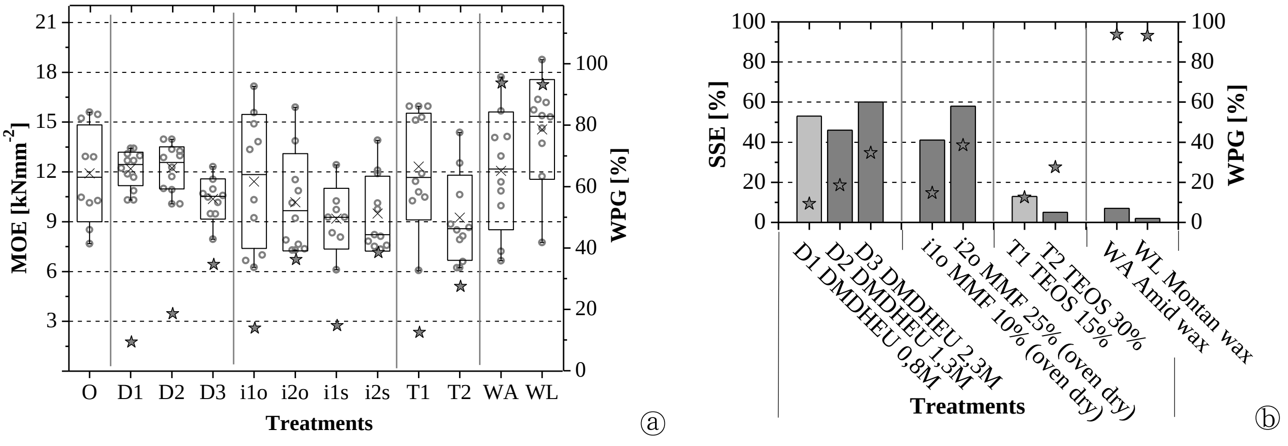


Figure 21. (a) - MOE determined according to DIN 52 186, (b) - SSE (between 87 and 30% of RH) and WPG (☆)

4.1.4.2 Bending strength ($f_{m,o}$)

Figure 22 shows the bending strength in three points bending according to DIN 52 186. The resin based modification with DMDHEU (D1, 0.8M) has shown a slight reduction in the strength, MOR and WML, statistically not significant. In the medium and high concentration levels of resin (D2 and D3 with 1.3M and 2.3M) a significant reduction up to 27% were found, despite the difference in the WPG found. Specimens modified with MMF resin did not show a significant reduction, up to 20% and no effect was found between both curing processes, oven and steam drier.

In the lumen fill modification, TEOS did not show any effect and for both types of wax, MOR increased up to 35%. The WML has shown similar behaviour as MOR did, for un- and modified wood specimens.

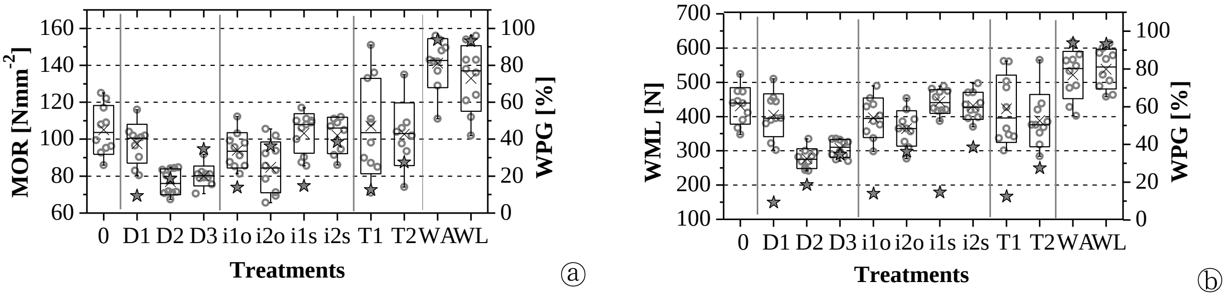


Figure 22. (a) - MOR, (b) - WML and WPG (✰). For abbreviations see Table 5

According to ASTM D143-83 different rupture patterns for unmodified wood (and modified) could be identified. In the cell wall modification with DMDHEU resin and different concentrations only one type of rupture was shown, a brash tensile rupture with the influence of *brittleness* material.

In the MMF resin modification with oven drier curing process, cross-grain and simple tensile rupture were presented at low level of modification. High concentration of MMF resin, and both types of curing process, typical brash tensile rupture was found. In the lumen fill modification (TEOS and wax) no difference in the rupture modes was presented to unmodified wood specimens. Simple tension and compression rupture were found.

4.1.4.3 Compression strength ($f_{c,o}$ and $f_{c,90}$)

Figure 23 shows the compression strength parallel to the grain. In the cell wall modification, different concentrations of DMDHEU resin have shown a significant increasing of compression strength, up to 55%. Specimens modified with MMF resin increased the compression strength up to 30%, and did not show significant difference between both curing processes.

In the lumen fill modification: TEOS did not show a significant effect in the compression strength but both types of wax (amid or montan) have shown a significant increase, up to 30%.

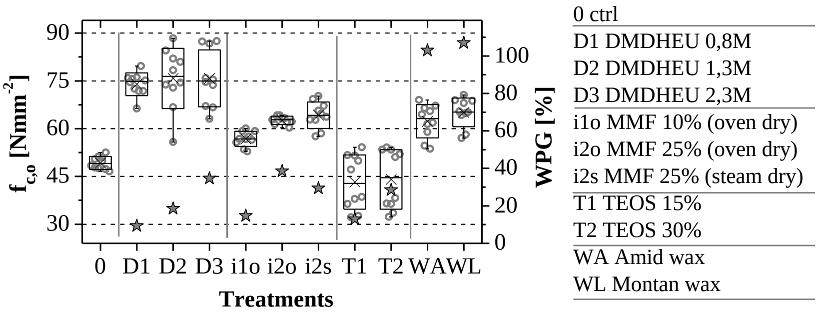


Figure 23. Compression strength parallel to the grain and WPG (☆)

Figure 24 shows the transversal compression strength and stiffness, perpendicular to the grain in the tangential direction. The compression strength in the cell wall modification with different concentrations, DMDHEU and MMF resin, showed a significant increase up to 125%, Figure 24a. Both curing processes in the MMF resin did not show significant differences.

In the lumen fill modified specimens: TEOS did not show a significant effect on the transversal compression (app. $10Nmm^{-2}$), but with both types of wax a significant increase was found, up to 250%(app. $30Nmm^{-2}$), see Figure 24a.

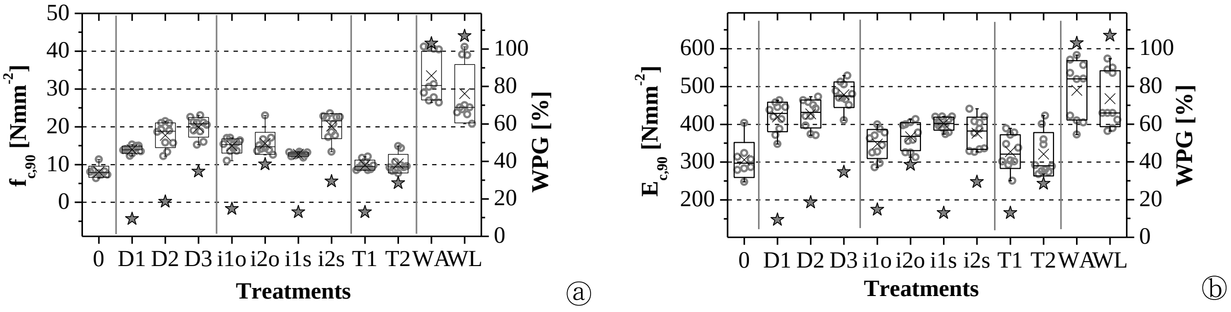


Figure 24. (a) - Perpendicular compression strength, (b) - MOE and WPG (☆). For abbreviations see Table 5

Figure 24b shows the corresponding *stiffness perpendicular* to the grain. In the cell wall modification with different concentrations of DMDHEU resin a significant increase was found, up to 60%. Specimens modified with MMF resin have shown an increase up to 30%. Both curing processes did not show significant difference.

In the lumen fill modification, TEOS has shown no significant effect and both types of wax (amid and montan) have shown a significant increase, up to 75%, Figure 24b.

4.1.4.4 Shear strength ($f_{v,o}$)

Figure 25 shows the shear strengths parallel to the grain according to DIN 52 187. In the cell wall modification (with DMDHEU and MMF resins) a significant reduction was found, up to 30%.

In the lumen fill modification the shear strength was increased. A significant effect was found on the wax modification and high concentration of TEOS, up to 30%.

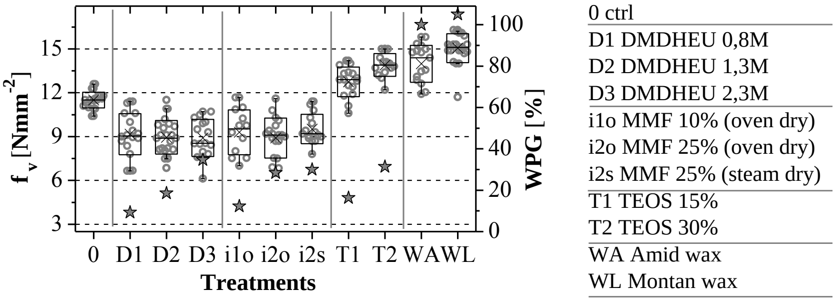


Figure 25. Shear strength parallel to the grain and WPG (☆)

It is *noted* that modified wood with both active principles have shown high scattered values. Cell wall reaction or lumen fill modification showed higher standard deviation with large size of rectangular boxes.

4.1.4.5 Impact bending strength (IBS)

Figure 26 shows the IBS determined using the Charpy pendulum. In the cell wall modified specimens: DMDHEU resin has shown a significant reduction up to 65% and MMF resin has shown a reduction up to 30% with significance for high concentration. Between both curing processes in MMF resin modified wood specimens, non-significant effect on the IBS was found. In the lumen fill modified specimens, TEOS did not show significant effect and both types of wax have shown a slightly increase of IBS, up to 22%, but it was not significant.

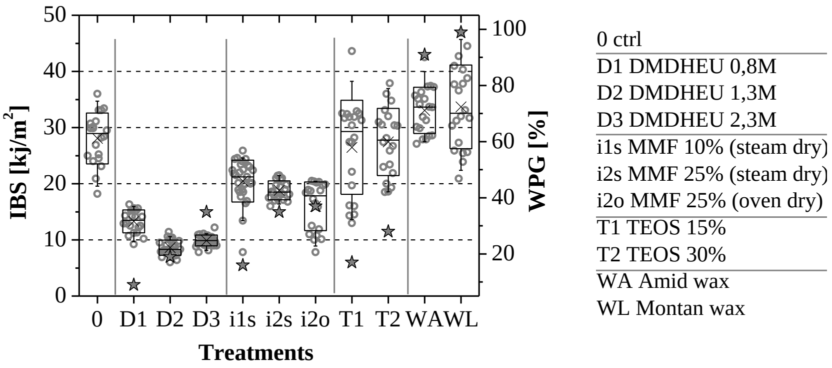


Figure 26. IBS and WPG (☆)

According to ASTM D143-83 different rupture patterns could be identified. Figure 27 shows the IBS rupture patterns for un- and modified wood with the most different behaviours.

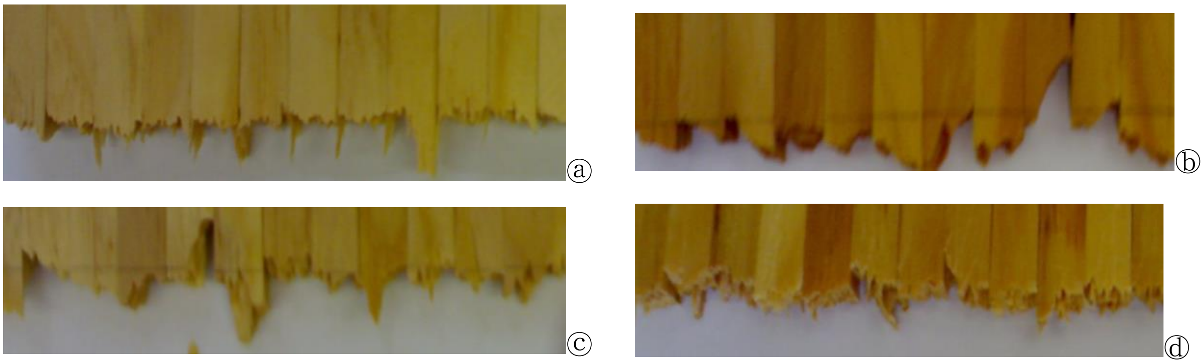


Figure 27. Rupture patterns for (a) - Unmodified, (b) - DMDHEU resin, D3 (2.3M), (c) - MMF resin (32% WPG) and (d) - Wax (108% WPG), for wood specimens with 10.10.150 RTL mm dimensions

In the unmodified pinewood a fibrous rupture in the compression fibres was found. The cell wall modified specimens with DMDHEU resin have shown two types of rupture modes with brittleness material influence: A *right broken* and a *blunt* rupture for low and other levels of modification, respectively. For both concentration levels of MMF resin and both curing processes, the rupture mode did not show significant difference and occurred in the *tensile* fibres. In the lumen fill modification specimens: TEOS did not show any difference to unmodified wood, despite the level of modification; And specimens modified with both types of wax, the rupture mode occurred in the *tensile* fibres.

4.1.4.6 Tensile strength ($f_{t,o}$)

Figure 28a shows the tensile strengths parallel to the grain. Wood specimens modified with cell reaction: DMDHEU resin has shown a significant reduction up to 45%, with associated small standard deviation, showed by the rectangular box plot dimension; Specimens modified with MMF resin did not show a significant difference between both curing processes and a slight reduction effect was demonstrated in the tensile strength, up to 10%, which was not significant.

In the lumen fill modification (with TEOS and wax), the increase of tensile strength was not significant, up to 22%.

Figure 28b shows the tensile stiffness parallel to the grain. For both active principles of modification, cell wall reaction with resin based (DMDHEU and MMF) and lumen fill modification (TEOS and wax), no significant effect on the tensile stiffness were found. Although, specimens modified with DMDHEU resin have shown less scattered results associated at slight reduction in the axial stiffness.

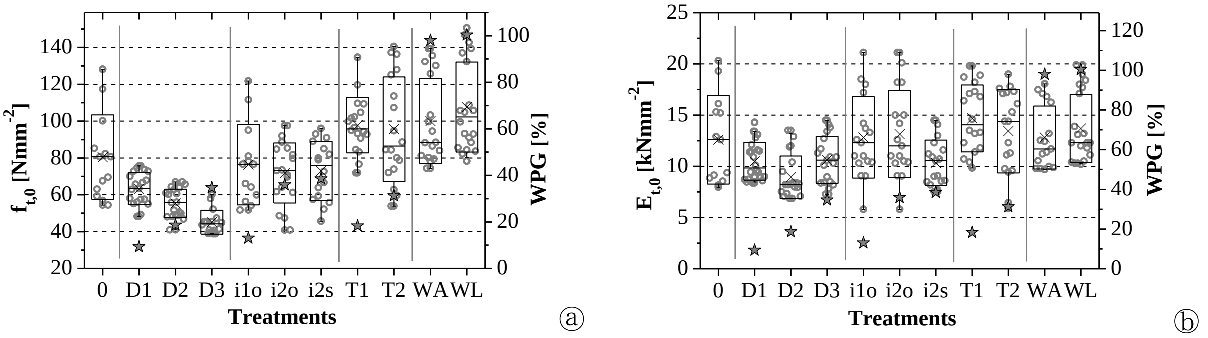


Figure 28. (a) - Tensile strength, (b) - stiffness in the longitudinal direction and WPG (☆). For abbreviations see Table 5

4.1.5 Mechanical properties, discussion

4.1.5.1 Stiffness (MOE)

From the literature it is known that some modified wood does not show significant effect on bending stiffness at indoor climate, 65% of RH. In the Scots pine and Beech wood species modified with DMDHEU and MMF resins, the MOE did not change as well (Bollmus 2011; Krause 2006). Short-term loads and low level of stress seems to be the main reason.

In the lumen fill modification, Scots pine modified with the same types of wax used in this study has shown similar results with a slight increasing of stiffness without be significantly (Scholz et al. 2009). Donath (2004) has shown unaffected MOE in the Scots pine modified with TEOS.

Epmeier et al. (2004) did a study with a well-documented provenance wood material and no significant effect was shown at indoor climate although the high variability in unmodified wood was kept in the modified wood, i.e. acetylation, MMF, heat modification and furfurylation. However, an enhanced behaviour will be expected in the stiffness between *wet* and *dry* climate - SSE, mainly in the resin based modification. In the cell wall modification as furfurylation, similar to DMDHEU modification, Lande et al. (2004) showed high up to moderate SSE, 30 and 60% with 15 and 47% of WPG, respectively. The good relation with moisture shown in the physical properties (low EMC and high ASE) is the main reason, Figure 16b and Figure 18 respectivelly.

In this study, different concentrations of DMDHEU resin showed similar SSE, 45 up to 60%. Regarding to unmodified wood, similar reduction was shown in the EMC variation between wet and dry environment rather than the ASE, in Figure 18 in 4.1.1.4.

Wood modified with MMF resin with different concentrations has shown different SSE, 40 up to 70%, respectively for low and high concentration. The SSE follows the outcome regard to the

ASE rather than the EMC variation between wet and dry climate. Because the EMC variation was in the less extend than SSE. However, three of them followed the same trend.

Epmeier et al. (2007a) and (2007b) showed an unexpected increase of MC in MMF resin related to unmodified control, despite the hight reduction under the MSE in bending. Epmeier et al. (2004) with specimens modified with MMF resin (15% of WPG) with similar environment variation has presented SSE on the other way around, SSE near null matched by own ΔEMC, in.

The lumen fill modification, TEOS and wax, has shown no effect in the ASE or ΔEMC between different environment climates related to unmodified wood as well as in the SSE. According to Norimoto et al. (1992) all modification methods that result in the highest SSE normally result in a reduction of ΔEMC. However, as the latter work told as well, an EMC changed by modification did not automatically produce a changing in MOE.

4.1.5.2 Bending strength (MOR, $f_{m,o}$)

Modulus of rupture (MOR) was changed in different ways by modification. Hard- and soft-wood species suffered similar changes on the strength. Negative or positive changes of MOR were found in the cell wall reaction or lumen fill modification, respectivelly. Beech modified with DMDHEU resin with similar concentrations has shown a MOR reduction up to 20% (Bollmus 2011). Scots pine modified with the same type of wax (amid and montan) has shown similar improvement of MOR, up to 28% (Scholz et al. 2009).

In bending strength, compression and tensile properties are involved. The *former* increased for all modification and the *latter* changed in different way, Figure 23 and Figure 28a, respectively. It seems that MOR was conditioned by the tensile strength behaviour. Normally, the reduction of MOR on the cell wall modification was associated to the *embrittlement* effect imparted by the resin, DMDHEU and MMF (Rowell 1983; Mai et al. 2007; Xie et al. 2007b; Dieste et al. 2008a).

4.1.5.3 Compression strength ($f_{c,o}$)

Gindl et al. (2003) with Scots pine modified with MMF resin has shown similar compression strength perpendicular to the grain in the tangential direction. Bollmus (2011) with Beech modified specimens with DMDHEU resin has shown an improvement up to 40%. For compression strength, it seems that the DMDHEU resin showed less effect on the hard- than on soft-wood. The compression strength tends to increase owing to the role of resin deposit in the cell wall as well as the *embrittlement* effect.

4.1.5.4 Shear strength ($f_{v,o}$)

Bollmus (2011) has shown reduction of shear strength, up to 60% in the Beech wood modified with different concentrations of DMDHEU resin. Similar shear reduction was also reported by Dreher et al. (1964) and Rowell (2005) in acetylated wood. In the cell wall modification (with DMDHEU and MMF resin), the shear strength had similar reduction as MOR in bending. That means, the embrittlement effect imparted by the resin based modification could also be seen on the shear strength. This reduction is the *greatest setback* to the use of the modified wood in truss connections.

4.1.5.5 Impact bending strength (IBS)

The IBS was reported as the most adversely affected property by cell wall modification. Rapp and Sailer (2001) have shown a reduction up to 60% on thermowood Scots pine and as weel Birch wood in Johansson and Morén (2006). In the furfurylated Southern Yellow pine a reduction up to 57% was reported by Goldstein (1955) in Lande et al. (2004). Scots pine venneers modified with glutaraldehyde has shown a significantly reduction of IBS, more than 60% (Xiao et al. 2010). The same tendency was shown with Scots pine furfurylated (Epmeier et al. 2004; Lande et al. 2004). Acetylated radiata pinewood did not show significant difference to the unmodified wood (Tjeerdsma and Pfeiffer 2006). Bollmus (2011) with Beech wood modified with DMDHEU resin has shown similar magnitude on shear of reduction to this study done with a different softwood species.

An opposite tend, with an improvement of mean IBS, was shown for Scots pine modified with wax by Scholz et al. (2009).

Portuguese pine behaved in a similar way as the reported wood species with some of these elementaries changes presented in the refered literature. However, in all these studies, the small dimension of specimens *must be kept in mind*. Lande et al. (2004) with furfurylated wood with standard size specimens has shown less reduction in the IBS than Epmeier et al. (2004) with small dimension specimens.

The embrittlement rupture mode in the DMDHEU resin was not surprising, because the effect of the acidic hydrolysis from the catalyst together with the effect of the resin deposit in the cell wall. The latter effect also appeared in the higher concentration of MMF resin where no acid was used. Probably this behaviour was due to others factors. So as the hardness / compression strength increase *masked* by the effect of the resin deposit in the cell wall. Compression and tensile strengths were involved for wax and MMF modification. Probably the tensile fibres rupture mode has occurred owing to the significant increase of hardness or compression strength material (MMF and wax modification). The role of the latter on the static equilibrium of the cross section was crucial, the neutral axis moves to the large imparted property. Compression strength increased significantly and the tensile strength did not change significantly in MMF and wax modification. The maximum tensile strength was reached more quickly.

If properties like *tensile* and *compression* strength were changed in different ways by both types of modification used in this study, cell wall or lumen fill modification, they help to explain the behaviour of the IBS at modified wood. The trend of the property tensile strength is followed by IBS.

The reinforcement of modified wood with other materials (steel or fibres as carbon, e.g.) could be an good approach to overcome the IBS, tensile and bending strength reduction.

4.1.5.6 Tensile strength ($f_{t,o}$)

Santos (2009) and Machado and Palma (2010) with standard specimens of unmodified Maritime pine have shown similar mean strength and stiffness in tensile strength parallel to the grain than small specimens in this study.

In the cell wall modification, MMF and especially with DMDHEU resin, tensile strength is expected to be reduced, as a consequence of the acidic hydrolysis of the cellulose and hemicelluloses (Xie et al. 2007b). Scots pine veneers modified with MMF resin did not cause any tensile strength loss compared to unmodified veneers (Mai et al. 2007). Specimens modified with MMF resin have shown less embrittlement effect in the IBS, however a reduction up to 30% were found (Figure 26). Therefore, no significant effect on tensile strength was found (Figure 28a). The embrittlement effect was not revealed in the tensile strength of modified wood with MMF resin.

As well in the bending stiffness, the short-term loads and lower SL seems to be the main reason to the unaltered stiffness in tensile (Figure 28b). Bollmus (2011) with Beech wood modified with DMDHEU resin with similar concentration levels showed a reduction in tensile strength up to 60%. Maritime pine wood has shown a reduction in the tensile strength up to 45%. Unlike what happens with modification in compression strength between soft- and hard-wood, it seems that the modification with DMDHEU resin showed a larger reduction in the tensile strength on the hard- than in soft-wood species. The changing on the tensile strength has followed closely the enhancement on the absorption energy (IBS) for all material in general and for DMDHEU modification in particular. The *embrittlement* effect associated with low EMC were the main diference.

In dry and wet environments, changes in the EMC as well as the ΔEMC presented by the modification did not fit to the tensile strength changes.

In the literature, different rupture patterns were found for tensile strength (Feio 2005; ASTM D143-83 2009). The rupture of unmodified wood in tensile test was related to the fibrous and irregularly line of rupture, where an *ash splinter* and *shear and tensile* rupture modes were found.

In the cell wall modification with low concentration of DMDHEU resin has shown *already* shear rupture mode. Medium and high concentrations of DMDHEU as well as MMF resin with high concentration showed pure tensile rupture in a *straight breakage line* almost perpendicular to the grain. The main reason for this *brittle behaviour* was the deposit of resin in the cell wall to avoid fibres mobilize the shear strength between them. A similar finding was presented in tensile strength studies of cotton and modified wood veneers with DMDHEU and $MgCl_2$ as catalizer by Zeronian et al. (1989); Som and Mukherjee (1989); Xie et al. (2007b); Mai et al. (2007).

Specimens modified with MMF resin with low concentration have shown two types of rupture: *Fibrous* or *splinter* rupture and shear and tensile rupture. No pure tensile ruptures were found. Wood specimens modified with MMF resin are less brittle than DMDHEU resin, see Figure 26a and Figure 27b and c. It seems that MMF resin displayed rupture morphology between pure tensile (found in the DMDHEU with high level of *embrittlement* effect) and *diversities* of patterns rupture for unmodified wood.

Mai et al. (2007) with wood veneers modified with MMF resin presented no reduction for MMF with different concentrations or pH solutions. To accept both results, the size of specimens needs to be kept in mind. In the lumen fill modification (TEOS and wax) the *diversity* of patterns ruptures was similar to unmodified wood. The deposit of TEOS and wax material in the lumen had no effect in the fibres *slippage*.

4.1.6 Mechanical properties, main conclusions

The most prospective modification methods are those that provide high dimensional stability with a large reduction in the EMC leading to high SSE, on one hand, but at the same time, do not lead to any shortcomings in terms of stiffness and strength properties (Epmeier et al. 2004). The resolution of that *dilemma* appears to be very difficult to achieve with the modification methods described before. The IBS appears to be affected more negatively with better dimensional stability, SSE. It is also the case that, when some properties increase, others decrease.

Stiffness at indoor climate (65% of RH) appeared to be relatively unaffected by modification, even though the EMC was significantly reduced and different ASE and SSE were obtained. The modification methods that had the highest SSE also reduced the EMC largely, Figure 16 in 4.1.1.2. For the resin based modification, the SSE changed substantially. The deposit material in the lumen fill modification (TEOS and wax), in dry and wet condition, showed no effects on SSE.

Strength was changed in different ways *with significant reduction* in the DMDHEU modified wood and a *slight positive improvement* in the wax modified wood, not significant. Frequently, rupture occurred *abruptly* and appeared *brittle* for cell wall modification (DMDHEU and MMF resin). In the lumen fill modification (TEOS and wax), the rupture mode features of the unmodified wood were kept.

Except for modification with TEOS solution, all modifications used in this study have shown an improvement in both directions LT of the compression strength.

A negative effect on shear and tensile strength as well as on the ability to absorb the impact energy (IBS) was shown only in the cell wall modification methods (DMDHEU and MMF resins).

4.1.7 Screening analysis between different mechanical properties

Mechanical properties are important to allow using wood for structural purposes. The full characterization of a wood species requires a *comprehensive* test campaign to hold the inherent material variability. According to EN 384, from experimental data and experiences of using unmodified softwoods, is possible to estimate the *lesser known* properties from the *reference* properties.

The concept of reference property and other less known properties is included in EN 384 standard and JCSS Code (2006): Density, MOE, MOR as reference properties, and compression, tensile and shear strengths, as less known properties.

The objective of this item is to evaluate the relation between less known and references properties for un- and modified wood. This analysis will show if all correlation between properties in the unmodified wood will be keep for modified ones.

4.1.7.1 Bending and tensile strength

To analyse the bending and tensile correlation, the data from Figure 22a and Figure 28 were used and presented in Figure 29a for reaction cell wall modification. For modified wood, the movement of the data of the modified wood to the beginning of the suggested curve (dot-line, EN 384) means a decreasing in the involved properties. In Figure 29a and b the dot-line indicates the suggested formula in EN 384 for unmodified wood to predict the 5% lower characteristic values of tensile strength *from the* bending strength values, equation (25).

$$f_{t,0,k} = 0.60 \cdot f_{m,o,k} \qquad (25)$$

Both reductions, in bending strength (up to 27%, Figure 22a) and in the tensile strength in the longitudinal direction of fibres (up to 45%, Figure 28), lead to a new approach to forecast the tensile property. To be on the safe side, a new approach could be formulated for modified wood with DMDHEU resin. The equation (26) was represented in Figure 29a at thin-dashed line.

$$f_{t,0,k} = 0.40 \cdot f_{m,o,k} \qquad (26)$$

Figure 29b shows the correlation between tensile and bending strengths for lumen fill modified wood specimens. The movement of the results away (to the upper side) of the suggested curve (with dot-line, EN 384), means that tensile strength imparted by modification was increased and the prediction are in the safe side. Specimens modified with wax have shown no significant increasing in tensile strength, up to 22%. The tensile strength prediction from the bending strength properties will be in the safe side. TEOS modified specimens had no effect in bending and tensile strength.

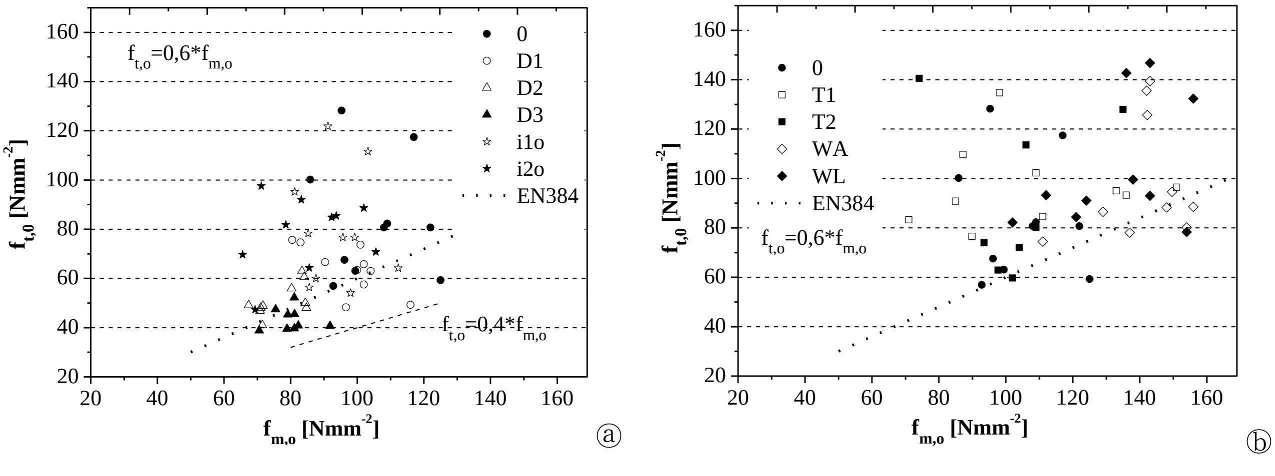


Figure 29. Correlation between bending and tensile strength for un- and modified wood with (a) - cell wall reaction, (b) - lumen fill and suggested curve (······ dot line, EN 384). For abbreviations see Table 5

4.1.7.2 *Bending and compression strength*

Figure 30 shows the correlation between bending and compression strengths where the data from Figure 22a and Figure 23 were used. The cell wall modification with DMDHEU and MMF resin has shown two different extended changes. In Figure 30a a movement of the results away from the suggested curve (with dot-line, EN 384) to the right-down side were shown. The increasing of compression strength moved the data to the right of the curve suggested in the EN 384 standard. The decreasing of bending strength moved the data down to the horizontal axis-xx. Specimens modified with DMDHEU resin, despite the concentrations, the significant increase of compression strength (Figure 23) together with the decreasing in bending (Figure 22a), lead to a significant data movement to the right-down side the EN 384 curve. Then, new curves were suggested (dashed-dot and thin-dashed line) in Figure 30a and b, where the coefficients k and η were shown in the Table 12.

If the suggested curve (27 equation, from EN 384 standard) was used to predict the compression from the bending strength in modified wood (in particular with DMDHEU resin) the results will be *underestimated* and full capacity of material would not be used.

$$f_{c,0,k} = 5 \,.\, (f_{m,o,k})^{0.45} \tag{27}$$

Figure 30b shows the correlation between bending and compression strength for lumen fill modification. Specimens modified with TEOS solution have shown no effect and modified specimens with wax have shown a slight increase effect, not significant.

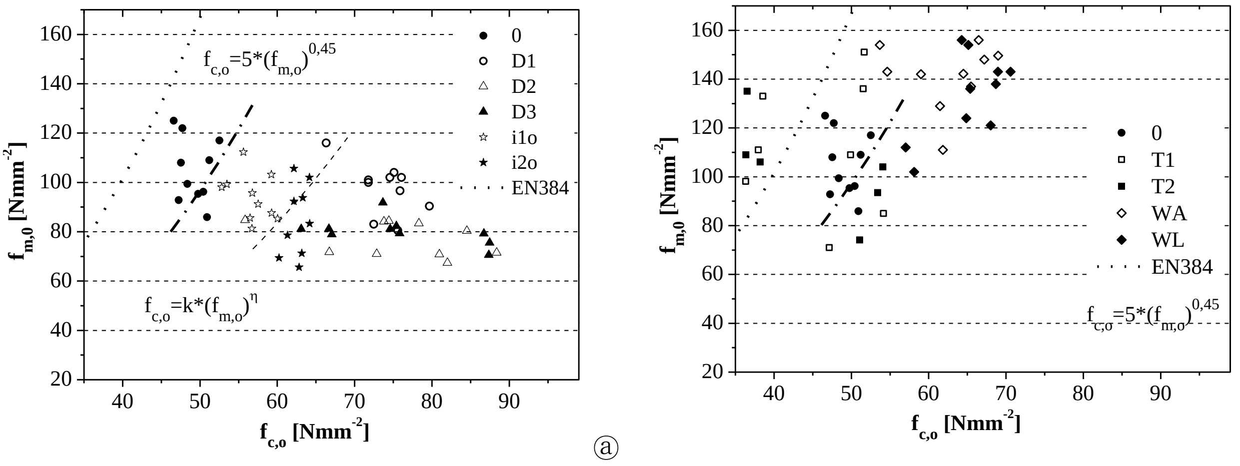


Figure 30- Correlation between bending and compression strength parallel to grain for un- and modified wood with (a) - cell wall, (a) - lumen fill and suggested curve (······ dot line, EN 384). For abbreviations see Table 5

Table 12 shows the coefficients for new suggested curves for correlation between compression and bending strengths in the modified wood.

Table 12. Suggested coefficients to estimate characteristic perpendicular compression strength from the bending strength

$f_{c,o,k} = k \cdot (f_{m,o,k})^{\eta}$	Modification	k	η	Line type
EN 384	0 *ctrl*	5	0.450	dot line
MMF and wax	i, WA and WL	7.5	0.415	dashed-dot line
DMDHEU	D	10	0.405	thin-dashed line

4.1.7.3 Tensile and compression strength

In order to correlate tensile and compression strengths shown in Figure 31, a new equation (28) was derived from the equations (25) and (27), where the compression, tensile and bending strengths were involved.

$$f_{c,0,k} = 5 \cdot \left(\frac{f_{t,0,k}}{0.6} \right)^{0.45} \tag{28}$$

If no change on the modified wood was incorporated (by the chemical or heat), their compression and tensile data should be around of the suggested curve (with dot line, EN 384), given by the last equation (28). Otherwise, movement of data away of the suggested curve EN 384 can occur.

In the resin-based modification, the increasing of compression strength (data from Figure 23) move the data to the right of the horizontal x-axis and the decreasing in tensile strength (data from Figure 28a) move the data down of the vertical y-axis, Figure 31a.

In the lumen fill modification (TEOS and wax) a slight increase of both properties, in the compression and tensile strengths (respectively in Figure 23 and Figure 28b), moves data to the up-right side of the suggested curve, in Figure 31b.

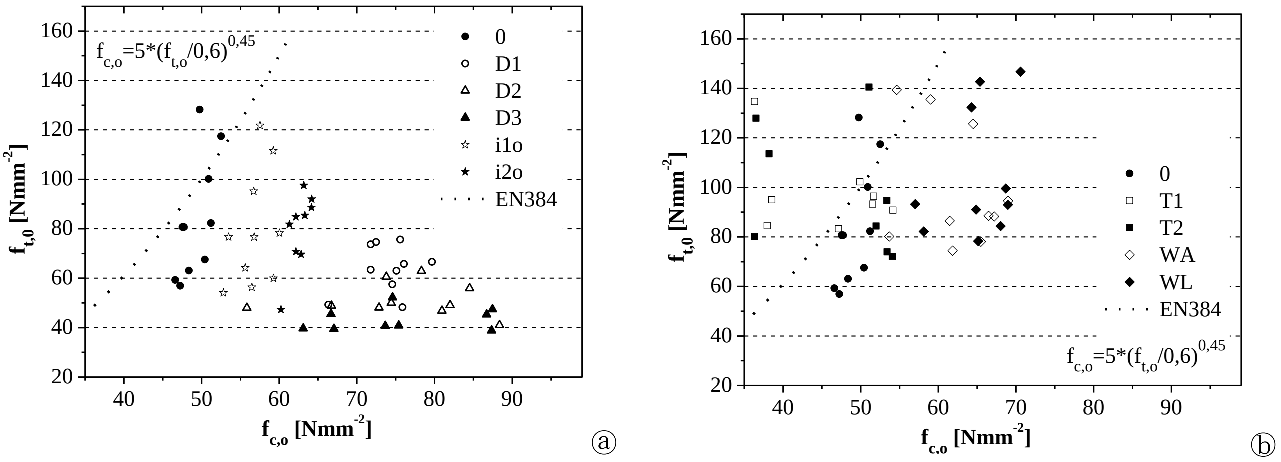


Figure 31. Correlation between compression and tensile strength parallel to the grain and *derived* suggested curves EN 384 for un- and modified wood with (a) - cell wall and (b) - lumen fill. For abbreviations see Table 5

Specimens modified with wax have shown a *slight* increase in tensile strength, however was not significant and does not justify an extensive test campaign.

In modified wood with DMDHEU resin, it was clear that the increasing of the compression strength conducts to *unsaved estimated* tensile values according to EN 384 standard. From this *screening study* and between both properties, compression and tensile strength are rarely mentioned in literature and an extensive test campaign needs to be done.

4.1.7.4 *Density and compression strength perpendicular to the grain*

In the wood structures design usually the perpendicular compression strength is obtained from the wood density. For chemical modified wood, the density increased according to WPG (✰) shown in Figure 21 up to Figure 28.

Figure 32 shows the relation between compression strength perpendicular to the grain in the T direction and the density of the wood material. The significant increase of the compression strength for resin based and wax modification was followed the density increasing but in different extent. On the other hand, in the lumen fill modification with TEOS solution, the density increasing for both WPG of different concentrations was not associated with.

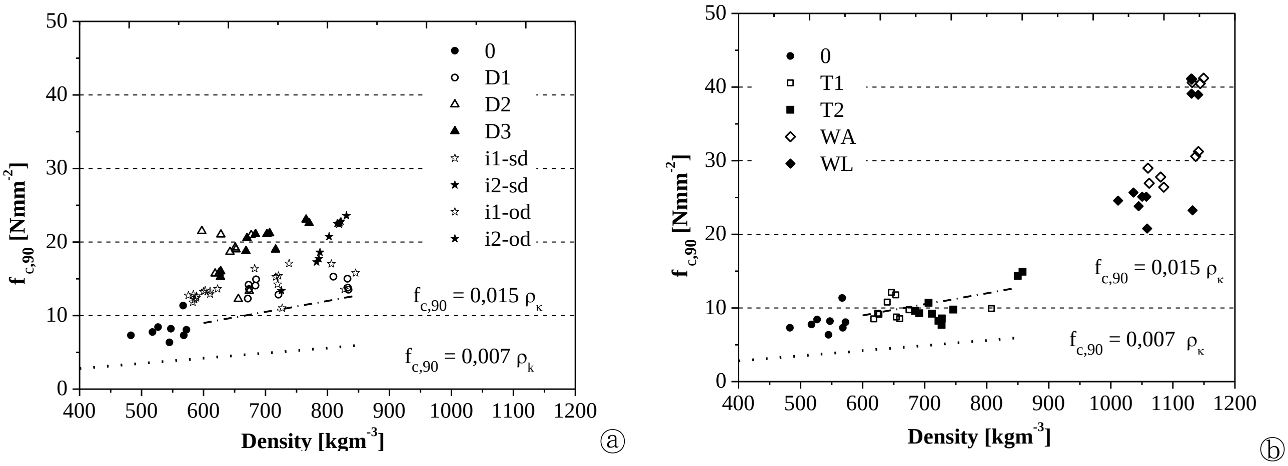


Figure 32. Correlation between density and compression strength perpendicular to the grain for un- and modified wood with (a) - cell wall and (b) - lumen fill and suggested curves, EN 384. For abbreviations see Table 5

In Figure 32 both curves (the dot-line curve for softwoods and the dashed-dot line for hardwood species) represent the suggested curves values according to EN 384 standard, quoted in equations (29) and (30), respectively. Where compression strength comes in N.mm^{-2} and density should be in kg.m^{-3}.

$$f_{c,90,k} = 0.007 \cdot \rho_k \qquad (29)$$

$$f_{c,90,k} = 0.015 \cdot \rho_k \qquad (30)$$

Except for specimens modified with TEOS, all modification applied to the pine softwood species used (DMDHEU or MMF resin and wax) increased significantly the compression strength perpendicular to the grain. However, despite the density increasing, the perpendicular compression strength prediction needs to be fit to the features imparted by the modification. An extensive test campaign is needed. For modified wood in general (with cell wall reaction and lumen fill with wax, exception done for TEOS), in Figure 32a and b, the suggested curve for hardwood species can be used to predict the compression strength from the density (dashed-dot line, EN 384).

4.1.7.5 Bending and shear strength

Figure 33 shows the correlation between shear strength parallel to the grain and MOR for un- and modified wood. Both properties have decreased by cell wall modification, in Figure 22a and Figure 25, respectively.

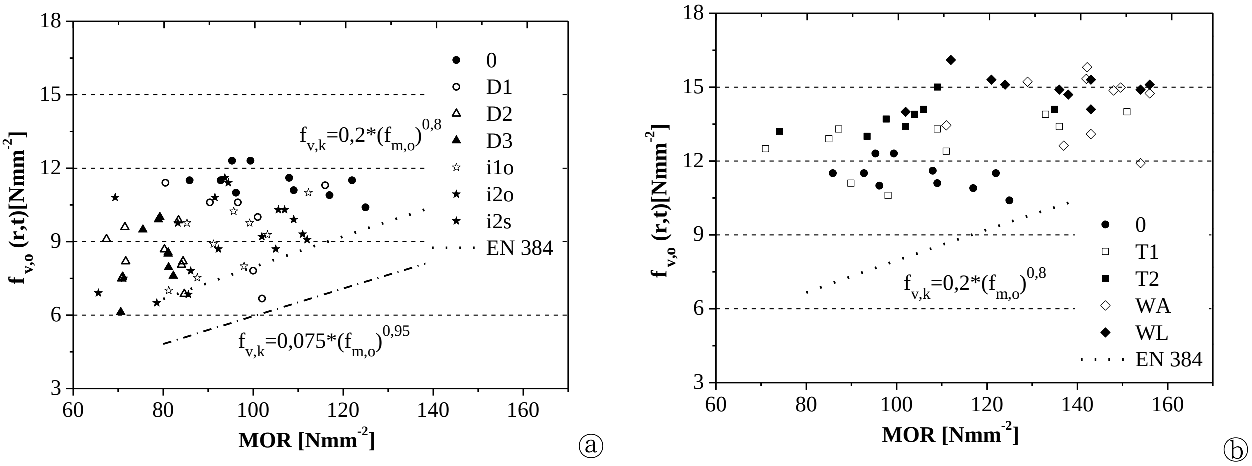


Figure 33. Correlation between shear strength parallel to the grain and bending strength (MOR) for un- and modified wood with (a) - cell wall, (b) - lumen fill and suggested curve, EN 384. For abbreviations see Table 5

In the Figure 33, the dot-line curve represents the suggested *characteristic* shear strength for unmodified softwood species, equation (31) according to EN 384. The shear strength reduction in the resin based modification lead to a new equation curve suggested at dashed-dot line and presented in the equation (32).

$$f_{v,0,k} = 0.2 \cdot (f_{m,o,k})^{0.8} \tag{31}$$

$$f_{v,0,k} = 0.075 \cdot (f_{m,o,k})^{0.95} \tag{32}$$

In the lumen fill modification (TEOS and wax) a slight increasing of shear strength moved up the data on the vertical y-axis. However, regarding to the higher variability of wood material and to obtain saved prediction data, no suggestion for new curves are presented.

4.1.8 Screening analysis, main conclusions

The screening analysis on *correlations* for predicting the *less known* mechanical properties from the *reference* properties were presented. To lead a better understanding of changes incorporated by chemical modification of Portuguese pinewood, the essential data were shown in an unknown way.

Density increased in all modification but any mechanical property was not improved in the same range, i.e. tensile, compression and bending strengths did not *follow* the improvement of density. The reaction cell wall modification with DMDHEU resin has shown a significant increase in *compressive strength* associated with a reduction in bending, tensile and shear strength.

The results obtained in different studies are encouraging but more work should be done to sustain the *suggested formulas* for modified wood.

From the correlation analysis some partial conclusions can be drawn and summarized in the Table 13. In the cell wall modified wood, the bending strength assumed the tendency of the *tensile* strength. To overcome the shortcomings introduced by modification and benefit from the enhanced properties in the structural components, reinforcement need to be considered, as the Glulam structural wood where *carbon fibres* were used, e.g. (FIRP 2012; Steiger et al. 2012). Moreover, this reinforcement has been followed in the XIXth century to solve the concrete brittle behaviour (Quintela 1989). In fact, the steel reinforcement in concrete improved their behaviour to nowadays known properties. It is also noted that laminations used in the structural elements of Glulam will help to surpass two unsolved problems in the wood modification industry: *Up-scaling* effect in large cross sections with *uneven distribution* of chemical and crack appearance in large cross section (Homan and Bongers 2004; Johansson 2005; Tjeerdsma et al. 2005).

Table 13. General overview about the effect of the modification in the mechanical properties

Strength property		DMDHEU	MMF	TEOS	wax
Bending	$f_{m,0}$	--	-		+
Compression	$f_{c,90}$	+++	++		++
Tensile	$f_{t,o}$	--	-		+

Legend: Increasing or decreasing, significantly +++/---, moderate ++/-- and slight +/-

4.2 Creep behaviour

Many materials experience a significant increasing in strain when loaded constantly over a period of time. It is believed that the creep behaviour of modified wood will differ from unmodified wood. Concerning the main changes introduced by the modification in the dimensional stability, EMC, *embrittlement* effect with changes in MOR on resin based modification, all these properties will influence the creep behaviour in a way, despite the MOE did not change.

During the period of creep measurements no ruptures occurred in both setups used:

- Bending in three points for different stress levels at indoor climate, 65% of RH, (setup in Figure 11a and results in 4.2.1 item).
- Bending in three points for saturated conditions, (setup in Figure 11b and results in 4.2.4 item).
- Bending in four points for environment changing conditions, to study the MSE (setup in Figure 12a and results in 4.2.5 item).

In full-scale wood structures, the creep phenomenon occurs at SL of 1.5 up to 2.1Nmm^{-2}, as suggestion at service limit state (SLS) according to EC 5 code (EN 1995:1). Therefore, a creep factor k_c of 0.60 is suggested for inddor conditions (65% of RH in a lifetime of 50years).

In laboratory conditions, SL of 10Nmm^{-2} was the most used (Epmeier et al. 2004; Ranta-Maunus and Kortesmaa 2000). The latter SL is the most close to the SL matched to the SLS of EC 5 and simultaneously can produce displacements to be captured by sensitive measurement instruments, LVDT's (see 3.5.2 item). However, in many wood applications, higher SL can be installed. Occasional *stock loads* at horizontal members and most of times in the wood columns. The latter's are never perfectly straight and when axial loaded, the creep phenomenon can arise due to the *secondary bending* moment from the slight column curvature, known as *P-δ effect*.

4.2.1 Stress level (SL) effect, indoor conditions

Under three SL over a period of 840h (35days), only unmodified pinewood and modified with medium concentration of DMDHEU resin (D2, 1.3M) were tested, Figure 34. Each darked-line shows one test specimen. The grey dashed-line shows the environmental conditions, assumed as constant RH in percent, between 55 to 60%.

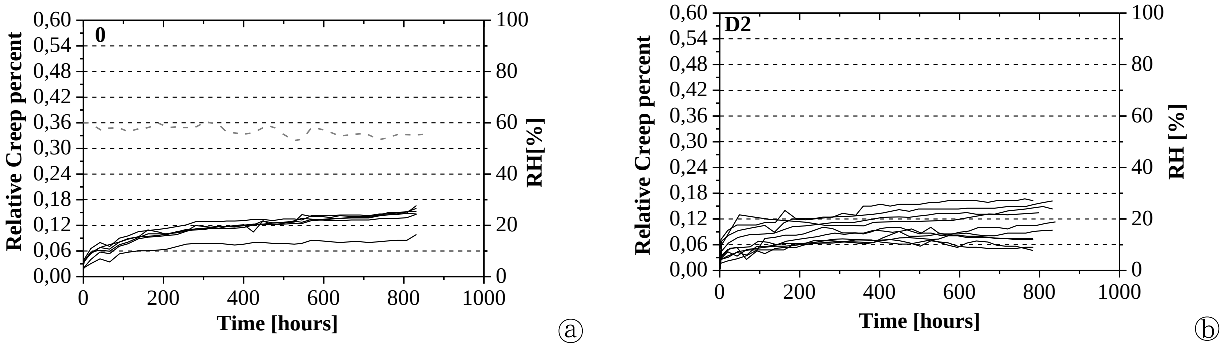


Figure 34. Relative creep percent for (a) - unmodified pinewood species and (b) - modified pine (DMDHEU D2, 1.3M) under low SL 8Nmm^{-2} at indoor conditions, 65% of RH [%]

Using the PFM model, listed in equation (3), the compliance of the creep curves can be decomposing in the constituent coefficients. Both creep coefficients, β_1 and β_2, have different meanings. In the creep strain, the coefficient β_1 describes the slope of the relative creep curve and β_2 is the power factor which represent the influence of time. From the creep coefficients of the PFM that leading to the creep factor (k_c) of each curve, Figure 35 shows the effect of the SL. Each box plot shows the chief creep coefficients of PFM used to fit all creep curves for each set of specimens and respective k_c, with the statistical analysis referred in 3.7 item.

In the unmodified pinewood (0) and modified with DMDHEU resin (D2) the k_c did not reveal the compliance creep curve of both materials, in Figure 35b and respectivelly d. Both creep coefficients (β_1, β_2) has shown constant tendencies, Figure 35a and c.

For unmodified pinewood: The average value of β_1 was set at 0.025 up to 0.040 for high SL; The average of β_2 was set at 0.10, despite the SL; And the k_c was set at 0.15 up to 0.22 for high SL.

For modified pinewood with DMDHEU resin (D2, 1.3M): The average value of β_1 was set at 0.025, despite the SL; The average of β_2 was set at 0.075 up to 0.11 for high SL; And the k_c was set at 0.11 up to 0.15 for high SL. However, under high SL the creep factor (k_c) has shown a slight increased tendency, statistically not significant.

In the low and medium SL the slope of the creep curve (β_1) was similar for both materials and the effect of the duration test (β_2) leads to a similar k_c as well, between un- and modified wood. For high SL (35Nmm^{-2}), the slope of the creep curve β_1 was higher for unmodified pinewood (0.075) than for modified pinewood (0.025). However, the duration test seemed to have no effect, where β_2 remained constant (0.24) for both, un- and modified wood. In the high SL for modified pinewood (DMDHEU resin, D2 - 1.3M) the slope curve was kept constant (β_1) and the role of the duration test (describe by β_2) had a slight effect, no significant.

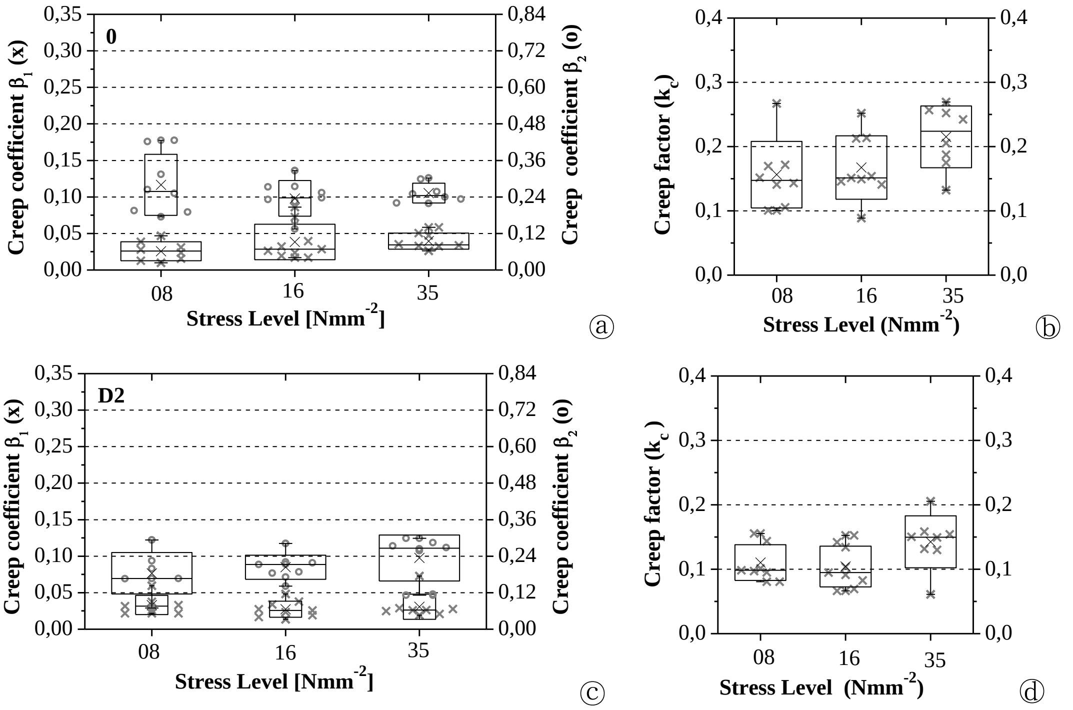


Figure 35. Creep coefficients (β_1 and β_2) and creep factors (k_c) at three stress levels for unmodified pinewood (a, b) and modified with DMDHEU (D2, 1.3M) (c, d)

The compliance of the slope curve did not show significant effect under three SL (8, 16 and 35Nmm^{-2}). Under low and medium SL (8 and 16Nmm^{-2}), the unmodified pinewood specimens did not show any difference on the k_c related to both SL, Figure 35b. However under high SL (35Nmm^{-2}), the mean of the k_c was higher, not significantly.

Specimens modified with DMDHEU resin showed lower and homogeneous k_c with significant difference under high SL (35Nmm^{-2}) in Figure 35d. Under low and medium SL (8 and 16Nmm^{-2}) k_c did not show significant effect (k_c of 0.15 up to 0.11 for un- and modified wood specimens, respectively). However, under higher SL (35Nmm^{-2}) significant less effect on the k_c

was found between un- and modified wood (k_c of 0.22 up to 0. 15, respectively), in Figure 35b and d.

Figure 36 shows the *SL effect for all modifications* on the creep compliance curves over a period of 35days (840hours). Specimens under low SL (8Nmm^{-2}, Figure 36a) did not show any difference on the creep factor between any *type of the modification*, cell wall reaction or lumen fill effect.

Under high SL (35Nmm^{-2}), specimens modified with resin were shown significant low k_c, in Figure 36b. Both modifications in cell wall (DMDHEU and MMF resin) have shown similar behaviour at indoor climate, a significant reduction up to 50% was found.

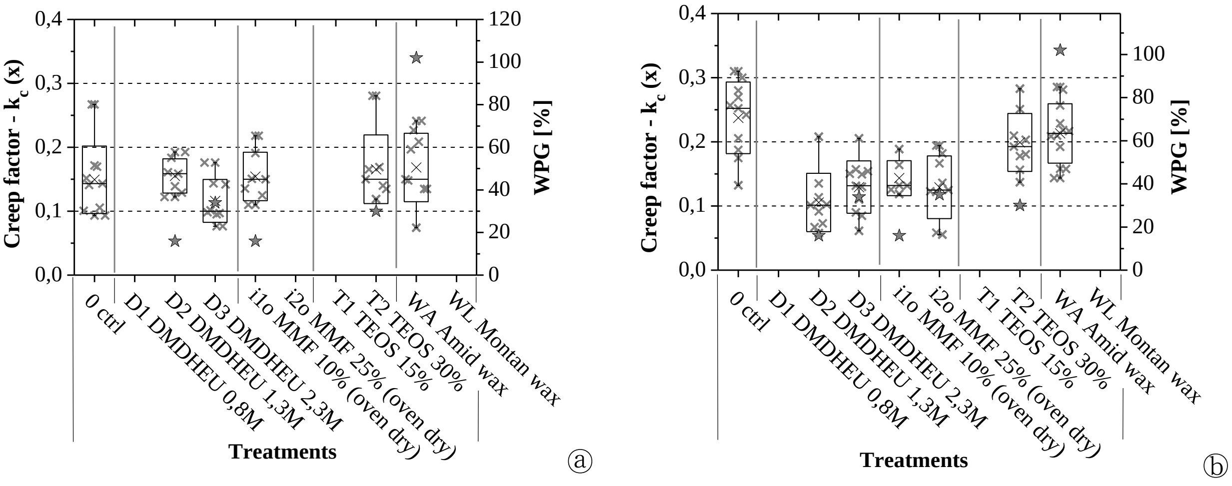


Figure 36. Creep factor for (a) - low SL, 8Nmm^{-2} and (b) - high SL, 35Nmm^{-2}

Both materials used in the lumen fill modification (TEOS and wax) did not show any effect compared to unmodified wood specimens, in Figure 36a and b.

4.2.1.1 Duration test effect

In the studies of creep is unanimously accept that results should demonstrate the strain obtained after a certain time. For comparative purposes, this philosophy is affordable, though the shape of the curves can lead to *newer* and *useful information* for future comparisons and support design standard data. On the other hand, the analyse of durations test allowing to see if the results will be *stable* or not, see also 4.2.5.3 and 4.2.5.4 items where the *creep limits* concept will be discussed.

For comparative purposes with pinewood curves previously presented in Figure 34a and b, two additional wood species, *Blue Gum* and *Beech*, were included. Figure 37 shows the compliance curves of relative creep in percent over a period of 35days//840h. Each dark line means one tested specimen and grey dashed-line showed the RH of the climate room.

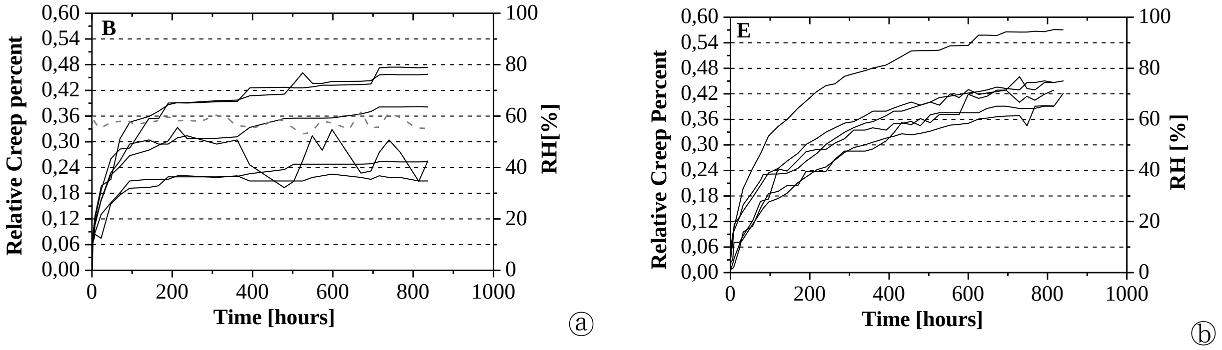


Figure 37. Relative creep percent for (a) - Beech and (b) - Blue Gum wood species under low SL 8Nmm^{-2} at indoor conditions, 60% of RH

Unmodified pinewood in small flawless wood stakes with 1:10 scale bending in three points has shown a k_c up to 1.15 (or 0.15 as a percent relative creep in Figure 34a). Roszyk (2005) with Scots pine 1:10 and Hoyle et al. (1985) with Douglas fir 1:1, both have shown similar creep results, up to 1.14 of k_c, despite four points bending setup was used.

In the same conditions, specimens with small scale 1:10 of Blue Gum wood species have shown an increase of k_c up to 0.42, in Figure 37b.

Comparatively both curves for unmodified pinewood species (in Figure 34a) and for Blue Gum (in Figure 37b), significantly less deformation in pinewood species was found.

Santos (2009) found similar results between both Portuguese species. He found less creep in the pinewood than in the Blue Gum species, despite full-scale specimens 1:1 and uncontrolled conditions were used.

Calvo et al. (2002) with Argentinean Eucalyptus with 1:10 has found a mean k_c up to 0.70, under uncontrolled condition (sheltered, service class 2 according to EC 5). With similar wood species of *Eucalyptus* and test conditions but with full-scale specimens 1:1, Piter et al. (2007) showed an k_c increasing up to 0.23. Both results are acceptable, according to EN 384, since specimens with 1:1 scale deflect less than 1:10 specimens (under the same SL conditions).

With constant indoor climate, despite small specimens 1:10 were used, Blue Gum showed k_c of 0.42. This result is in the middle of 0.7 and 0.23 showed by Calvo et al. (2002) and Piter et al. (2007), respectivelly.

Santos (2009) with pinewood 1:1 bending in four points under *uncontrolled* conditions (sheltered) presented higher relative creep. He showed a mean creep of three times of k_c (200% of the *initial strain*) compared to 0.15 of k_c in this study with small specimens 1:10. Environmental conditions should be the main reason to lead a higher deformation. At sheltered conditions, high variation of RH can occured. A difference of 20% of RH is enough to reach the MSE. Either, in the same wood species, it is unexpected that full-scale specimens showed higher creep deformation than small-scale specimens.

Figure 38 shows the compliance curves of the creep coefficients, β_1 and β_2, obtained using the PFM in equation (4), over tests differents duration. In each duration (of 100, 200, 400, 800 and 1400h), the fitting curves were done by the ORIGIN software. The mean coefficients of all creep curves were recorded and analyzed (•,▲,-,✕ means the median value of 10 specimens). Each curve translated the compliance curve of the PFM coefficients (creep coefficients, β_1 and β_2) for creep tests with different durations.

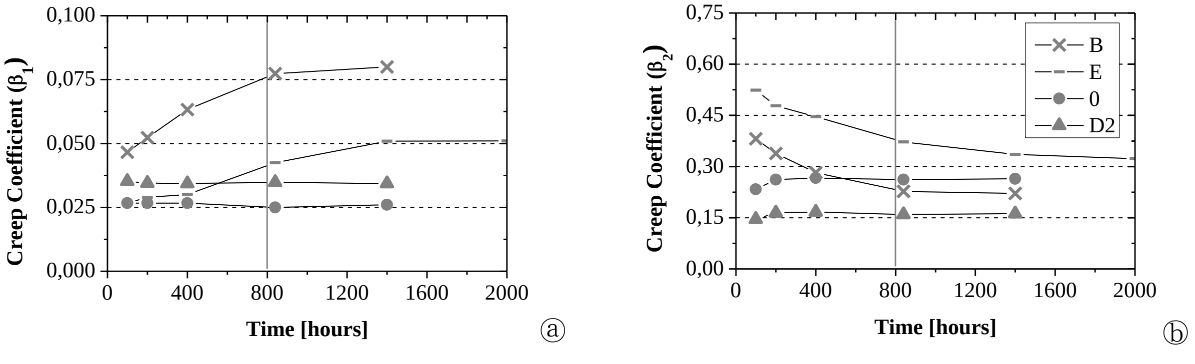


Figure 38. Mean creep coefficients (a) - β_1 and (b) - β_2 of the PFM, dependent upon the duration of the creep test (*legend*: -B Beech, -E Blue Gum, -0 unmodified pinewood, -D2 DMDHEU 1.3M)

4.2.1.2 β_1 - Creep coefficient

The coefficient β_1 describes the slope of creep curve, 2.4.1. In this study done with small beams 1:10 bending in three points (Figure 11a), all unmodified wood species (Pine, Beech and Blue Gum) and modified pinewood with DMDHEU has shown higher slopes in the creep curves than full scale specimens (Hoyle et al. 1985). It starts at 0.025 in modified pine, up to 0.077 for Beech specimens. Hoyle et al. (1985) with Douglas-fir 1:1 presented 0.0210 for β_1. Pinewood species in scale 1:10, un- or modified with DMDHEU resin, were the most close of Hoyle's results 1:1, app. 0.025.

When different sizes are compared, as Calvo et al. (2002) and Piter et al. (2007) did with Eucalyptus, higher slopes of creep curves are expected in small-scale specimens 1:10.

Above 200h of duration test, creep coefficient β_1 was stabilized, 0.025 and 0.0325 for un- and modified pinewood, respectively. The flat tendency of β_1 was reached in Beech and Blue Gum species within 800h and 1400h, respectively.

To find stabilized creep coefficient for pinewood species, modified or not, the duration test does not need to be extended up to 840h, only 200h is enough. However, the stabilization with hardwood species was reached for longer period, 1400h for Bluegum.

4.2.1.3 β_2 - Creep coefficient

The creep coefficient β_2 describes the effect of test duration on the creep factor, k_c, see 2.4.1. Hoyle et al. (1985) and Kliger (1986) with full-scale specimens 1:1 found similar exponential creep coefficient (β_2), 0.3240 and 0.2845, respectively. Unmodified wood species, Beech and pine wood has shown a tendency towards the creep coefficient β_2 presented by Kliger, and Blue Gum converge to the β_2 presented by Hoyle, with an average value of 0.3240.

As higer is the creep coefficient β_2 as significant is the duration test in creep. In the Blue Gum hardwood species, with fast grown, the duration creep test assumes an important role in the creep results comparatively to Beech and pinewood species. A minimum of 1400h was required to find stable creep coefficients for Blue Gum wood species.

For all species, un- and modified, the increase of the duration test showed a stabilization of both creep coefficients (β_1, β_2). For comparative reasons between Pine wood species modified or not, stabilized creep coefficients were found over one-week of duration test. For DMDHEU modified specimens a stabilization of β_2 at 0.170 was found up to 200h. The stabilization of the exponential term (β_2) in the similar period (for un- and modified wood) corroborated that the creep test duration doesn't need to be extended to obtain stablized results.

4.2.1.4 k_c - Creep factor

The k_c is the *ratio* of the strain increasing with time related to the *initial elastic strain*, 2.4.6. Figure 39 shows the compliance curves of the k_c for the duration creep tests and forecast for 840h and 50years. The k_c forecasting, at 840h (in Figure 39a) and 50years (in Figure 39b), used the theoretical creep coefficients (β_1, β_2 of the PFM) from Figure 38, see in 2.4.1 the equation (4).

In the pinewood species, un- or modified with DMDHEU resin, all creep parameters were stabilized in the same range above 200h of duration test, β_1, β_2 in Figure 38 and concomitantly k_c in Figure 39a. The duration test increasing has shown a stabilization of all k_c. Between 100h up to 2000h, hardwood species has shown the highest reduction up to stabilize values were found 30%, Figure 39a. However, Beech stabilizes early than Blue Gum wood specimens. Features of the wood species, with a normal- and fast-growing, seem to be the main reason.

In the long-term prediction, forecast at 50 years in Figure 39b, each symbol means the average of the k_c obtained with the relative creep fitting curves using the PFM in ORIGIN software. The average of 10 specimens was presented when the duration creep tests were 100 up to 1400h (2000h for Blue Gum wood species).

Pinewood and Beech specimens showed 0.9 and 1.6 of k_c (at the expected end-life of building, 50years), respectively. Specimens of Blue Gum have shown significantly higher k_c (3.5) than the EC 5 suggestion (0.6).

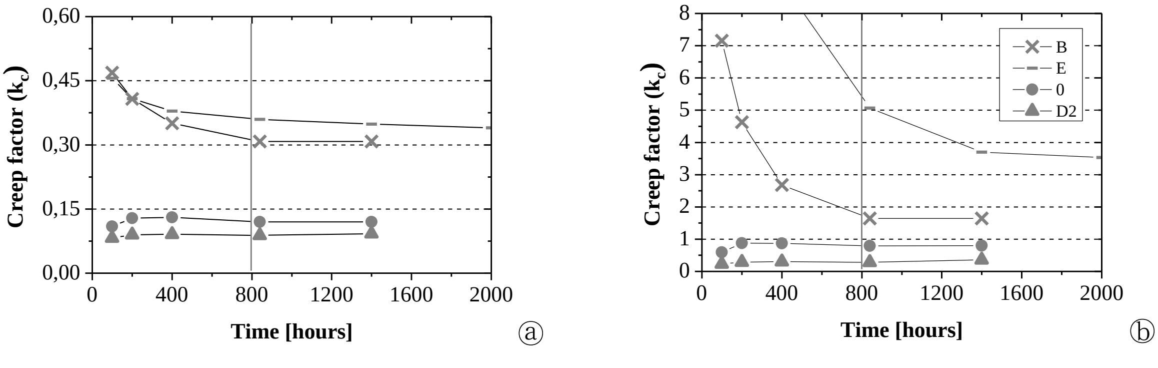


Figure 39. Creep factor (k_c) forecasting at (a) - 840hours and (b) - 50 years, dependent upon the creep tests duration, n=10 (*Legend*: -B Beech, -E Blue Gum, -0 unmodified pinewood , -D2 DMDHEU 1.3M)

Small-scale specimens of all *unmodified* species has shown higher k_c than the EC 5 suggestion (at the same indoor climate, first service class, k_c assume 0.6). Modified wood (DMDHEU D2, 1.3M) was the *only one* that has shown less k_c (0.43) than EC 5 suggestion (k_c 0.60).

In the pinewood species, modified or not, the creep factor k_c stabilized up to 200h of duration test (app. 8days). In the shorter- up to long-duration test (100h and 840h) only a slight difference were found, up to 10%. Comparative studies with modified pinewood request no longer duration for creep tests than 200h, app. 8days, to obtain stabilized creep coefficients results.

Cell wall modified wood has shown a significant *enhancement* in the creep behaviour comparable to the reduction: In the IBS or the EMC reduction in wet conditions, 87% of RH environment. Always compared to unmodified wood.

4.2.1.5 Analysis of correlations, indoor conditions

Often, wood density is regarded as being closely related to the strength or deformation. Table 14 shows the main correlations between density, stiffness and deformations in the creep tests under differents SL (8, 16, 35Nmm^{-2}) at indoor conditions.

Table 14. Coefficients of correlation for un- and modified pinewood specimens at each SL and different variables (n=10), [non-significant values]. For abbreviations see Table 5

ctrl / Modification			0	D2	D3	i1	i2	T2	WA
SL - 8Nmm^{-2}									
Creep strain	Vs.	MOE_{dyn}	[-0.34]	-0.89	[-0.46]	-0.80	-0.63	-0.56	-0.72
Relative creep	Vs.	MOE_{dyn}	[-0.13]	[-0.03]	[-0.27]	-0.67	-0.59	[-0.44]	-0.62
SL - 16Nmm^{-2}									
Creep strain	Vs.	MOE_{dyn}	[-0.06]	[-0.51]	[-0.03]	---	---	---	---
Relative creep	Vs.	MOE_{dyn}	[-0.32]	[-0.40]	[-0.41]	---	---	---	---
SL - 35Nmm^{-2}									
Creep strain	Vs.	$MOE_{st,3pb}$ [a]	[-0.37]	-0.80	[-0.50]	[-0.51]	[-0.05]	-0.67	-0.78
Relative creep	Vs.	$MOE_{st,3pb}$	[-0.43]	[-0.31]	[-0.10]	[-0.09]	[-0.27]	[-0.35]	-0.68
All SL (8, 16, 35Nmm^{-2})									
Density	Vs.	$MOE_{st,3pb}$	[+0.49]	[+0.34]	[+0.31]	[+0.53]	[+0.06]	[+0.13]	[+0.39]
Density	Vs.	MOE_{dyn}	[+0.51]	+0.61	+0.64	[+0.48]	[+0.30]	[+0.30]	+0.57
MOE_{dyn}	Vs.	$MOE_{st,3pb}$	+0.97	+0.71	+0.93	+0.97	+0.85	+0.95	+0.92
Creep strain	Vs.	MOE_{dyn}	[-0.53]	-0.61	[-0.46]	-0.77	[-0.43]	-0.65	-0.77
Relative creep	Vs.	MOE_{dyn}	[-0.50]	[-0.06]	[-0.16]	-0.57	[-0.45]	[-0.41]	-0.66

(a) These relationships are shown in Figure 40.

As far as unmodified wood is concerned in the vertical column (o-*ctrl*), moderate correlations were found, not significant. In modified wood specimens, the correlations were lower and not significant, in the most cases. The correlation between relative creep and MOE_{dyn} was moderate for unmodified wood and modified wood with TEOS. However, significant correlation between relative creep and MOE_{dyn} was found for modified specimens with wax (0.62 and 0.68 R). In the cell wall modification under low SL, the correlation between relative creep and MOE_{dyn} was significant for specimens modified with MMF resin (0.67 and 0.59 R). However, between the same properties, minor correlations for DMDHEU resin (0.03 and 0.27 R) were found. Moreover, at high SL the MMF resin has shown minor correlation (0.09 and 0.27 R).

For relative creep and stiffness, the following pattern can be drawn: Un- and modified with lumen fill (with TEOS and wax) have shown the best correlations, moderate up to significant staticscally. In the resin-based modification, correlation presented by specimens with MMF resin was not confirmed by specimens with DMDHEU resin.

Any pattern for correlations *can not be* extracted from this analysis for modified wood with resin based at indoor conditions.

As a summary, *the prediction of the creep performance criteria based exclusively on density should not be formulated for modified wood*. Although, the stiffness obtained with vibration technique (MOE_{dyn}), for un- and modified with wax and DMDHEU resin, showed significant correlations.

Specimens of un- and modified wood with deposit material in the lumen fill (TEOS and wax) showed better correlations than the modified ones, with resin-based, DMDHEU and MMF.

Epmeier and Kliger (2005) showed high significant correlation for unmodified wood specimens too, but at the same time they presented minor correlations for modified wood, i.e. acetylation, MMF resin, *thermowood* and furfurylation. The *varied* environmental conditions (MSE), SL and different size of the specimens used are the main distinctions between both studies and will be addressed latter, see item 4.2.5.6.

Creep strain and stiffness has shown the best correlations. Moderate up to significant for unmodified wood specimens and all modifications (with both active principles, resin based and lumen fill). Exception need to be done for resin based modifications with high concentration.

The high correlation between creep strain and MOE_{st} could be expected, as the MOE_{st} was calculated from the (creep test) strain after 60s. In fact, two strains were compared: The strain after 60s (with *short-term* load) and the strain after 5 weeks under a sustained load. On the other hand, the low and medium SL used in this study, both are not enough to mobilize the same SL needed to match the SL standard to measure the MOE according to DIN 52 186.

The obtained short-term deformation correlated moderately to-significantly to the long-term deformation. This indicates that, by measuring the stiffness of a structural member, it should be possible to predict its long-term performance under loading.

In the cell wall modification (DMDHEU and MMF resin, with medium concentration) moderate correlation were found, statistically not significant. However, it seems that for high level of concentration in the same resin based modification, the correlation disappeared.

In the Figure 40, scatter plots of the correlation between creep strain (on the horizontal x-axis) and $MOE_{st,3pb}$ (on the vertical y-axis) are shown. The corresponding coefficients of correlation can be consulted in the Table 14 with creep strain vs. $MOE_{st,3pb}$. Specimens modified with lumen fill (TEOS and wax) have shown significant correlation and unmodified wood has shown moderate correlation.

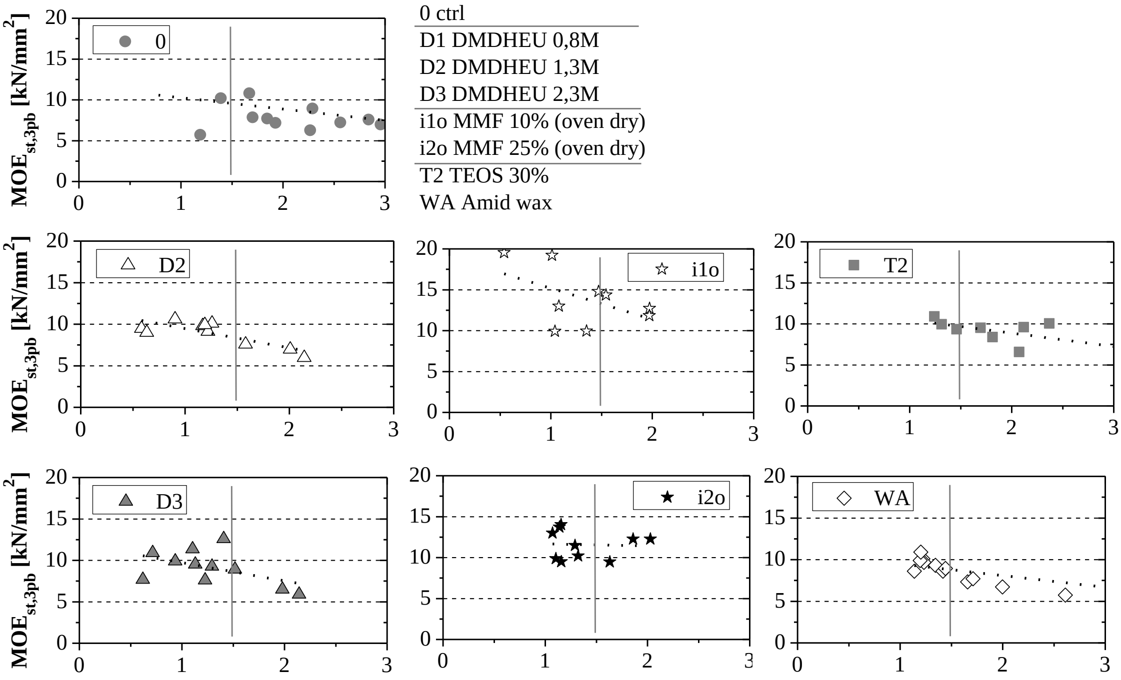


Figure 40. Correlation scatter plots between creep strain [mm] and $MOE_{st,3pb}$ [$kNmm^{-2}$//GPa] under SL of $35Nmm^{-2}$ over a period of 850h (35days) at indoor condition.

4.2.2 Stress level effect, discussion

When this study started, mainly for resin based modified wood, the assumption was that chemical modification of wood would change the bending creep behaviour. The main reasons to contribute for that were changes in EMC, SSE and IBS / *embrittlement effect* imparted in the modified wood material.

For unmodified wood, it is known the minor effect of the MC (under certain limits) and the SL in the bending creep under constant environmental conditions. Clouser (1959) conducted a creep study with small beams (1:10 scale) of Douglas fir wood species with 6 and 12% of moisture under very high SL, greater than 60 up to 95% of MOR. He has shown that the *time to rupture* increased as the SL was decreased and a *slight effect* of MC was shown at indoor climate (but not significant). Dinwoodie et al. (1990) showed a slight effect of the SL on the relative creep with red wood under SL between 30 up to 50% of MOR.

Despite resin-based modification reduced the EMC (or showed high dimension stability, ASE and SSE), their creep results did not differ from unmodified wood under low and medium SL (8 and 16Nmm^{-2}). Under high SL (35Nmm^{-2}), both types of resin (DMDHEU and MMF) have shown less creep, with a reduction close to the SSE, 50% (app.). However, these resin based modifications has showed *lower* EMC and the *embrittlement* effect was involved as well in different extend. On the other hand, saturated condition has shown the isolated *embrittlement effect* imparted by the modification. The experiment did with *moisture content* above the FSP allows to neglect the effect of the MC in unmodified wood and in the resin based modification.

The lumen fill modification (TEOS and wax) has not shown any effect on the EMC and SSE as well as in the relative creep presented at constant enviroment, indoor or saturated conditions.

Table 15 shows the mean k_c accessed experimentally under three SL (8, 16 and 35Nmm^{-2}) over a period of 840h//35days with non-significant values in [square brackets] and significant values *italicized*.

Cell wall reaction or lumen fill modification under low SL has shown no significant effect, regardless the WPG imparted by the modification. For cell wall modification (with medium and high concentration of DMDHEU resin) similar creep results were found.

Specimens modified with medium and high concentrations of DMDHEU resin, or high concentration of MMF resin, under high SL they have shown significant less creep than unmodified specimens. The embrittlement effect, imparted by the resin deposit in the cell wall modification (DMDHEU and MMF resin), can be seen as the main *explanation* by the significant reduction in the long-term creep behaviour. At each set of wood specimens, modified wood or not under various SL, no significant effect were found. The last two lines in the Table 15 showed all dates in square brackets, which means, no significant effect between them.

On one hand, the wood MC and its changes (ΔMC, app. 50% for modified wood with resin based) could be assumed to be a parameters that influence the creep behaviour. However, on the other hand, the experiment done with cell wall modification (by DMDHEU and MMF resins) two effects were mixed:

- The EMC reduction;
- Resin deposit in the cell wall.

The *latter* acts as arrested-fibres by it self, *embrittlement effect*, according to Rowell (1996), Mai et al. (2007) and Xie et al. (2007b). Therefore, the former low EMC, and small ΔEMC between climate changes, imparted by modification, such as resin based modification, more in DMDHEU than in MMF resin, only displayed reduced primary creep behaviour under high SL (35Nmm^{-2}), app. 50%.

Table 15. Results of creep tests at indoor cilmate, creep factor (k_c) under 8, 16 and 35Nmm^{-2} SL over 850h (35days) by un- and modified pine (mean, standard deviation, coefficient of variation and p-value). For abbreviations see Table 5

Stress Level, k_c	0	D1	D2	D3	i1	i2	T1	T2	WA
SL 8Nmm^{-2}, k_c	0.15	--	0.16	0.11	0.19	--	--	0.18	0.18
stdv	0.05	--	0.03	0.03	0.03	--	--	0.07	0.06
cv	35	--	17	23	18	--	--	37	34
p-value	--	--	[0.61]	[0.21]	[0.78]	--	--	[0.84]	[0.67]
SL 16Nmm^{-2}, k_c	0.14	--	0.12	0.11	--	--	--	--	--
stdv	0.02	--	0.05	0.04	--	--	--	--	--
cv	18	--	43	33	--	--	--	--	--
p-value	--	--	[0.37]	[0.08]	--	--	--	--	--
SL 35Nmm^{-2}, k_c	0.22	--	0.11	0.14	0.14	0.13	--	0.18	0.21
stdv	0.05	--	0.05	0.04	0.03	0.05	--	0.03	0.05
cv	22	--	43	28	19	38	--	14	21
p- value	--	--	*0.00*	*0.02*	[0.07]	*0.01*	--	[0.24]	[0.79]
p-value[a]									
SL 8Nmm^{-2}	--	--	--	--	--	--	--	--	--
SL 16Nmm^{-2}	[0.27]	--	[0.24]	[0.11]	--	--	--	--	--
SL 35Nmm^{-2}	[0.10]	--	[0.12]	[0.11]	[0.28]	--	--	[0.96]	[0.58]

(a) Correlation between each modification but at different stress level

To clarify and separte both latter effect, a new experiments were done, see 4.2.4 item.

4.2.3 Stress level effect, main conclusions

At indoor climate and up to medium SL (8 and 16Nmm^{-2}), cell wall modified specimens with DMDHEU resin did not show significant reduction in creep, represented by creep coefficients (β_1 , β_2) and creep factor (k_c). However, at high SL (35Nmm^{-2}) the cell wall modification has shown significant k_c reduction. This creep behaviour was similar to the SSE, with a reduction up to 50%.

Specimens modified with lumen fill (with deposited material of TEOS and wax) under constant conditions (indoor and saturated) as well under various SL (8 up to 35Nmm^{-2}) have shown no difference at creep behaviour compared to unmodified wood. In other words, the material deposit in the lumen *has no effect* in the creep behaviour.

Unmodified pinewood has shown a slight not significant increase of the relative creep at high SL (35Nmm^{-2}). In general, for un- and modified-wood with resin based (DMDHEU and MMF resin), TEOS and wax, the relative creep over 800hours/35days appears to be *unaffected* in the domain of stress up to 35Nmm^{-2} (0.40 of MOR). The creep seems to be roughly independent of the SL.

In the analysis of the compliance creep curves related to the duration test with constant environmental conditions, some conclusions can be drawn:

- A *minimum duration* of creep tests is required to reach stabilized creep coefficients. A results comparison in the future can be done, independent of the unmodified wood species or type of modification.

- Above 200h of duration creep test, pinewood species showed stabilized creep values. Through the creep analysis with PFM (un- and modified pine wood with DMDHEU in small clear specimens 1:10) has shown constant creep coefficients (β_1, β_2) and creep factor (k_c).

- For Blue Gum wood species (*Eucalyptus globulus*), creep test duration has a decisive role to obtain stabilized creep results. Blue Gum and Beech wood species showed a required minimum duration creep test, of 1400h and 840h as necessary, respectively.

4.2.4 Creep in saturated conditions

Applications in wet conditions (swimming pools, e.g.) and the significant increase in compression strengths (Figure 23 and Figure 24) or hardness (Figure 61 and Figure 62) are the *strengths* of chemically modified wood. Comparatively the creep behavior of modified wood under constants environmental conditions was evaluated by the setup presented in Figure 11b.

In order to uniform the results presentation of these both experiments in saturated conditions, only the relative creep was presented. In these experiments, displacements are greater than displacements obtained at indoor conditions. However, as relative creep is the ratio of the strain at any time related to the initial strain, values in the charts are compensated.

Figure 41a shows the *relative creep* of small beams bending in three points with upper compression zone saturated over the test duration, 35days//840h.

Specimens modified with lumen fill (TEOS and wax) have shown no effect on the creep performance compared to unmodified wood.

The cell wall modified specimens, with DMDHEU and MMF resins, have shown a significant reduction of the relative creep, Figure 41a.

Figure 41b shows the creep behaviours under constant *full-saturated* conditions. The mean MC was higher than the FSP, 62% and 48% for un- and modified wood with DMDHEU resin, respectively.

Between both types of specimens, modified or not, 0 and D2, creep performance were assumed to be alone resultant of the *embrittlement effect* by chemical modification (effect of the resin deposit and reaction with cell wall). Because the MC was above the FSP, its effect can be neglected and only the deposit of resin in the cell wall remained as difference.

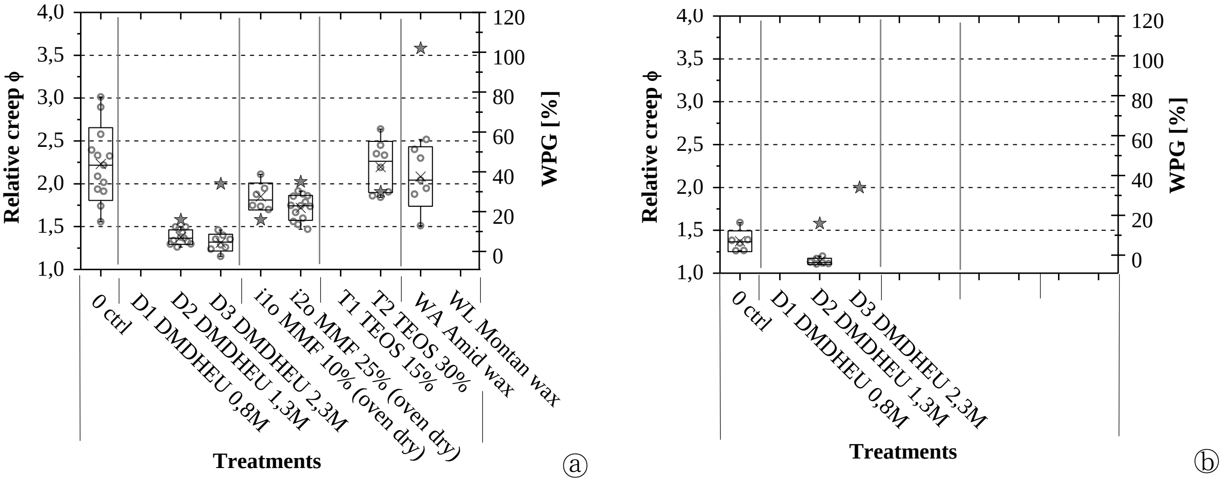


Figure 41. Relative creep, ϕ, with (a) - saturated compression zone and (b) - full saturated, for un- and modified pinewood specimens (WPG, ✰) under SL 16Nmm^{-2}

Under wetted conditions in the compression zone Figure 41a, reduction of the relative creep (ϕ_t) was roughly similar to the reduction in the IBS (energy absorption) experienced by both modifications: 60% for DMDHEU and 30% for MMF resin, see also Figure 26 in the item 4.1.5.5.

The IBS is the best property to describe the *embrittlement effect* imparted by the cell wall modification (with DMDHEU and MMF resins). Both setups, saturated compression zone in Figure 41a or *full-saturated* conditions in Figure 41b (see also the loading arrangement in Figure 11b), led to a similar conclusion regarding the *relative creep* results and IBS behaviour.

Under full-saturated conditions, cell wall modification (with DMDHEU and MMF resin) has shown less creep with different extend, 50% and 25%, respectively. The reduction in the k_c was roughly similar to the decreasing in EMC in both type of resins (DMDHEU and MMF) for wet conditions, 87% of RH, see Figure 16.

Epmeier and Kliger (2005) with similar modified wood (furfurylation and MMF resin) could not settle any correlation between their own results in the MSE and the ΔEMC. However, in the study *under saturated* compression zone in bending, specimens modified with MMF resins has shown similar creep reduction as Epmeier and kliger (2005) in the MSE.

Specimens modified with wax have shown a slight *positive effect* in the IBS and a significant in the compression strength, Figure 23 in 4.1.5.3 and Figure 26 in 4.1.5.5, respectively. However, both latter changes were not revealed in the saturated bending creep. Specimens modified with TEOS did not show any effect in the creep behaviour as well in the EMC, see Figure 16b.

4.2.5 Mechano-sorptive effect (MSE)

MSE is called when the results of creep are obtained under constant load and simultaneously varying the MC of the material. The visco-elastic deformation is also possible to obtain in creep in constant condition. Hunt and Gril (1998) showed some empirical evidence between visco-elastic deformation and MSE. Both types of creep are considered irreversible. The MSE is the way to accelerate the deformation in a shorter period of time.

The strain from the MSE is largely time-independently. It depends on the applied stress, amount of moisture change and parameters of previous hygro-mechanical loading history (Hauska and Bucar 1996). Duration have less influence on the MSE part of strain than the moistening change (Navi et al. 2002).

4.2.5.1 Moisture content distributions

To check the MC distributions in the cross section of the wood specimens moistening in asymmetric conditions (see Figure 12b), a preliminary experiment was done to clarify some doubts:

- The *first* one, it was how far the moistening process is suitable to produce a MC changing. Special care was taken in the study of the modified wood specimens.

- The *second* one, it was an attempt to establish the length of the cycle for the duration creep-test, in a way to reach the wood MC stabilization after the wet-and-drying cycle.

- The *third* and last one, it is checked the MC above and below of the neutral axis (n.a.). In other words, which level of MC is reached with this asymmetric moistening procedure, Figure 12.

Figure 42 shows the mean of the MC distributions at different depths on the cross section during the upper surface moistening, see also Figure 12b. The mean of MC values were obtained with five specimens and showed by ★, ☆ and ✳.

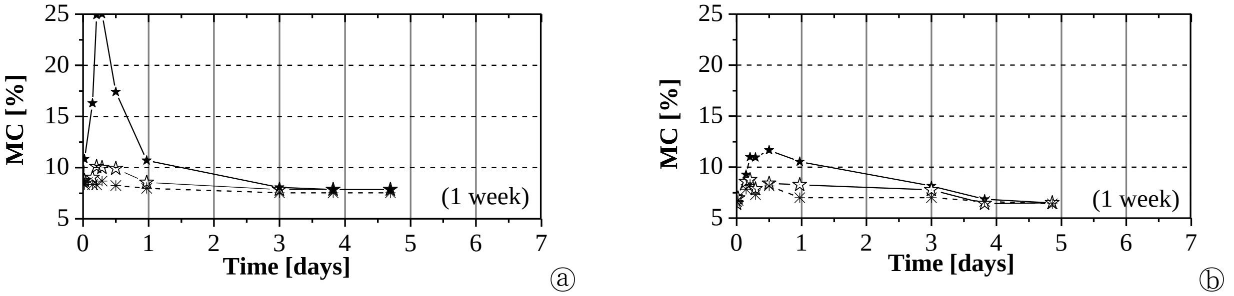


Figure 42. Profile of the MC in the specimens cross section with moistening process on the top radial surface, (a) - unmodified pinewood and (b) - DMDHEU D2, 1.3M. See also Figure 12b (★3mm, ☆ 8mm, ✳ 15mm) - depths

Below the n.a., the MC was unaffected by the moistening where the dased line done with ∗ did not change its flat trend. However, above n.a. of both materials, (unmodified pinewood, in the Figure 42a and modified wood with DMDHEU in the Figure 42b), the MC reached were similar to the EMC found in the wetted stabilized conditions, RH of 87% (see Figure 16). Only one part of the cross section changed the MC, from the n.a. up to upper side of the moistening. This effect produces the MSE only at one part of the bending beam - compression or tensile zone.

Modified wood specimens with resin took five days to reach and stabilize the preliminary EMC, before moistening. On the other hand, unmodified pine took three days to stabilize, despite higher MC was reached.

One week for the length of the cycle in the MSE of the bending creep tests was taken.

It should be keep in mind that moisture-meter was able to access the MC in the pine wood and other species well identified, Protimeter MMS system. Therefore, it is not the most appropriated equipment to access directly the MC for the modified wood, despite similar density was used. In Figure 42, the MC should be considered a *rough* approach. In fact, Pfeffer (2011) with unmodified Scots pine and specimens modified with DMDHEU has shown significant correlations between the MC measured by *gravimetric* and electrical *resistivity* methods.

4.2.5.2 Creep curves development

The standard behaviour of creep curves under the MSE is the *increasing* strain during the drying cycle and *decrease* during the wetting cycle, see Figure 43. The recovered or the negative deformation observed during absorption was due to the reversible behaviour of the MSE. Over the running trials, different types of creep curves were obtained. Based on the relative creep, creep curves were classified as type A, B and C:

- Type A or standard, increasing deformation during drying (desorption stage) and decreasing deformation during wetting (adsorption stage).
- Type B, decreasing deformation during drying (desorption stage) and increasing deformation during wetting (adsorption stage).
- Type C, increasing deformation during both sorption and desorption or indecisive.

When the moistening effect took place in the *compression zone,* moisture increasing caused compression stresses in the wood-matrix and the strain decreased. Then, whilst the moisture decreased - dry state, the strain increased because the *softening* of wood material and the tensile zone remained constant, below the n.a..

When the moistening effect took place in the *tensile zone*, moisture increasing caused swelling / tensile stresses in the matrix and the strain increased. Whilst the moisture decrease - dry state, the strain decreased. The compression zone remains constant below the n.a..

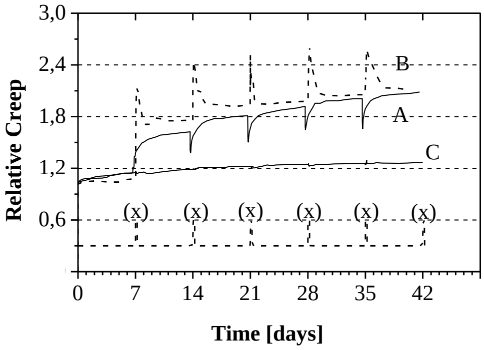


Figure 43. Typical curves in MSE with moistening with distillated water over 5hours (x). See the meanings of the letters in the paragraphs behind

From the literature, most of the creep curves should performe as type A, named as *standard behaviour*. Creep curves with *non* standard behaviour are rarely reported. Despite all specimens were chosen flawless//defects free, MSE in bending creep has shown non-standard curves as presented in the Table 16.

Table 16. Distribution of types of creep curves for both moistening processes: In compression and tensile stress zone in bending (n, specimens)

Compression / Modification	n	A	B	C
0 *ctrl*	[23]	14	8	1
D2 DMDHEU 1.3M	[15]	12	1	2
D3 DMDHEU 2.3M	[12]	8	2	2
i1 MMF 10% (oven dry)	[19]	18	1	0
i2 MMF 25% (oven dry)	[14]	13	0	1
TEOS 30%	[7]	7	0	0
WA Amid wax	[7]	0	0	7

Tensile / Modification	n	A	B	C
0 *ctrl*	[8]	3	5	0
D2 DMDHEU 1.3M	[9]	1	7	1
D3 DMDHEU 2.3M	[8]	0	8	0
i1 MMF 10% (oven dry)	[-]	-	-	-
i2 MMF 25% (oven dry)	[-]	-	-	-
TEOS 30%	[7]	1	6	0
WA Amid wax	[-]	-	-	-

The MSE in the *compression zone* of the unmodified wood specimens have shown a predominant curve type - A. However, curves type B and C were found as well. In the resin based modification (DMDHEU and MMF) and specimens with TEOS, a predominant curve type A was found. In the same conditions, wax modified wood has shown creep curves type C as a predominant. The *hydrophobic effect* of the wax on the specimen surface could be the main reason. In others words, 5hours of moistening exposition did not allow *any* change of the MC in the modified wood with wax.

The MSE in the *tensile zone* moistening, unmodified wood specimens have shown *no predominance* of the type curves A or B. Specimens modified with DMDHEU has shown creep curve type B as a predominant as well as TEOS modified wood specimens.

According to the moistening process did in bending, most of curves performed as type A and B, in the compression and tensile zone, respectively. For practical applications, it’s not necessary to make any division into standard and non-standard curves, as their long-term forecast does not differ significantly (Bengtsson 2001).

Epmeier et al. (2007a) suggested that material properties did not show significant differences between types of the creep curves. Density, MOE, MC or others features of wood as annual rings orientation or provenance material, such as tree and position within stem, type of the modification, i.e. acetylation, MMF, thermowood with oils bath and furfurylization are some of this wood properties.

For both moistening setups showed in Figure 12 at 12Nmm^{-2} of SL no rupture occurred.

4.2.5.3 Moistening in compression zone

Figure 44 shows the compliance curves of the relative creep in four points bending (4pb) according to EN 408 (and ENV 1156, Figure 12) when the moistening process was done in the compression zone.

An increase of MC means a creep strain variation for all used specimens. Exception needs to be done for specimens modified with wax that had a particular behaviour under these experiments. All others specimens, modified or not, showed a creep deflection variation under MC changing. Therefore, drying process tends to have a different displacement recover. Between, cell wall and lumen fill modification, the MC and displacement has shown different extend, see Figure 44 and Figure 46. On the 2nd day of the cycle, unmodified wood and TEOS modified specimens have shown stabilized creep strain despite higher MC was found. In the resin based modification, the stabilization strain took place in the middle of the 2nd and 3rd day of the cycle.

The slope of the compliance creep curve describes the *creep limit*, which has a particular interest to analyze and compare the creep behaviour (Hunt and Shelton 1988). Mohager and Toratti (1993) showed no *creep limit* with different sizes (1:1 and 1:15) of unmodified Scots pine specimens under MSE over long-term, eight years. That means, with successive wet-and-drying cycles, the creep deformation increases *indefinitely*, is unstable.

Between un- and modified wood (with resins, DMDHEU and MMF) the difference of the slope in the creep curves was clearly lower in modified ones. A possible explanation is that moisture in unmodified wood acts as a plasticizer (Holzer et al. 1989), i.e. the strain increases with moisture as a result of the MC and MOE variation.

In creep test of unmodified wood and at the beginning of each cycle, the wetting causes swelling and concomitantly a larger moment of inertia responsible for the *negative peak* on the strain. The first *sorption* causes an increasing deformation in different extend from the next ones. The following cycles have caused a less extend strain, see Figure 44a.

Modified wood has shown the same instability between the *first* and *next cycles* as unmodified wood did. However, the difference (or *instability*) was in the less extention. The best performances of the resin-based modification in the ASE and SSE help to explain its lesser extent strain in the curve of the relative creep, in Figure 44b and c compared to Figure 44a for unmodified wood.

In resin-based modified wood, the MSE has shown the same tends than stiffness stabilization efficiency (SSE, in Figure 21b) and as well the anti-swelling efficiency (ASE, in Figure 18). Norimoto et al. (1992) and Epmeier and Kliger (2005) with resin based modified specimens, with different dimensions and setups, showed similar results.

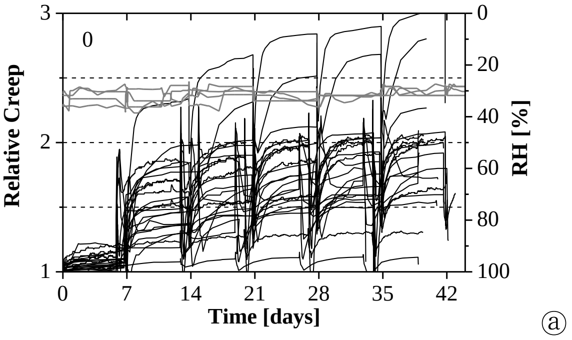
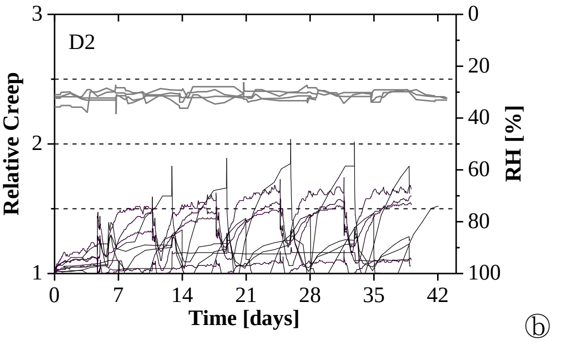


Figure 44. Compliance curves of the relative creep and RH environmental conditions for pinewood

(a) - 0, *ctrl*

(b) – D2 DMDHEU 1.3M

(c) - i1 MMF 10%



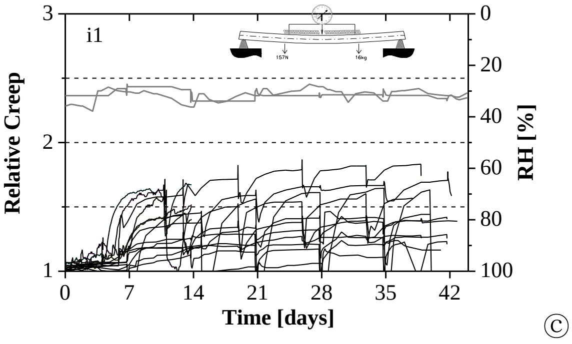


Figure 45 shows the relative creep for wax modified wood in bending. Specimens were tested under similar moistening process in the compression zone. The load arrangement can be seen in Figure 12. Wax modified wood specimens have shown a hydrophobic behaviour in the surface. For that reason no experiment was done with specimens moistening in the tensile zone.

The hydrophobic effect of the wax and the *slower* water penetration presented by Scholz et al. (2009) with similar wax, can be the explanation of the creep behaviour of wax specimens. The evaporation took place *firstly* than the capillarity water uptake/absorption into the wood material. The sealer effect of the wax did not let show the MSE. Actually, the MSE does not judge completely eradicated. However, the environmental RH changes will have a less effect and move forward the MSE with *phase*. This means, when the wood start to wet, the surround environment conditions start to dry. It is *credible* for practical applications that the deposited of wax in the lumen of the cells *avoids the water* circulation through the wood material.

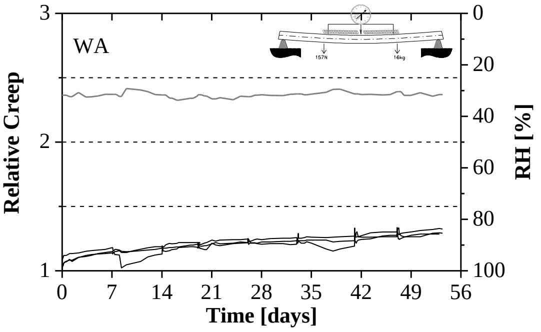


Figure 45. Compliance curves of the relative creep and change RH environmental conditions for pinewood modified with Amid wax (WA, 95% WPG). For moistening process, the Figure 43 need to be seen

4.2.5.4 Moistening in tensile zone

Figure 46 shows the compliance curves of relative creep with moistening process in the tensile zone. Also as can be seen for wetting process in the compression zone, the unmodified wood has shown no *creep limit*. On the other hand, modified wood has shown *creep limit* and with less amplitude (wet and dry strain) than unmodified wood. It can be said that, the MSE behaviour was characterized by the *constant-balance* between wet and dry compliance strain. At the end of the experiments (42days/1000hours), the slope (or the *creep limit*) can be represented by the k_c, in Figure 47b.

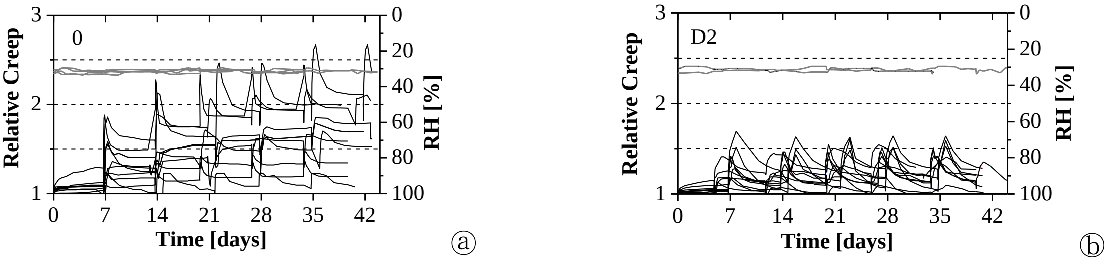


Figure 46. Compliance curve of relative creep for (a) - unmodified pinewood and (b) – D2 DMDHEU 1.3M and RH conditions. Figure 43 showing the moistening process

4.2.5.5 *Creep factor (k_c)*

The k_c is the *ratio* of the increasing creep strain related to instantaneous strain, see 2.4.6. To represent the mean strain and achieve the mean relative creep, the compliance creep curves obtained from the creep tests were fitted by PFM.

Figure 47 shows k_c over 42days/1000hours under 5 cycles of wet-and-drying. In the resin based modification (DMDHEU and MMF resins), both types of resins have shown similar behaviour with significant less creep compared to unmodified wood, 60%. In the lumen fill modified wood, specimens with TEOS have shown no effect compared to unmodified wood. Wax specimens have shown a particular behaviour in the MSE, with the most homogeneous and lower k_c, Figure 47a.

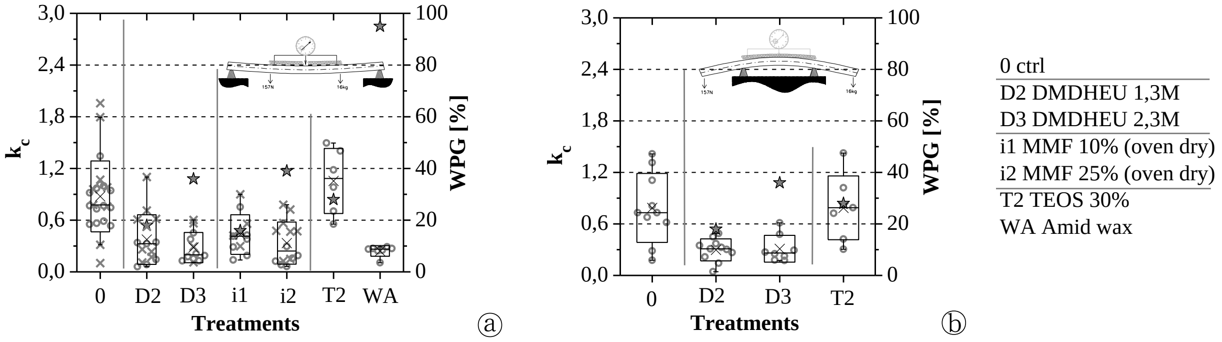


Figure 47. Creep factor (k_c) over 42days with moistening at, (a) - compression zone and (b) - tensile zone with 4pb and WPG (✰)

Wood modified with resin has shown lower and less scattered k_c under MSE at forecasting of 42days, whilst the lumen fill modified specimens with TEOS did not show any difference compared to unmodified pinewood.

In this study with asymmetric moistening, the MSE in the tensile zone with *unmodified pinewood* has shown similar results than Roszyk (2005) with Scots pine and *similar setup*. He presented a mean k_c up to 0.80. On the other hand, under similar setup, he showed a slight-higher k_c for the moistening in the compression zone, app. 1.3 against 0.9 in this study.

Usually, uniforme or symmetric moistening is the most environmental conditions used, with RH between 30 and 90%. When applied to unmodified pinewood, it showed similar k_c compared to asymmetric moistening process. Mohager and Toratti (1993) with small specimens $10 \cdot 10 \cdot 330$mm RTL of Scots pine has found a k_c of 1.05. Under similar conditions but with full-scale specimens 1:1, they showed an increasing of k_c of 0.80. It was expected that full scale specimens showed less creep than small scale specimens 1:15. Epmeier (2006) conducted a study with a large and well-documented provenance material in full scale 1:1 and showed a range of k_c between 1. up to

1.35. Bengtsson (2001) with material from different positions of the stem (heart- and sapwood) and type of trees (fast- and slow-growth) showed a range of k_c between 0.9 up to 1.57.

In this study where small scale specimens 1:10 were used, results of MSE became in line with results consulted in literature. For other pines in full 1:1 or small 1:10 scale specimens. Although, differents creep test setups were used.

For un- and modified wood tested, the creep behaviour under the MSE in bending is lower in tensile than in compression mechanism (15% app.), compared k_c between Figure 47a and b. Roszyk (2005) showed the same conclusion for unmodified wood - Scots pine and similar setup. He showed 35% less creep with moistening in tensile than in compression zone.

Unidirectionaly, the MSE showed lower creep strain in tensile than in the compression creep behaviour, with a ratio 1:2, respectively (Bengtsson 2000). Comparatively, the MSE in bending for unmodified pinewood has shown low k_c for tensile than for compression zone moistening (app. 15% in average). The difference between both results can be explained mainly for two reasons: The V/A ratio exposed to the moistening and the higher SL (app. 50%, $18Nmm^{-2}$). Schniewind (1967) and (1968) suggested that as the lower V/A ratio exposed to the moistening variation, as higher pronounced of MSE is.

Table 17 shows the k_c in the MSE for both moistening setups used in this study and the difference compared to unmodified wood with p-value. Wood specimens modified with DMDHEU resin did not show significant difference between both setups of moistening (62-69% up to 62-60%). Modified specimens with TEOS showed a k_c 25% lower in tensile moistening 1.05 up to 0.79 between compression and tensile zone moistening, respectively.

Table 17. Mean of the creep factors (k_c) and difference between modified and unmodified wood with [non significant values]

Wet / Modification	0-*ctrl*	D1	D2	D3	i1	i2	T1	T2	WA
k_c $(f_{c,o})^a$	0.89	--	0.33	0.28	0.41	0.29	--	1.05	0.24
Difference [%]	--	--	-63	-69	-54	-68	--	+18	-73
p-value	--	--	0.00	0.00	0.00	0.00	--	[0.32]	0.00
k_c $(f_{t,o})^b$	0.79	--	0.30	0.31	--	--	--	0.79	--
Difference [%]	--	--	-62	-60	--	--	--	+0.08	--
p-value	--	--	0.01	0.01	--	--	--	[0.77]	--

Creep factor with moistening (a) in the compression zone and (b) moistening in the tensile zone of bending tests over 42days/1000hours according to ENV 1156

Over 42days and five wet-and-drying cycles, resin based modification (DMDHEU and MMF) has shown a significant reduction on creep (k_c), higher than 50%, see also Figure 47a. Specimens modified with MMF resin with low concentration (i1) has shown less reduction than DMDHEU resin with similar concentration. Both levels of modification with DMDHEU resin (D2 and D3 with 18 and 36% of WPG) have shown a slight decrease in the creep factor, up to 2%. Similar results, with no significant difference, were shown with MMF (with 15% and 30% of concentrations). Both latter results came in line with Epmeier and Kliger (2005). They used full-scale specimens 1:1 modified with both concentrations of MMF resin (with 7.5 and 15%) and they showed no significant difference in the MSE of bending creep.

The latter results have an *important meaning* in the industrial scale of chemical modification where the dimension of specimens plays an important role. Modified wood with large cross section has the propensity to establish internal *chemicals gradient*. Homan and Bongers (2004) showed a gradient of app. 50% with uneven chemical distribution in the cross section (greater than 50mm). On the other hand, to achieve the enhancement of the MSE on the bending creep, only a minimum level of cell all modification is required.

Furfurylated wood is similar to modified wood with DMDHEU resin with high concentration. Epmeier et al. (2007b) with furfurylated specimens, in full-scale 1:1 under symmetric moisture change, found a k_c up to 0.75. Specimens modified with DMDHEU resin have shown a mean k_c up to 0.30. Problems with the process of modifications - furfurylation should be the main reasons to justify the difference.

In this study, specimens modified with MMF with medium concentration have shown similar k_c, up to 0.41, as Epmeier and Kliger (2005) and Norimoto et al. (1992) with similar concentrations. Nevertheless the setup difference of the V/A ratio, in the *former* with full scale 1:1 (k_c 0.47) and the *latter* authors with small-scale 1:15 (k_c 0.40) were found. Under different setups conditions but with acetylated wood, the latter's authors found similar k_c up to 0.30. It seems that the size of the specimens in the MSE in creep (1:1 or 1:15) did not assume any effect.

4.2.5.6 Analysis of correlations

The *density* is an important wood feature and often regarded as being closely related to deformation (stiffness or strength). In the creep test of the unmodified wood, several authors correlated the stiffness (short-term wood property) or wood quality (MOE/density) to the long-term performance with significant correlation (Hoyle et al. 1985; Bengtsson 2001). Epmeier and Kliger (2005) corroborated the later results for Scots pine but found minor correlations with modified wood, i.e. acetylation, MMF, heat modification in oil bath. Epmeier et al. (2007b) presented the same *minor correlation* for furfurylated wood.

Table 18 shows the correlations between density, stiffness and creep deformations found under the MSE of the creep tests. As far as unmodified wood were concerned, moderate up to significant correlations were found. In the lumen fill modification (with TEOS) the tendency of the correlation remained between *density* and *other properties*.

In the cell wall modification (with DMDHEU and MMF resins), the correlations were lower (in the most cases). Occasionally significant correlations were found, but not confirmed for others concentrations or similar modification.

Correlation between *creep strain* and *relative creep* is moderate for un- and modified wood with DMDHEU D2 and significant for DMDHEU D3, MMF and TEOS. Despite the particular hydrophobic behaviour, the modified wood with wax has shown no significant correlation. The surface wax isolates the wood material of RH changing from the exterior environment. However, in the lumen fill modification with wax at constant climates, the EMC and ASE did not change, see Figure 16 and Figure 18.

High correlation between creep strain vs. $MOE_{st,4pb}$ could be expected, as the $MOE_{st,4pb}$ was calculated from the strain after 60s (in the creep test). In fact, two strains were compared: The strain after 60s (under a short-term load) and the strain after 6 weeks with five wet-and-drying cycles under a sustained load (long term loading behaviour). The short-term deformation ($MOE_{st,4pb}$ or MOE_{dyn}) is moderate to significantly correlated to the long-term creep strain. This indicates that, from the stiffness measurement of a structural member, it should be possible to *predict roughly* its long-term performance under load.

In both moistening processes, the results of this study confirmed the suggestions from the literature, where the main correlation fitted (moderate up to significantly) for unmodified pinewood (Bengtsson 2001; Epmeier 2006).

The lumen fill modification with TEOS has no effect on the MSE, however, it kept the best correlation (moderate up to significant) with different variables.

The correlations presented by specimens modified with MMF resin (i2, high concentration) are not confirmed by similar modification with DMDHEU resin.

Creep strain and stiffness are the variables that have shown the best correlations, moderate up to significant for unmodified and TEOS modified wood mainly in the moistening tensile zone.

Table 18. Coefficients of correlation for modified wood specimens and unmodified pine at each moistening process, [non-significant values]. For abbreviations see Table 5

Moistening	/	Modification	0	D2	D3	i1o	i2o	T2	WA
($f_{c,o}$) - Compression side									
Density	vs.	MOE_{dyn}	0.69	[0.10]	0.61	[0.07]	0.60	0.56	[0.37]
Density	vs.	$MOE_{st,4pb}$	0.77	[0.30]	[0.50]	[0.32]	[0.47]	[0.11]	[0.28]
Density	vs.	$MOE_{st,3pb}$	0.69	[0.14]	[0.40]	[0.54]	0.56	0.91	[0.33]
Density	vs.	relative creep	-0.86	[-0.05]	[-0.54]	[-0.25]	[-0.18]	-0.78	[-0.02]
Density	vs.	creep strain	-0.70	[-0.01]	[0.15]	[-0.42]	[-0.26]	-0.68	[-0.44]
creep strain	vs.	relative creep	[0.43]	[0.35]	0.74	0.64	0.62	0.85	[0.01]
creep strain	vs.	$MOE_{st,4pb}$/DEN	[-0.33]	[-0.45]	[-0.36]	[-0.48]	[-0.18]	[-0.26]	-0.80
creep strain	vs.	$MOE_{st,4pb}^{(a)}$	-0.67	[-0.35]	[-0.54]	-0.80	[-0.35]	[-0.39]	[-0.37]
($f_{t,o}$) - Tensile side									
Density	vs.	MOE_{dyn}	0.67	[0.24]	[0.32]	---	---	0.84	---
Density	vs.	$MOE_{st,4pb}$	0.78	[0.09]	[0.14]	---	---	0.60	---
Density	vs.	$MOE_{st,3pb}$	0.73	[0.16]	[0.11]	---	---	0.68	---
Density	vs.	relative creep	-0.72	[-0.01]	[-0.04]	---	---	-0.64	---
Density	vs.	creep strain	-0.63	[-0.11]	[0.04]	---	---	[-0.42]	---
creep strain	vs.	relative creep	[0.54]	0.64	0.81	---	---	0.56	---
creep strain	vs.	$MOE_{st,4pb}$/DEN	-0.84	[-0.08]	[-0.04]	---	---	[-0.49]	---
creep strain	vs.	$MOE_{st,4pb}$	-0.62	[-0.48]	[-0.44]	---	---	-0.93	---

(a) These correlation are shown in Figure 48

The unaffected MSE behaviour for lumen fill modified wood specimens with TEOS confirms the significant correlation for unmodified wood. On the other hand, for cell wall modified specimens (with DMDHEU and MMF resins) *any clear pattern* can be drawn for relative creep.

Epmeier (2006) with cell wall modified wood, i.e. acetylation, MMF resin and thermowood in oil bath, full scale specimens 1:1 under MSE have shown moderate up to significant correlation for MOE_{dyn}, density and creep strain. However in the same work, they were not confirmed with relative creep vs. MOE_{stat} nor in furfurylated wood specimens.

In Figure 48, scatter plots are shown for the correlations between creep strain (on the x-axis) and $MOE_{st,4pb}$ (on the y-axis). The corresponding coefficients of correlation can be found in Table 18 (Creep strain vs. $MOE_{st,4pb}^{(a)}$). In the lumen fill modified wood (with TEOS and wax) significant correlations were found as well as unmodified pinewood with moderate correlation.

In the cell wall modified wwod specimens with medium concentrations of DMDHEU and MMF resins, moderate correlations were found, statistically not significant. In the resin based modification, it seems that for high concentration the correlation disappeared.

The unmodified and lumen fill modified wood specimens (with both materials, TEOS and wax) correlated better than the cell wall modified specimens (with DMDHEU and MMF resins).

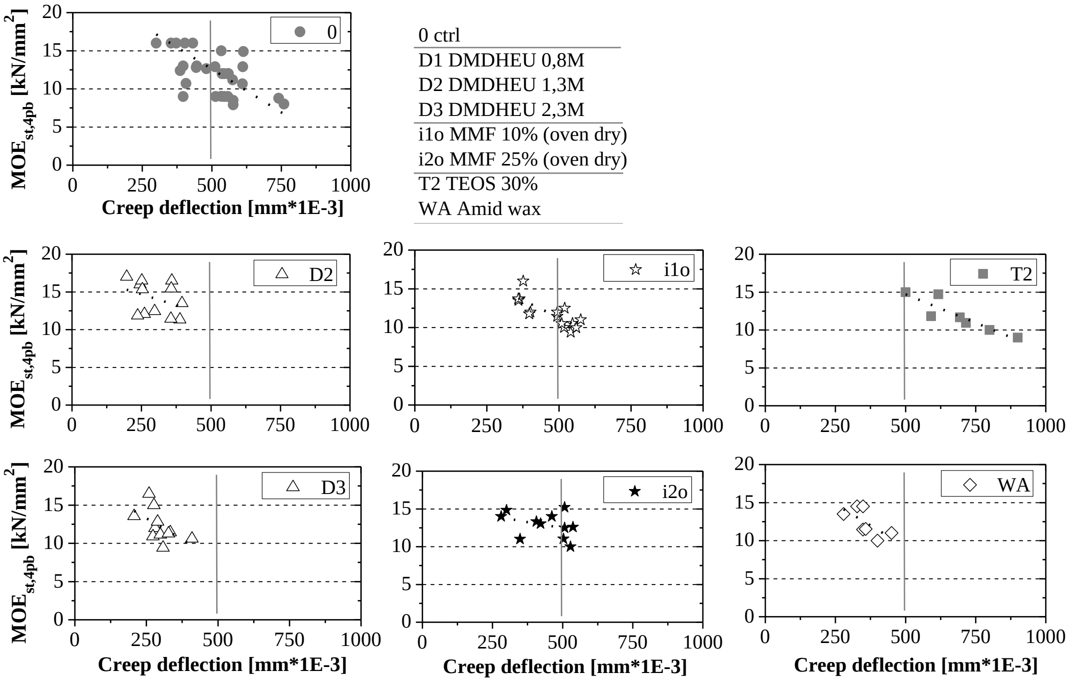


Figure 48. Correlation scatter plots between creep strain [mm*1E-3] and MOE$_{st,4pb}$ under SL of 12Nmm^{-2} over a period of 42days/1000h

To summarise, the prediction of performance criteria based exclusively on density should not be formulated for modified wood. Although, with stiffness accessed with vibration technique (MOE$_{dyn}$) significant correlations were found for un- and modified wood with high concentration of resins (DMDHEU and MMF).

4.2.5.7 Anti-creep efficiency (ACE)

The effect of chemical modification on the MSE can be characterized by the ACE factor, which quantifies the ability of the *modification* to reduce the strain in the MSE. The higher ACE, the larger reduction the creep strain is (Norimoto et al. 1992).

Figure 49 shows the ACE for all modification methods in both moistening processes. The lumen fill modified wood with TEOS has shown low ACE, near zero. Whilst the moistening in the compression zone showed a negative result (-10%), the moistening in the tensile zone showed a positive value of ACE, up to +9%. The unaffected bending creep strain by TEOS chemical was consistent with ASE and SSE, in Figure 18 and Figure 21b, respectivelly. Despite both properties, ASE and SSE expressed different behaviours.

Modified wood with wax has shown a particular behaviour. High ACE presented by specimens modified with wax were *a surprise in contrast* with ASE and SSE. The wax acts as a *hurdle* to the moisture change. The wax effect in the lumen fill modification *clearly reduced* the capillary water uptake in a ratio of 5:1 (Scholz et al. 2009). Similar results were found by Ranta-Maunus and Kortesmaa (2000) with full scale beams 1:1 under *service conditions* with surface coating with alkyd paint. Santos (2009) showed lower creep for Glulam beams 1:1 with protected surface than unprotected ones.

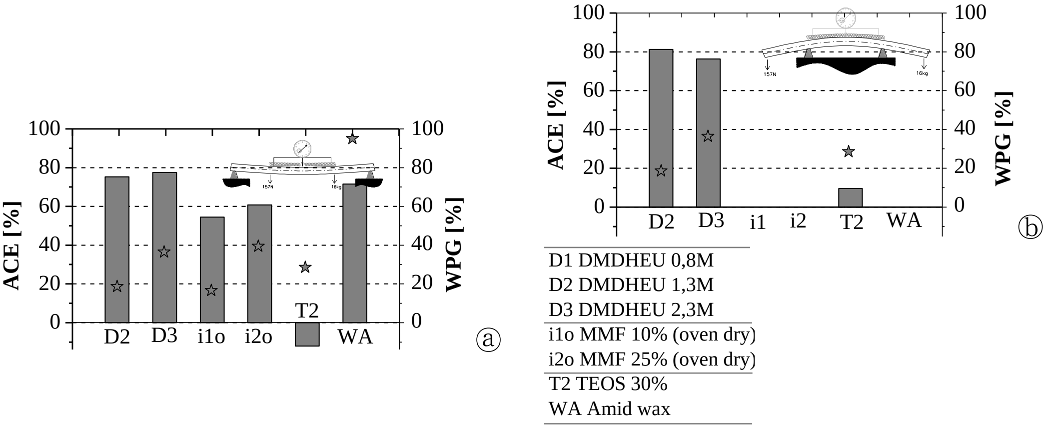


Figure 49. Anti-creep efficiency (ACE) for (a) - compression and (b) - tensile zone moistening

In MSE, the most effective modification methods were cell wall reaction, where DMDHEU performed best than MMF resin. However, in different concentrations of resin, significant differences in the ACE were not found.

Based on some references in bending creep and MSE of modified wood, Table 19 shows a summary regarding the type of modified wood used and physical features (WPG and ASE).

The furfurylation, with 40% of WPG, can be compared with cell wall modification with DMDHEU D3, 2.3M. In this study, modified wood in the cell wall (with DMDHEU and MMF resins) showed comparable ACE as furfurylated and MMF resins in Epmeier et al. (2007b), respectively.

Relating to ACE and changes in the MC or ΔMC, in order to predict the effect of modification on the creep behaviour does not seem feasible (Epmeier et al. 2007a). The resin based modification (DMDHEU and MMF) has shown reductions to a different extend in EMC, with 40% and 20% in wet or dry conditions, respectively for both types of resin, Figure 16a. No significant correlations between ACE and the EMC or ΔEMC were found, although specimens of wood modified with DMDHEU has shown best performance than MMF resin in ACE, EMC and ΔEMC. In general, for specimens modified in the cell wall, the ACE is in the same tendency than changes in ASE. The higher ASE is, higher the ACE is. Modification that leads to high ASE and to negative ACE at the same time may exist. Norimoto et al. (1992) presented some examples: Etherification with propylene oxide and polyethylene glycol impregnation.

Table 19. Weight percent gain, anti-swelling efficiency and anti-creep efficiency of different modifications

Modification	WPG [%]	ASE [%]	ACE [%]	Authours
Acetylation	23	66	48	(Norimoto et al. 1992)
Acetylation	13	70	53	(Epmeier et al. 2004; 2007b)
Heat T. (180ºC/3-10h) (a)	-2.4/-3.5	11/17	16 / 22	(Norimoto et al. 1992)
Heat T. (160/190ºC) (b)	--	--	22 / 25	(Epmeier et al. 2007a)
MMF 7.5%	10	--	59	(Epmeier and Kliger 2005)
Phenol Resin	13	30	47	(Norimoto et al. 1992)
MMF 15%	16	--	64	(Epmeier and Kliger 2005)
i1 MMF 15%(c)	16	30(d)	53 / --	---
i2 MMF 30%(c)	39	38	61 / --	---
Furfurylation	35	67	58	(Epmeier et al. 2004; 2007a)
D2 DMDHEU 1.3M(c)	18	45(d)	75 / 81	---
D3 DMDHEU 2.3M(c)	36	60(d)	77 / 76	---

(a)Heat modification with the same temperature and different durations, 3 and 10hours; (b)Heat modification in vegetable oil bath; (c),(d)ACE found with moistening process in compression and tensile zone in bending, respect.

4.2.5.8 *Duration test effect*

The test duration is one of the major impediments/*hurdles* to the study of creep because it requires facilities/equipments for long. In the point of view to optimize and reducing the duration of creep tests, correlation between results after the 2nd and 5th cycle was analyzed. In paragraphs behind it was shown that modified wood in the cell wall (DMDHEU and MMF resins) has shown a creep limit, 4.2.5.3. On the other hand, lumen fill modified wood with TEOS had no effect on the MSE behaviour. The latter modification, together with unmodified pinewood, both have shown no *creep limit* over the MSE procedure.

Figure 50 shows correlations between k_c obtained after the 2nd and 5th cycle. Based on the *creep limit*, correlations were presented for: Cell wall modified wood with *creep limit* (DMDHEU and MMF) as *Resin* (R 0.95); And unmodified pinewood and TEOS with *no creep limit* as *Pine* (R 0.96). To help a better understanding, the Figure 44 and Figure 46 should be revisited. Specimens with no *creep limit* have shown low creep in the first two cycles. The *creep limit* in the cell wall modification (DMDHEU and MMF resin for both moistening process) was responsible for closer results between the 2nd and 5th cycle.

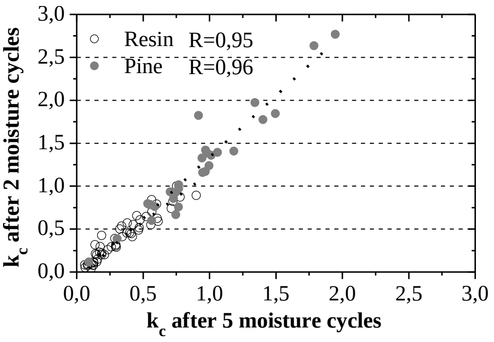


Figure 50. Correlations between the creep factor after 2^{nd} and 5^{th} cycle of the moistening

It can be concluded that, for both types of *active principle* of modified wood and unmodified one, between the k_c obtained in the 2^{nd} and 5^{th} cycle significant correlations were found (R 0.95). That means, after loading and completed two wet-and-drying cycles were enough to obtain the k_c prediction of the MSE obtained after additional moisture cycles.

4.2.6 Mechano-sorptive effect, conclusions

The results of this study with un- and modified Portuguese pinewood using small scale 1:10 specimens seem to fit with results found in the literature, with lower scale 1:15 by Norimoto et al. (1992) and higher scale 1:1 by Epmeier and Kliger (2005) and Epmeier et al. (2007b) was weel as Santos (2009).

Relative creep after 42days/1000hours appears to be clearly identified with these setups (asymmetric moistening). Unmodified wood and lumen fill modified wood with TEOS presented no *creep limit*. The latter chemical had no effect in the creep strain, at one hand.

On the other hand, MSE of the modified wood with resin has shown a *creep limit* presented by stable displacement with constant amplitude (0.30). Cell wall modified wood (DMDHEU and MMF resins) decreased significantly the creep strain / relative creep (up to 60%). The homogeneity of results in the creep factor was enhanced, as well.

From the correlations studied here, MOE_{dyn} has the best chance of becoming a functional indicator of the relative creep. However, to prove this, a much broader statistical analysed is needed to enhance the significance of this correlation.

The density for modified wood cannot be used to predict the creep performance in the same way as they can for unmodified wood.

The effect of wood modification on MSE of creep has been characterized by the ACE factor, analogous to ASE. However, only in the cell wall modified wood (DMDHEU and MMF resin) were found a good correlation between ASE and ACE.

The changing in EMC imparted by the modification, mainly in the cell wall modification, did not correlate well with creep results under the MSE in bending.

Modified wood in the *cell wall* and not filling the lumen *alone*, is required to affect the MSE in bending creep.

The creep behaviour *depends* more of the material relation with water than the enhanced mechanical strengths imparted by modification. The latter are represented by the increasing of compression and decreasing in tensile strengths, *in general*, and *in particular* the wood material relation in changed environment is represented by the physical and mechanical properties, as ASE and SSE, respectivelly.

4.3 Performance of wood against to marine borers

The activity of two main marine borers, with surface galleries and tunnels inside the wood material, will be referred as *Limnorids* and *Teredinids* attacks according to EN 275, respectively.

4.3.1 Inspections

The *Limnorids* and *Teredinids* attack is evaluated distinctly, according to EN 275. The first makes the galleries on the surface and was accessed visually (Figure 58b). The latter, after the deposit of larval stage of Teredos on the wood surface, makes their tunnels inside the wood and was accessed by x-ray (Figure 58a and Figure 57).

4.3.1.1 1st inspection, 6 months (half year)

The *first* inspection took place in October 2009, after six months of exposure. All wood specimens were already covered by biofouling. Thirty-eight specimens randomly chosen were inspected. Slight or trace signs of attack were found. Small holes became visible with a diameter of 1.5 up to 2mm caused by *Teredinids* larvae incoming. Figure 51 shows the number of holes visually inspected for different unmodified wood species (pinewood included) and modified wood (with associated WPG).

The number of holes was scarce. A maximum of three holes in a few specimens were recorded. However, the x-ray did not show any tunnels by *Teredinids*. Attack by *Limnorids* was not visually detected. No holes or another sign of attack were detected in unmodified wood species and modified wood with different levels.

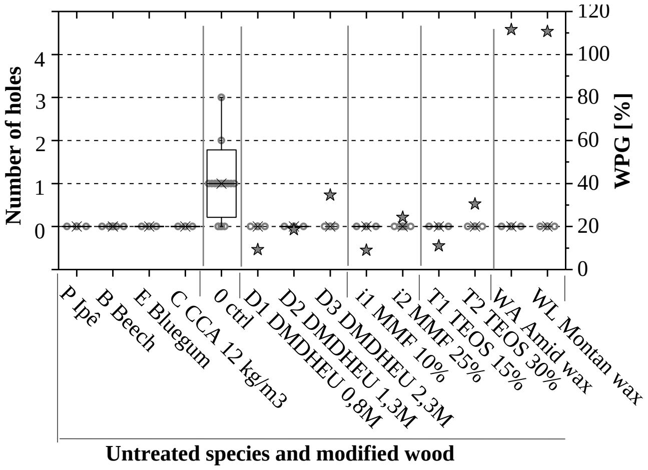


Figure 51. Number of holes with 1.5 up to 2mm of diameter at each specimen of Maritime pinewood species. Star with five nozzle shows the WPG for modified wood

4.3.1.2 2nd inspection, 12 months (1 year)

The *second* inspection was carried out in February 2010. Sixty specimens were extracted and inspected. No signs of attack were recorded for wood species, Ipê, Beech, Bluegum, CCA treated pine and modified wood with resin (DMDHEU and MMF). In the unmodified pinewood and lumen fill modified wood (both concentrations of TEOS and amid wax) slight or trace attack of *Limnorids* were detected visually. The x-ray has shown only a small number of *Teredinids* in the unmodified pinewood. It is notes that some of these organisms have shown large dimensions, 13mm of diameter and 18cm in length.

Figure 52 shows on vertical axis the marine borers activity, stand on the 1st year for unmodified wood species, including pinewood and modified wood with WPG associated (☆ - on the right vertical axis).

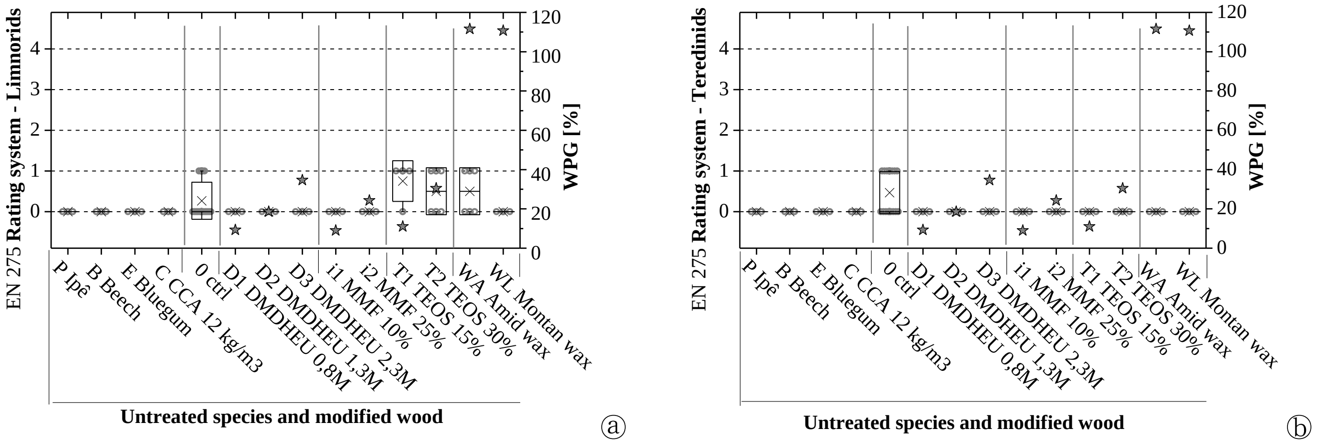


Figure 52. Marine borers attack rating according to EN 275 (a) - *Limnorids* and (b) - *Teredinids* activity after 12 months (1year) of exposition

It was noted at the end of the 1st year:

- No attack by *Teredinids* for all wood materials (except for unmodified pinewood);
- Slight attack by *Limnorids* in unmodified pinewood and lumen fill modified wood, TEOS and wax.

At the end of the 1st year, low activity of marine borers was found at any wood species and type of modified wood.

The lower activity of marine borers in this study was surprising, when compared to recent results in temperate or cold waters. Over the same exposition time, specimens completely destroyed were found by Gambetta (1986) and Westin et al. (2007).

4.3.1.3 3rd inspection, 24 months (2 years)

The *third* inspection took place in the second year, February 2011, 24 months rather than after 18 months because the low activity detected in the 2nd inspection (12th month). Heavy activity was recorded in the 3rd inspection compared to the others earlier inspections (1st and 2nd). Similar burst of marine borers activity from one inspection to another (at 6 up to 12 months of intervals) was recorded by Beesley (1980).

Figure 53 shows on the vertical axis the marine borers attack of the 2nd year for wood species and modified wood on the horizontal axis, and associated WPG (✫) on the right-vertical axis.

At the end of the second year, it is noted by *Limnorids*, see also Figure 53a:

- No attack in tropical hardwood species, Ipê;
- Sligth attack in Beech and Blue Gum wood species;
- Moderate attack in CCA treated pine;
- Moderate to severe attack in unmodified pinewood;
- Slight to moderate attack in the lumen fill modification, TEOS, amid and montan wax;
- No attack in the resin based modified wood was not found, regardless type of resin and level of modification.

By *Teredinids,* see also Figure 53b:

- No attack in tropical hard wood species, Ipê;
- Moderate attack in Beech and Blue Gum wood species;
- Moderate attack in CCA treated pine;
- Severe attack in unmodified pinewood;
- Slight attack in low level of modification with DMDHEU resin (D1);
- No attack for medium and high levels of modification with DMDHEU resin, respectivelly (D2 and D3);
- Moderate to slight attack for low and high level of modification with MMF resin, respectively (i1 and i2);
- Sligth attack in the lumen fill modified wood with TEOS;
- Moderate up to severe attack in wax modification, amid and montan wax.

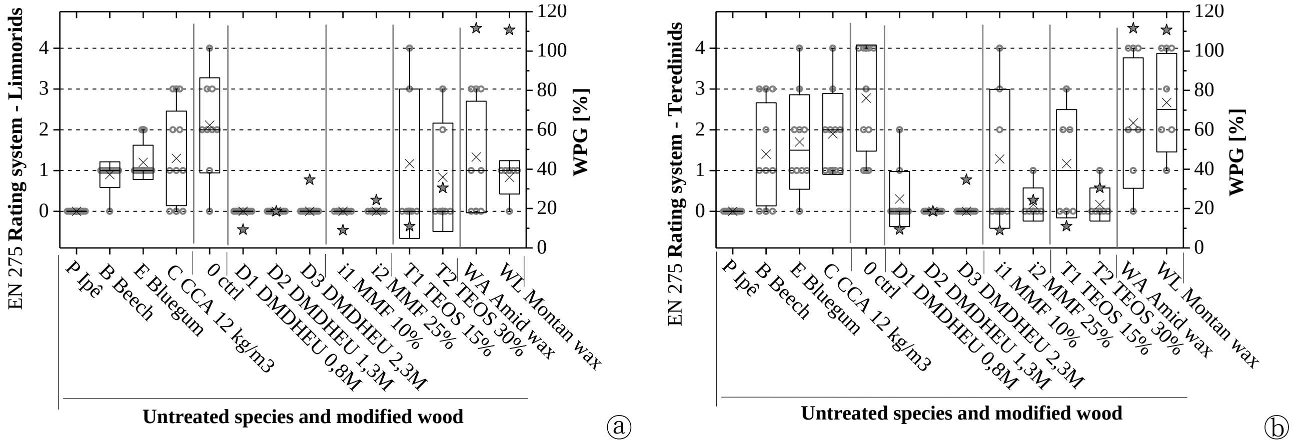


Figure 53. Marine borers attack rating according to EN 275 (a) - *Limnorids* and (b) - *Teredinids* activity after 24 months (2years) of exposition

At the end of the second year, high activity of marine borers was found in all unmodified wood species and modified wood. In the unmodified wood species, attack by *Limnorids* was on comparable level than attack by *Teredinids*.

4.3.1.4 4th inspection, 36 months (3 years)

The *fourth* inspection took place at the end of the third year, March 2012. Figure 54 shows the marine borers activity, stand on the 3rd year of exposition for unmodified wood species and modified wood. The trend for infestation remained on the third year of exposition, at the fourth inspection. Figure 54a shows the main remarks for *Limnorids* activity:

- No attack in the tropical hardwood species, Ipê;
- Slight to moderate attack in the wood species of Beech and Bluegum;
- Severe attack in treated pine with CCA (12 kgm^{-3});
- Severe attack up to failure in the unmodified pinewood;
- No attack was detected in the resin based modified wood, regardless of the resin type and the level of the modification;
- Moderate to severe attack in the lumen fill modified wood with TEOS;
- Severe up to failure in the wax modified specimens;

Figure 54b shows the main remarks for *Teredinids* activity:

- No attack in the tropical hard wood species, Ipê;
- Severe attack in the wood species of Beech and Bluegum;
- Severe attack in treated pine with CCA;
- Unmodified pinewood, used as control, was completely destroyed;

- Slight attack in low level of modification with DMDHEU resin;
- No attack for medium and high level of modification with DMDHEU resin;
- Slight up to severe attacks in the modified wood specimes with MMF resin;
- Slight to severe attack for both concentration of TEOS solution;
- Moderate up to severe attack in the wax modified specimens, amid and montan wax.

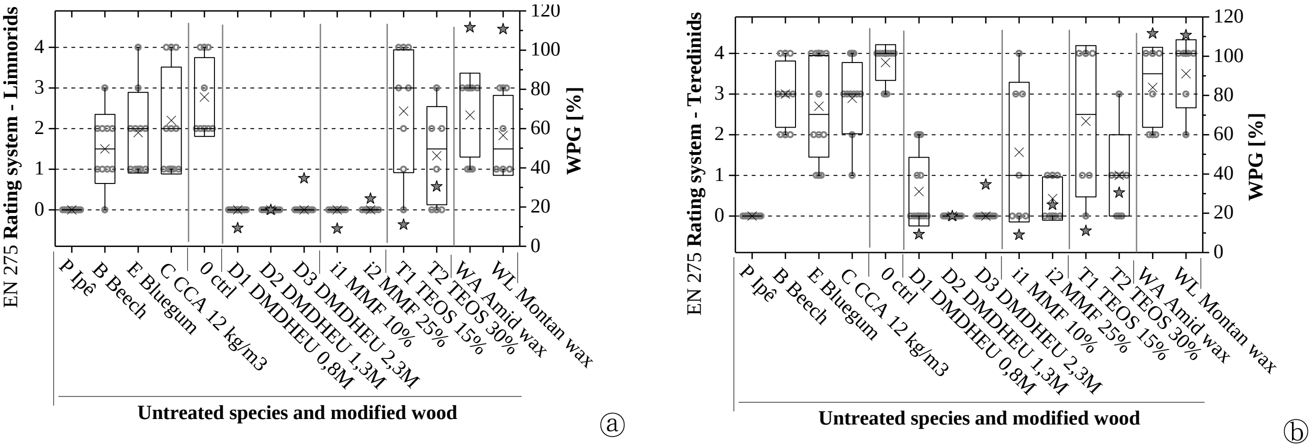


Figure 54. Marine borers attack rating according to EN 275 (a) - *Limnorids* and (b) - *Teredinids* activity after 36 months (3years) of exposition

A new set of five test specimens were left to replace the unmodified pinewood completely destroyed.

4.3.2 Screening of the marine borers activity up to the 3rd year

Figure 55 shows the *Limnorids* activity up to the 3rd year of exposition for unmodified wood species and modified wood. The hardwood species Ipê has shown no attack by *Teredinids*, however Beech, Bluegum, CCA treated pinewood and unmodified pinewood were stepwise attacked, slight to severe increased. Medium and high concentrations of DMDHEU resin have shown protection against attack by *Teredinids*. Resin based modification, DMDHEU and MMF resins, was not attacked by *Limnorids*. Lumen fill modified wood, TEOS and wax, showed a slight not significant decrease in *Limnorids* infestation compared to unmodified wood.

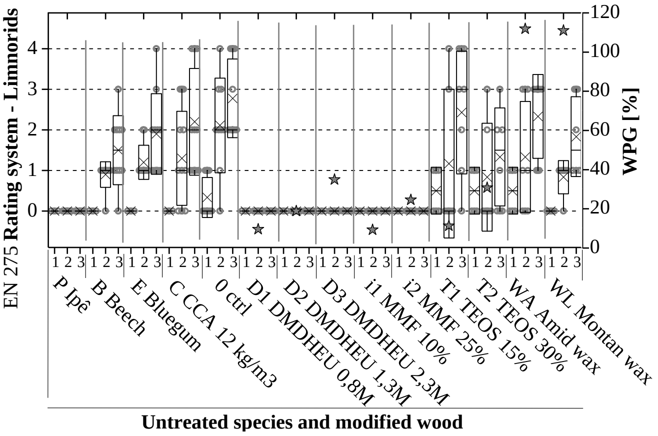


Figure 55. Annual *Limnorids* activity in the first three inspections

Figure 56 shows the *Teredinids* activity up to the 3rd year of exposition for unmodified wood species and modified pinewood. The Ipê hardwood species has shown no attack by *Teredinids*, however Beech and Blue Gum wood species were severely attacked. Unmodified pinewood and CCA treated pinewood has shown severe up to completely destroyed specimens. Medium and high concentration of DMDHEU resin showed no attack by *Teredinids*. Low concentration of DMDHEU and high concentration of MMF resin showed a slight attack by *Teredinids*, and a moderate attack for medium concentration of MMF resin. High concentration of TEOS has shown high activity of *Teredinids* but with smaller size, Figure 57(T21 specimen). Wax modification performed similar to the unmodified pinewood specimens.

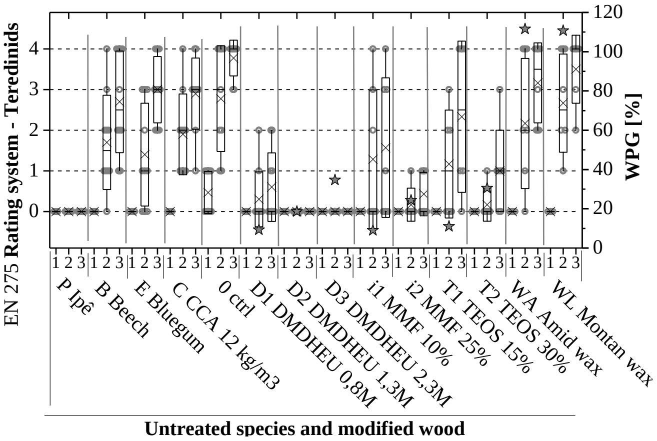


Figure 56. Annual *Teredinids* activity in the first three inspections

In the unmodified wood species the *Teredinids* activity was slightly more aggressive than *Limnorids* activity as well as in the modified wood with wax. In the lumen fill modified wood with TEOS, both marine borers activities were similar, irrespective the solution concetration.

4.3.3 Biofouling

At each inspection, the organisms, animals and fouling, were examined and compared. Between unmodified wood species, modified wood and pinewood with different shapes, the wood surface material did not show any difference in the organisms.

Fouling was moderate at the site. Fouling organisms were mainly barnacles and members of the families of marine organisms - Terebellidae, Sabellidae, Serpulidae, Nereidae and Nephtydae. Calcareous tubes of Serpulidae family (Annelida, Polychaeta), *Mytilus edulis* L. - (Mollusca, Bivalvia), *Balanus amphitrite* Darwin (Artropoda, Crustácea) and *Ciona intestinalis* (L.) - (Chordata. Tunicata). Two Teredinidae (molluscan species, *Lyrodus pedicellatus* and *Teredo Navalis*) and two Limnoridae (Crustacean Borers or Gribbles, *Limnoria tripunctata* Menzies and *Limnoria quadripunctata* Holthuis) were identified.

To illustrate the activity of the main marine borer (*Teredinids*), Figure 57 shows the x-rays of some specimens: DMDHEU (D1, 9%WPG), MMF (i1, 9%WPG) and (i2, 25%WPG), Tetra-ethoxy (T1, 13%WPG) and (T2, 32%WPG) and amid wax (WA, 110%WPG). The activity of *Limnorids* is already exemplified in Figure 58b.

In the TEOS modified specimens, it seems that *Teredinids* individuals did not grow inside the wood material, although the large number of colonies, see specimens T11 and T21 in Figure 57.

In the cell wall modified wood, with DMDHEU or MMF resin, *Teredinids* individuals grew normally, see specimens D14 and i17 in Figure 57, and tunnels with 13mm of diameter and 26cm in length were found.

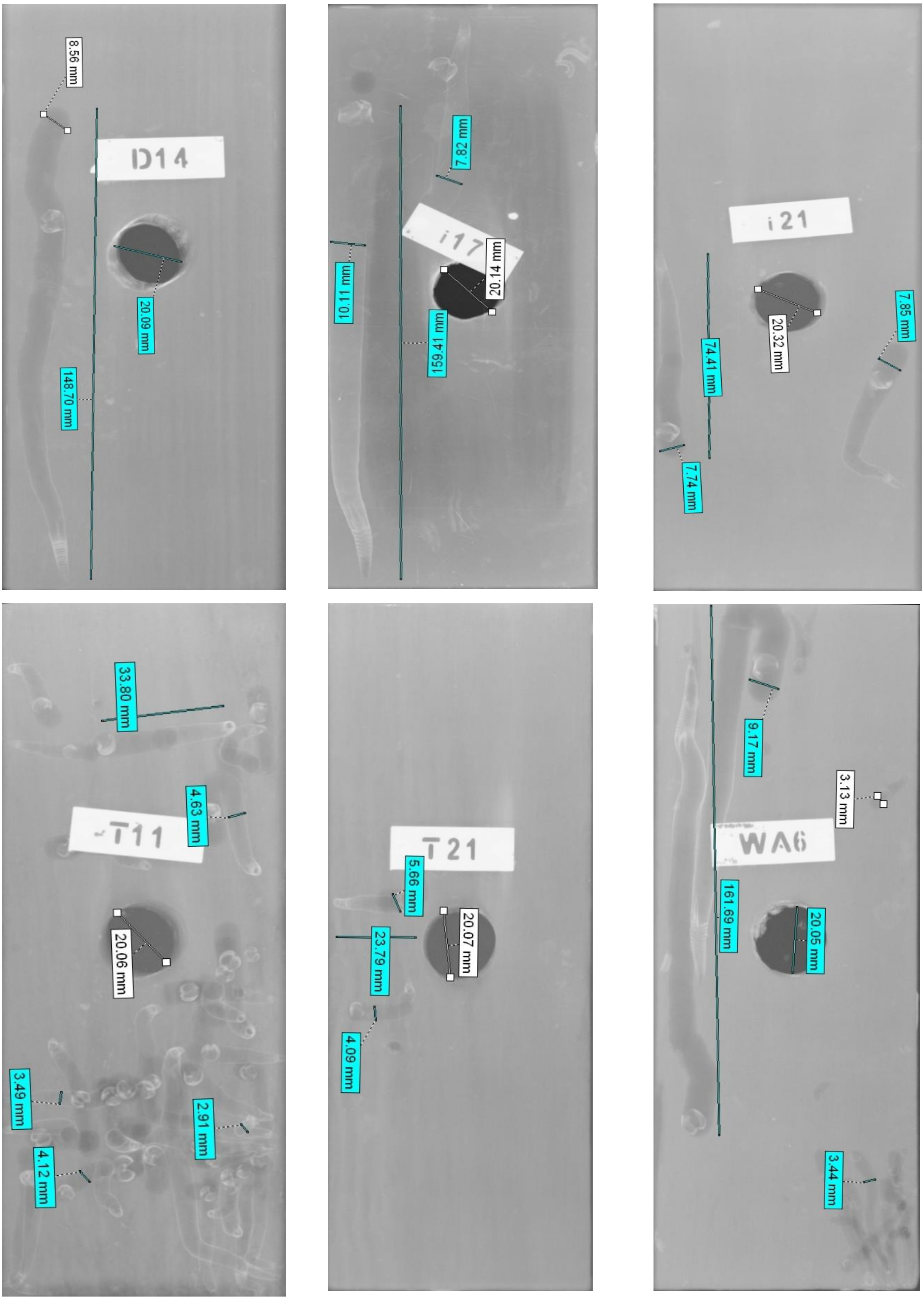


Figure 57. X-ray of the *Teredinids* activity after 2 years exposition. Images were modified with Philips software DiagNET 2.2 (Eindhoven, Netherlands)

4.3.3.1 Gradient of copper and chromium content

Table 20 shows the biocide gradient of CCA penetration in the cross section of the treated logs (in industrial scale) with 15cm of diameter. The treatment with 1.75% CCA (mass/mass) corresponding sapwood retentions of 12kgm^{-3} app..

The chemical content at different depths has shown a gradient up to 52%. However, *Teredinids* individuals did not show any preference behaviour by any part of the specimens, whilst the near part of the pith was preferred by *Limnorids*.

Table 20. Copper and chromium content ($CuSO_4 5H_2O$ [35%]; $K_2Cr_2O_7$ [45%]; $As_2 O_5$ $2H_2O$[20%])

Depth[a] [mm]	Cu [mg/g]	Gradient [%]	Cr [mg/g]	Gradient [%]
11	6.4	---	12.9	---
11	6.4	---	13.5	---
22	4.8	-25	10.4	-19
35	3.3	-52	7.5	-42
35	3.3	-52	7.7	-40

[a] Depth, from the outer surface to the pith

4.3.4 Contribution of the size of specimens on the resistance

According to Figure 14, the influence of the shape of specimens on the marine resistance was analyzed, with 180 specimens of unmodified pinewood. However only 110 specimens were recovered and identified for inspection. At least, eight specimens per thickness and width remained.

Nearly 40% of the exposed specimens were missing. Biological action or mechanical action of water or both were the main reasons. The level of destruction was so extent that turned the rating impracticable, see Figure 58c. The degree of *Teredinids* or *Limnorids* attack was undetermined. Small pieces involved by bio-fouling were found, nevertheless no classification were done and recorded as missing.

Figure 58a shows the typical x-ray of wood specimen infestations by large amount and big *Teredinids* animals, while Figure 58b shows a heavy attack by *Limnorids* on the surface of material.

Comparing the x-ray from the wood specimens exposed in cool waters of the North Sea (Westin et al. 2007 and Klueppel et al. 2010) and temperate waters (in this study), animals are larger in temperate waters. The environment temperature seems to take an important role on the recorded attack.

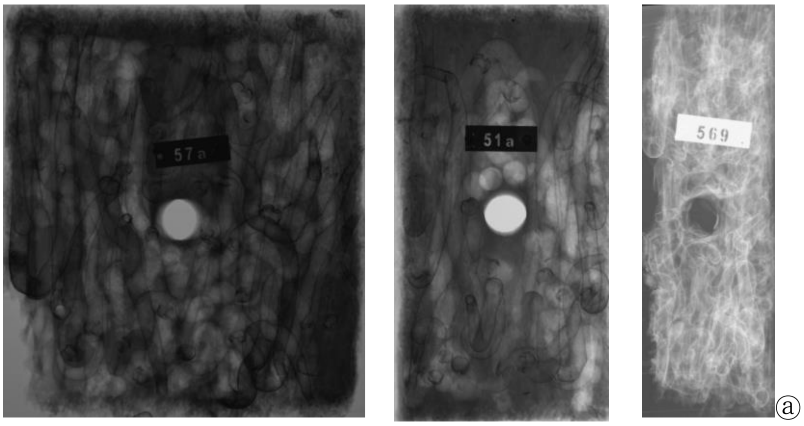


Figure 58. Typical attack by marine borers in the pinewood over 2 years,

(a) - x-ray to detect tunnels by *Teredinids* inside of the wood material;

(b) - visual inspection to detect superficial galleries by *Limnorids*;

(c) - unclassified specimens;

[*Scale*: Central hole have a diameter of ϕ 20mm]

Figure 59 shows the marine borers attack over a period of two years in pure sapwood of the Maritime pine species, tested in the open sea field (Leixões harbour, Portugal). On the horizontal axis, thicknesses and withs, any tendency was found for both marine bores.

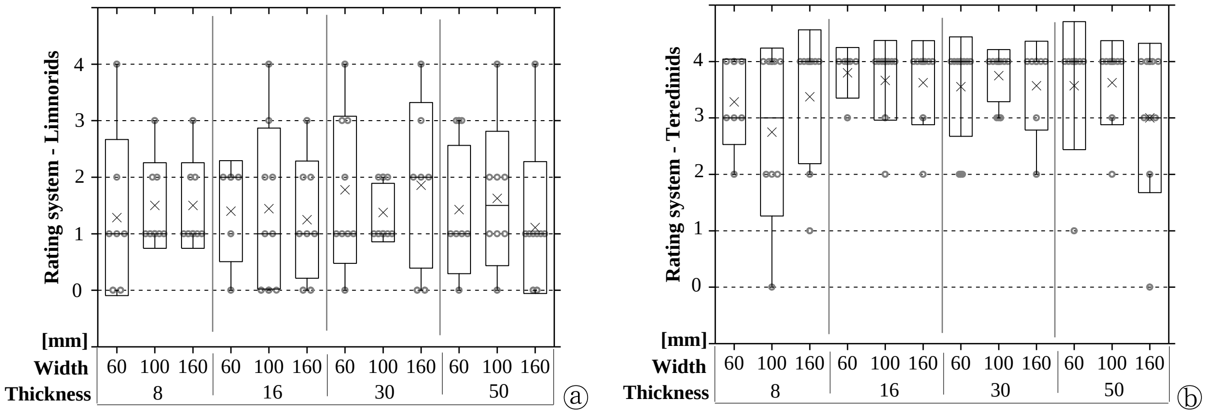


Figure 59. Attack of marine borers for different thicknesses and widths, (a) - activity of *Limnorids* and (b) - activity of *Teredinids* (n=8)

In general, a moderate up to severe attack by *Limnorids* was found, Figure 59a. Forty percent of the specimens have showed moderate attack by *Limnorids*. A major attack by *Limnorids* was detected in 6% of all specimens.

The attack by *Teredinids* prevailed over the *Limnorids* in 94% of all specimens. From the *Teredinids* attack, in Figure 59b, all wood material were completely destroyed or rejected over two years. Only two wood specimens remained intact, without any attack by *Teredinids*, and two were evaluated with slight/trace attack.

Related to the shape of specimens, Figure 60 shows an alternative analysis carried out regarding some variables: End area exposed in longitudinal direction (A_{end}, cross section), tangential direction (A_t) and radial direction (A_r), total area (A_{tot}) and total volume (V) as well as the ratio area and volume (A/V). All the latter variables are in vertical axis.

The marine borers attack is on the horizontal axis. The mean attack by *Teredinids* is set on the right side at range 2.5 up to 3.75 and the mean attack by *Limnorids* is in the range of 1.0 up to 2.0 (in the left side of the horizontal axis).

Each thickness (8, 16, 30 and 50mm) matches one line with three figures for each width. Thicknesses together with widths (60, 100 and 160mm) of test specimens match differents ratio A/V (on top-left of the vertical axis). Different lines of *Limnorids* and *Teredinids* attacks did not assume any tendency. The same conclusion can be drawn for all isolated variables on the vertical axis, i.e. top area or cross section area, radial and tangential area exposed, total area and volume exposed.

From both evaluations, in Figure 59 and Figure 60, it can be seen that the severeness of attack from both marine borers, *Teredinids* or *Limnorids*, is comparable in all sample dimensions.

In the open sea exposure, organisms (*Limnorids* and *Teredinids*) have shown no shape preference during their biological action. This allows concluded that any size of specimens can be used to access the durability performance of wood materials.

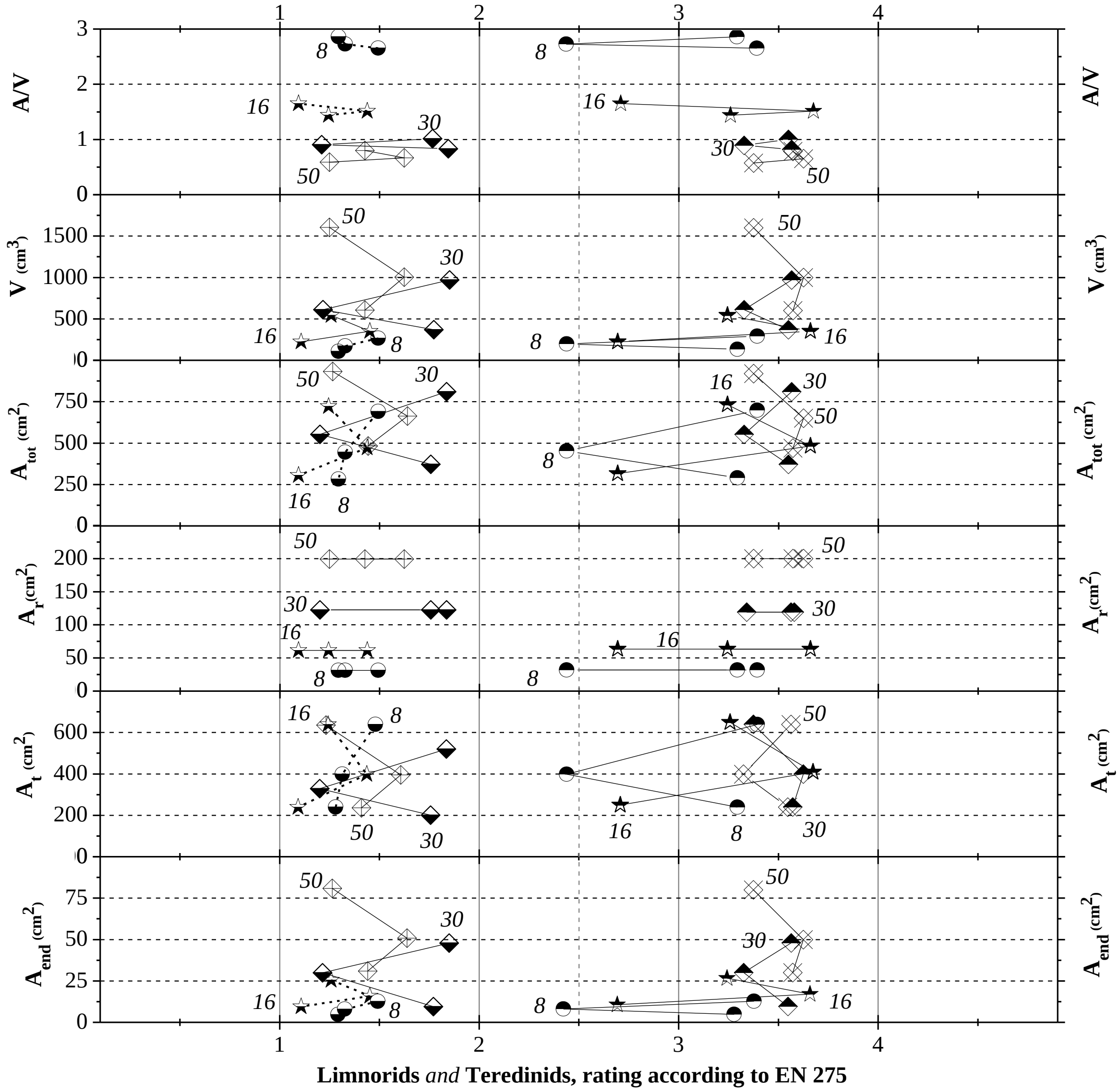


Figure 60. Attack of *Limnorids* (on the Left), *Teredinids* (on the right) and mean variables analyzed of the attack in Pinewood: 50mm◇-diamond with vertical and rotate cross; 30mm◇-diamond (down shadow ◒ and upper ◓); 16mm☆-star with five nozzle and 8mm○-circle, for *Limnorids* and *Teredinids*, respectively (n=8)

4.3.5 Hardness contribution on the marine resistance

Density correlates with hardness in the same- and different-wood species (Filho et al. 1992; Cragg et al. 2007; Unsal and Candan 2008; Lahr et al. 2010). When this study started the assumptions was that hardness plays an important role in the wood durability of marine and terrestrial wood-boring arthropods respectively in Green et al. (2004) and Cragg et al. (2007).

Figure 61 shows the correlations between density, hardness and marine borers attack. A range of density of 425 up to 675kgm^{-3} was found. The density was categorized into six intervals with box plot. Box plot showed the marine borers attack related to the wood density. To keep the picture as clear as possible, individual data of density and *Limnorids* attack (showed by the box plots) were not shown. Between density and *Limnorids* attack no significant correlation was found (R -0.095), despite to be negative. That means, no tendency was found in the mean value of the *Limnorids* attack, matched with the increasing of the BH more than 400%, Figure 61a. The superficial hardness did not show any correlation with *Limnorids* attack (surface galleries). On the other hand, density has shown a significant correlation with BH (R +0.66).

Figure 61b shows the correlations between density, Janka hardness and *Teredinids* attack. Density was significantly correlated with JH (R +0.63). The increasing of JH (up to 200%) matched with a slight increase on *Teredinids* infestation (not significant, R +0.12).

Unlike what has been found for *Teredinids* and hardness, pinewood has shown a negative correlation between BH and a slight decrease on *Limnorids* infestation.

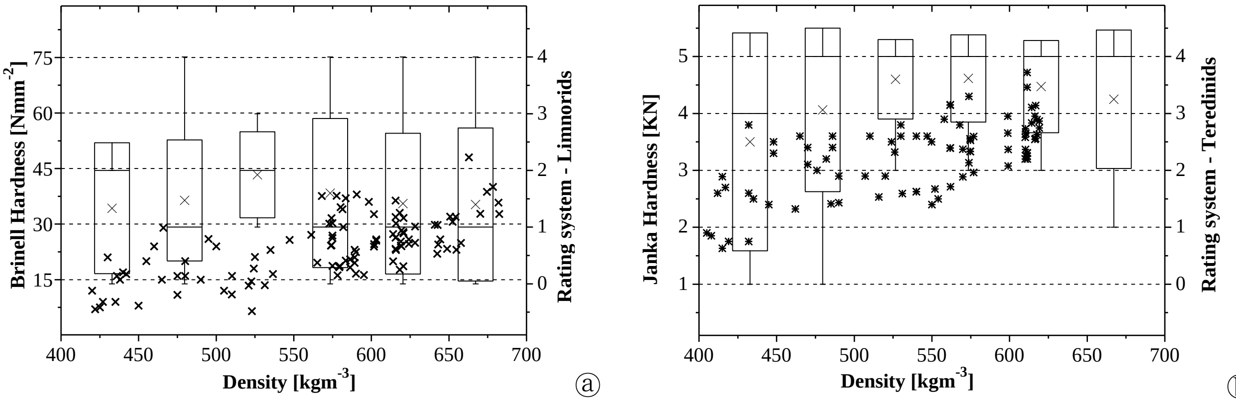


Figure 61. (a) - Density and Brinell hardness (×), (b) - density and Janka hardness (✳). Box plot shows the marine borers activity in Maritime pine rating according to EN 275, exposed ober two years (Leixões, Portugal)

Between *Limnorids* activity and the increase of BH (app. 400%), the negative correlation does not fit with the suggestions done by Cragg et al. (2007) and Borges et al. (2008). In laboratory trials, these authors showed a moderate correlation between micro-hardness (in various wood species and a wide range density, 400 up to 1050kgm^{-3}), and faecal pellet production by *Limnorids*, *L. quadripunctata*. However, with the same procedure, the same marine borers and pellet production, Sivrikaya et al. (2008) found a minor correlation between densities of Turkish woods. In marine field conditions, Sen et al. (2008) in Mediterranean and Black sea waters with tropical hardwood with high natural durability has shown that the best performance was not dependent on the hardness but more of the extractives content. It seems that hardness play a role together with the amount of extractives content in the wood species.

In this study, because the same pinewood species is used, the amount of extractives content was in the same range and can be neglected. Then, the role of hardness appeared as isolated variable and without any effect on the durability of the pinewood, Figure 61a and b.

The extractives content for Pinewood species are mainly compounds soluble in ethanol and water, between 1.1 up to 3.0% for sapwood and 2.6 up to 13% for heartwood (Esteves 2006). The heartwood was avoided as much as possible, then the effect of extractives was neglected.

Machado et al. (2003) with the same Portuguese wood species showed similar correlations between density and hardness. Esteves et al. (2009) showed slight higher mean hardness with Janka procedure. Undifferentiated provenance material, sap- and heartwood, should be the main reason per the mean value difference.

4.3.6 Hardness and chemicals contribution to the marine borers resistance

The main marine organisms, *Teredinids* and *Limnorids*, act to the wood in different ways. The *former* drilling tunnels in the wood material and affects large area, with undifferentiated early- or latewood. Teredo animal is the most usual and largest known xylophagous tunnelling diameters with 10 up to 20mm. The *latter Limnorids* produces galleries at the wood surface with preference for the paler early-wood rather than the darker latewood of the annual growth rings. Limnoria animal has a few millimetres, 2 up to 4mm.

The connection between both marine borers and both hardnesses, i.e. surface Brinell hardness and Limnoria action as well as the depth Janka hardness and Teredo action, seems to be a reasonable approach to access the contribution of hardness to the marine durability.

Figure 62 shows the hardness for un- and modified wood specimens and the rate of marine borers attacks according to EN 275.

The Brinell hardness (BH) had the following performance comparing to the unmodified pinewood, Figure 62a:

- DMDHEU resin modified wood increased the BH between 80 up to 140%, for low and high concentrations, respectively.
- MMF resin modified increased the BH 40 up to 60%, for low and high concentrations, respectively.
- TEOS modified wood increased the BH between 30 up to 50%, for low and high concentrations, respectively.
- Wax modified wood increased the BH between 180 up to 210%, for amid and montan wax, respectively.

The Janka hardness (JH) had the following performance, Figure 62b:

- DMDHEU resin modified wood increased the JH 40 up to 75%, for low and high concentration, respectively.
- MMF resin modified wood increased the JH up to 50%.

- TEOS modified wood increased the JH up to 40%.
- Both types of wax increased the JH up to 180%.

Unmodified wood species (Ipê, Beech and Bluegum) have shown similar mean hardness found in the literature (on the surface BH and in the depth JH), respectively in Machado et al. (2003) and Kretschmann (2010). Wood specimens treated with CCA did not shown any effect on the hardness.

The highest degree of attack by *Teredinids* occurred in the unmodified pine, Beech and Blue Gum wood species as well as in the modified wood with both types of wax.

The *Limnorids* attack was more frequent than *Teredinids* attack in 6.5% of the 170 specimens inspected. In particular, modified wood with TEOS (28% WPG, T2 high concentration) has shown *Limnorids* attack more frequent than *Teredinids* attack.

In the saturated conditions, all material decreased the JH. In the modified wood, the wetted JH decreased by 25% for DMDHEU resin regardless the concentration; MMF resin decreased the wetted JH up to 40%. In the modified wood with lumen fill, regardless the concentration of TEOS solution, the wetted JH decreased up to 45% and in the wax modified wood the wetted JH decreased up to 30%. Unmodified wood species has shown a reduction up to: 40% for pinewood and Bluegum; 30% for Beech and 10% for Ipê, Figure 62b.

In the unmodified wood species (Ipê, Beech, Blue Gum and Maritime pine) a clear reduction of attacks by marine borers occurred with the increase of surface and depth hardness (Figure 62a and b). However, the role of extractives content was not taken in to account. Then, to avoid the marine borers attack, any conclusion about the contribution of hardness between wood species can not be extracted, only by accident.

On the other hand, lumen fill modified wood with wax had a key role to explain the contribution of hardness on the marine durability. The surface hardness increasing (BH, up to 210%) resulted in a slight decreasing of the attack by *Limnorids* (not significant). The BH did not play a significant role for marine borer activity on the surface of the wood material.

In the resin based modification, regardless the resin concentrations or type, no attack of *Limnorids* was recorded.

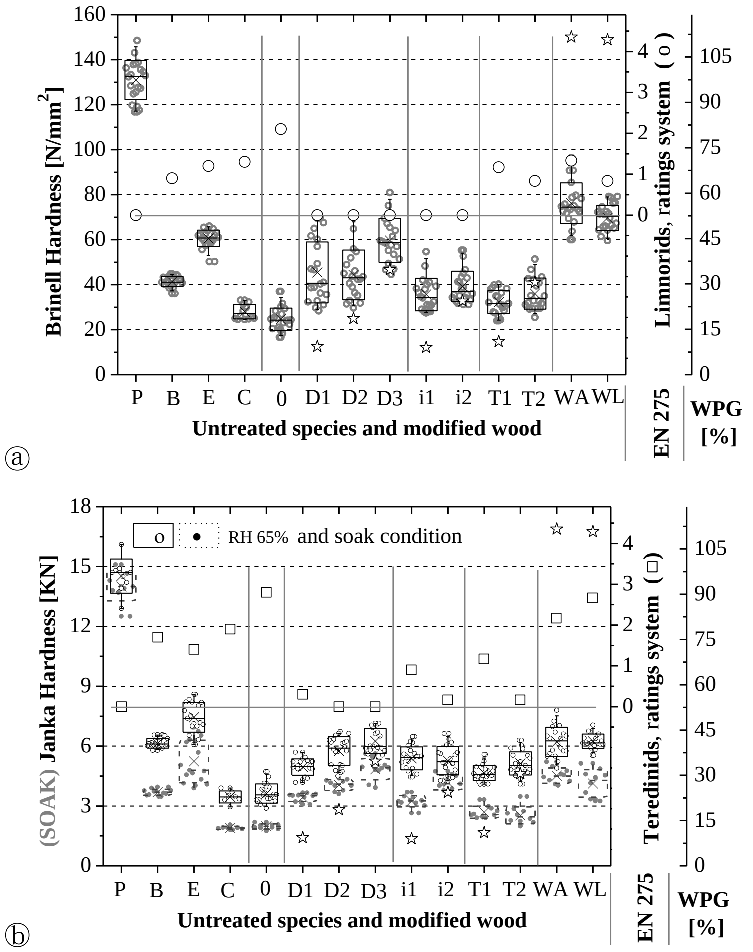


Figure 62. (a) - Brinell hardness and *Limnorids* attack, O, (b) - Janka hardness and *Teredinids* attack, □, at 65% RH and wet conditions, and WPG ☆ (n=10) of wood specimens exposed in Leixões harbour, Portugal (0-no attack and 4-maximum severity of attack). For abbreviations see Table 8 and Table 9

The JH and *Teredinids* activity supports the latter conclusion of the hardness contribution in the *Limnorids* behaviour, Figure 62b and a, respectively. In the modified wood with both types of wax, the *Teredinids* attack has not shown significant difference to unmodified pinewood, despite the depth JH increased up to 100%. Whilst, the JH decreasing in unmodified wood species (Ipê, Beech, Blue Gum and pinewood) match an increasing of the *Teredinids* attack. However, once again, the contribution of extractives content was not taken in to account.

In the resin-based modification, hardness increase matched with a smaller attack, from severe up to trace/slight attack by marine borers, comparing un- and modified wood with low resin concentration (D1 and i1), respectively. For high concentrations (DMDHEU and MMF, D2 and i2), conclusions can not be drawn until the fifth year of exposition is reached. But in this case, the hardness has not play the main role but the protective function and the amount of the resin embedded.

In the lumen fill modified wood, regardless the wax type, no effect on *Teredinids* activity was found despite the high increase of hardness. In the TEOS modified specimens the *Teredinids* attacks were decreased in proportion to the level of modification. However, the length of individuals, not the number, into the wood seems to corroborate the abrasive role of silica material imparted by the modification. Over the time, TEOS modification does not induce sufficient resistance to *Teredinids* or *Limnorids*, see specimens T11 and T21 in Figure 57. Cookson et al. (2007) conducted an experiment over long-term exposition in Australian seawater. He did not find significant differences between CCA treated pine, combined or not to the silica content (0 up to 15%). The silica particles of the lumen fill material of TEOS solution may render the wood abrasive to the denticulate of bivalves and did not allow the organisms to grow up normaly. Nevertheless, no contribution was shown regarding the resistance to the crustaceans *Limnorids* activity. It seems that resistance was not attributable to the hardness increase by the modification (up to 20%, see Figure 57 and Figure 62).

4.3.6.1 Discussion of the contribution of hardness and chemicals

The results of the unmodified wood species (Ipê, Beech, Blue Gum and Maritime pine) used in this study were not unexpected. However, feature of new site, water temperature and salinity mainly, provided relevant data. Similar results were found in the literature in different environmental conditions and period (Palma 1980; Beesley 1980; Gambetta and Orlandi 1980; Eaton and Hale 1983; Cookson et al. 1998; Brelid et al. 2000; Cookson and Scown 2003; Westin et al. 2004; Cookson et al. 2007).

Regarding the type and amount of extractives content involved, but not determined in this case, no special attention was done for the correlation between the marine borer performance of wood species and density or hardness.

To prevent leaching of biocidal chemicals, the wax modification was used before by MacLean (1959). Southern yellow pine modified with parafin, montan wax mixtures (with low retention, 30%) and creosote has shown relative low effectiveness after long-term exposition at Pensacola, FL USA (MacLean 1959). Modified specimens with wax have shown high hardness increasing and helped to clarify that, despite the increasing of hardness, their contribution on marine bores resistance was null or can be neglected.

Johnson and Rowell (1988) and Brelid et al. (2000) found some severe and trace attack by *Limnorids* and *Terebrans* and *Shaeroma* in acetylated wood exposed at different seawater sites. In the acetylated wood, the hardness increased up to 25% (Larsson and Simomson 1994; Epmeier et al. 2004). The slight increase of hardness was not helped by the toxicity of the chemical to impart a better marine performance.

In the modified wood, the assumption is that the chemicals action/toxicity associated with an hardness increasing, both were played an important role in the marine borers resistance. Good predictions in short term laboratory test with DMDHEU and phosphobutane tricarboxylic acid PBTC were obtained (Borges et al. 2005). In field trials, similar results to the latter study were shown with low level of DMDHEU resin modified wood in Olhão (Algarve, Portugal) in Borges et al. (2005).

From the literature, furfurylated modified wood has similar features to the DMDHEU modified wood specimens (Krause 2006). In the furfurylated wood with low concentration (10% WPG) all specimens were severely attacked after 4 years of exposition in the North Sea (Lande et al. 2004). The same modification with medium level of modification (30% WPG) under the same condition has a good performance over seven years (Westin et al. 2007). That means, a minimum level of modification was required. Similar conclusion can be drawn for DMDHEU in this study. The low concentration of modified wood with DMDHEU resin has shown trace attack of *Teredinids*. Whilst, wood modified with medium and high concentration of DMDHEU, it has not shown attack by *Teredinids* and *Limnorids* (D2 and D3).

Some references describe the role of hardness on terrestrial wood-boring arthropods (Behr et al. 1972; Green et al. 2004; Morales-Ramos and Rojas 2005). In the unmodified wood species, density correlated with hardness and in the same line with marine borers performance, *Teredinids* and *Limnorids*, respectively in Figure 62b and Figure 62a. For four species in this work (Ipê, Beech, Blue Gum and Maritime pine), they have shown the same tendency as Cragg et al. (2007) did with a variety of wood species in laboratory studies. Where, they have revealed significant correlation between wood species micro-hardness and faecal pellet production by *Limnoria quadripunctata* (Cragg et al. 2007). Sivrikaya et al. (2008) found a minor correlation between density of Turkish wood and pellet production in laboratory screening test for the same *Limnorids* organism. Sen et al. (2008) reported that high natural durability did not depend on hardness but more on the extractives content of tropical hardwood in the field conditions (Mediterranean and Black sea). Similar conclusion can be drawn in this work. However, because different amount and type of extractives content are involved at different wood species, no conclusion can be drawn if the main protective effect derived from the extractives or hardness (or combinations).

The type and amount of extractives content varies tremendously between species of wood (Hill 2006). The Maritime pine extractives content are mainly compounds soluble in ethanol and water. The extractives content varies between 1.1 up to 3.0% for sapwood and 2.6 up to 13% for heartwood (Esteves 2006).

The Blue Gum extractives are mainly water soluble (2.1 to 3.1%) and ethanol soluble compounds (1.8 up to 3.1%) according to Pereira and Miranda (1991) in Esteves 2006).

In Beech wood species there are more extractives content in sapwood (3%) than in heartwood (1.5%) (www.holzlexikon.de). Accidentally in Leixões exposition, in the unmodified wood species the marine borers attack correlated better with the density (hardness) than with the amount of extractives, see Figure 62a and b.

4.3.7 Conclusions on the performance of the marine borers

By this study on the durability of wood exposed in marine environment, relevant information influencing the marine borers resistance was obtained. In the open sea exposure, both type of marine borers (*Limnorids* and *Teredinids*) showed no shape preference during its biological action. This allows concluded that any size of specimens can be used to access the durability performance of wood materials.

Un- and modified pinewood specimens were significantly attacked by the common shipworm, *Teredo navalis* and *Lyrodus pedicellatus* (*Teredinids*). Comparatively crustacean borers, *Limnoria tripunctata* Menzies and *Limnoria quadripunctata* Holthuis (*Limnorids*) were less frequent.

After the exposition in temperate waters over three years, the modification with thermosetting resins has shown the best performance against marine borers, *Limnorids* and *Teredinids*. No trace attack was recorded by *Limnorids*. Slight/trace attack was recorded by *Teredinids* in modified wood with low level. A minimum WPG level seems to be required.

The lumen fill modification did not increase the marine-borers durability despite the significant increase of hardness imparted by both types of wax (amid and montan wax). Both levels of modification with TEOS did not reduce the number of boring organisms infection on the surface but slow down their growth in the interior wood.

Hardness did not play the main role in marine resistance as the chemical toxicity does. In the same pinewood species, where the contribution of the extractives content can be neglected, *Teredinids* activity was unaffected by the hardness and the *Limnorids* activity had a slight effect (statistically not significant).

In the analysis of the marine borers performances of the unmodified wood species, the amounts and type of extractives and type of chemical need to be taken in to account. The local hardwood species, Blue Gum *Eucalyptus globulus*, did not have satisfactory performance and the tropical hardwood Ipê confirmed its good performance.

4.4 Applications for modified wood

With regard to the application of modified wood in the construction industry, a brief SWOT analysis can be done, where the strength and the opportunities are summarized:

- Wood modification with cell wall reaction (especially resin based) had good relation with moisture-change. At the same time, stiffness did not change significantly. Then, modification of the cell wall at the molecular level, and not filling the cell-wall cavities alone, was required to affect properties where moisture was involved, like MSE, ACE, SSE, ASE and EMC.

The weakness and threats are focused in:

- Strength properties, MOR and IBS reduction.

From this assumption, one of the most accepted reasons for the use of modified wood in building applications is that modified wood may contribute at lower the running costs through significantly longer maintenance intervals, thus returning the higher investment cost for modified wood after a few years. However, the use of modified wood in a specific application depends on which demands for safety, serviceability and other requirements have to be met. The most important requirements for the structural purposes used in the building industry are:

- Strength, such as MOR, IBS and creep in regard to appearance and to risk for structural rupture.
- Fastening with nails, screws, bolts, etc…, often related to density and hardness.
- Stiffness, mainly when regard with moistening change environment (where the deformation related properties such as SSE and ACE are important).
- Durability against biological deterioration.

The main field of application of modified wood lies in SLS design or in non-load bearing applications, where durability, stiffness, appearance and supplemnentary properties are governing. The reduced moisture sensibility of modified wood provides new opportunities for constructions. Less moisture movements lead to reduce the impact on others moisture-related properties.

With regard to durability, stiffness and dimensional stability, modified wood can be used when SLS is governing the design of a wood component.

With considerable higher dimensional and shape stability, modified wood meets the requirements for sustained geometry. Even the workability is often better for modified wood than for unmodified wood.

4.4.1 Cell wall modification, with DMDHEU and MMF resins

Resin based modification can be used in many outdoor applications above ground (outdoors structures, claddings and windows) but also in ground contact (piles and fences) and as well in marine environment (piles, dolphins, fenders, jetties and piers). In the latter, DMDHEU is the most advisable of the tested ones. Its high dimensional stability (ASE) makes resin based modification suitable for e.g. wall studs and ground plates. Special care need to be taken when the bending strength is governing the ULS. If so, DMDHEU in particular and MMF resin also appears to be more brittle than unmodified wood. Despite, its excellent long-term behaviour (represented by ACE) makes the resin-based modification in wood suitable for e.g. floor joists in loft and crawl space, where high dimensional and stiffness stability (ASE, SSE), even under highly varying moisture conditions, is required. Others applications within the field of residential buildings are structural components such as outdoor stairs and patios. Supplementary applications are e.g. bridges, decks, bearing studs in water contact, railway sleeper, fence, garden furniture, carport and playground facilities. Non-load bearing components such as front wall claddings, windows and windows frames are as well recommended.

Additional studies on fastening and reinforcement to solve the brittle behaviour should therefore be carried out before using both cell wall modification (DMDHEU and MMF resins) for structural purposes.

4.4.2 TEOS and wax

Lumen fill modification applied in wood, in a structural point of view, does not appear to offer any major advantage compared to unmodified wood, even though mechanical properties, such as MOE, MOR, SSE and ACE, remain statistically unchanged. Regard to moisture behaviour, the hygroscopicity leads to similar MC, EMC, ASE, swelling strain in all directions to unmodified wood in the long term contact with moisture, at one hand. However, in the other hand, since the water uptake speed changed, according to Scholz et al. (2009) and Donath et al. (2004) good behaviour will be expect under user class 3- EN 335-2 where short time of exposition to the moisture are available. To substantiate the latter assumption is the particular behaviour that was seen for the wax modified specimens in the MSE in creep. It can be questioned wether the excellent long-term performance remains in outdoor applications where different variable are involved such wearing, abrasion, temperature, photo-degradation and swelling effect.

5 CONCLUDING REMARKS

The *Technological improvement of Portuguese pinewood by chemical modification* was reached in different ways. *Physical* and *mechanical* properties as well as the *marine resistance* were researched. Four chemical modification methods applied to Maritime pine (*Pinus pinaster* Ait.) were used: 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) and methylated melamine (MMF), both resin-based modification, with cell wall reactive principle; TEOS and wax modification with lumen fill active principle were as well usedas model compounds.

Maritime pine is an important wood species in Portugal for constructional purposes. From this reason, *several* related wood *properties* were assessed. From this work, the following *conclusions* can be drawn about the physical and mechanical performances:

- The *cell wall* modified wood were the *most effective* methods to achieve high dimensional stability, low equilibrium moisture content and low swelling rate, where DMDHEU had higher extent than MMF resin. On the other hand, the lumen fill modification (with TEOS and wax) *has not shown* any effect.
- Modification methods with high reduction in the equilibrium moisture content also resulted in the highest stiffness stabilization efficiency.
- Except for TEOS, all modifications have shown a significant improvement on the compression strength in both directions (longitudinal and tangential).
- MOR was affected in different extention by modification. A *negative* influence was seen in DMDHEU resin modified specimens and a *positive* in wax modified ones. Frequently, rupture occurred *abruptly* and appeared brittle for cell wall modification (DMDHEU and MMF resin).
- In addition, for cell wall modified wood, a negative effect was shown on *shear* and *tensile* strengths as well as on the *ability to absorb energy* (impact bending strength).

The following conclusions about the creep behaviour can be drawn:

- At indoor conditions and up to medium stress level (of 16Nmm^{-2}), all modifications had no influence in the creep factor (k_c). At high stress level (of 35Nmm^{-2}), cell wall modification (DMDHEU and MMF resin) has shown significant reduction. The enhanced relative creep is *roughly* similar to the reduction in the equilibrium moisture content in wet conditions, RH 87%, imparted by resin-based modification.
- In the modification with lumen fill active principle (with TEOS and wax), creep results did not show significant difference to unmodified pinewood in both climates (indoor and saturated) as well as under high stress level (35Nmm^{-2}).

- At saturated conditions, cell wall modification has shown the *relative creep* reduction *roughly* similar to the reduction in the *impact bending strength*.

- For Pinewood species under various stress levels (8 up to 35Nmm^{-2}) only a slight not significant relative creep increase was found in the higher stress level. In general, in the domain of stresses and over a period of 800hours/35days, the relative creep appears to be independent of the stress level for un- and modified wood.

- The change of the equilibrium moisture content imparted by the modification (ΔEMC), mainly in the cell wall modification, did not correlate with the creep results at indoor climate.

- Unmodified wood and lumen fill modification with TEOS presented higher creep strain under the mechano-sorptive effect with no *creep limit*.

- Resin based modified wood has shown lower creep strain with *creep limit*.

- The effect of modification on the mechano-sorptive effect in bending has been characterized by the *anti-creep efficiency* factor (ACE), analogous to anti-swell-efficiency (ASE).

To improve the mechano-sorptive effect in bending, the modification on the wood cell wall was required, not filling the lumen cells alone. The creep behaviour depends more on the material *relation* with moisture than from the *improvement* in mechanical properties done by modification on the wood material (increase in compression and decrease in tensile strength). In the former relation was showed in the *physical* and *mechanical* properties, anti-swelling efficiency and stiffness stabilization efficiency, respectively. The latter improvement was showed by increasing compression and decreasing tensile strength.

For comparatives purposes and forecasting results, *stable creep* were obtained from data measured over a period of two weeks, in the pinewood species, modified or not.

Marine trials in the Leixões harbour after 3years showed that unmodified pine wood and lumen fill modification (with TEOS and wax) were destroyed. On the other hand, in the cell wall modified wood with DMDHEU resin, a minimum level of modification was required. High concentration of DMDHEU (D3, 2.3M) performed well against both marine borers (against to *Limnorids* and *Teredinids*). Medium and low concentration of DMDHEU and MMF resins performed well *only* against to *Limnorids*.

To identify any influence of the size, shape and hardness of the tested material in the marine resistance, this research showed that was not the case for marine trials. All specimens of unmodified pinewood were attacked even severely. Both marine borers (*Limnorids* and

Teredinids) showed no shape preference and less influenced by the pine wood hardness instead of the toxicity of the chemicals used. Beyond this level of hardness, *any conclusion* about its effect on marine borers resistance could not be elaborated.

5.1 Further work

All *creep factors* found in this study are overestimated, because severe tested conditions, thus they are not suitable to use as deformation factors for *design* purposes. Altered creep behaviour and reduced creep factor will demand adaptation of the design codes (EC 5) as suggested by EN 384 and Abdul-Wahab et al. (1998). *Further* research is needed to fill the gaps of knowledge regarding how to adapt the test methods / standardisation and how to adjust the *design codes* for modified wood in creep.

Modified wood is characterized by the increased density and bulking effect. To help the understanding of the MSE in the modified wood or not, the *swelling* effect on the creep due to the moistening and due to the modification need to be clarified.

MOR reduction will affect the ultimate limit state design (EC 5, load bearing capacity, ULS). The bending strength of wood is determined by *several* factors imparted by modification in opposite directions, such as the compression and tensile strength. The material behaviour in bending was *still influenced* by the weakest part, *tensile* strength. It seems to be one of the main *setbacks* to be solved in the wood modification field. Associated to the latter *brittle* behaviour, the non-uniformity (or up-scaling effect) of the chemical distribution for large cross sections will be *surpassed* with Glulam *reinforced* modified wood. Similar problem has been *solved* already in concrete and its reinforcement. Aramid, Kevlar and Carbon fibre polymers and steel plates / sheets are the most used materials to reinforce concrete structures. In the modified wood, aluminium together with fibre polymers and steel will give a possibility to overcome these shortcomings and use the modified wood efficiently.

In the *stresses* domain, a new approach can be conducted with *very high* SL (near the rupture, over 0.75 up to 0.90 of MOR). Columns buckling and ULS in beams would be clarified and covered.

High *durability* performances, the dimensional stability *improvement* and the *predictable* rupture behaviour will make modified wood an even better *building material*. Well-established *correlations* between different material properties as well as *reliable* data on the strength and stiffness properties for structural purposes are applied only to unmodified wood (EN 384). As they cannot simply be transferred to modified wood, these changes in modified wood are necessary to take into account when using modified wood for building purposes. This is a prerequisite for ensuring that a designer can use the same design routines for modified wood as for unmodified wood, although with adapted coefficients and factors.

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5.3 Curriculum vitae - Lebenslauf

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I, Duarte Barroso Lopes, declare for my honour that is true the one that does consist of my *Curriculum Vitae*, and I commit to supply any eventual lack of documents to prove that is true.