

# Adhesive systems for low formaldehyde emission wood-based panels

*Nuno José Alves da Costa*



**Dissertation presented for the degree of  
Doctor of Philosophy in Chemical and  
Biological Engineering**

**by**  
University of Porto

**Supervisors**  
Adélio Miguel Magalhães Mendes  
Luisa Maria Hora de Carvalho

**Enterprise coordinator**  
João Miguel Macias Ferra

**LEPAE – Laboratory of Engineering Processes, Environment and  
Engineering**

Chemical Engineering Department  
University of Porto – Faculty of Engineering  
Porto, 2013



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A humanidade divide-se em cétricos e fanáticos. Os fanáticos são os crentes, os cétricos, por outro lado, são os que desconfiam criticamente. O meu objetivo é ganhar adeptos para a causa dos cétricos.

*Juan Fontcuberta*

*In: O Beijo de Judas*



## ***ACKNOWLEDGEMENTS***

I would like to acknowledge to the financial support of the Fundação para a Ciência e Tecnologia (FCT) and EuroResinas – Indústrias Químicas, S.A. for my PhD grant (SFRH/BDE/33655/2009) as well as the financial support of E0\_formaldehyde and ECOUF projects. I would also like to thank to: Chemical Engineering Department (FEUP), LEPAE – Laboratory for Process, Environmental and Energy Engineering, Department of Wood Engineering from the Polytechnic Institute of Viseu, all the Sonae Indústria group and ARCP – Competence Network in Polymers for giving me the conditions to carry out my work.

I am particularly thankful to my supervisors Professor Adélio Mendes and Professor Luisa Carvalho for believing in me, for your guidance, knowledge and experience. I would also like to express my thanks to my enterprise coordinator Dr. João Ferra for all the suggestions and essential contributions given.

My sincere appreciation and thanks to Dr. Paulo Cruz, Professor Jorge Martins and Professor Fernão Magalhães, for your endless contribution of ideas, daily challenges and hard questions. Thank you also for your encouragement and insightful comments.

I also want to thank to Professor Joaquim Agostinho Moreira for opening his laboratory and equipment as well as his essential time and support for Raman spectra interpretation.

A special thanks to Dr. Martin Ohlmeyer for having received me at Thünen-Institut of Wood Research, in Hamburg, Germany. Thank you for the hospitality and for the generosity on sharing your knowledge. Thanks to all the Thünen-Institut staff, to Jonas Vagt which never hesitate to help me. Thank you all for supporting me, and I will always support FC St. Pauli!

To all the staff from LEPAE and ARCP, specially to my labmates João Pereira, Daniela Martins, Ana Henriques and Nádia Paiva for the

fantastic working environment, help and contribution to the present work. Without you all this work would be harder! To all my friends, thank you for your support and advice, but mostly for the joy and optimism that you always gave to me.

For their unconditional love and never-ending support, my deepest gratitude to my lovely family, my parents José and Amélia and my sister Diana.

Finally, a special thanks to Lúcia. Thank you for your patience and for showing me that there is always a solution for each problem. Thank you for all your love, for support, for believing, for everything. Thank you for being my “Porto Seguro”!

## ***ABSTRACT***

This work is focused on new solutions for the production of low formaldehyde emission wood-based panels. Wood is a renewable material of excellence, contributing positively to the life cycle of carbon. In Portugal the forest-related economy is responsible for 9 % of the industrial jobs and contributes for 12 % of the total exports. Portugal is also the headquarter one of the largest global wood-based panels producers, Sonae Indústria SA.

In the last years, wood-based panel industry came across a big challenge: formaldehyde emission. Since the publication, by the International Agency for Research on Cancer (IARC) from World Health Organization (WHO) in 2006, of the reclassification of formaldehyde as “carcinogenic to humans (Group 1)”, panel producers and, consequently, wood adhesive producers were compelled to reduce significantly the formaldehyde emission, to avoid losing market share to other products from non-natural sources, such as plastic or metal.

The thesis begins with a general introduction followed by five parts reporting the various aspects of the developed work. The second part concerns the study of urea-formaldehyde (UF) resins synthesis. The effect of the most important parameters (pH and temperature) is studied and the polymeric structure formed characterized. Adhesive performance of the resins applied onto particleboards is assessed. In order to improve the adhesive properties of these resins, the addition of compounds containing hydroxyl groups, such as sucrose, is studied. Advanced characterization techniques, namely Nuclear Magnetic Resonance (NMR), Raman spectroscopy and Size-Exclusion Chromatography (SEC) are essential to assess the chemical reactions involved.

The third part of this thesis focuses the cure of UF resins. Conventional hardeners - so called latent catalysts, namely ammonium sulphate and ammonium nitrate, at high temperature, react with existing free formaldehyde in the resin, forming a strong acid that promotes resin cure.

Currently, these hardeners present low performance due to the lower free formaldehyde concentration in resin. On the other hand, this reaction produces hexamine as by-product, which decomposes when exposed to heat and moisture conditions during the lifetime of the panel. The performance of phosphoric, citric and oxalic acids as UF resin cure catalysts is evaluated. In addition, hexamine contribution to the formaldehyde emission is demonstrated.

The fourth part of this thesis deals with formaldehyde emission determination methods and the use of formaldehyde scavengers. The most used methods for determining formaldehyde emissions were compared: perforator (EN 120), gas analysis (EN 717-2) and desiccator (JIS A 1460). The performance of different formaldehyde scavengers, their application methods, and the relation between data from different emission methods are discussed.

In the fifth part, Volatile Organic Compounds (VOCs) emission of two different wood species is studied: a softwood (*Pinus pinaster*) and a hardwood (*Populus* spp.). In addition, the performance of the most promising formaldehyde scavengers in terms of total VOCs emission reduction is assessed.

Finally, in the sixth part, the general conclusions were formulated from the knowledge acquired during this thesis, which permitted to propose future investigation trends.



## ***SUMÁRIO***

A presente tese visa o estudo de novas soluções para a produção de painéis de derivados de madeira de baixa emissão de formaldeído. A madeira é um material renovável por excelência, contribuindo positivamente para o ciclo de vida do carbono. Na economia portuguesa, o setor florestal representa 9 % do emprego industrial e 12 % das exportações totais. Portugal é também sede de um dos maiores produtores mundiais de painéis de derivados de madeira, a Sonae Indústria SA.

Nos últimos anos, a indústria de painéis de derivados de madeira deparou-se com um grande desafio: reduzir a emissão de formaldeído. Desde a publicação por parte da *International Agency for Research on Cancer* (IARC) da *World Health Organization* (WHO), em 2006, da reclassificação do formaldeído para “carcinogéneo para humanos (Grupo 1)”, os produtores de painéis e, conseqüentemente, os produtores de adesivos, viram-se obrigados a reduzir consideravelmente a emissão de formaldeído dos seus produtos, sob pena de perderem quota de mercado para produtos de fontes não naturais, tais como o plástico ou o metal.

Esta tese é composta por uma introdução geral seguida por cinco partes relativas aos diferentes tópicos abordados neste trabalho. A segunda parte aborda o estudo da síntese das resinas de ureia-formaldeído (UF). Foi estudado o impacto dos parâmetros mais importantes (pH e temperatura) e foi caracterizada a estrutura polimérica das resinas sintetizadas. O desempenho das resinas foi avaliado através da produção de painéis de aglomerado de partículas. De forma a melhorar as propriedades adesivas destas resinas, foi estudada a adição de compostos contendo grupos hidroxilo, nomeadamente a sacarose. As técnicas de caracterização avançada, tais como a Ressonância Magnética Nuclear (RMN), a espectroscopia Raman e a Cromatografia por Exclusão de Tamanhos, revelaram-se fundamentais para compreender as reações químicas envolvidas.

Na terceira parte desta tese aborda-se a cura das resinas UF. Endurecedores convencionais, também chamados de catalisadores latentes, nomeadamente o sulfato de amónio e nitrato de amónio, reagem com o formaldeído livre existente na resina, a altas temperaturas, formando um ácido forte e acelerando a cura da resina. Atualmente estes endurecedores apresentam um baixo rendimento, devido à redução da concentração de formaldeído livre na resina. Por outro lado, esta reação produz hexamina como produto secundário, que se decompõe, libertando formaldeído, quando exposta ao calor ou à humidade ao longo do tempo de vida do painel. Foi avaliado o desempenho dos ácidos fosfórico, cítrico e oxálico como catalisadores da cura da resina UF, assim como a contribuição da hexamina para a emissão de formaldeído.

A quarta parte desta tese foca os métodos de determinação da emissão de formaldeído e a utilização de captadores de formaldeído. Foram comparados os métodos mais usados na determinação da emissão de formaldeído, nomeadamente: perforador (EN 120), análise de gás (EN 717-2) e exsicador (JIS A 1460). O desempenho de diferentes captadores, a sua forma de aplicação e a relação entre dados de diferentes métodos são também discutidos neste capítulo.

Na quinta parte, estudou-se a emissão de Compostos Orgânicos Voláteis (COVs) de duas espécies de madeira: uma da família das resinosas (*Pinus pinaster*) e outra da família das folhosas (*Populus spp.*), bem como o desempenho dos mais promissores captadores de formaldeído na redução da emissão total de COVs.

Finalmente, na sexta parte, são formuladas as conclusões gerais a partir dos conhecimentos adquiridos durante a realização desta tese, o que permitiu propor investigações futuras.

## **RÉSUMÉ**

Cette thèse porte sur l'étude de nouvelles solutions pour la production de panneaux à base de bois de basse émission de formaldéhyde. Le bois é un matériel renouvelable par excellence, contribuant positivement pour le cycle de vie du carbone. Dans l'économie portugaise, le secteur forestier représente 9 % de l'emploi industriel et 12 % du total des exportations. Le Portugal est aussi le siège social d'un des plus grands producteurs mondiaux de panneaux dérivés du bois, Sonae Indústria SA.

Dans les derniers années, l'industrie des panneaux à base de bois a été confronté à un grand défi: réduire l'émission de formaldéhyde. À partir de la publication pour l'*International Agency for Research on Cancer* (IARC) de la *World Health Organization* (WHO), en 2006, du reclassement du formaldéhyde comme "cancérogène pour l'homme (Grupo 1)", les producteurs de panneaux et par conséquence les producteurs d'adhésifs ont été forcés à réduire considérablement l'émission de formaldéhyde dans leurs produits, sous peine de perdre part de marché pour les produits de sources artificielles, tels que le plastique ou le métal.

Ce rapport de thèse est organisé par une introduction générale suivi par cinq parties contenant les différents thèmes couverts par cette étude. La deuxième partie présente l'étude de la synthèse des résines urée-formol (UF). L'effet des paramètres plus importants (pH et température) a été étudié et la structure polymérique des résines synthétisées a été caractérisée. La performance des résines a été évaluée par la production de panneaux de particules. Pour améliorer les propriétés adhésives des résines, l'addition de composés contenant des groupements hydroxyles, notamment le saccharose, a été étudié. Les techniques de caractérisation avancées, tel que la Résonance Magnétique Nucléaire, spectroscopie Raman et la Chromatographie d'Exclusion Stérique se sont avérées fondamentales pour comprendre les réactions chimiques impliquées.

La troisième partie porte sur le durcissement des résines UF. Des durcisseurs conventionnels, également appelés de catalyseurs latents, à savoir le sulfate d'ammonium et le nitrate d'ammonium, réagissent avec le formaldéhyde libre de la résine à hautes températures en formant un acide fort et accélérant le durcissement de la résine. Actuellement, ces durcisseurs présentent un faible rendement dû à la réduction de la concentration de formaldéhyde libre dans la résine. Par contre, cette réaction forme hexamine comme produit secondaire qui se décompose lors qu'il est exposé au chaleur ou à l'humidité au cours de la durée de vie du panneau. La performance des acides phosphorique, citrique et oxalique en tant que catalyseurs du durcissement de la résine UF, a été évaluée, ainsi comme la contribution de l'hexamine pour l'émission de formaldéhyde.

La quatrième partie se rapporte sur les méthodes de détermination de l'émission de formaldéhyde et l'utilisation de capteurs de formaldéhyde. Les méthodes plus utilisées dans la détermination de l'émission de formaldéhyde ont été comparées, notamment: perforateur (EN 120), analyse de gaz (EN 717-2) et dessiccateur (JIS A 1460). La performance des différents capteurs, leur mode d'emploi et la relation entre les données obtenues avec les différentes méthodes, ont été aussi discutés dans ce chapitre.

Dans la cinquième partie, l'émission des composés organiques volatils (COVs) d'une essence de la famille des résineux (*Pinus pinaster*) et d'une de la famille des feuillus (*Populus* spp.), a été étudié, ainsi comme la performance des plus intéressants capteurs de formaldéhyde pour la réduction de l'émission totale de COVs.

Enfin, dans la sixième partie, des conclusions générales sont formulées à partir des connaissances acquises pendant la réalisation de cette thèse, qui a permis d'envisager de futures recherches.

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# ***CHAPTER 1***

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## CHAPTER 1 – INTRODUCTION

### 1.1. WOOD ADHESIVES

According to SRI Consulting [1], the production of urea-formaldehyde (UF), MF (melamine-formaldehyde) and PF (phenol-formaldehyde) resins accounted 63 wt.% of the world demand of formaldehyde in 2009. Merchant Research & Consulting Ltd. [2], in their report “Formaldehyde: 2012 World Market Outlook and Forecast up to 2017” states that formaldehyde-based resins consumes 66 wt.% of the formaldehyde world production.

In wood-based panels market, these resins are the most common adhesive due to their competitive price, reactivity and performance. Particleboard is still one of the most important products in this industry, with a total world capacity around 100 million cubic meters, being Europe the largest producer with a market share of more than 50 % [3].

Portugal has three particleboard mills with a total capacity of 850 thousands of cubic meters. Sonae Indústria is one of the world largest wood-based panels producers and its headquarters is located in Portugal [4].

Moreover, forest and wood have an important impact in the Portuguese economy: one third of the Portuguese territory is covered by forest, representing 165,000 jobs, contributes 5.5 % to the gross national product (GNP) and represents 14 % of the industrial GNP, 12 % of the Portuguese total exportations and 9 % of the industrial jobs [5]. Wood and furniture industry is responsible for more than 54,000 jobs distributed among 5000 companies and revenue of 2500 million euros. Portuguese industrial production of wood-based panels is evaluated in 450 million euros per year [5].

In 2006, after the reclassification by International Agency for Research on Cancer (IARC) of formaldehyde as “carcinogenic to humans (Group 1)” [6], several efforts have been made in order to reduce formaldehyde emission from wood-based panels. Currently, attention is being paid not only to formaldehyde issues, but also to all volatile organic compounds (VOC) emitted by wood-based panels [7].

### **1.1.1. Introduction to wood adhesives**

“An adhesive may be defined as a material which when applied to surfaces of materials can join them together and resist separation” [8]. This is a definition proposed by Kinloch, but the use of adhesives is reported since the early days of humankind. The oldest known adhesives used by modern humans are dated over 8000 years ago. The artefacts found in excavations at northwest of Mount Sedom in Israel have shown residues of collagen-based material believed to be derived from animal skins. Studies of burial sites dated before 4000 B.C. revealed vessels made from broken pottery repaired with sticky resins from trees [9].

The process of bonding wood materials with glue is also known since the early periods of civilization. The first glues were made from a wide range of natural sources, such as starch, collagen and blood. Proteins from milk curd, fish skins and legumes were used as adhesive substances for gluing wood and paper [10]. The bonds formed were strong and durable although moisture induced a faster deterioration. Alternatives were natural thermoplastics such as bitumen and tree pitch, but neither of them permitted to attain rigid bonds.

The first commercial glue plant was installed in Holland, around 1690, as reported by Delmonte [11]. Casein glues were used during the World War I to construct wood main-frames of aircraft, but these were found to have limited resistance to moisture and to mould growth. These limitations were a driving force for the development and expansion of new adhesives based on other materials and synthetic sources, since the 1930s [12]. The first U.S Patent on casein glue was registered in 1876

[13], despite the manufacturing of casein glues appear only at the beginning of nineteenth century in Germany and Switzerland [14].

### *Formaldehyde based adhesives*

In the first formaldehyde monograph, J. Frederic Walker reports that formaldehyde was first prepared by Butlerov in 1859 and obtained by the reaction of methylene iodide with silver acetate [15]. Despite Butlerov had noticed the characteristic odour of formaldehyde, he was not able to isolate it. In 1868, A. W. Hofmann prepared formaldehyde by passing a mixture of methanol vapours and air over a heated platinum spiral. Formaldehyde was definitely identified. Moreover, this synthesis route was the forbear of the modern methods of formaldehyde production [15].

In the “golden age of organic chemistry” (last decades of the 19th century), Adolf von Baeyer and co-workers condensed formaldehyde with phenol and produced non-crystalline solids that they described as useless “goos and gunks” [16]. Leo Hendrik Baekeland, a Belgian chemist and his assistant Nathaniel Thurlow, invented the Bakelite, a condensate of formaldehyde and phenol under mild alkaline conditions [16].

The first study known about the condensation of formaldehyde and urea is dated from 1884 and was carried out by a German chemist, Bernard Tollens [17]. More than 10 years later, melamine-formaldehyde adhesive started being commercialised by American Cyanamid Corp., although the first report of condensation between these two monomers dated from 1933 by Ciba (now Ciba-Geigy) [16].

### *Urea-formaldehyde resins*

Urea-formaldehyde (UF) resins were first synthesized in 1880s, when the production of urea was not well developed. At this time, UF resins were more expensive than phenol-formaldehyde (PF) resins and other natural

adhesives, which explains why the commercial application of UF resins as wood adhesive, did not occur until late 1920s [18]. Earlier studies about the reactions between urea and formaldehyde, published in the last years of the XIX century, such as the studies by Carl Goldschmidt, published in 1896, reported the formation of a precipitate as the result of the reaction between urea and formaldehyde under acidic conditions [19]. This precipitate was empirically identified as  $C_5H_{10}O_3N_4$  and later identified as a cyclically structured condensation product [20]. The basic chemistry of amino resins was established around 1908 [21, 22].

The first patent disclosing the UF polymer is dated around 1918 and issued to Hanns John [23], but the first commercial products were manufactured by E. C. Rossiter of British Cyanides Co. in 1924. In 1925 this company developed moulding materials that are still in use nowadays. A major step forward in the industrialization of amino resins became possible after the patent by A. Schmid and M. Himmelheber in 1932, in which the authors establish the basis for resin-bonded particleboard [22].

### *Melamine-formaldehyde resins*

Melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF) resins are among the most used adhesives for exterior wood-based panels and for the production and bonding of low- and high-pressure decorative laminates and overlay sheets. Their benefit, when compared with UF resin, is the significantly higher water and moisture resistance, despite the higher price and slight lower reactivity [14]. MUF resin, however, is cheaper than MF resin being the choice in most applications without compromising significantly its performance.

### *Phenol-formaldehyde resins*

Phenol-formaldehyde resins (PF) are the polycondensation products of the reaction between phenol and formaldehyde. It was the first synthetic

polymer to be developed commercially, since the latest 1910s. Today, it has a vast and differentiated industrial uses [14]. Despite the higher price and lower reactivity, PF resins exhibit strong water resistance. In wood-based panels industry, it is used mainly in plywood manufacture for exterior conditions [12].

### *Other Adhesives*

Isocyanates are applied in combination with several classes of wood adhesives. They are widely used because their reactivity with groups that contain reactive hydrogens, such as amine or alcohol groups. Despite isocyanates increase the reactivity and the cure rate of the adhesive, they react so rapidly with water present in wood that competes with desired reactions with wood, such as with the hydroxyl groups from cellulose and hemicellulose fractions, as well as the phenols and hydroxyl groups in the lignin domains [24]. They also react quickly and irreversibly with many compounds present in human bodies, especially when volatile isocyanates are present, being this the major disadvantage [25].

Epoxy adhesives are less common owing to their excessively high price and also due to their limited durability. They are mostly used for on-site repair of wood structures.

Tannins, despite the recent attention paid to bio-based adhesives, are difficult to be isolated or their extraction is extremely costly. Lignin, despite their large availability and low price, presents much slower reactivity and a large chemical variation in the feedstock, not being, at present, an efficient substitute of conventional formaldehyde-based resins.

Table 1.1.1 – Advantages and disadvantages of the main adhesives used in the manufacturing of wood-based panels (adapted from [26])

Properties	Adhesive			
	UF	MUF	PF	pMDI
Price	Low	Medium/ High	Medium	High
Cure temperature	Low	Medium	High	Low
Press time	Short	Medium	High	Medium
Susceptibility against wood species	High	Medium	Low	Low
Efficiency	Low	Medium/ High	Medium/ high	High
Manipulation	Easy	Easy	Easy	Difficult
Water and moisture resistance	Low	Medium	High	High
Formaldehyde emission	High	Low	Very Low	No emission

### 1.1.2. Urea-formaldehyde synthesis process

Classically the production of UF resins is carried out in a batch reactor, as shown in Figure 1.1.1. The maximum volume could be greater than 50 tons, but usually it is between 20 tons and 50 tons. Beyond heating and cooling systems and mechanical stirrer, industrial reactors usually present continuous additions of raw materials and vacuum systems.

The most important variables in UF resins synthesis are: purity of raw materials, formaldehyde to urea molar ratio at the different steps and production parameters (e.g. pH and temperatures profile, duration of each step, etc.) [27, 28].

Reaction between urea and formaldehyde is very complex. The combination of these two monomers results in both linear and branched polymers, as well as tridimensional network polymeric matrixes due to the tetrafunctionality of urea (four replaceable hydrogen atoms) and bifunctionality of formaldehyde. According to Pizzi [14], the most important factors that determine the UF polymer properties are: 1)

relative molar proportion of monomers, 2) reaction temperature and 3) condensation pH.

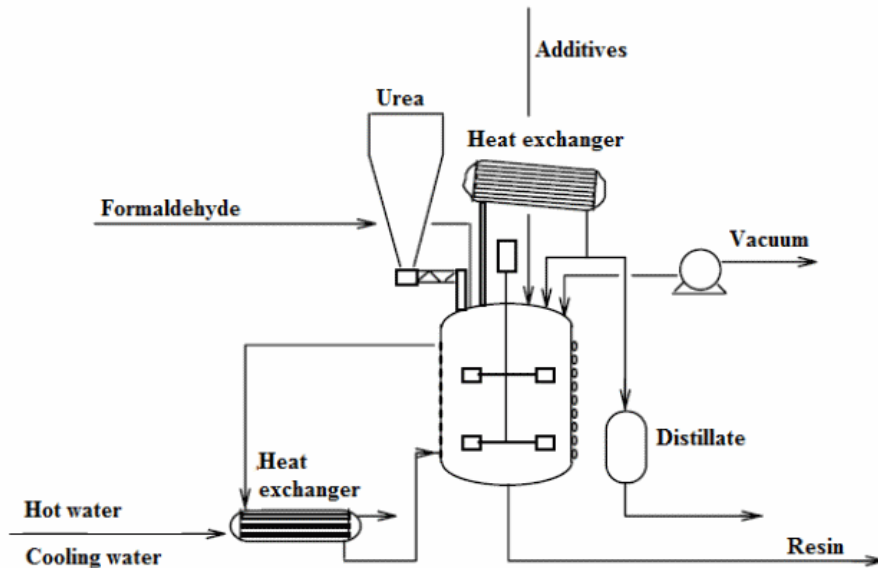


Figure 1.1.1 – Scheme of UF resin reactor [26]

UF resin production is based in two main steps: methylation and condensation reaction. Methylation is the reaction between urea and formaldehyde to form urea-formaldehyde oligomers, generally under excess of formaldehyde [23]. Urea is hydroxymethylated by the addition of formaldehyde to the amino groups of urea, forming mono-, di-, and trimethylolureas (Figure 1.1.2). Tetramethylolureas, apparently are not formed [14, 29]. At the same time, these oligomers react together forming a continuous linear and/or branched structure – the UF polymer. The growth of polymer occurs as methylene ether bridges ( $-\text{CH}_2\text{-O-CH}_2-$ ) and/or methylene bridges ( $-\text{CH}_2-$ ) are been formed. Conner [29] states that the formation of methylene ether bridges occurs as a result of the reaction between: 1) two methylol groups and the formation of methylene bridges by the reaction between: 2) methylol and amino groups, 3) splitting out of formaldehyde from methylene ether bridges and 4)

splitting out water and formaldehyde in the reaction between methylol groups. The two first schemes are presented in Figure 1.1.3.

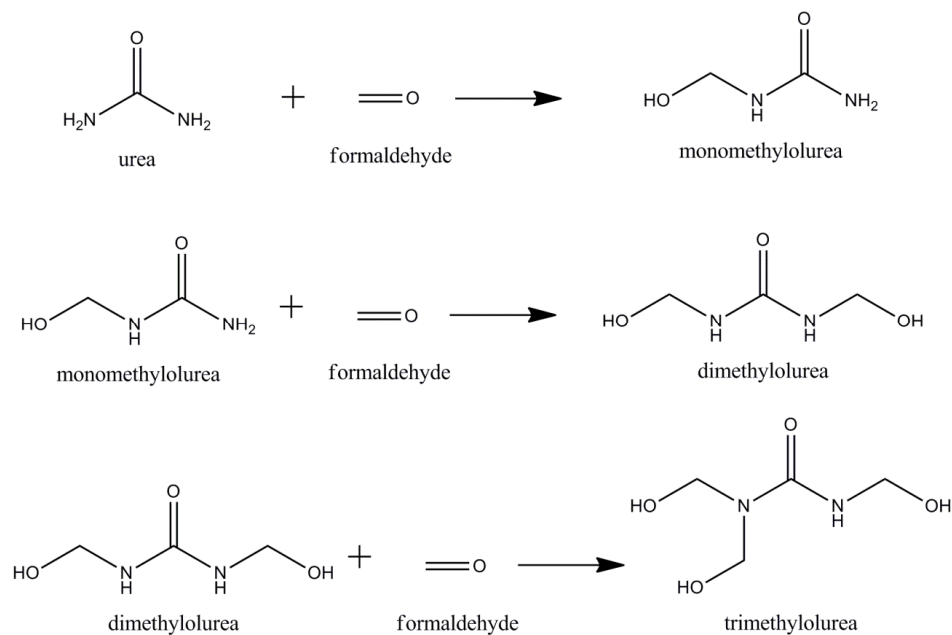


Figure 1.1.2 – Formation of methylolureas (adapted from [29])

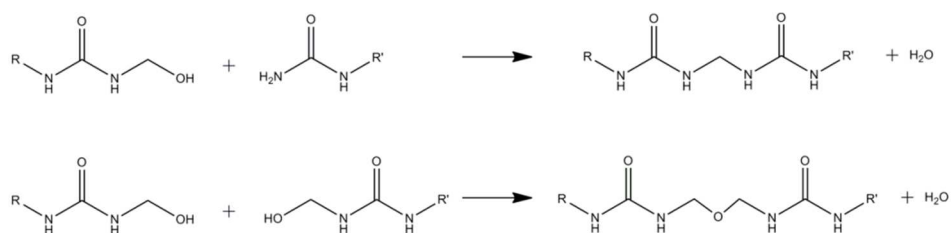


Figure 1.1.3 – Formation of methylene and methylene ether bridges (adapted from [29, 30])



Figure 1.1.4 presents the effect of pH in methylation and condensation steps; pH plays a major role on the kinetics of these stages. Some authors [31-33] have also identified the formation of cyclic structures, also called urons, essentially under low pH environments. Despite their strongly influence on adhesive performance, up to date, less attention has been given to these structures.

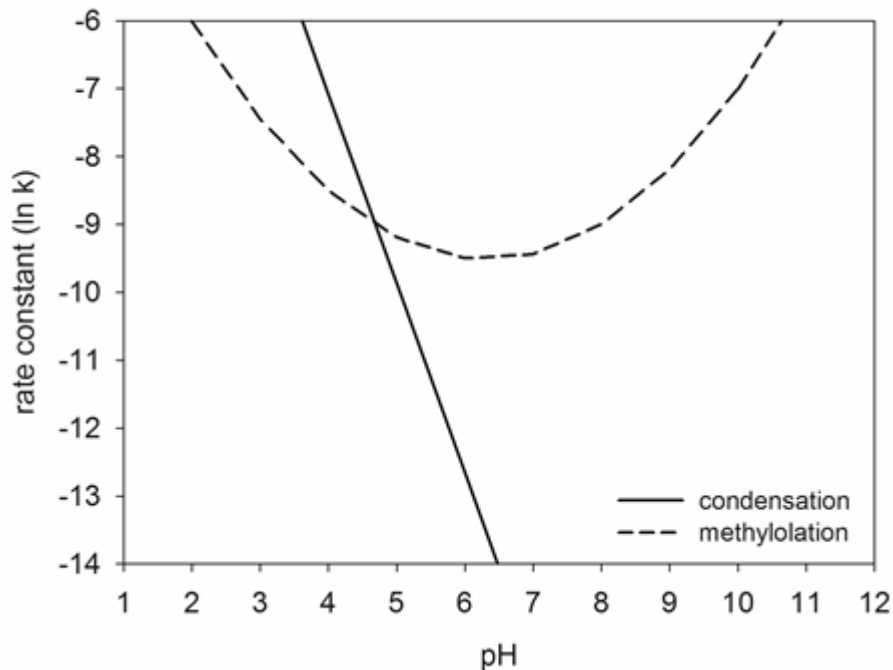


Figure 1.1.4 – Rate constant of condensation and methylation reactions under different pH (adapted from [14, 29])

At industrial level, several processes can be used for UF resins production. Despite innovative processes, such as continuous processes [34], they present higher downtimes associated with the charging and discharging of reactor, disabling the possibility of producing different types of resins in the same reactor. Indeed, wood adhesives manufacturers produce more than one type of UF adhesive to fulfil the

expected properties and type of board to be produced. The production of products with different specification is a common practice among adhesive producers.

The most common process uses then a batch reactor to run the alkaline-acid process. In the following section, only the batch process is analysed.

### **1.1.2.1. Alkaline-acid process**

Alkaline-acid is the most common process for UF resins synthesis. It consists in a first methylation under alkaline environment, followed by a condensation step under slightly acid pH, neutralization and addition of the last urea to consume free formaldehyde (second methylation).

The synthesis protocol starts with charging the reactor with formaldehyde, followed by pH adjusting to slight alkaline environment. Then, the first urea is added under controlled temperature (generally above 90 °C) until attaining the desired F/U molar ratio, usually around 2.2 to 2.0 [14]. Methylation reaction occurs while the exothermic effect is observed. The pH is then adjusted to ca. 5.0, moderate acid, and the second urea is added. As a consequence the condensation reaction is activated, as shown in Figure 1.1.4; the condensation step is monitored by viscosity measurement. When the desired viscosity is reached (normally between 400 cP to 800 cP), pH is adjusted to slightly alkaline, stopping the condensation reactions. Cooling operation starts and the last urea is added until the desired F/U molar ratio is reached (between 1.1 and 0.9). Last urea will consume unreacted formaldehyde and the endothermic dissolution effect will facilitate the cooling operation. An entire cycle of production takes approximately 8 hours.

The condensation step plays a major role during the synthesis process. Due to the complexity of on-line viscometers and their low reliability, the condensation step is normally monitored off-line. Samples are taken every 10 to 15 minutes, cooled to 25 °C and then the viscosity and pH

measured. The sampling time contributes to measurement uncertainty and consequently to the variability of the final product properties.

#### **1.1.2.2. Strongly acid process**

In the strongly acid process, the condensation step is carried out under strongly acidic conditions and takes place simultaneously with the first methylation step. The synthesis protocol starts with charging the reactor with formaldehyde and adjusting pH usually to a value below 2.0, with sulphuric acid. The urea feed starts then at controlled feed rate; the temperature increase is controlled during the feed process, following a previously established temperature program. When desired F/U molar is reached, pH is adjusted to neutral or slight alkaline conditions with sodium hydroxide and the second urea is added. To increase the degree of condensation, a second condensation step, under moderate acidic conditions can be performed, following a similar procedure of the condensation step of the alkaline-acid process. After reaching the desired viscosity, pH is again adjusted to slight alkaline and the cooling step begins. The third (last) urea is added to consume unreacted formaldehyde.

According to Williams [35], the strongly acid process entails minimal energy consumption and involves a shorter batch time reaction, when compared with the conventional process. The shorter time is due to the simultaneous initial methylation and condensation steps. Hatjiissaak and Papadopoulou [36] reported that the reaction occurring during the strongly acid step is extremely exothermic and difficult to transpose from the laboratory to the industrial scale. Ferra *et al.* [37] also observed the high exothermicity of the reaction and compared the reactivity of resins obtained by both strongly acid and alkaline-acid processes. Despite the difficulties of the acid synthesis protocol, this process is nowadays applied in some formaldehyde-based adhesives companies. However, a rigorous feed rate of raw materials (namely urea) and a powerful cooling system are needed.

### 1.1.3. UF resin cure

According to IUPAC [38], a thermosetting polymer, also known as a thermoset, is a prepolymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing. A thermosetting polymer cure can be induced by the action of heat or suitable radiation, or both.

During UF polymer synthesis, the condensation step is stopped by neutralization and cooling. The crosslinking process can be restarted by acidification and temperature increase (Figure 1.1.5). Generally, the acidification is carried out by the addition of catalysts to resin. According to the definition of a catalyst as a substance which increases the rate of chemical reaction without being consumed in the process, providing a new reaction mechanism [39], catalysts for UF resins are not in fact “true” catalysts. They are involved in the curing reaction, being consumed and generating an acid that reduces the pH. Due to this ambiguity, these compounds are also called hardeners. However, the terms catalyst and hardener are used indiscriminately in wood and wood adhesive science [14, 40].

The most common catalysts are the latent (ammonium sulphate, ammonium chloride and ammonium nitrate) [41-45]. Latent catalysts, in the presence of water (which promotes dissociation), react with formaldehyde forming an acid, hexamine and water (equations 1.1 to 1.3). During the blending operation (mixing of wood particles with adhesive), the presence of free water is residual since the moisture content of the blended particles is around 11 %, below the fibre saturation point of wood (around 30 % for most wood species) [46]. The absence of free water avoids the pre-cure reaction. During the hot-pressing operation, water vapour is formed, and the formation of acid takes place, promoting the cure reaction.

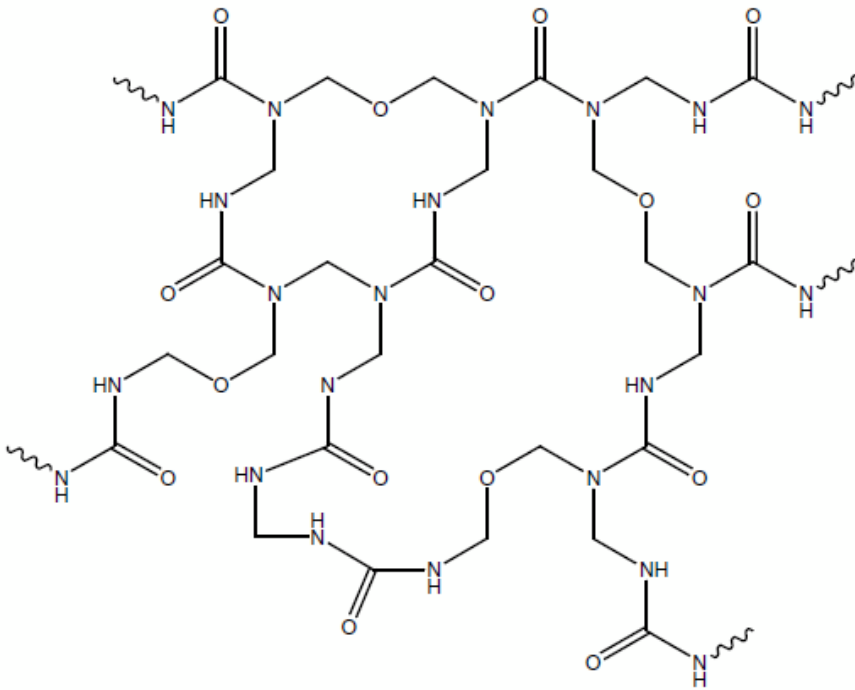
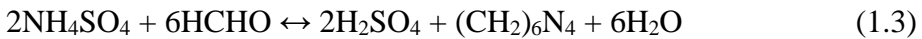
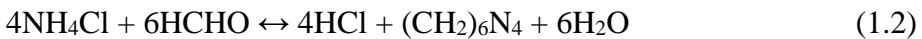
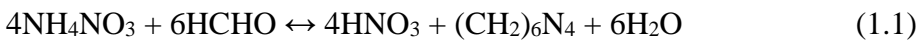


Figure 1.1.5 – Example of urea-formaldehyde polymerization forming a cross-linked network (adapted from [25])



Beyond the requirement of free formaldehyde availability, these catalysts led to the formation of hexamine, which in presence of moisture and heat decomposes releasing formaldehyde (equation 1.4) [10, 15, 47].



In the last years, the reduction of the final F/U molar ratio due to formaldehyde emission issues led to a decrease of free formaldehyde in commercial resins. Residual free formaldehyde results from an insufficient curing reaction and affects also the curing rate [43]. New catalytic systems with no requirement of free formaldehyde are being studied. In North America, the use of buffered catalyst systems is more spread than in Europe and was implemented where ammonium sulphate was unsuccessfully used. Despite the lower reactivity of these systems, they are usually more stable towards premature cure [40].

Direct application of acids such as maleic, acetic, oxalic, formic, nitric [18, 27, 43, 48] have been proposed by several authors. However, the use of strong acids promotes the resin pre-cure (reduction of the adhesive pot-life) and could originate corrosion problems in the equipment, as well as wood degradation.

### **1.1.4. Resin Characterization**

As mentioned before, UF resins are very complex polymeric structures mostly because the number of bonds that urea can originate. Besides that reversible reactions and structural rearrangements occurs during resin production and storage. For obtaining a product with uniform properties, a very accurate control during production and to the final product is needed. Although the characterization of formaldehyde-based resins is being performed for more than 60 years, only recently analytical methods are allowing distinguishing resins with relevant practical differences. Old characterization methods involve the control of physical properties that relate poorly with the resin performance, such as viscosity and solid content, and chemical properties such as reactivity, pH and buffer capacity [49]. New characterization methods are now being developed/used that give a more precise picture of the resin performance as adhesive, namely spectroscopy and chromatographic techniques.

### *Basic characterization*

The usual characterisation of the resin is made using inexpensive methods. The most common characterisation methods are:

**Solid content (%)** is evaluated by oven drying. During the process not only the existing water, but also formaldehyde and water from the on-going condensation are released. Usual values for solid content ranges from 60 % to 64 %.

**Density ( $\text{kg}\cdot\text{m}^{-3}$ )** of an adhesive is usually determined based on the weight/volume ratio and it can be measured using a pycnometer or a hydrometer.

**Viscosity (cP or  $\text{mPa}\cdot\text{s}$ )** gives a rough indication of the polymerization degree. Lower viscosities are expected to induce excessive wood penetration, increasing resin consumption, while higher viscosities will bring flow problems. Nominal values of viscosity at 25 °C are comprised between 150 cP and 400 cP.

**pH-value** is related to the resin stability until its application. pH-values for UF resins are usually between 7.5 and 9.0.

**Buffer capacity** is evaluated by acid-base titration and measures the amount of acid (or base) needed to reduce (or increase) resin pH.

**Curing time and gelation time**, also called **resin reactivity (s)**, is the time needed for the resin gelification under similar conditions of the hot-pressing process (at 100 °C). Usual values of gel time range between 50 s to 100 s.

### *Advanced analyses*

Advanced techniques have been developed for characterizing UF resins. Thereafter is referred some spectroscopic and chromatographic techniques as well as mechanical tests and corresponding relevant studies for UF resins, providing useful information about their structure,

functional groups composition, existing chemical bonds, curing behaviour, etc.

### *Spectroscopic techniques*

There are several spectroscopic techniques useful for characterizing UF resin.

**Fourier Transform Near-InfraRed spectroscopy** (FT-NIR, 13000 – 4000  $\text{cm}^{-1}$ ) is a non-destructive, reliable, fast, versatile technique and no sample preparation is required [50, 51]. There are several studies concerning the application of FT-NIR spectroscopy to UF resins. Chimar Hellas S.A. [52] developed a commercial methodology for on-line monitoring of the industrial resin production, called GNOSSI<sup>TM</sup>. This software can be applied for the determination of formaldehyde concentration, as well as during UF resins production [53]. Application of NIR spectroscopy for on-line assessment of the reaction progress [54] as well as off-line measurements for quality control, namely F/U molar ratio [55, 56] or viscosity [57]. Combined with information collected from other techniques, it is also possible to study the polymeric structure of resin by FT-NIR [58].

**Fourier Transform InfraRed spectroscopy** or **Mid-InfrarRed (FT-IR/MIR)** detect functional groups by measuring fundamental molecular vibrations in the range of 4000 – 400  $\text{cm}^{-1}$  [59], namely carbonyl groups (e. g. amide bonds) that have a high molar absorptivity.

**Raman spectroscopy**, as FT-MIR, involves the study of the interaction of radiation with molecular vibrations. However, while MIR and NIR spectroscopy are based on the absorption of radiation, Raman spectroscopy is a scattering technique [50]. Normally used as complement to FT-IR, Laser Raman spectroscopy was introduced by Hill *et al.* [60] to analyse the structure of UF resins. Minopoulou *et al.* [58] also studied the UF structure by Raman spectroscopy, while



Carvalho *et al.* [61] studied the UF oligomers and curing which permitted to obtain kinetic data as the basis for an empirical kinetic model.

Among the **Nuclear Magnetic Resonance (NMR) spectroscopy** methods, liquid-state  $^{13}\text{C}$  NMR provides the most complete information on the chemical structures present in UF resins, allowing the identification of several functional groups and its quantitative determination [62]. Several authors have studied UF resins by  $^{13}\text{C}$  NMR under different synthesis conditions [31-33, 61, 63-65].

**Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry** allows fast and efficient analysis of complex synthetic polymers, which always exhibit varying degree of polydispersity, including molar mass distribution and chemical composition distribution [66]. Several types of mass analysis instruments can be coupled, being the most common the Time of Flight (MALDI-TOF). For polymer characterization, MALDI provides useful information, such as weight average molecular weight ( $M_w$ ), number average molecular weight ( $M_n$ ), the number of repeating units, and end group determination can be obtained from MALDI data [67]. Zanetti *et al.* [68] have studied with success formaldehyde-based resins by MALDI-TOF.

### ***Chromatographic techniques***

Chromatography is essentially a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (stationary phase) while the other (the mobile phase) moves in a definite direction. When the stationary phase is a solid with a controlled pore size distribution solutes are separated by size differences and the technique is referred to as size-exclusion chromatography (SEC) [69]. Among SEC techniques, Gel Permeation Chromatography (GPC) is the chromatographic separation of macromolecules with the use of porous gels or rigid inorganic packing particles [70, 71]. GPC/SEC allows the determination of the molecular weight distribution (MWD) of a wide range of polymers. The mechanical

and bonding properties of an adhesive are strongly dependent on its molecular weight distribution [49].

High Performance Liquid Chromatography (HPLC) is widely used to analyse the monomer content or to characterize oligomers and additives in adhesives. Components in a mixture are separated by their affinity between the mobile and stationary phase, migrating along the column at different speeds and emerging from the column at different times, thus resulting in a mixture separation. This method is very effective in establishing and identifying low molecular weight components in resins [41, 72-74].

### *Cure evaluation techniques*

The bond strength of thermosetting adhesives develops during the hardening or curing process, which is usually carried out in a hot-press at a defined pressure and temperature, and for a defined period of time. Bond strength between the wood substrate and the adhesive develops during the hardening or curing of the adhesives, which involves conversion of a liquid adhesive through gelation and vitrification to fully cured adhesive [75].

Hardening and gelling of thermosetting adhesives and resins can usually be monitored by exo- or endothermic behaviour during gelling and hardening (chemical curing); suitable test methods are Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC). The solidification of the adhesive during curing by building up the three-dimensional network, also described by the achievable degree of cross-linking; usual test methods for this mechanical curing are Dynamic Mechanical Analysis (DMA), Thermal Mechanical Analysis (TMA), Torsional Braid Analysis (TBA), Thermal Scanning Rheometry (TSR), Dielectric analysis (DEA). The formation of the bond strength between two adherents (materials being bonded) can be followed by methods such as Automated Bonding Evaluation System (ABES), Composite Testing

System (ComTeS) and Integrated Pressing and Testing System (IPATES).

**Differential Scanning Calorimetry (DSC)** measures the change of the difference in the heat flow rate between a sample and into the reference sample, while they are subjected to a controlled temperature program [76]. The original idea of DSC technique born from the **Differential Thermal Analysis (DTA)**. **Thermogravimetric Analysis (TGA)** is a test performed on samples that determines change in weight as a function of a temperature program under a controlled atmosphere. The weight loss of the sample is recorded as a function of the temperature, which is related to the volatile content (including dehydration and chemical reactions involving mass variation), but phenomena related with heat flux transitions are not detected [77].

**Thermomechanical analysis (TMA)** involves measurements of the dimensional changes of material under controlled conditions of force, atmosphere, time and temperature. **Dynamic mechanical analysis (DMA)**, sometimes referred to as **Dynamic mechanical thermal analysis (DMTA)**, analysis the response of a material subjected to a sinusoidal stress, which generates a corresponding sinusoidal strain. **Torsional braid analysis (TBA)** is the predecessor of DMA and characterizes cure properties of polymeric materials. Torsional oscillations are induced by applying a torque.

**Dielectric analysis (DEA) or dielectric cure monitoring** involves measuring changes in the dielectric properties of the material by using an impedance analyser over many decades of frequency. Tests on polycondensating binders used in wood-working industry show that this method is also suited for curing characterization of aminoplast resins. DEA is based on changes in the dielectric properties caused by cross-linking reactions. Immobile groups originated by polymeric processes result in dielectrical conductance decrease. In recent years, DEA technique has been described for the characterization of polycondensating phenoplast and aminoplast wood binders [78, 79].

Furthermore, DEA was also used for testing UF bonded particle boards [80].

The so-called **Automated Bonding Evaluation System (ABES)** has been developed and patented by Humphrey [81]. The ABES enables the determination of strength development characteristics of different adhesives in combination with an adherent. The system includes bonding and testing of a lap-shear specimen under controlled conditions. The system uses a pair of relatively thin adherent strips and the adhesive, which is applied to the end of one strip. The strips are put together to form a lap-shear specimen. The specimen is put in the testing device and pressed by side like in a small hot-press. After a certain pressing time, this small press opens and the specimen is immediately (or after a defined cooling interval of few seconds) tested in shear mode. The technique provides valuable data on the shear strength of the adhesive bond as a function of the pressing parameters (e.g. time and temperature) and conditions (e.g. the cooling effect) [82]. ABES and similar adapted methods have been found to be useful for determining the development of bond strength for various adhesive types under different pressing conditions [83-86].

The so-called **Integrated Pressing and Testing System (IPATES)** was developed for the determination of the adhesive cure in wood fibre and particle mats. The working principle is similar to the one of ABES. A disc mat is formed on a steel press platen with 100 mm in diameter. The mat is heated by two electrically heated blocks and compressed by a universal testing machine. A special adhesive is used to ensure the proper linkage between the press platens and the sample being tested. After pressing, the specimen is destructively tested in tensile mode for determination of the internal bond [87]. A similar method, the **Composites Testing System (ComTeS)** has been used for testing wood composites [88].

## 1.2. WOOD-BASED PANELS

Wood is one of the most popular building materials in the world. However, it has some drawbacks that made it undesired for certain applications. Wood-based panels is a general term for a variety of board products, which have an impressive range of engineering properties overcoming some of the wood restrictions [89].

Solid wood is usually related to high quality products while wood-based panels are, errantly, often classified as a low quality product. Wood-based panels are distinct from solid wood products in their characteristics and applications, although can partially substitute solid wood products. Beyond the environmental benefits of wood products, wood-based panels are an alternative to wood products, due to their versatility, engineered properties and price. They convince by their higher versatility of shapes and dimensions, absence of defects, higher isotropy of properties and higher dimensional stability.

### **1.2.1. Raw materials for wood-based panels**

Products made from particulate woody materials, in the shape of fibre, shaving, chips or other types of particles, can be made from woodworking waste, non-commercial or low value tree species or agricultural wastes [90]. Recovering forest and sawmills residues for manufacture of wood-based panels, particularly particleboards and fibreboards are the success of particleboard industry, presenting the advantage of reduction of raw materials cost, but also environmental benefits, extending the carbon cycle.

Besides the production process, raw-materials have a strong effect on panel performance. The qualities of wood may vary strongly depending on the regional differences and the assortment used, but also over time within the individual process [91]. Therefore, recycling wood is a common practice in a number of countries throughout Europe [92]. The

particleboard industry took up this challenge already quite some time ago. More recently, MDF manufacturers started to use recycled wood in their production processes. Wood-based panels industry is clearly responding positively to the aim of sustained industrial development, in other words, to create more value with less environmental impact [93]. In Portugal, the two major companies implemented strategies for sustainable use of forest resources through recycling of clean wood residues (sawmill), but also industrial wood waste (secondary transformation and wood-based panels manufacturers) and packaging [94].

### **1.2.2. Particleboard manufacture**

Particleboard, as defined in EN 309, is a “wood-based panel manufactured under pressure and heat from particles of wood (wood flakes, chips, shaving, sawdust and similar) and/or other lignocellulosic material in particle form (flax shives, hemp shives, bagasse fragments and similar) with the addition of an adhesive”.

Particleboard raw-materials comprise not only logs but also sawmill residues, recycled wood as well as recycled fibres. These materials are stored in the plant raw-materials store, sorted by species and size. First, large samples are chipped in the Primary Breakdown Machines and later in the Secondary Breakdown Machines sectors, where wood particles are converted in smaller sizes through the hammer mills and flakers. Then, particles are sent to the dryer to achieve the desired moisture content and particles are then sorted according to their sizes. Some manufacturers sort their particles before drying in order to minimize the energy consumption. After these stages, wood particles are mixed with resin and other additives (gluing operation) in a continuous process. Additives could be added directly to wood particles or mixed previously with the resin. Moisture content of the blended particles plays a major role during the pressing stage. Particles in the surface layers present higher moisture content than the core layer particles. This gradient will allow the steam flow to the core, inducing a faster heating of the core section. Core layer particles are usually larger than the in the surface; longer particles

provide better mechanical properties, namely in bending while the lower size of surface particles confers homogeneity to post-processes, such as laminating. After mattress formation, mat is pre-pressed and pre-heated in order to improve the efficiency of pressing operation, reducing the operational costs and improving the line speed. After pressed, boards are cut, their edges trimmed and finely are cooled in a star cooler and then stacked and stored. Prior to shipping, boards are sanded and cut-to-size. A schematic example of a particleboard plant can be seen in Figure 1.2.1. An exhaustive description of the overall process are also reported in the reviews written by Maloney [90] and Irle and Barbu [95].

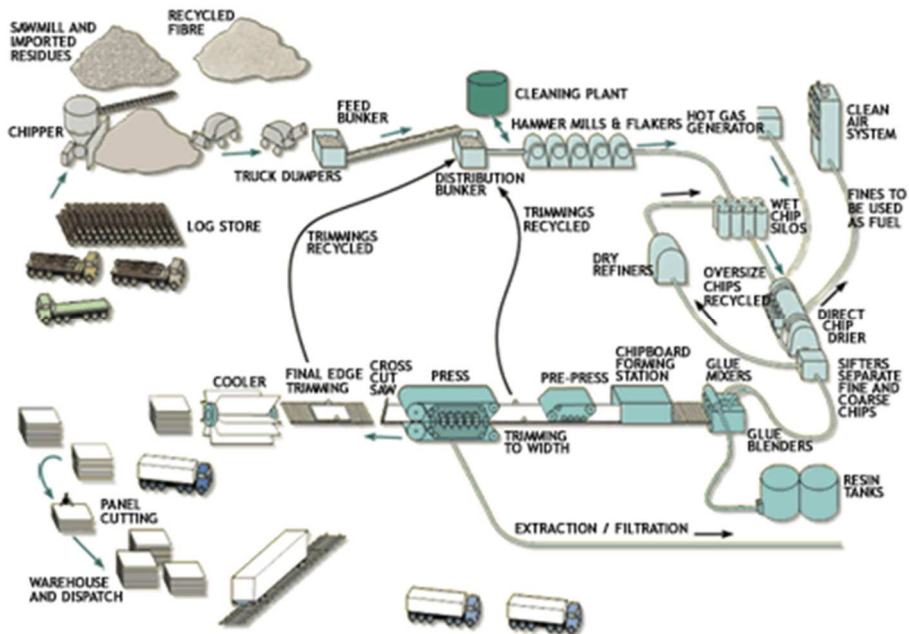


Figure 1.2.1 – Particleboard process diagram [96]

### 1.2.3. Characterization of wood-based panels

Wood-based panels, and more specifically particleboards, can be characterized by several tests and methods. Usually, boards are assessed

according to methods defined by recognized international organizations, such as European Committee for Standardization, also known as Comité Européen de Normalization (CEN), American Society for Testing and Materials (ASTM), Japanese Industrial Standards (JIS) and other regional standard organizations. Each organization defines, sometimes, different tests or experimental conditions for evaluating similar properties.

In this work, all physico-mechanical properties were evaluated according to the European standards (EN), except for formaldehyde emission that was also considered Japanese standards.

Regarding to the EN 312, particleboards can be classified according to different grades, from P1 to P7, where the minimal requirements are defined according to the product final application. For each grade it is defined general requirements, such as the range of moisture content or specific requirements. As example, a P1 grade refers to “General purpose” and a P2 is for “Interior fitments – dry conditions” while a P7 is for “Heavy duty load bearing – humid conditions”. The common tests and corresponding standards to evaluate particleboards properties are defined in Table 1.2.1

Table 1.2.1 – Common test methods to evaluate particleboard properties

<b>Properties</b>	<b>EN standards</b>
Modulus of elasticity in bending	EN 310
Bending strength	EN 310
Tensile strength perpendicular to the plane	EN 319
Swelling in thickness after immersion in water	EN 317
Moisture Content	EN 322
Density	EN 323

Modulus of elasticity in bending, also called modulus of elasticity ( $E_m$ ), and bending strength ( $BS$ ) are determined according to the EN 310.



Modulus of elasticity is calculated from the slope of the linear region of the load-deflection curve. Bending strength is calculated from the ratio of the bending moment ( $M$ ) and the maximum load ( $F_{max}$ ) to the moment of its full cross section, as stated in EN 310 standard. The test piece is supported by two roller-bearing parallel and then a load is applied to the test piece by an equidistant and parallel cylindrical load head capable to measure the deflection and the load applied. An example of a testing apparatus is shown in Figure 1.2.2 (left). Tensile strength perpendicular to the plane of the board is also commonly called “internal bond” ( $IB$ ) and is determined according to EN 319. Figure 1.2.2 (right) shows the apparatus of an internal bond test.

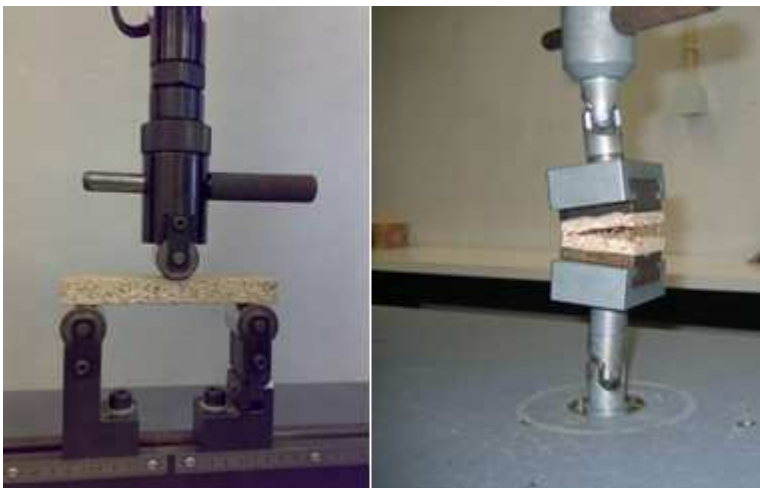


Figure 1.2.2 – Example of determination of a bending (left) and an internal bond test

Swelling in thickness after immersion in water, “thickness swelling” ( $TS$ ) is determined by measuring the increase in thickness of a test piece after complete immersion in water after 24 hours. Figure 1.2.3 (top left) shows a running test apparatus according to the EN 317. Moisture content ( $MC$ ) of boards is determined by the loss of mass of a test piece dried in an oven at  $103 \pm 2$  °C and density is determined from the ratio between mass

of a test piece and its volume. Apparatus of these tests are also shown in Figure 1.2.3.



Figure 1.2.3 – Example of thickness swelling determination (top left), moisture content (top right) and density (below)

### 1.2.4. Particleboard Market

Particleboards market has changed since the last few decades. In 1956 there were 106 European mills producing 724 000 cubic meters of particleboard. In 1973, the production increased about 27 times when compared with 1956 [90]. This period was a period of great developments in wood-based panels and particleboards industry, with substantial increase on relevance of particleboards on global production of wood-based panels, as shown in Table 1.2.2.

Table 1.2.2 – World production of wood-based panels (values in millions of cubic meters, adapted from [90])

<b>Year</b>	<b>1950</b>	<b>1960</b>	<b>1970</b>	<b>1971</b>	<b>1972</b>	<b>1973</b>
Particleboards	0.02	3.1	19.3	22.9	27.2	31.5
Fibreboards	5.4	9.5	14.4	16.1	17.1	18.1
Total Wood-based panels	265.4	343.7	412.6	427.3	438.3	444.2

Currently, wood-based panels and particleboards market has changed completely. Present world capacity is around 100 million cubic meters distributed around the world in different proportions. Europe is the largest producer, with a market share of more than 50 %. However, two clear different trends are found in Europe. In the EU-15 countries there is been a negative trend in the last years, with a production of 31.2 million cubic meters in 2008 and 26.9 million cubic meters expected in 2014, while the production in the European countries outside the EU-15 in 2008 was 19.9 million cubic meters and 25.9 million cubic meters expected in 2014 [3]; this reduction in capacity is related to the European crisis, which led to the closing of industrial plants. Production of particleboards in North America also observed a reduction of around 5 %. Contrasting with Europe and North America, emerging regions such as South America and Asia observed a significant increase on their production capacity with several new plants being planned namely for Brazil and China [3]. Table 1.2.3 shows the particleboard world capacity and the expectations up to 2014.

Portugal has three particleboards mills with an overall capacity of 850 thousands of cubic meters. Sonae Indústria is one of the world largest wood-based panels producers. Their product range includes not only particleboards, but also medium and high density fibreboard, OSB, among other products.

Table 1.2.3 – Historical and prospective world production capacity (values in millions of cubic meters [3])

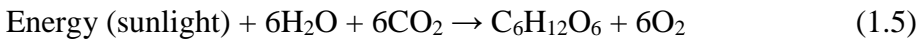
	<b>2008</b>	<b>2009</b>	<b>2010</b>	<b>2011</b>	<b>2012</b>	<b>2013</b>	<b>2014</b>
North America	11.7	11.8	11.3	10.4	11.2	11.2	11.2
South America	4.9	6.0	6.0	6.0	6.6	7.4	8.3
Europe	51.1	53.9	54.6	50.2	52.4	52.8	52.8
Asia	19.8	21.1	21.3	21.8	24.5	24.9	24.9
Australasia	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Africa	2.1	2.0	2.0	2.0	2.0	2.0	2.0
Total	90.7	95.9	96.3	91.5	97.8	99.4	100.3

Forest and wood has an important impact in the Portuguese economy. One third of Portuguese territory is covered by forest, representing 165 thousand jobs and contributes 5.5 % to the gross national product (GNP) and represents 14 % of the industrial GNP, 12 % of the Portuguese total exportations and 9 % of the industrial jobs. Wood and furniture industry is responsible for more than 5000 Portuguese companies and 54 000 jobs and a revenue of 2500 million euros. Portuguese industrial production of wood-based panels is evaluated in 450 million euros per year [5].

### 1.3. ENVIRONMENTAL IMPACT

#### 1.3.1. Green carbon cycle

Forests present a positive impact on carbon storage. Biomass on forest and other green vegetation remove carbon from atmosphere through the photosynthesis process, converting carbon dioxide and water into sugars for tree growth and release oxygen into the atmosphere [46] (equation 1.5):



Carbon in wood remains stored until wood deteriorates or is burned; wood products store carbon while in use. On the other hand, if the tree remains on forest and dies, it releases a portion of carbon retained during lifetime to the atmosphere by decomposition [46]. Processing recovered materials into new long-lived products can extend the storage life of wood carbon already removed from forest.

Figure 1.3.1 represents the green carbon cycle, since the forest through the sawmills and panel factories, the use of wood as building material, recycling wood as raw material for panel manufacture and energy recovery when wood residues are no longer suitable for recycling and consequent release of carbon dioxide that will return to forest. Notwithstanding, there are countries where panels are sent to landfills.

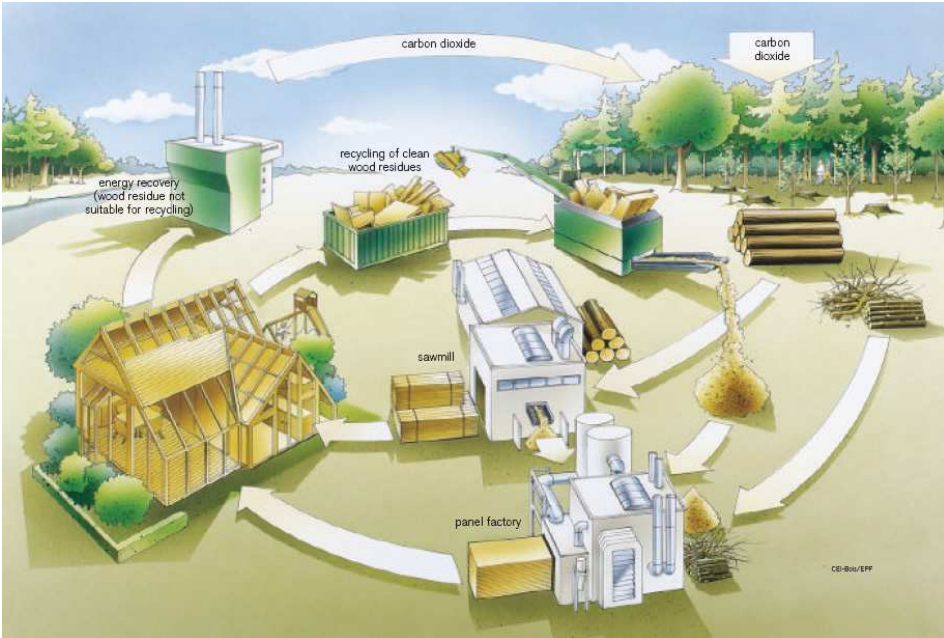


Figure 1.3.1 – The green carbon cycle of the wood-based panels [97]

### 1.3.2. Formaldehyde emission concerns

Formaldehyde is toxic by inhalation, ingestion and skin absorption [7], causing nasal and eye irritation at higher concentrations. The first considerations about indoor air quality and formaldehyde emissions happened in the end of 1970s, during the energy crisis due to the building insulation. The encouragement of the insulation of houses to avoid additional energy consumption has reduced the air exchange with exterior, reducing the ventilation rates and consequently entrapping the gaseous pollutants inside home air atmosphere [98]. This situation led to an increase of some health problems related to the exposure to formaldehyde by inhalation [99, 100]. Indoor air pollution and its sources are considered as possible causes for the sick building syndrome (SBS) and building related illness (BRI) [101].

Formaldehyde emissions became an important subject of public opinion. Since then, wood panels industry has reduced consecutively formaldehyde emission from its products (Figure 1.3.2).

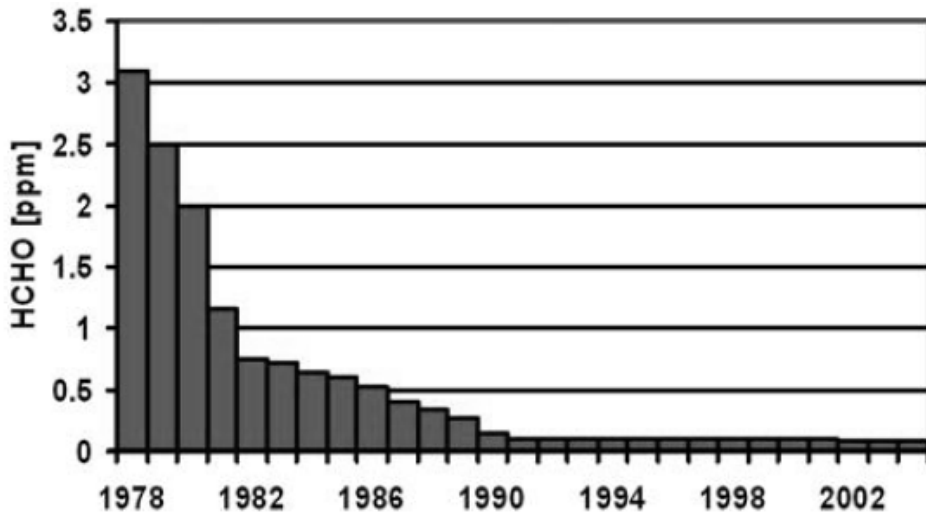


Figure 1.3.2 – Decrease of formaldehyde emission in wood panels (adapted from [101])

In the late 1980s, the U.S. Environmental Protection Agency (EPA) has classified formaldehyde as a probable human carcinogen under conditions of unusually high or prolonged exposure [100]. Prior to 2006, World Health Organization (WHO) classified formaldehyde as probably carcinogenic to humans (Group 2A). In 2004, the International Agency for Research on Cancer (IARC) of WHO, recommended the reclassification of formaldehyde as “carcinogenic to humans (Group 1)”. Despite not being a legal document, this recommendation was received with concern, triggering several reactions from producer associations, “green” organisms, and regulation authorities [7]. IARC recommendation was finally published in 2006, stating that “there is sufficient evidence in human and in experimental animals for the carcinogenicity of formaldehyde” and that “formaldehyde is carcinogenic to humans

(Group 1) [6]. As a consequence, various authorities and institutions have been concerned about formaldehyde as an indoor priority pollutant and new regulations have emerged considering increasingly lower exposure limits. Within European Union, formaldehyde is currently classified as 3-R40 substance (“limited evidence of carcinogenic effect”), but the classification has been reviewed under the new regulation for chemicals Registration, Evaluation, Authorization and Restrictions of Chemicals (REACH). For this purpose, FormaCare (formaldehyde sector group of the European Chemical Industry Council) established a REACH taskforce to facilitate the creation of a consortium allowing European formaldehyde manufacturers to work together as a unified group for their REACH compliance activities [101].

Lately, a study reported by Formacare (Formaldehyde sector group of the European chemical Industry Council), estimated that 10-50 % of the formaldehyde found in indoor air nowadays comes from organic uses such as candles, incense, cooking, outdoor air, gas heaters, indoor chemical reaction, cigarette smoke, etc. [102].

### **1.3.2.1. Emission methods**

Determination of formaldehyde emission in wood-based products can be performed by several methods and standards, basically emerged in Europe, United States and Japan. Each method measure a slightly different emission characteristic and frequently produces results in different and non-interchangeable units, causing confusion among government regulators, consumers and industry personnel [7]. Furthermore, the formaldehyde emission values in 70s and 80s were substantially higher, being necessary to adapt and improve the existing characterization methods. Lately, new test methods have been proposed in order to comply with the new requirements: higher accuracy, lower detection limits, faster and reliable.

Formaldehyde released from wood-based panels in service is caused, not only by residual formaldehyde trapped as gas in the structure of substract,



but essentially due to hydrolysis (reversibility of reactions) of weaker formaldehyde bonds, namely methylol groups, acetals and hemiacetals, as well as methylene ether bridges [27]. Formaldehyde release is affected by internal and external factors. Internal factors include the type of wood and resin employed, operating conditions and parameters during press as well as panel age. External factors are related to the place in which panels are located, such as temperature, air humidity, air exchange rate, as well as the total panel area in relation to the total volume of the room [7].

Existing characterization methods concerning formaldehyde emission can be divided into: measurable emission (“really emitted” amount of formaldehyde under the test conditions) and the “emittable potential” of formaldehyde in the panel (maximum emittable formaldehyde under conditioning at forceful conditions) [41]. Table 1.3.1 summarizes the most important test methods and related standards for the determination of formaldehyde from wood-based panels.

Table 1.3.1 – Test methods and standards for determination of formaldehyde from wood based panels (adapted from [7]).

<b>Test method</b>	<b>Standard, standard draft or method name</b>
Chamber	ASTM E 1333, ASTM D 6007, EN 717-1, JIS A 1901, JIS A 1911, ISO 12460-1, ISO 12460-2
Gas analysis	EN 717-2, ISO 12460-3
Flask method	EN 717-3, method AWPA
Desiccator	ASTM D 5582, ISO 12460-4, JIS A 1460, JAS MAFF 235, JAS 233, AS/NZS 4266-16
Perforator	EN 120, ISO 12460-5

### *Chamber method*

The quantification of the formaldehyde emission of a product under typical indoor conditions in real-life and over defined time scales requires the use of a climate-controlled chamber. Formaldehyde concentration is determined by drawing air from the outlet of chamber through two gas washing bottles containing water that absorbs the formaldehyde. Figure 1.3.3 shows an apparatus of a 1 m<sup>3</sup> chamber.



Figure 1.3.3 – Apparatus a chamber method (EN 717-1), including the chamber and air source (left) and collecting system (right) – (Department of Wood Engineering, IPViseu)

### *Gas analysis method*

Gas analysis (EN 717-2) is a derived test used to determine formaldehyde released at accelerated conditions during 4 hours. Collecting system is similar to the apparatus used in the chamber method (EN 717-1), where formaldehyde released from test piece is continually drawn from the chamber passing through gas wash bottles containing water. Figure 1.3.4 shows an apparatus of a gas analysis method.

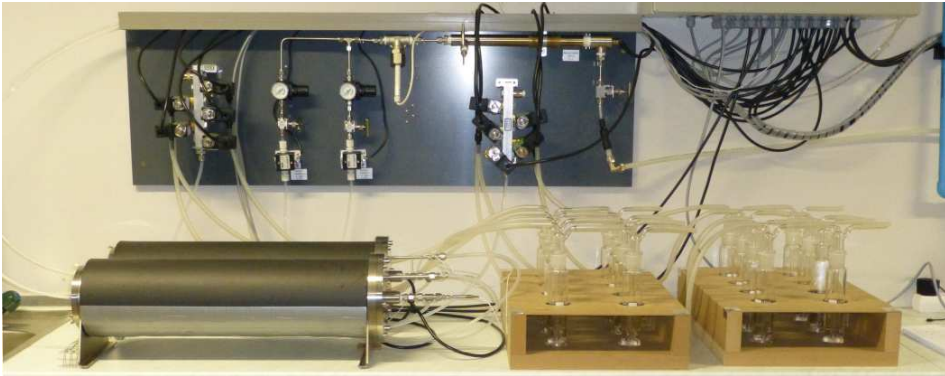


Figure 1.3.4 – Apparatus of gas analysis method according to the standard EN 717-2 (two closed chambers at left and corresponding collecting systems at right) – (Department of Wood Engineering, IPViseu)

### *Desiccator method*

Desiccator method, commonly used in Japan is described in the Japanese standard JIS A 1460 and is one of the cheapest methods. Figure 1.3.5 shows the apparatus of the desiccator test method.



Figure 1.3.5 – Apparatus of desiccator testing, according to JIS A 1460 (on left an open desiccator with test pieces and an example of a test running at right) – (Department of Wood Engineering, IPViseu)

### *Perforator method*

Perforator method (EN 120) measures the formaldehyde content of wood-based panels potentially emitted under forceful conditions. While the chamber method may take several days until samples attain the equilibrium stage, perforator method is a quick and expeditious method, being indicated to a daily factory production control. The drawback of this method is the environmental impact of the toluene used for formaldehyde extraction. Figure 1.3.6 shows the perforator equipment and the testing apparatus according to the EN 120.



Figure 1.3.6 – Perforator equipment used in EN 120. Lower image shows test samples boiling in toluene and upper image shows the collecting system for formaldehyde dissolved in water – (Department of Wood Engineering, IPViseu)

All previously reported methods use water to trap the emitted formaldehyde, due to its ability to absorb formaldehyde. Formaldehyde retained in water is afterwards quantified by analytical methods. The most used quantifying methods are based on derivatization, being the acetylacetone and chromotropic acid methods generally adopted. European methods employ the photometrical quantifying method (by UV/Vis spectrometry) using the acetylacetone method. This method is based on the Hantzsch reaction which involves the cyclization of 2,4-pentadione, ammonium acetate and formaldehyde to form dihydropyridine 3,5 diacetyl-1,4-dihydropyridine (DDL), presenting a maximum absorbance at 412 nm [99, 103].

### **1.3.2.2. Emission regulations**

Standards of formaldehyde testing methods usually do not mention any classification of wood based panels according to the results of formaldehyde emission or release. This classification is established in the specification standards of each product. The harmonized European standard EN 13986 (Wood-based panels for use in construction) classifies formaldehyde emission into two classes: E1 and E2. Internal discussion within the European wood-based panel associations, lead EPF (European Panel Federation) to launch its own formaldehyde standards EPF-S, that corresponds to a perforator value below 4 mg/100 g oven dry board for PB and 5 mg per 100 g oven dry board for MDF (thickness > 8 mm). Driven by IKEA (IOSMAT 0003), an equivalent class with half E1 formaldehyde emission limit was introduced, the so-called E0 (or E0.5); this class has not yet been recognized officially by CEN [104]. Recently, members of EPF agreed to only produce E1 class.

In Japan, more strict limits are defined by standards JIS A 5908 and 5905, F\*\*, F\*\*\* and F\*\*\*\*. The F\*\* is more or less equivalent to European E1 class, while the F\*\*\* and F\*\*\*\* correspond to much lower formaldehyde emission limits, being the last one close to the emission of solid untreated wood, between 0.5 and 2.0 mg/100 g [7].

In the United States, ANSI A208.1 & 2 were the guidelines for formaldehyde emission limits. More recently, CARB established more stringent formaldehyde limits for wood-based panels, being nowadays as reference on wood-based panels market. Phase 1 limits are roughly equivalent to E1 class (and F\*\*) while Phase 2 limits are similar to F\*\*\*. CARB regulation states that, beyond the compliance of those emission limits, wood-based panels and finishing goods for sale or used in California must also be certified by CARB approved third party certification laboratory, unless they are approved Ultra Low Emission Formaldehyde (ULEF) or No Added Formaldehyde (NAF) products. NAF and ULEF products must demonstrate a 90 % or better compliance with a 0.04 ppm (ASTM E 1333) limit.

Different authors have attempted to establish correlations between formaldehyde testing methods (desiccator, perforator and chamber). Due to the different operating conditions used in each method, it is not possible to obtain a relation, although approximate correlations can be found in literature [105-107]. In the very low region of emissions, there is a poor correlation between perforator values and the emission of boards [108]. Table 1.3.2 shows relations by Harmon that are generally accepted.

Table 1.3.2 – Relationship between different methods and standards limits (<sup>a</sup>values obtained by correlation; adapted from [109])

Method	Japan		Europe	IKEA	USA (CARB)	
	F***	F****	E1	E0.5	Phase 1	Phase 2
EN 120 [mg/100 g o.d.b.]	≤ 4.5 <sup>a</sup>	≤ 2.7 <sup>a</sup>	≤ 8.0	≤ 4.0	≤ 11.3 <sup>a</sup>	≤ 5.6 <sup>a</sup>
EN 717-1 [mg·m <sup>-3</sup> air]	≤ 0.054 <sup>a</sup>	≤ 0.034 <sup>a</sup>	≤ 0.124	≤ 0.050	≤ 0.176 <sup>a</sup>	≤ 0.088 <sup>a</sup>
ASTM E 1333 [ppm]	≤ 0.055 <sup>a</sup>	≤ 0.035 <sup>a</sup>	≤ 0.127 <sup>a</sup>	≤ 0.051 <sup>a</sup>	≤ 0.180	≤ 0.090
JIS A 1460 [mg·L <sup>-1</sup> ]	≤ 0.5	≤ 0.3	≤ 0.9 <sup>a</sup>	≤ 0.4 <sup>a</sup>	≤ 1.3 <sup>a</sup>	≤ 0.6 <sup>a</sup>

### 1.3.3. Volatile Organic Compounds emission concerns

Besides formaldehyde, wood and wood-based panels also release detectable amounts of other volatile organic compounds (VOCs) [7, 110]. Wood contains several free compounds in its interlinked main constituents of cell walls. The frequent use of wood-based panels in the construction of houses can often lead to high VOC concentrations, mainly terpenes and aldehydes [111]. Softwoods are usually rich in extractives and therefore can release substantial amounts of VOCs, mainly terpenes and aldehydes [112]. Terpenes and acids are strongly dependent on wood species, while formaldehyde is related to the adhesive. Other aldehydes are formed under certain conditions, by autoxidative splitting of free unsaturated fatty acids and triglycerides [113-115]. Makowski and co-workers [115, 116] observed an increase in the first days followed by a decrease in the last week of testing aldehyde concentration during test emissions. Terpenes are essential components for defence against insects and fungi and occur naturally in softwood oleoresin. Due to their relatively high vapour pressure at ambient temperatures terpenes are volatile and contribute to the characteristic odour from different wood species [112]. Hardwoods release mainly acetic and formic acids and less terpene compounds [117].

VOCs emission from wood-based panels depends from the type of the adhesive used (mainly formaldehyde), production parameters, such as pressing time and temperatures, surface structure, storage conditions as well as storage conditions [115, 118].

In last years, the emission issues have been focused on VOCs. Germany and France were pioneers on VOCs regulations. In Germany, the health impact of VOCs is under evaluation by AgBB (Ausschuss zur gesundheitlichen Bewertung von Bauprodukten). Currently, German requirements are only enforced for flooring products; ISO 16000 defines limits to emissions after 3 and 28 days of test pieces stored in a test chamber. AgBB establishes limits for carcinogen compounds, for each VOC as well as for total volatile organic compounds (TVOC). French regulation on VOC emission from construction products published on

May 25<sup>th</sup> 2011 regards a mandatory labelling of construction products installed indoors, floor and wall coverings, paints and lacquers with their emission classes based on emission methods. Emission classes are C, B, A and A+, corresponding the later to the lowest emission. This labelling includes a maximum for TVOC and for each of the organic compounds. No mandatory upper limits for C class are established yet.

### 1.4. REFERENCES

1. SRI Consulting, Urea-Formaldehyde (UF) Resins. 2009.
2. Merchant Research & Consulting, Formaldehyde: 2012 World Market Outlook and Forecast up to 2017. 2012.
3. Wood-Based Panels International, Focus on Particleboard: Capacity growth goes ahead in rest of world, in Wood Based Panels International. February 2013.
4. Observatório para as Fileiras Florestais, Relatório de Síntese. 2012. Direção Nacional das Fileiras Florestais, Autoridade Florestal Nacional, Ministério da Agricultura, Mar, Ambiente e Ordenamento do Território, 28 Junho de 2012
5. Portugal Global, Madeira e Cortiça: a excelência em materiais de construção, in Portugal Global nº 48. September 2012.
6. IARC, Monographs on the Evaluation of Carcinogenic Risk to Humans. 2006, World Health Organization - International Agency For Research On Cancer.
7. Athanassiadou, E. and M. Ohlmeyer, Emissions of Formaldehyde and VOC from Wood-based Panels, in COST Action WG3 (E49)-Performance in use and new products of wood based composites, M. Fan, et al., Editors. 2009, Brunel University Press: London. p. 219-240.
8. Kinloch, A.J., Adhesion and adhesives: science and technology. 1987: Chapman and Hall.
9. Adams, R.D., Adhesive bonding: science, technology and applications. 2005: CRC Press.
10. Pizzi, A., Wood adhesives: chemistry and technology, Vol. 2. 1989: Marcel Dekker Inc., New York
11. Delmonte, J., The technology of adhesives. 1947: Reinhold Publishing Corporation.
12. Shields, J., Adhesives handbook. 1984: Butterworths.



13. Ross, J.H. and C.D. Ross, Improvement in processes of preparing glue. 1876, Albion (New York): United States.
14. Pizzi, A. and K.L. Mittal, Handbook of adhesive technology. 1994: Marcel Dekker Inc.
15. Walker, J.F., Formaldehyde. American Chemical Society Monograph Series. 1944, New York: Waverly Press, Inc.
16. Seymour, R.B. and G.B. Kauffman, Formaldehyde: A simple compound with many uses. *Journal of Chemical Education*, 1992. 69(6): p. 457.
17. Tollens, B., I. Ueber einige Derivate des Formaldehyds. *Berichte Der Deutschen Chemischen Gesellschaft*, 1884. 17(1): p. 653-659.
18. Graves, G., Urea-Formaldehyde Resins: Yesterday, Today, and Tomorrow, in 1998 Resin & Blending: Seminar Proceedings, J. Bradfield, Editor. 1998: Portland, Oregon. p. 3-10.
19. Goldschmidt, C., Ueber die Einwirkung von Formaldehyd auf Harnstoff. *Berichte Der Deutschen Chemischen Gesellschaft*, 1896. 29(3): p. 2438-2439.
20. Carlson, J.E., Cross-linked urea-formaldehyde polymer matrix compositions containing cyclic intermediate structures. 1984, United States Patent 4429075.
21. Einhorn, A. and A. Hamburger, The methylol compound of the urea. *Berichte Der Deutschen Chemischen Gesellschaft*, 1908. 41: p. 24-28.
22. Diem, H., G. Matthias, and R.A. Wagner, Amino Resins, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2000, Wiley-VCH Verlag GmbH & Co. KGaA.
23. Fink, J.K., Urea/formaldehyde Resins, in *Reactive Polymers Fundamentals and Applications*. 2005, William Andrew Publishing: Norwich, NY. p. 283-298.
24. Rowell, R.M., *Handbook of Wood Chemistry and Wood Composites*. 2012: Taylor & Francis Group.
25. Frihart, C.R., Wood adhesion and adhesives, in *Handbook of wood chemistry and wood composites*. 2005, CRC Press: Boca Raton, Fla. p. 215-278.
26. Ferra, J.M., Optimization of Urea-Formaldehyde resins for the manufacture of wood-based panels, PhD thesis, Department of Chemical Engineering, Faculty of Engineering, University of Porto. 2011. Porto.
27. Dunky, M., Urea-formaldehyde (UF) adhesive resins for wood. *International Journal of Adhesion and Adhesives*, 1998. 18(2): p. 95-107.
28. Ferra, J.M., et al., Optimization of the Synthesis of Urea-Formaldehyde Resins using Response Surface Methodology. *Journal of Adhesion Science and Technology*, 2010. 24(8-10): p. 1455-1472.

29. Conner, A.H., Urea-Formaldehyde Adhesive Resins, in *Polimeric Materials Encyclopedia*, J.C. Salamone, Editor. 1996, CRC Press. p. 8496-8501.
30. Conner, A.H., Wood Adhesives. *Encyclopedia of materials : science and technology*. 2001. Elsevier Science, Ltd., Amsterdam, New York
31. Gu, J.-Y., et al., Synthetic Conditions and Chemical Structures of Urea-Formaldehyde Resins I. Properties of the resins synthesized by three different procedures. *Japan Wood Research Society*, 1995. 41(12): p. 1115-1121.
32. Soulard, C., C. Kamoun, and A. Pizzi, Uron and uron-urea-formaldehyde resins. *Journal of Applied Polymer Science*, 1999. 72(2): p. 277-289.
33. Tohmura, S., C.Y. Hse, and M. Higuchi, Formaldehyde emission and high-temperature stability of cured urea-formaldehyde resins. *Journal of Wood Science*, 2000. 46(4): p. 303-309.
34. Gann, M. and M. Tveter, Process for the Continous Production of High Efficient Aqueous Formaldehyde Resin Solutions. 2011, United States Patent US 2011/0014487 A1.
35. Williams, J.H. and K. Louisville, Hydrolytically stable urea-formaldehyde resins and process for manufacturing them. 1983, United States Patent 4410685.
36. Hatjiissaak, A. and E. Papadopoulou, Aminoplast Resin of High Performance for Lignocellulosic Materials. 2007, Patent WO/2007/138364.
37. Ferra, J.M.M., et al., Comparison of UF synthesis by alkaline-acid and strongly acid processes. *Journal of Applied Polymer Science*, 2012. 123(3): p. 1764-1772.
38. Horie, K., et al., Definitions of terms relating to reactions of polymers and to functional polymeric materials - (IUPAC Recommendations 2003). *Pure and Applied Chemistry*, 2004. 76(4): p. 889-906.
39. Figueiredo, J., M. Pereira, and J. Faria, *Catalysis from Theory to Application*. 2008: Imprensa da Universidade de Coimbra.
40. Gunnells, D. and K. Griffin. *Catalyst Systems*. in *Resin & Blending Seminar Proceedings*. 1998. Portland, Oregon and Charlotte, North Carolina: Forest Products Society.
41. Dunky, M., *The Chemistry of Adhesives*, in *COST Action E13: Wood Adhesion and Glued Products*, State of the art Report, M.E. Dunky, Editor. 2001.
42. Stefke, B. and M. Dunky, Catalytic influence of wood on the hardening behavior of formaldehyde-based resin adhesives used for wood-based panels. *Journal of Adhesion Science and Technology*, 2006. 20(8): p. 761-785.

43. Dongbin, F., L. Jianzhang, and M. An, Curing Characteristics of Low Molar Ratio Urea-Formaldehyde Resin. *Journal of Adhesion and Interface*, 2006. 7(4): p. 45-52.
44. Xing, C., et al., Urea-formaldehyde-resin gel time as affected by the pH value, solid content, and catalyst. *Journal of Applied Polymer Science*, 2007. 103(3): p. 1566-1569.
45. Shumigin, D., Ammonium Nitrate Based Catalysts for the Production of Particleboards. 2010: Lambert Academic Publishing.
46. Anonymous, Wood handbook: Wood as an engineering material. General Technical Report FPL-GTR-190. General Technical Report FPL-GTR-190. 2010, Madison, WI: U.S.: Forest Products Laboratory. Department of Agriculture, Forest Service, Forest Products Laboratory.
47. Dreyfors, J.M., S.B. Jones, and Y. Sayed, Hexamethylenetetramine - a Review. *American Industrial Hygiene Association Journal*, 1989. 50(11): p. 579-585.
48. Motter, W.K. and D.M. Harmon, Polymerization-Enhancing Composition for Urea-Formaldehyde Resin, Method of Manufacture, Method of Use, and Articles Formed Therefrom. 2006. United States Patent US 20060057353 A1
49. Grunwald, D., Analysis of resins and adhesives, in COST Action E13: Wood Adhesion and Glued Products, State of the art Report, M.E. Dunky, Editor. 2001.
50. Burns, D.A. and E.W. Ciurczak, Handbook of Near-Infrared Analysis. Practical Spectroscopy Series Volume 35. 2008 CRC Press.
51. Jerry Workman, J. and L. Weyer, Practical Guide to Interpretive Near-Infrared Spectroscopy. 2008. CRC Press
52. Chimar Hellas. Available from: <http://www.chimarhellas.com>, accessed on April 8, 2013
53. Papapetros, D., et al., A new generation of methodologies for on-line monitoring of the industrial production, in 6th European Wood-Based Panel Symposium. 2008: Hanover, Germany
54. Dessipri, E., et al., Use of FT-NIR spectroscopy for on-line monitoring of formaldehyde-based resin synthesis. *European Polymer Journal*, 2003. 39(8): p. 1533-1540.
55. Henriques, A., et al., Determination of formaldehyde/urea molar ratio in amino resins by near-infrared spectroscopy. *Journal of Applied Polymer Science*, 2012. 124(3): p. 2441-2448.
56. Costa, N., et al., Assessment of resin formulations and determination of the formaldehyde to urea molar ratio by near- and mid-infrared spectroscopy and multivariate data analysis. *Journal of Applied Polymer Science*, 2013. 128(1): p. 498-508.
57. Henriques, A., et al., Viscosity determination of amino resins during synthesis using near-infrared spectroscopy *International Wood Products Journal*, 2012. 3(1): p. 64-66.

58. Minopoulou, E., et al., Use of NIR for structural characterization of urea-formaldehyde resins. *International Journal of Adhesion and Adhesives*, 2003. 23(6): p. 473-484.
59. Socrates, G., *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*. 2004: John Wiley & Sons.
60. Hill, C.G., et al., Raman-Spectroscopy of Urea-Formaldehyde Resins and Model Compounds. *Journal of Applied Polymer Science*, 1984. 29(9): p. 2749-2762.
61. Carvalho, L.M.H., M.R.P.F.N. Costa, and C.A.V. Costa, A very simple empirical kinetic model of the acid-catalyzed cure of urea-formaldehyde resins. *Journal of Applied Polymer Science*, 2006. 102(6): p. 5977-5987.
62. Rammon, R.M., et al., The Chemical Structure of UF Resins. *The Journal of Adhesion*, 1986. 19(2): p. 115-135.
63. Hse, C.Y., Z.H. Xia, and B. Tomita, Effects of Reaction pH on Properties and Performance of Urea-Formaldehyde Resins. *Holzforschung*, 1994. 48(6): p. 527-532.
64. Park, B.-D., et al., Reactivity, chemical structure, and molecular mobility of urea-formaldehyde adhesives synthesized under different conditions using FTIR and solid-state <sup>13</sup>C CP/MAS NMR spectroscopy. *Journal of Applied Polymer Science*, 2003. 88(11): p. 2677-2687.
65. Martins, D., et al., Characterization of Urea-Formaldehyde Resins Using <sup>13</sup>C NMR, in *Minimizing the Environmental Impact of the Forest Products Industries*, F. Caldeira, Editor. 2011, University Fernando Pessoa: Porto.
66. Mautjana, N.A. and H. Pasch, Matrix-Assisted Laser Desorption Ionization Mass Spectrometry of Synthetic Polymers. *Macromolecular Symposia*, 2012. 313-314(1): p. 157-161.
67. Stump, M.J., et al., Matrix-assisted Laser Desorption Mass Spectrometry. *Applied Spectroscopy Reviews*, 2002. 37(3): p. 275-303.
68. Zanetti, M., et al., Acetals-induced strength increase of melamine-urea-formaldehyde (MUF) polycondensation adhesives. II. Solubility and colloidal state disruption. *Journal of Applied Polymer Science*, 2002. 86(8): p. 1855-1862.
69. Poole, C., Book review: *The Essence of Chromatography*. *Analytical and Bioanalytical Chemistry*, 2004. 378(1): p. 24-25.
70. Kostanski, L.K., D.M. Keller, and A.E. Hamielec, Size-exclusion chromatography—a review of calibration methodologies. *Journal of Biochemical and Biophysical Methods*, 2004. 58(2): p. 159-186.
71. Barth, H.G., B.E. Boyes, and C. Jackson, *Size Exclusion Chromatography and Related Separation Techniques*. *Analytical Chemistry*, 1998. 70(12): p. 251-278.

72. Ferra, J.M., et al., Characterization of Urea-Formaldehyde Resins by GPC/SEC and HPLC Techniques: Effect of Ageing. *Journal of Adhesion Science and Technology*, 2010. 24(8-10): p. 1535-1551.
73. Ludlam, P.R., J.G. King, and R.M. Anderson, Liquid-Chromatographic Procedure for the Separation and Characterization of Simple Urea - Formaldehyde Reaction-Products. *Analyst*, 1986. 111(11): p. 1265-1271.
74. Kumlin, K. and R. Simonson, Urea-Formaldehyde Resins. Separation of Low-Molecular Weight Components in Urea-Formaldehyde Resins by Means of Liquid-Chromatography. *Angewandte Makromolekulare Chemie*, 1978. 68(May): p. 175-184.
75. Sernek, M. and M. Dunky, Adhesive Bond Strength Development, in *Wood-based Panels: An Introduction for Specialists*, H. Thoemen, M. Irle, and M. Sernek, Editors. 2010, Brunel University Press: London. p. 123-176.
76. Höhne, G., W.F. Hemminger, and H.J. Flammersheim, *Differential Scanning Calorimetry*. 2003: Springer.
77. Sperling, L.H., *Introduction to Physical Polymer Science*. 2005: John Wiley & Sons.
78. Sernek, M. and F.A. Kamke, Application of dielectric analysis for monitoring the cure process of phenol formaldehyde adhesive. *International Journal of Adhesion and Adhesives*, 2007. 27(7): p. 562-567.
79. Pretschuh, C., et al., Dielectric analysis as curing control for aminoplast resins—correlation with DMA. *European Journal of Wood and Wood Products*, 2012. 70(5): p. 749-753.
80. Wang, S.Q. and P.M. Winistorfer, Monitoring resin cure during particleboard manufacture using a dielectric system. *Wood and Fiber Science*, 2003. 35(4): p. 532-539.
81. Humphrey, P.E., Device for testing adhesive bonds. 1993, United States Patent 5176028 A.
82. Humphrey. Temperature and reactant injection effects on the bonding kinetics of thermosetting adhesives. in *Wood Adhesives/Section 3B: Composite Products*. 2006. San Diego, CA.
83. Kreber, B., P.E. Humphrey, and J.J. Morrell, Effect of Polyborate Pretreatment on the Shear-Strength Development of Phenolic Resin to Sitka Spruce Bonds. *Holzforschung*, 1993. 47(5): p. 398-402.
84. Prasad, T.R.N., P.E. Humphrey, and J.J. Morrell, The Effects of Chromated Copper Arsenate and Ammoniacal Copper-Zinc Arsenate on Shear-Strength Development of Phenolic Resin to Sitka Spruce Bonds. *Wood and Fiber Science*, 1994. 26(2): p. 223-228.
85. Chowdhury, M.J.A. and P.E. Humphrey, The effect of acetylation on the shear strength development kinetics of phenolic resin-to-wood bonds. *Wood and Fiber Science*, 1999. 31(3): p. 293-299.

86. Lecourt, M., A. Pizzi, and P. Humphrey, Comparison of TMA and ABES as forecasting systems of wood bonding effectiveness. *Holz Als Roh-Und Werkstoff*, 2003. 61(1): p. 75-76.
87. Heinemann, C., A. Fruhwald, and P.E. Humphrey. Evaluation of adhesive cure during hot-pressing of wood-based composites. in *COST E13 - 3rd Workshop*. 2002. Vienna.
88. Heinemann, C., R. Lehnen, and P.E. Humphrey. Kinetic response of thermosetting adhesive systems to heat: Physico-chemical versus mechanical responses. in *Sixth Pacific Rim Bio-Based Composites Symposium*. 2002. Oregon State University, Corvallis.
89. Thoemen, H., *Wood-based Panels - An Introduction for Specialists*. 2010: Brunel University Press.
90. Maloney, T.M., *Modern particleboard & dry-process fiberboard manufacturing*. 1977, San Francisco, California: Miller Freeman Publications.
91. Thoemen, H. Competition for wood resources-impact on wood-based panels. in *Proc. of the COST E44-E49 Conference on Wood Resources and Panel Properties*. 2006. 12-13 June, AIDIMA, Valencia, Spain.
92. Magic, C., et al. Recycling of urban wood waste into quality board products: trends and prospects for the future. in *Proc. of 5th European Panel Products Symposium*. 2001. Llandudno, Wales, U. K.
93. European Panel Federation. The use of recycled wood for wood-based panels. Available from: [http://www.europanel.org/pdf/Environment\\_WoodRecycling\\_Standard\\_2.pdf](http://www.europanel.org/pdf/Environment_WoodRecycling_Standard_2.pdf), accessed on January, 2012
94. Martins, J., et al. Effect of recycled wood on formaldehyde release of particleboard. in *COST Action E49 Conference "Measurement and Control of VOC Emission from Wood-Based Panels*. 2007. Braunschweig, Germany.
95. Irle, M. and M.C. Barbu, *Wood-Based Panels Technology*, in *Wood-Based Panels: An Introduction for Specialists*, H. Thoemen, M. Irle, and M. Sernek, Editors. 2010, Brunel University Press.
96. SonaeIndústria. Production process: particleboard. Available from: [http://www.sonaeindustria.com/image\\_bank/products/pb\\_flowsheet.png](http://www.sonaeindustria.com/image_bank/products/pb_flowsheet.png) accessed on April 8, 2013.
97. Ward, R., *Tackle Climate Change - Use Wood*. 2009: BC Forestry Climate Change.
98. Zhang, L., et al., Formaldehyde exposure and leukemia: A new meta-analysis and potential mechanisms. *Mutation Research/Reviews in Mutation Research*, 2009. 681(2-3): p. 150-168.
99. Salthammer, T., S. Mentese, and R. Marutzky, Formaldehyde in the Indoor Environment. *Chemical Reviews*, 2010. 110(4): p. 2536-2572.

100. United States Environmental Protection Agency, Office of Air and Radiation. Report to Congress on Indoor Air Quality, Volume II: Assessment and Control of Indoor Air Pollution 1989.
101. FormaCare. Wood panels & formaldehyde. Available from: <http://www.formaldehyde-europe.org/fileadmin/formaldehyde/PDF/BS.Wood.pdf>, accessed on January, 2012.
102. FormaCare. Health & Safety. Available from: <http://www.formacare.org/about-formaldehyde/health-safety>, accessed on January, 2012.
103. Salthammer, T. and S. Mentese, Comparison of analytical techniques for the determination of aldehydes in test chambers. *Chemosphere*, 2008. 73(8): p. 1351-1356.
104. Carvalho, L., F. Magalhães, and J. Ferra, Formaldehyde Emissions from Wood-Based Panels -Testing Methods and Industrial Perspectives, in *Chemistry, Applications and Role in Polymerization*, C.B. Cheng and F.H. Ln, Editors. 2012, Nova Science Publishers, Inc.: Hauppauge, NY
105. Risholm-Sundman, M., et al., Formaldehyde emission—Comparison of different standard methods. *Atmospheric Environment*, 2007. 41(15): p. 3193-3202.
106. Que, Z. and T. Furuno, Formaldehyde emission from wood products: relationship between the values by the chamber method and those by the desiccator test. *Wood Science and Technology*, 2007. 41(3): p. 267-279.
107. Park, B.-D., et al., Empirical correlations between test methods of measuring formaldehyde emission of plywood, particleboard and medium density fiberboard. *European Journal of Wood and Wood Products*, 2011. 69(2): p. 311-316.
108. Roffael, E. and B. Johnsson, Perforator method in balance. *International Wood Products Journal*, 2012. 3(1): p. 43-50.
109. Harmon, D.M., *CHANGE - Its Challenges and Opportunities*, in *Engineered Wood Products Association of Australasia Conference*. 2008: Caloundra, Australia.
110. Roffael, E., Volatile organic compounds and formaldehyde in nature, wood and wood based panels. *Holz als Roh- und Werkstoff*, 2006. 64(2): p. 144-149.
111. Hodgson, A.T., D. Beal, and J.E.R. McIlvaine, Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house. *Indoor Air*, 2002. 12(4): p. 235-242.
112. Fengel, D. and G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*. 1989: Walter De Gruyter Incorporated.
113. Fischer, M. and K. Aehlig, Emission of VOC from wood and wood products – two case studies, in *COST Action E49 Conference "Measurement and Control of VOC Emissions from Wood-Based Panels"*. 2007: Braunschweig.

114. Steckel, V., W. J., and M. Ohlmeyer, Emissions of volatile organic compounds from convection dried Norway spruce timber, in COST Action E53 Conference “The Future of Quality Control for Wood & Wood Products”. 2010: Edinburgh.
115. Makowski, M. and M. Ohlmeyer, Influences of hot pressing temperature and surface structure on VOC emissions from OSB made of Scots pine. *Holzforschung*, 2006. 60(5): p. 533-538.
116. Makowski, M., M. Ohlmeyer, and D. Meier, Long-term development of VOC emissions from OSB after hot-pressing. *Holzforschung*, 2005. 59(5): p. 519-523.
117. Risholm-Sundman, M., et al., Emissions of acetic acid and other volatile organic compounds from different species of solid wood. *Holz als Roh- und Werkstoff*, 1998. 56(2): p. 125-129.
118. Ohlmeyer, M., et al., Influence of panel thickness on the release of volatile organic compounds from OSB made of *Pinus sylvestris* L. *Forest Products Journal*, 2008. 58(1-2): p. 65-70.



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## ***CHAPTER 2***

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## CHAPTER 2 – RESIN SYNTHESIS

### 2.1. EFFECT OF URONS STRUCTURES OF AMINO ADHESIVES ON WOOD-BASED PANELS PERFORMANCE<sup>1</sup>

#### *Abstract*

Concentration of cyclic polymeric structures (urons) plays an important role on the adhesive properties, such as viscosity and gel time, but also on physico-mechanical properties and formaldehyde content of particleboards. Higher urons concentration presents lower viscosity and reactivity. Particleboards produced with resins with higher uron concentration present lower formaldehyde content, but lower internal bond strength.

The wood-based panels produced fulfil E1 class requirements for formaldehyde emissions, indicating that strongly acid process is an interesting alternative to the conventional alkaline-acid process.

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<sup>1</sup> N. A. Costa, D. Martins, J. Pereira, J. Martins, J. Ferra, P. Cruz, A. Mendes, F. D. Magalhães and L. H. Carvalho, *Journal of Applied Polymer Science*, 2013. 130(6):4500-4507

### 2.1.1. Introduction

The conventional UF resins synthesis procedure, so called alkaline-acid process, consists in two main steps: an alkaline methylation followed by an acid condensation [1]. After these, urea is usually added under alkaline environment, reacting with free formaldehyde and forming new methylolureas. Williams studied the alternative strongly acid process [2, 3], which consists on simultaneous methylation and condensation under highly acidic environment and large excess of formaldehyde, followed by a neutralization and addition of more urea (known as second urea). Then, a second condensation under moderate acidic environment takes place until the desired viscosity is attained. Finally, the resin is neutralized with sodium hydroxide and more urea (known as final urea) is added to attain the desired final F/U molar ratio. According to Williams [2], the strongly acid process entails minimal energy consumption and involves a shorter batch time reaction, when compared with the conventional process. Hatjiissaak and Papadopoulou [4] reported the extremely exothermic reaction of the strongly acid step and the difficulty to transpose this process from the laboratory to the industrial scale. Ferra *et al.* [5] also observed the high exothermicity of the reaction and compared the reactivity of resins obtained by both processes, reporting lower reactivity of resins produced by the strongly acid process when compared with the alkaline-acid procedure.

The complex structure and chemistry of UF resins has been subject of numerous research studies, but their physical, morphological and chemical properties are not yet fully understood. The large variety of structural elements such as methylene bridges, ether bridges, methylol and amide groups or possible cyclic compounds makes their analysis very difficult [6]. In the same way, the effect of changing synthesis parameters (for example, pH, temperature, F/U molar ratios) on the chemical structure of the resin has not been well established.

Among the NMR spectroscopy methods, liquid-state  $^{13}\text{C}$  NMR has provided the most complete information on the chemical structures present in UF resins (that can be dissolved in appropriate solvents) and

the reactions occurring in their formation. In a  $^{13}\text{C}$  NMR experiment, the chemical shift ( $\delta$ ) is a sensitive probe of the chemical structure and the large chemical shift range makes  $^{13}\text{C}$  NMR an attractive technique for the analysis of these resins. In addition, this analytical method allows the identification of several functional groups present in the resins and its quantitative determination [7]. Over the years, many works have been performed by different researchers using  $^{13}\text{C}$  NMR to identify the chemical structure of UF resins synthesized under different pH conditions [6, 8-12]. Some authors have shown that uronic structures are present in the resins when strongly acidic conditions are employed. Gu *et al.* [9] showed that substituted uronic structures are formed only for resins synthesised at pH equal to 1 and a smaller amount of methylol group than the other resins produced at higher pH. Soulard *et al.* [10] determined that the pH ranges that favour formation of urons and its derivatives are above 6 and below 4 and that the reactivity of methylol groups in uronic structures is much lower than for methylol groups on the noncyclic structures of urea. Tohmura *et al.* [11] concluded that resins prepared under strongly acidic conditions have better heat stability than those produced under weakly acidic and alkaline conditions, possibly due to some aromatic character present in the urons formed.

However, the influence on physico-mechanical properties and formaldehyde emission of wood-based panels are not well understood. Hse *et al.* [8] reported that resins produced in strongly acid environment produce boards with lower internal bond strength, lower bending strength and lower formaldehyde emission. Gu *et al.* [9] found that resins produced under strongly acid environment were less reactive and wood-based panels produced with these resins had lower bond strength and lower formaldehyde emission. Park *et al.* [12] also reported the lower viscosity and lower free formaldehyde concentration in UF resins produced at low pH. Obviously, the results of formaldehyde emissions reported by these authors are significantly higher than those nowadays considered as “low”, since the emissions levels on wood-based panels have been continuously reduced along the last decades [13].

This work uses liquid state  $^{13}\text{C}$  NMR to study the chemical structure of liquid UF resins synthesized under different pH and temperature conditions. This information was related to the performance of the resins, in terms of viscosity and reactivity. Particleboards produced with these resins were characterized in terms of physico-mechanical properties and formaldehyde content by perforator method.

### 2.1.2. Material and methods

#### *Materials*

Seven UF resins were provided by EuroResinas S. A. (Sines, Portugal). These were produced by the strongly acid process, according to the procedure described by Ferra *et al.* [5]. These resins were divided in two series. Resins in the first series (resin A, B, C and D) were produced under different pH environments, between 2.0 and 0.5. The resins in the second series (resins E, F and G) were produced under different condensation temperatures, between 80 and 90 °C.

Wood particles, paraffin and ammonium sulphate were supplied by Sonae Indústria PCDM (Oliveira do Hospital – Portugal) for the production of particleboards.

#### *Methods*

##### **Liquid $^{13}\text{C}$ NMR experiments**

The  $^{13}\text{C}$  NMR spectra of the liquid resins were obtained with a Bruker Avance III 400 NMR spectrometer, at a frequency of 100.6 MHz. Chemical shifts ( $\delta$ ) were calculated relative to TSP (3-(trimethylsilyl) propionic acid sodium salt), as the external reference, dissolved in  $\text{D}_2\text{O}$  for NMR control. At about 1 mL of liquid 63% solids resin was added 0.4 mL of deuterium oxide and then the mixture was placed in an NMR tube. The high concentration of the samples allowed very good signal/noise ratios.

### **Resin characterization**

Viscosity was measured with a Brookfield DV-III Ultra viscometer with a 62 spindle at 60 rpm. Samples were previously cooled until 25 °C.

The gel time of the final resins was measured in a laboratory test tube immersed in boiling water, corresponding to the time necessary to attain the onset of gelification. A 20 wt.% ammonium sulphate solution was used as catalyst.

UF resins were analysed by GPC/SEC using a Gilson Differential RI detector and a Rheodyne 7125 injector with a 20 µL. The columns were PSS Protoma 100 and 300 µm placed in an external oven at 60 °C. A flow rate of 1 mL·min<sup>-1</sup> of dimethylformamide (DMF) was used as mobile phase. Samples for analyses were prepared dissolving a small amount of resin in dimethylsulfoxide (DMSO), followed by vigorous stirring. Subsequently, the sample was left to rest and filtered with a 0.45 µm nylon syringe filter, following the protocol described by Ferrá *et al.* [14].

### **Particleboards production and characterization**

Wood particles were blended with resin, catalyst and a hydrophobic agent (paraffin) in a laboratory glue blender. Surface and core layers were blended separately. The amount of solid resin was 7.0, in surface and core layers (based in oven dry wood). The catalyst level in the core layer was 3 wt.% (g dry catalyst per g solid resin).

After blending, a three-layer particleboard mat was hand formed in a deformable aluminium container (220 x 220 x 80 cubic millimetres). Wood amount was determined in order to obtain boards with target densities of 650 kg·m<sup>-3</sup>. Surface and core layer differ in particle size distribution and moisture content. The mass distribution was 20 % for the upper surface layer, 62 % for the core layer and 18 % in the bottom surface layer.

The mats were pressed in a computer-controlled laboratory batch hot-press equipped with a linear variable displacement transducer (LVDT), a pressure transducer and thermocouples. Five boards were produced for each synthesized resin.

After production, boards were hermetically conditioned until performance evaluation. All tests were carried out according to the European Standards for particleboard testing: internal bond (IB) (EN 319), moisture content (MC) (EN322). Formaldehyde content (FC) was evaluated according to EN 120. The values were corrected for 6.5 % of moisture content, according to the EN 312 standard.

### **2.1.3. Results and discussion**

#### ***Liquid $^{13}\text{C}$ NMR interpretation***

The interpretation of the spectra is complex, but can give a good indication on the structure and nature of the linkage groups present in the resins, and can also help in relating the synthesis conditions with the resulting structures. Thus, each signal observed in the spectra of all resins was identified according to chemical shifts reported earlier by other authors [10, 15, 16].

Uronic structures (cyclic compounds of urea and formaldehyde) were also identified in all spectra of resins. These assignments have been also previously reported by many authors [8, 10, 15].

This work allowed studying the effect of reaction pH of the UF resins synthesised by the strongly-acid process on the final resin structure and on the relative amount of produced urons. As shown in Figure 2.1.1, the quantitative amount of uronic structures increases as the acidity conditions increase.

Uronic structures were also identified in all spectra of the UF resins prepared under different reaction temperatures. Figure 2.1.2 shows that



the relative quantity of urons increases with the condensation temperature.

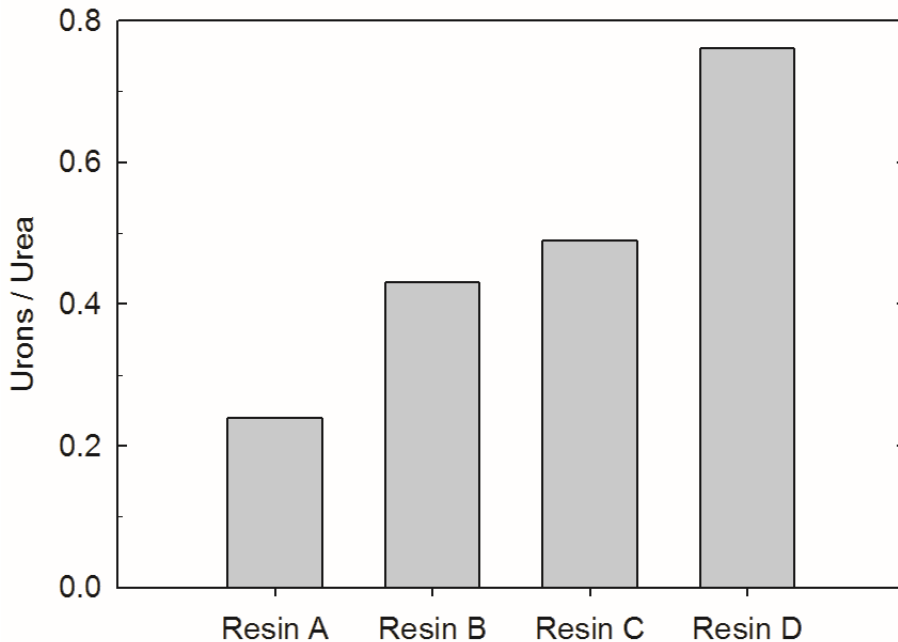


Figure 2.1.1 – Relative proportion between urons and urea for resins produced under different acidic environments

Soulard *et al.* [10] prepared UF resins using a procedure based on the conventional alkaline-acid process, in order to maximise the proportion of urons present at the end of the reaction. During the synthesis the pH was monitored. They found that the maximum quantity of urons at the end of reaction (pH 2.3) approached almost 50% of total urea present (uron + urea). These authors also stated that the uron amounts do not change much during the final neutralization procedure. In our work, and at pH values near 2, we achieved lower concentration values, which could indicate that, depending on reaction conditions, it is possible to decrease the formation of urons, even for the strongly acid process.

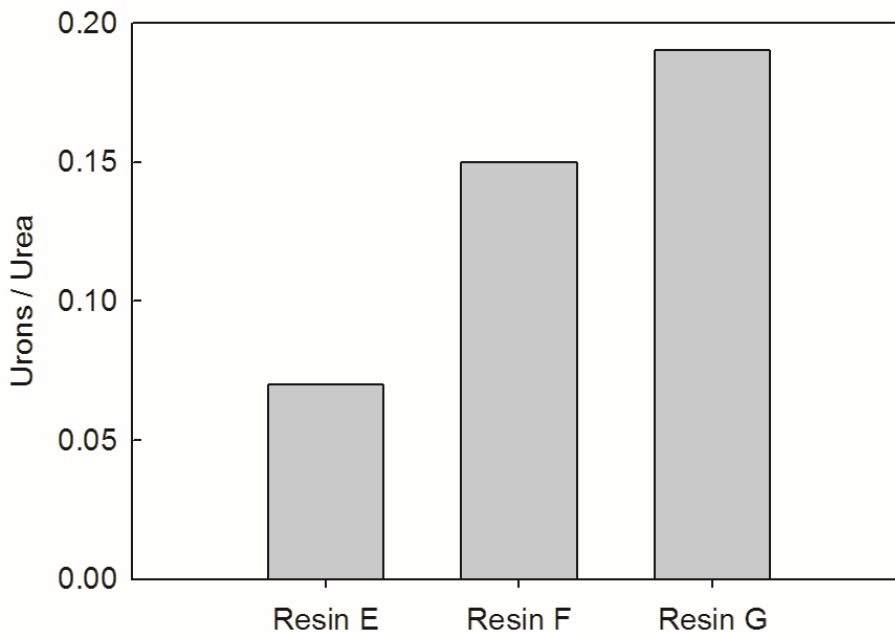


Figure 2.1.2 – Relative proportion between urons and urea for resins produced under different condensations temperatures

### *Resin properties*

Figure 2.1.1 shows that increasing acidic conditions during condensation leads to an increase in urons concentration. The resins with higher urons concentration present lower viscosity and higher gel time, as seen for resins A to D in Table 2.1.1.

Table 2.1.1 – Relative amount of urons, viscosity and gel time of the produced resins and corresponding particleboard properties; a) Particleboards were not produced due to the lower adhesive viscosity that will cause excessive penetration on wood particles

Resin	Resins properties			Particleboards properties	
	Urons/Urea	Viscosity (cP)	Gel time (s)	Internal bond (N·mm <sup>2</sup> )	Formaldehyde content (mg/100g oven dry board)
A	0.24	150	56		
B	0.43	100	66		
C	0.49	80	97	a)	a)
D	0.76	70	104		
E	0.07	170	41	0.47	6.0
F	0.15	190	53	0.39	5.8
G	0.19	230	57	0.39	5.4

An increase in gel time corresponds to a decrease in resin reactivity. Soulard *et al.* [10] and Gu *et al.* [9] have also shown that higher amount of urons implies lower reactivity. Resins A, B, and C presented a final viscosity below the standard requirements for adhesives for particleboards production. Usually, the target viscosity must lie between 150 cP and 500 cP, since lower viscosities cause excessive penetration of adhesive on wood, increasing the consumption of resin, and higher viscosities will bring flow problems in adhesive spray on the industrial plant [17, 18]. On the other hand, lower reactivity will increase pressing time and therefore decrease productivity. As these resins presented reactivity and viscosity values below standard requirements for commercial manufacture, particleboards production was not performed.

Figure 2.1.2 shows the effect of condensation temperature on urons formation during synthesis. Higher temperatures increase urons concentration in the final resin. In this study, a reduction of 10 Celsius degrees has reduced the urons concentration by one third. These resins

were produced at a pH near to the resin A, to obtain a lower concentration of urons and maximize reactivity and viscosity properties. As seen in Figure 2.1.3, a linear relation was found between urons concentration and gel time. The gel time of these resins is below 60 seconds and viscosity above 150 cP.

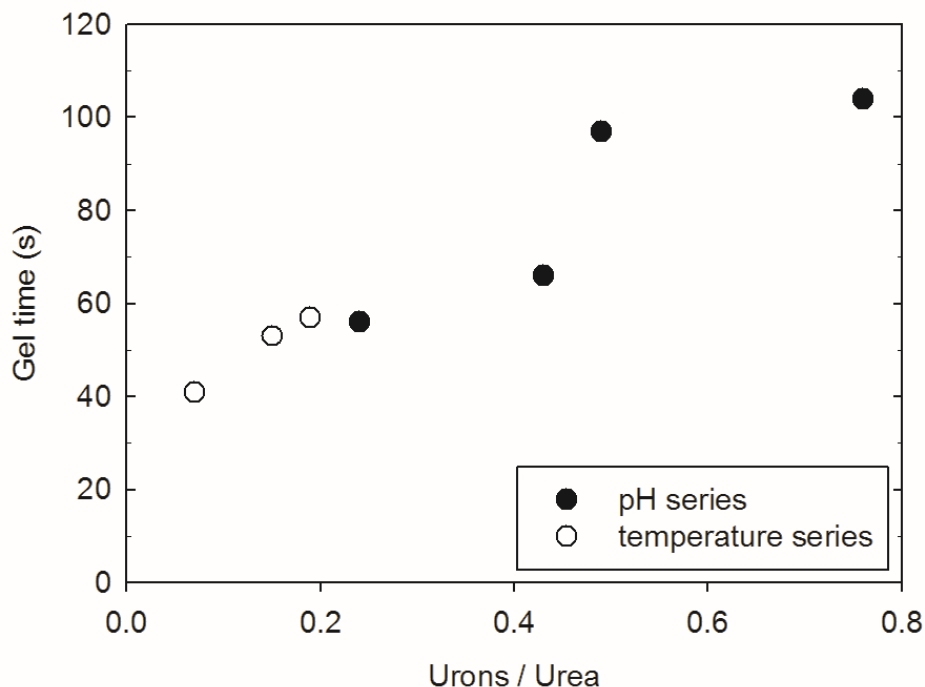


Figure 2.1.3 – Relation between concentration of urons and gel time of resins produced

Gel Permeation Chromatography (GPC) technique has been shown to allow differentiation of formaldehyde-based resin based on polymeric structure [19]. Chromatograms shown in Figure 2.1.4 evidence that the polymeric structure of resins E, F and G is similar, supporting that the main differences are related to small oligomers, namely uron structures, as suggested.

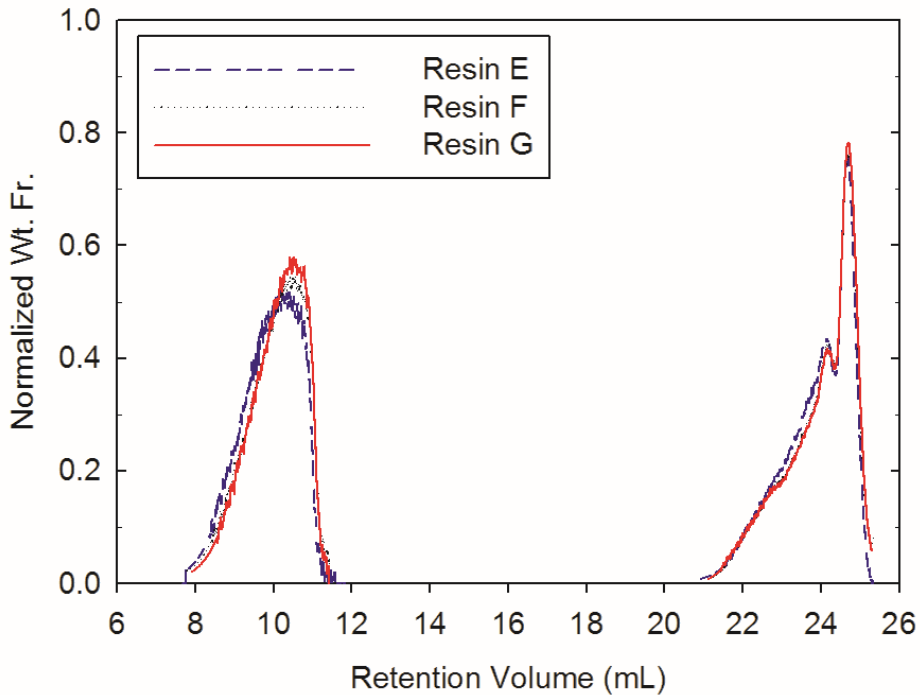


Figure 2.1.4 – GPC/SEC chromatograms of resins E, F and G

The particleboard properties presented in Table 2.1.1, for resins E, F and G, shows that resins with higher urons concentration present lower formaldehyde content, but also lower internal bond strength. Hse *et al.* [8] and Gu *et al.* [9] also obtained lower free formaldehyde on resins with higher amount of cyclic structures. These authors found that resins produced under strongly acid environments exhibited lower reactivity and the boards produced thereof presented lower formaldehyde emissions and internal bond strength. The apparent relation between decreasing formaldehyde content and increasing urons concentration may be due to the higher stability of these species. On the other hand, lower internal bond strength may be related to lower reactivity.

#### 2.1.4. Conclusions

$^{13}\text{C}$  NMR spectroscopy was applied in the analysis of the amino adhesives synthesized by the strongly acid process at different reaction pH and temperature. The formation of cyclic structures (urons) was related to the properties of the adhesives and particleboards.

Lower pH and higher temperatures originate higher concentrations of uronic structures. Resin properties are strongly related to the concentration of uronic structures. Higher concentration of urons leads to a decrease on resin viscosity and reactivity. Higher condensation temperatures also induce the formation of urons. However, these reduce the reactivity of the resins, penalizing the particleboard internal bond strength, despite also reducing formaldehyde content of particleboards.

All boards produced were according to the class E1 requirements, meaning that strongly acid process can be an alternative to the conventional alkaline-acid process and should not be disregarded in future studies.

## 2.2. THE ROLE OF SUCROSE IN AMINO POLYMERS SYNTHETIZED BY THE STRONGLY ACID PROCESS<sup>2</sup>

### ***Abstract***

This article studies the incorporation of sucrose in amino polymers produced by the strongly acid process and its role on the physico-mechanical properties and aldehyde emission of the resulting particleboards. The incorporation of sucrose at different pH environments was studied and differences on molecular weight of resins were analysed by Gel Permeation Chromatography/Size Exclusion Chromatography (GPC/SEC) and characteristic chemical bands by Raman spectroscopy. A reaction mechanism was proposed to explain the observed differences in GPC/SEC chromatograms and supported by Raman spectra. It was observed that small amounts of sucrose incorporated in polymeric matrix are sufficient to improve the physico-mechanical properties of particleboards; the sucrose addition protocol plays a key role of these improvements.

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<sup>2</sup> N. A. Costa, J. Pereira, J. Ferra, P. Cruz, J. A. Moreira, J. Martins, F. D. Magalhães, A. Mendes and L. H. Carvalho, *Journal of Adhesion Science and Technology*, 2012. 27(7):763-774

### 2.2.1. Introduction

Additives in UF products are used since the early decades of last century for improving mechanical properties [20], namely the use of compounds with hydroxyl groups [21-23]. Sucrose was already been reported as a modifying agent for improving adhesive performance [24]. Tondi *et al.* [25] observed an adhesion synergy between sugar and starch in wood adhesion.

There are a wide variety of spectroscopic and chromatographic techniques that can be helpful for the characterization of UF resins, such as  $^{13}\text{C}$  NMR [6, 7, 10, 15], FT-IR [26], FT-NIR [27, 28], Raman [6, 29], MALDI-TOF [30], HPLC [14]. GPC/SEC is a well-known technique [14, 31-33] for the determination of molecular weight distributions (MWD). GPC/SEC is a controlled separation technique in which molecules are separated by their hydrodynamic molecular volume or size [32]. The MWD is relevant to predict the mechanical and bonding properties of the adhesive [1, 34].

Raman spectroscopy has shown good ability for the interpretation of chemical interactions in polymers and identification of functional groups, such as methylene group, ether linkage or identification of chemical bonds, namely single, double or triple carbon links. Hill *et al.* [29] were the first authors to study urea-formaldehyde and phenol-formaldehyde polymers using this technique. Carvalho *et al.* [6] studied the cure of UF polymers by Raman spectroscopy, obtaining kinetic data which permitted to develop an empirical model of reaction cure.

This work studies the effect of sucrose addition during the synthesis of UF resins at different pH environments and their influence on performance of particleboards. GPC/SEC chromatograms were related to particleboard properties and formaldehyde emissions. A mechanism describing reactions between sucrose, formaldehyde and urea is proposed and supported by GPC/SEC chromatography and Raman spectroscopy.



### 2.2.2. Material and methods

#### *Materials*

Formaldehyde (55 wt.% solution), urea (prills) and sucrose for the production of UF resins were provided by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal). Wood particles, paraffin and ammonium sulphate were supplied by Sonae Indústria PCDM (Oliveira do Hospital – Portugal) for the production of particleboards.

#### *Methods*

##### **Resin preparation**

UF resins were produced in a 5 L glass reactor. All resins were produced according to the strongly acid process [2, 3, 5]; the second condensation step of the original procedure was eliminated since it is not relevant for the present study and shorts the synthesis protocol. The reaction consists basically in the following steps:

- i) methylation and condensation in strongly acid environment (below pH 2) at controlled temperature and urea feed rate until a desired F/U molar ratio is reached;
- ii) second methylation step at slightly alkaline environment, with addition of a second urea at controlled feed rate until a desired F/U molar ratio is reached;
- iii) fast cooling and final addition of urea until desired final F/U molar ratio.

Each of the studies reported in the different parts of the section 2.2.3 was performed with a different batch of formaldehyde and wood mixes. In first part resins had a final F/U molar ratio of 1.10 and the particleboards were pressed during 120 s. In the second and third sections F/U molar ratio was 1.00 and the press time was 150 s. For all resins, the catalyst used was ammonium sulphate 30 wt.% solution.

### **GPC/SEC analysis**

UF resins were analysed by GPC/SEC equipped with a Gilson Differential RI detector and a Rheodyne 7125 injector with a 20  $\mu\text{L}$  to determine MWD [14]. The columns were PSS protema 100 and 300  $\mu\text{m}$  placed in an external oven at 60  $^{\circ}\text{C}$ . A flow rate of 1  $\text{mL}\cdot\text{min}^{-1}$  of dimethylformamide (DMF) was used as mobile phase. Samples for analyses were prepared dissolving a small amount of resin in dimethylsulfoxide (DMSO), followed by vigorous stirring. Subsequently, the sample was left to rest and filtered with a 0.45  $\mu\text{m}$  nylon syringe filter.

### **Raman analysis**

The unpolarized Raman spectra of the samples were obtained under ambient conditions using a 514.53 nm line of an Ar + laser, in a right-angle scattering geometry. The solutions were placed inside an optical polished amorphous quartz cell. The spatial resolution is better than 2  $\mu\text{m}$ . The laser power was kept below 15 mW on the sample in order to avoid heating. The scattered radiation was analysed using a Jobin–Yvon T64000 triple spectrometer equipped with a CCD. The spectral resolution is better than 4  $\text{cm}^{-1}$ . Details of the experimental set-up could be found in [35].

The Raman spectra were numerically processed using a user developed Octave script.

### **Particleboards production**

Wood particles were blended with resin, paraffin and catalyst in a laboratory glue blender. Three layers particleboards were hand formed in a square aluminium deformable container with 220 x 220 x 80 cubic millimetre. Wood mass distribution was 20 % in upper face layer, 62 % in the core layer and 18 % in the bottom face layer. The pressing

schedule of an industrial continuous process (16 mm boards) was adapted to a batch cycle in a laboratory scale press with computer controlled equipped with a linear variable displacement transducer (LVDT) and equipped with a pressure transducer and thermocouples. For all series, five boards replicates were prepared.

All boards produced were hermetically conditioned until tested. The boards were tested according to the European standards for density (D) (EN 323), internal bond (IB) (EN 319), moisture content (MC) (EN 322) and thickness swelling (EN 317). For each series, one board was randomly selected for the analysis of formaldehyde content (FC) according to EN 120 (perforator method).

### **2.2.3. Results and discussion**

#### ***Effect of sucrose addition at different pH***

Two different resins were produced according to the strongly acid process [2, 3, 5]. Same amount of sucrose (6.0 wt.%, based on total mass of final product) was added at different stages of synthesis. In resin A, sucrose was added at the beginning of step i), after acidification and before starting urea addition. In resin B, sucrose was added at the beginning of step ii), immediately after neutralization. Samples for GPC/SEC analysis were taken during synthesis: sample 1 at the beginning of step ii); sample 2 at the end of step ii); and sample 3 at the end of production.

Figure 2.2.1 and Figure 2.2.2 shows the GPC/SEC chromatograms collected for the two resins. As reference, aqueous sucrose and urea solutions were previously analysed, showing elution peaks at 24 and 25 mL retention volumes, respectively (not shown here). Resin B shows a peak with retention volume 24 mL, for samples 2 and 3, associated to the presence of sucrose or related substances in the liquid medium. Sample 1 does not show this peak, since sampling was done before sucrose addition. On the other hand, in resin A that peak is not so evident,

indicating that sucrose reacts with formaldehyde or urea (or both) and is incorporated in the polymeric matrix. In this resin, sucrose, a disaccharide, was added at strongly acidic pH, undergoing inversion into monosaccharides fructose and glucose [36] (Figure 2.2.3). These products exist as an equilibrium between the corresponding cyclic and open structures (Figure 2.2.4). The open structures of fructose and glucose react with formaldehyde forming acetals (Figure 2.2.5), which are unstable at strongly acid environment [37]. Added urea will react with formaldehyde and with carbonyl groups of glucose and with ketone groups of fructose (open structures) by nucleophilic addition. These reactions will displace the cyclic/open structure equilibrium in order to form more open structures, extending the reaction with urea (Figure 2.2.6). The species formed in these reactions have an amine group that is reactive towards formaldehyde and will therefore be incorporated in the UF polymer structure. The attached hydroxyl groups will be available for interaction with wood surface (hydrogen bonding) [34, 38]. After the addition of the second urea (step ii), low molecular weight polymer and oligomers remain reactive, increasing the amount of moderate molecular weight (retention volume between 19 and 23 mL) and high molecular weight polymer is still forming (samples 2 and 3 in Figure 2.2.1 and Figure 2.2.2).

This sucrose consumption mechanism does not occur in resin B, where sucrose is added in step ii). Sucrose dissociation into monosaccharides is not promoted at slightly at alkaline pH. Hydroxyl groups of sucrose can react with free formaldehyde, forming chemically stable cyclic hemiacetals [37] (Figure 2.2.7), during the second methylation at high temperature.

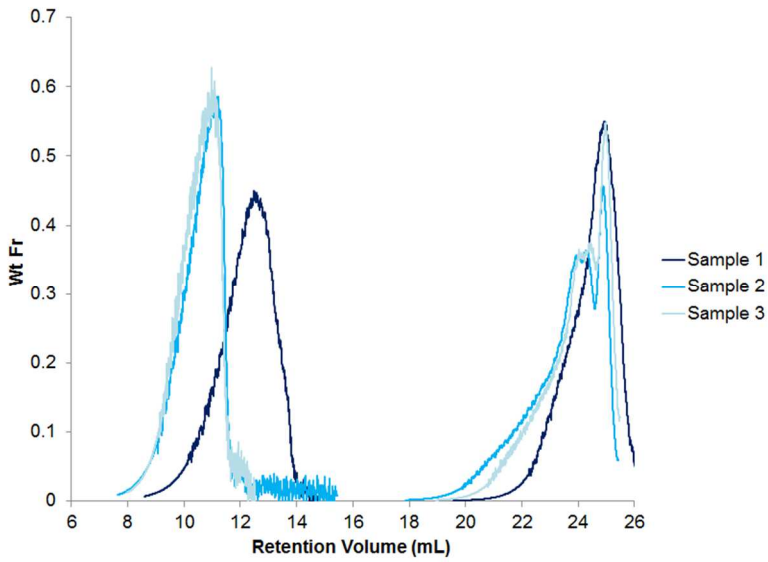


Figure 2.2.1 – GPC/SEC chromatograms of the samples taken of resin A

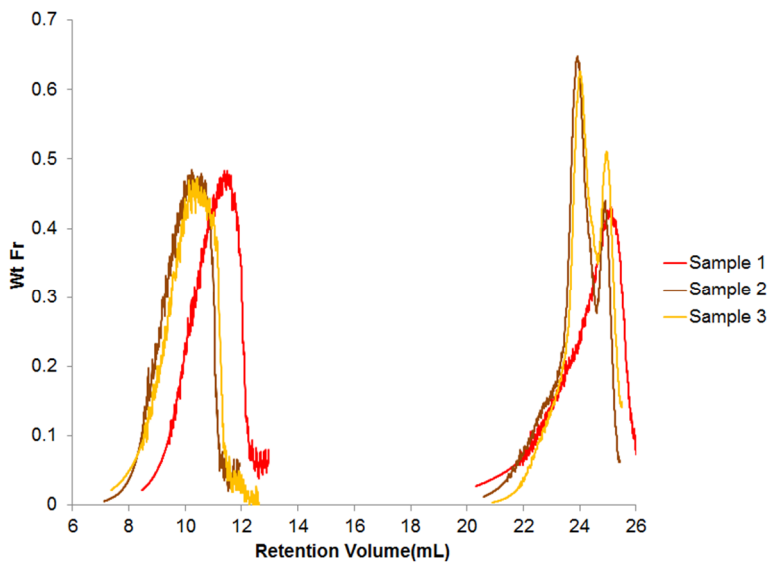


Figure 2.2.2 - GPC/SEC chromatograms of the samples taken of resin B



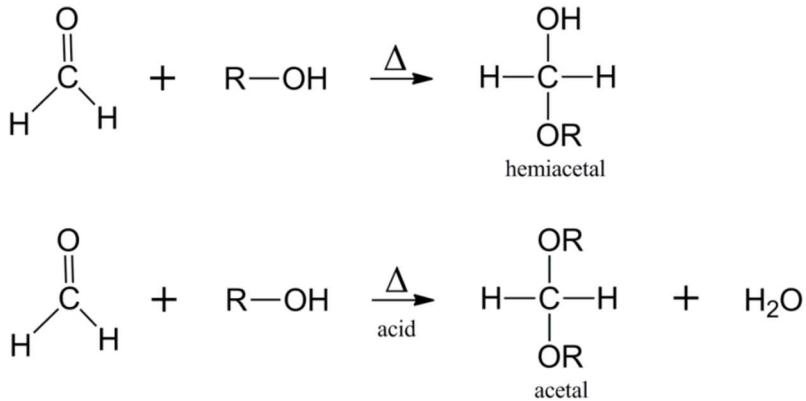


Figure 2.2.5 – Scheme of reactions between formaldehyde and hydroxyl groups

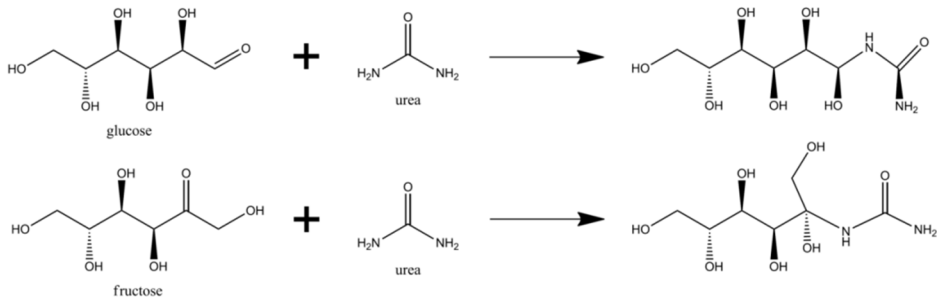


Figure 2.2.6 – Reactions of glucose and fructose with urea

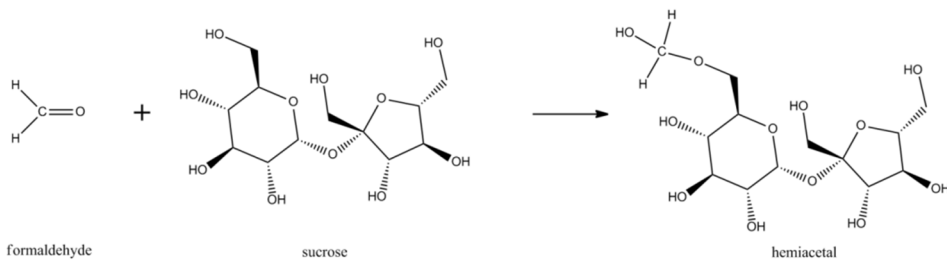


Figure 2.2.7 – Example of a cyclic hemiacetal formed by reaction of hydroxyl group of sucrose and formaldehyde

To support our assumptions, UF resins were analysed by Raman spectroscopy. New UF resins, with same F/U molar ratio, were produced: resins A2 (sucrose added in beginning of first step, under strongly acidic conditions), C2 (no sucrose added) and F2 (sucrose added at the end synthesis). The amount of sucrose in these resins (when added) was 3 wt.%. Based on studies by Carvalho *et al.* [6], we focused our analysis in the 900-1000  $\text{cm}^{-1}$  and 1300-1400  $\text{cm}^{-1}$  spectral ranges, where the urea-formaldehyde linkage vibration is expected. According to the reported data, the Raman bands assigned to vibrations of the group  $-\text{NCH}_2\text{N}-$  appear at 920-955  $\text{cm}^{-1}$  and at 1320-1330  $\text{cm}^{-1}$ , while for the bending vibration of the  $\text{CH}_2$  in the  $-\text{NCH}_2\text{N}-$  group, appears at 1430-1436  $\text{cm}^{-1}$ . The spectroscopic data in the 2800-3600  $\text{cm}^{-1}$  were not considered in this work, as the strong Raman bands arising from the stretching vibration of the water molecule overlap with the ones assigned to the C-H and N-H stretching vibrations, hindering a reliable quantitative analysis of these bands.

Figure 2.2.8a shows the Raman spectrum of resins A2, C2, and F2. The average Raman spectrum of resin C2 will be taken as standard. Numerical processing was applied in the following order: a) correction of discretization errors; b) baseline correction; c) normalization by total spectral area. Figure 2.2.8b presents the derivative of the Raman spectra shown in Figure 2.2.8a. We can see clear difference between the derivatives in the 850-1150  $\text{cm}^{-1}$  range. Even though Carvalho *et al.* [6] refer that the range 1300-1440  $\text{cm}^{-1}$  contains some bands assigned to urea-formaldehyde linkages, our derivatives do not show remarkable differences, due to the strong band overlapping. Moreover, the 850-1150  $\text{cm}^{-1}$  spectral range exhibits well resolved Raman bands, enabling at performing accurate analysis.



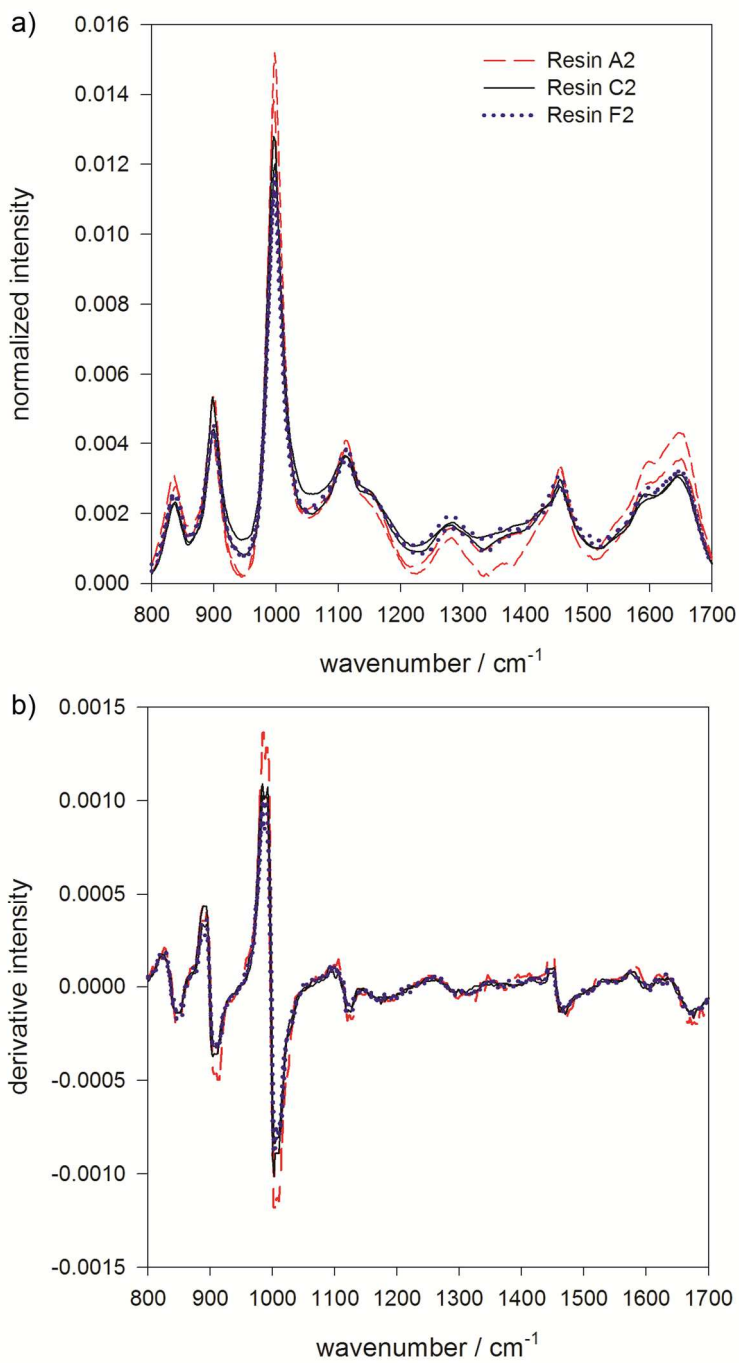


Figure 2.2.8 – a) Spectra of resins A2, C2 and F2; b) corresponding derivative spectra

Each measured spectrum for resins A2, C2 and F2, in the 850-1150  $\text{cm}^{-1}$  spectral range, was divided by the average spectrum of resin C2. The results are shown in Figure 2.2.9. Resin A2 shows a noticeable depression at about 950  $\text{cm}^{-1}$ . As referred to above, the band at 958  $\text{cm}^{-1}$  is assigned to urea-formaldehyde linkage (-NCH<sub>2</sub>N-) [6]. The reduction of intensity of this band for resin A2, relatively to the standard spectrum, evidences for the competitive reaction of sucrose with urea, incorporating the saccharides in the polymeric matrix. The results concerning resins F2 and C2 do not show significant differences, pointing out for the reaction of sucrose with urea under alkaline conditions does not take place to significant extent, as previously discussed.

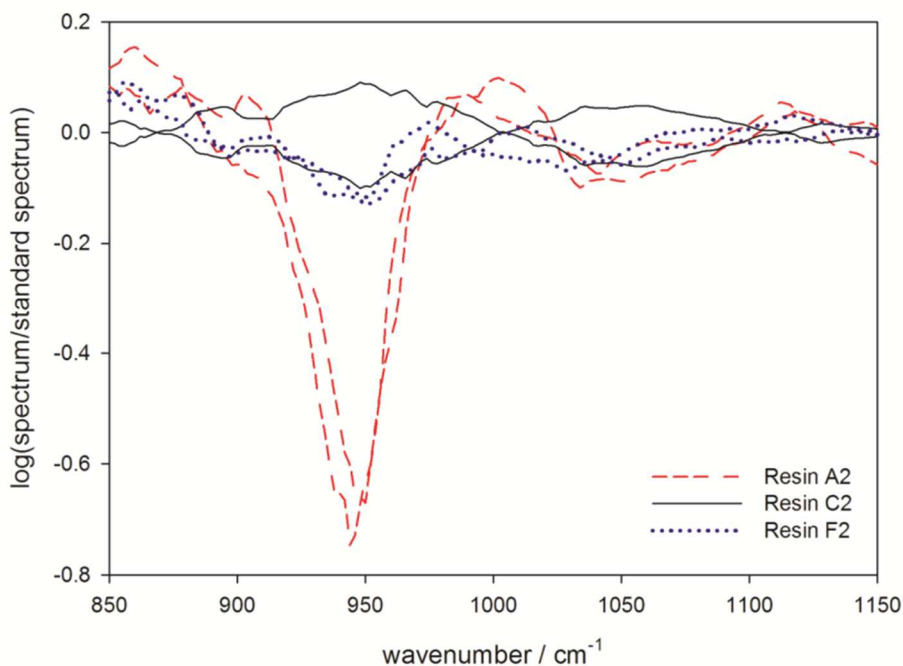


Figure 2.2.9 – Logarithm of the quotient between resin spectra and standard spectrum

The Raman analysis, along with the GPC/SEC results, supports the reaction mechanism presented above for the synthesis of the UF resins reinforced with sucrose, under strongly acid conditions.

Therefore, Raman analysis supports the reaction mechanism presented above for the synthesis of the UF resins reinforced with sucrose, under strongly acid conditions.

Table 2.2.1 shows the properties of particleboards produced with resins A and B. Resin A presents higher internal bond and lower thickness swelling, although higher formaldehyde emission. Higher internal bond may be associated with higher amount of polymer with high molecular weight, but may also be related to the contribution of hydroxyl groups to internal cohesion of board. This effect was already reported by other authors that used bio-based formaldehyde scavengers with hydroxyl groups [21, 22]. In resin B, the formation of hemiacetals consumes formaldehyde needed for cross-linking. This originates low formaldehyde emission of particleboards, but also causes lower internal bond.

Table 2.2.1 – Particleboards properties of resins A and B

	<b>Resin A</b>	<b>Resin B</b>
Internal Bond (N·mm <sup>-2</sup> )	0.34	0.16
Thickness Swelling (%)	34.5	46.6
Formaldehyde content (mg/100 g oven dry board)	5.9	2.9

### *Effect of amount of sucrose*

The previous results show that the addition of sucrose under acidic conditions, before the condensation step, produces boards with better performance. Four new resins were then produced in the same conditions as resin A. In resin C, no sucrose was added during synthesis. In resins D and E, 0.3 and 3.0 wt.% sucrose was added, respectively. Resin F is the

same as resin D, with 2.7 wt.% sucrose added at room temperature to the final product.

The GPC/SEC chromatograms (Figure 2.2.10) are similar for all resins in the low retention volume region. However, some differences are noticeable for the high retention volume range (low molecular weight fraction). Addition of sucrose (resins D and E) increases the amount of polymer with moderate molecular weight (retention volume between 20 and 23 mL) in relation to resin C (no sucrose added). When sucrose is added to the final product (resin F), an increase of oligomers with retention volume of about 24 mL is observed (Figure 2.2.11). This result is similar to the one obtained previously with resin B, where sucrose was added at the beginning of step ii). This is an indication that in both cases sucrose is not being incorporated in the UF polymer, therefore not contributing towards mechanical resistance.

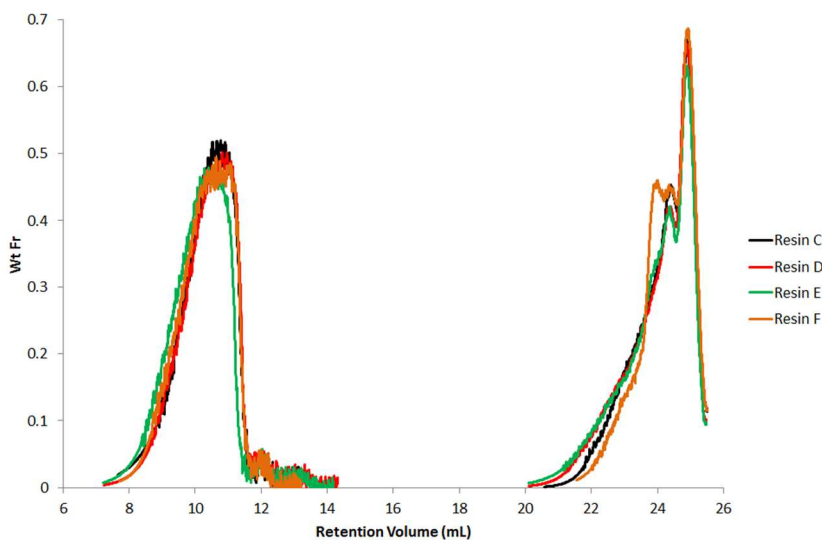


Figure 2.2.10 – GPC/SEC chromatograms of resins C, D, E and F

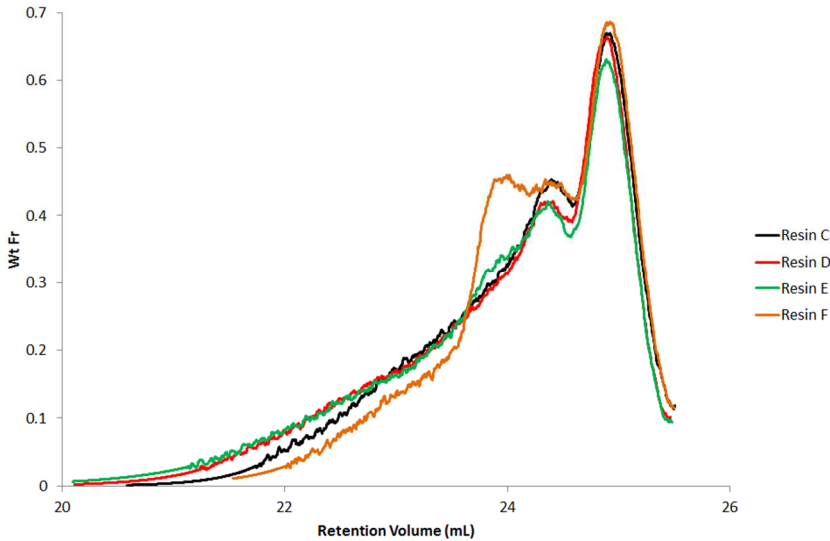


Figure 2.2.11 – High retention volume fraction of Figure 2.2.10

Table 2.2.2 shows that panels produced with resins D and E have better performance in terms of internal bond strength and formaldehyde emission, confirming the previous observations. Resin D, with less added sucrose, seems to have the best overall performance. This indicates that small sucrose additions are sufficient to obtain relevant improvements.

Table 2.2.2 – Particleboards properties of resins with different amount of sucrose

	<b>Resin C</b>	<b>Resin D</b>	<b>Resin E</b>
Sucrose (wt.%)	0.0	0.3	3.0
Internal Bond ( $\text{N}\cdot\text{mm}^{-2}$ )	0.25	0.40	0.36
Thickness Swelling (%)	40.4	30.7	32.1
Formaldehyde Content (mg/100 g oven dry board)	4.6	3.3	3.5

### *Reaction of sucrose with formaldehyde*

Resin G was prepared with 0.3 wt.% of sucrose added after acidification, at pH below 2.0, being equivalent to resin D above. Resin H was prepared adding 0.3 wt.% of sucrose to the formaldehyde solution (pH  $\approx$  3.0-4.0) before acidification, to avoid Cannizzaro reaction [37]. In this case, reaction with sucrose was allowed to run for 20 min, after which the pH was decreased to below 2.0 and urea addition was started. The remaining production protocol was equal for both resins.

Table 2.2.3 shows the particleboards properties prepared with resins G and H. The addition of small amounts of sucrose to an acid environment with a large excess of formaldehyde produces acetals that, despite being unstable could prevent the reaction between the monosaccharides with urea. However, from Table 2.2.3 it can be seen that both resins show quite similar properties. The GPC/SEC chromatograms are also similar (not shown here). This means that the possible formation of acetals between formaldehyde and monosaccharides does not compete with the reaction between monosaccharides and urea in acid environment.

Table 2.2.3 – Resin and particleboards properties of resins G and H

	<b>Resin G</b>	<b>Resin H</b>
Sucrose (wt.%)	0.3	0.3
pH of addition of sucrose	< 2.0	$\approx$ 3.5
Reaction time (min)	0	20
Internal Bond (N $\cdot$ mm <sup>-2</sup> )	0.38	0.36
Thickness Swelling (%)	34.4	32.6
Formaldehyde content (mg/100 g oven dry board)	4.1	4.2

#### **2.2.4. Conclusions**

This work assesses the performance of sucrose as an additive for the synthesis amino polymers by the strongly acid process. It was concluded

that sucrose affects positively the properties of the particleboards if added at strongly acid environment, even at low sucrose concentrations (0.3 wt.%). In these conditions, monosaccharides obtained from sucrose inversion react with urea becoming incorporated in the polymer structure, as supported by GPC/SEC chromatography and Raman spectroscopy. On the other hand, when sucrose is added under alkaline conditions, it reacts with aldehydes, forming hemiacetals, and is not incorporated in the polymer. The aldehyde consumption penalizes physico-mechanical properties of the particleboards.

It was also concluded that at low pH the reaction between monosaccharides and aldehyde do not compete with reaction between monosaccharides and urea.

### 2.3. REFERENCES

1. Dunky, M., Urea-formaldehyde (UF) adhesive resins for wood. *International Journal of Adhesion and Adhesives*, 1998. 18(2): p. 95-107.
2. Williams, J.H. and K. Louisville, Hydrolytically stable urea-formaldehyde resins and process for manufacturing them. 1983, United States Patent 4410685.
3. Williams, J.H. and K. Louisville, Low emitting aqueous formulations of aminoplast resins and processes for manufacturing them. 1984, United States Patent US 4482699 A.
4. Hatjiissaak, A. and E. Papadopoulou, Aminoplast Resin of High Performance for Lignocellulosic Materials. 2007, Patent WO/2007/138364.
5. Ferra, J.M.M., et al., Comparison of UF synthesis by alkaline-acid and strongly acid processes. *Journal of Applied Polymer Science*, 2012. 123(3): p. 1764-1772.
6. Carvalho, L.M.H., M.R.P.F.N. Costa, and C.A.V. Costa, A very simple empirical kinetic model of the acid-catalyzed cure of urea-formaldehyde resins. *Journal of Applied Polymer Science*, 2006. 102(6): p. 5977-5987.
7. Rammon, R.M., et al., The Chemical Structure of UF Resins. *The Journal of Adhesion*, 1986. 19(2): p. 115-135.

8. Hse, C.Y., Z.H. Xia, and B. Tomita, Effects of Reaction Ph on Properties and Performance of Urea-Formaldehyde Resins. *Holzforschung*, 1994. 48(6): p. 527-532.
9. Gu, J.-y., et al., Synthetic Conditions and Chemical Structures of Urea-Formaldehyde Resins I. Properties of the resins synthesized by three different procedures. *Japan Wood Research Society*, 1995. 41(12): p. 1115-1121.
10. Soulard, C., C. Kamoun, and A. Pizzi, Uron and uron-urea-formaldehyde resins. *Journal of Applied Polymer Science*, 1999. 72(2): p. 277-289.
11. Tohmura, S., C.Y. Hse, and M. Higuchi, Formaldehyde emission and high-temperature stability of cured urea-formaldehyde resins. *Journal of Wood Science*, 2000. 46(4): p. 303-309.
12. Park, B.-D., et al., Reactivity, chemical structure, and molecular mobility of urea-formaldehyde adhesives synthesized under different conditions using FTIR and solid-state <sup>13</sup>C CP/MAS NMR spectroscopy. *Journal of Applied Polymer Science*, 2003. 88(11): p. 2677-2687.
13. Carvalho, L., F. Magalhães, and J. Ferra, Formaldehyde Emissions from Wood-Based Panels -Testing Methods and Industrial Perspectives, in *Chemistry, Applications and Role in Polymerization*, C.B. Cheng and F.H. Ln, Editors. 2012, Nova Science Publishers, Inc.: Hauppauge, NY
14. Ferra, J.M., et al., Characterization of Urea-Formaldehyde Resins by GPC/SEC and HPLC Techniques: Effect of Ageing. *Journal of Adhesion Science and Technology*, 2010. 24(8-10): p. 1535-1551.
15. Tomita, B. and S. Hatono, Urea-formaldehyde resins. Constitutional characterization by <sup>13</sup>C Fourier Transform NMR spectroscopy. *Journal of Polymer Science: Polymer Chemistry Edition*, 1978. 16(10): p. 2509-2525.
16. Angelatos, A.S., et al., NMR structural elucidation of amino resins. *Journal of Applied Polymer Science*, 2004. 91(6): p. 3504-3512.
17. Christjanson, P., et al., Structural changes in urea-formaldehyde resins during storage. *Holz als Roh - und Werkstoff*, 2002. 60(6): p. 379-384.
18. Kumar, R.N., et al., Studies in the process optimization and characterization of low formaldehyde emission urea-formaldehyde resin by response surface methodology. *Journal of Applied Polymer Science*, 2007. 103(4): p. 2709-2719.
19. Paiva, N.T., et al., Production of melamine fortified urea-formaldehyde resins with low formaldehyde emission. *Journal of Applied Polymer Science*, 2012. 124(3): p. 2311-2317.
20. Smidth, L., Method of Plasticizing Urea-Formaldehyde Condensation Products. United States Patent 1886600.



21. Eom, Y.-G., et al., Reduction of Formaldehyde Emission from Particleboards by Bio-Scavengers. *Mokchae Konghak*, 2006. 34: p. 29-41.
22. Kim, S., et al., Effect of bio-scavengers on the curing behavior and bonding properties of melamine-formaldehyde resins. *Macromolecular Materials and Engineering*, 2006. 291(9): p. 1027-1034.
23. Alexander, J.R., D. Burton, and F. Hausmann, Plasticized Urea-Formaldehyde Resins. 1948, United States Patent 2443368.
24. Ghanbarzadeh, B., et al., Effect of plasticizing sugars on rheological and thermal properties of zein resins and mechanical properties of zein films. *Food Research International*, 2006. 39(8): p. 882-890.
25. Tondi, G., et al., Starch-sugar synergy in wood adhesion science: basic studies and particleboard production. *European Journal of Wood and Wood Products*, 2012. 70(1): p. 271-278.
26. Zorba, T., et al., Urea-formaldehyde resins characterized by thermal analysis and FTIR method. *Journal of Thermal Analysis and Calorimetry*, 2008. 92(1): p. 29-33.
27. Minopoulou, E., et al., Use of NIR for structural characterization of urea-formaldehyde resins. *International Journal of Adhesion and Adhesives*, 2003. 23(6): p. 473-484.
28. Henriques, A., et al., Determination of formaldehyde/urea molar ratio in amino resins by near-infrared spectroscopy. *Journal of Applied Polymer Science*, 2012. 124(3): p. 2441-2448.
29. Hill, C.G., et al., Raman-Spectroscopy of Urea-Formaldehyde Resins and Model Compounds. *Journal of Applied Polymer Science*, 1984. 29(9): p. 2749-2762.
30. Gavrilovic-Grmusa, I., et al., Molar-mass distribution of urea-formaldehyde resins of different degrees of polymerisation by MALDI-TOF mass spectrometry. *Journal of the Serbian Chemical Society*, 2010. 75(5): p. 689-699.
31. Ludlam, P.R. and J.G. King, Size exclusion chromatography of urea formaldehyde resins in dimethylformamide containing lithium chloride. *Journal of Applied Polymer Science*, 1984. 29(12): p. 3863-3872.
32. Barth, H.G., B.E. Boyes, and C. Jackson, Size Exclusion Chromatography and Related Separation Techniques. *Analytical Chemistry*, 1998. 70(12): p. 251-278.
33. Billiani, J., K. Lederer, and M. Dunky, Investigation of the Molar Mass-Distribution of Urea-Formaldehyde Resins Via Gpc Coupled with Light-Scattering Measurements. *Angewandte Makromolekulare Chemie*, 1990. 180: p. 199-208.
34. Pizzi, A. and K.L. Mittal, *Handbook of adhesive technology*. 1994: Marcel Dekker Inc.

35. Moreira, J.A., et al., Coupling between phonons and magnetic excitations in orthorhombic  $\text{Eu}_{1-x}\text{Y}_x\text{MnO}_3$ . *Physical Review B*, 2010. 81(5): p. 054447.
36. Chen, J.C.P. and C.C. Chou, *Cane Sugar Handbook: a manual for cane sugar manufacturers and their chemists*. 1993: John Wiley & Sons, Inc.
37. Clayden, J., et al., *Organic chemistry*. 2001: OUP.
38. Anonymous, *Wood handbook: Wood as an engineering material*. General Technical Report FPL-GTR-190. General Technical Report FPL-GTR-190. 2010, Madison, WI: U.S.: Forest Products Laboratory. Department of Agriculture, Forest Service, Forest Products Laboratory.

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## ***CHAPTER 3***

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## CHAPTER 3 – RESIN CURE

### 3.1. ALTERNATIVE TO LATENT CATALYSTS FOR CURING UF RESINS FOR THE PRODUCTION OF LOW FORMALDEHYDE EMISSION WOOD-BASED PANELS<sup>3</sup>

#### *Abstract*

This paper studies alternative catalysts to ammonium sulphate for curing urea-formaldehyde (UF) resins. When using a latent catalyst like ammonium sulphate, ammonium nitrate or ammonium chloride, hexamine is formed as a by-product of curing reaction. It is believed that hexamine hydrolysis may contribute to formaldehyde release during the life-time of wood-based panels produced with UF resins. Orthophosphoric acid, on the other hand, catalyses resin cure without by-product formation and was compared to ammonium sulphate. The pot-life of adhesive with both catalysts was evaluated at 40 °C with a Brookfield rheometer. Mechanical resistance tests with ABES (Automated Bonding Evaluation System) showed that orthophosphoric acid effectively catalyses UF resins cure. Particleboards were produced using both catalysts and the most important properties evaluated, according to European Standards: formaldehyde content, internal bond, moisture content, thickness swelling and density. Particleboards cured with orthophosphoric acid and stored under forceful conditions of humidity and temperature presented similar internal bond and lower formaldehyde content than those produced with ammonium sulphate.

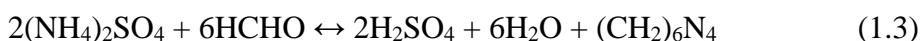
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<sup>3</sup> N. A. Costa, J. Pereira, J. Martins, J. Ferra, P. Cruz, F. D. Magalhães, A. Mendes and L. H. Carvalho, *International Journal of Adhesion and Adhesives*, 2012. 33:56-60

### 3.1.1. Introduction

Different strategies for producing low formaldehyde emission boards have been attempted, such as reducing formaldehyde to urea (or amine groups,  $(\text{NH}_2)_2$ ) ratios [1] and addition of formaldehyde scavengers to the resin or glue system [2]. These, however, impair physico-mechanical properties. New processes for resin synthesis have been exhaustively studied in order to understand the major factors that affect the formaldehyde emission [3]. Relevant factors for panel manufacture were also studied, like nature of wood mixes, resin content, platen temperature and pressing programs [4]. Alternative gluing systems with formaldehyde substitutes (e.g. dimethoxyethanal) are expensive and present weaker properties than formaldehyde based resins [5].

Reducing the formaldehyde/urea (F/U) molar ratio is an alternative for decreasing formaldehyde emissions from panels, but the minimum limit has already been attained, since further lowering the molar ratio impairs resin cure due to the excessively low free formaldehyde content [6, 7]. The conventional catalysts (also called latent catalysts) consume formaldehyde to create an acid environment, essential for the cure reaction [8]. Latent catalysts like ammonium sulphate react with formaldehyde, forming sulphuric acid, water and hexamine [9] (equation 1.3).



An excess of latent catalyst can act also as formaldehyde scavenger, because it may consume unreacted formaldehyde after the cure. However, under acidic conditions and heat, hexamine formed may decompose releasing formaldehyde [10]. Hexamine may also react slowly with water, forming ammonia and formaldehyde [11, 12]. Both mechanisms may lead to formaldehyde emission during the lifetime of the panel.

Resins with low F/U molar ratio have a low free formaldehyde content, which may impair the action of a conventional latent catalyst and not

allow the generation of a sufficiently acid environment for resin cure. Decreasing pH prior to application is not a solution since the resin would start reacting in the time span between blending with the wood particles and the start of the hot press cycle. The pressure applied would destroy the early-formed cross-linked structures.

Scarce information can be found in literature about alternative catalysts for UF resins. The use of buffer solutions was tried in the past [13], but the results obtained did not convince the industrial producers due to the low reactivity of the glue mix compared to conventional catalysts.

Orthophosphoric acid is a non-toxic inorganic triprotic acid. Increasing temperature accelerates the hydrolysis reactions considerably, decreasing pH. With pKa's of 2.12, 7.21 and 12.68 [14], orthophosphoric acid can provide a sufficiently acidic environment to induce cure of UF resins. Some studies made on the use of orthophosphoric acid as fire retardant additive revealed a decrease in physical properties of wood and plywood [15, 16]. At high temperatures, the high content of phosphoric acid caused significant acid hydrolysis on wood, therefore damaging performance [17]. More recently, studies with lower fire-retardant contents of orthophosphoric acid in MDF panels (about 2 and 6 % based on oven dry fibre weight) exhibited more satisfactory results, showing that for contents above 2 % the panels with orthophosphoric acid still present the quality parameters of internal bond [18].

In this paper, the performance of orthophosphoric acid as an urea-formaldehyde resin catalyst is compared to a latent catalyst (ammonium sulphate). ABES tests were made and particleboard panels were produced with both catalysts and their properties evaluated.

### **3.1.2. Material and methods**

#### ***Materials***

Standard UF resins for production of E1 boards were supplied by Euroresinas – Indústrias Químicas, SA (Sines - Portugal). Wood

particles, paraffin and ammonium sulphate were supplied by Sonae Indústria PCDM, SA (Oliveira do Hospital – Portugal). Analytical grade orthophosphoric acid 85 wt.% solution was purchased from Panreac.

Beech veneer strips for ABES tests were supplied by Sonae Indústria, PCDM S.A. (Mangualde – Portugal).

### *Methods*

The press program was optimized for adhesives with reactivity (gel time) of about 60 s. To determine the amount of orthophosphoric acid needed, 200 g of a standard UF resin with 63 % solid content was titrated with orthophosphoric acid (85 % w/w), recording the pH value for each addition. Samples with 250  $\mu$ L were removed and the reactivity of the sample was measured in a laboratory test tube immersed in boiling water. A stirring rod was used to detect the onset of gelification. The reactivity corresponds to the time necessary for attaining this state.

The amount of orthophosphoric acid used in all subsequent tests corresponded to quantity needed to promote resin gelification in 60 s.

To evaluate pot-life, the resin catalysed with orthophosphoric acid or ammonium sulphate was kept at controlled temperature (40 °C) and the viscosity was measured with a Brookfield DV-III Ultra viscometer, with a 62 spindle at 60 rpm until 500 cP, and at 30 rpm until 1000 cP.

Tests with the ABES apparatus were made for both catalyst systems. 15  $\mu$ L of adhesive were spread on beech veneer strips with 0.5 mm thickness, 20 mm wide and 117 mm in length, stored at 20 °C and 65 % RH. Adherent pairs were mounted in the ABES machine with an overlapping area of 60 mm<sup>2</sup>. The veneers were prepared using a pneumatically driven precision sample-cutting device supplied by Adhesive Evaluation Systems Inc (Corvallis, Oregon). Four different temperatures (85, 95, 105 and 115 °C) were considered with press times between 50 and 600 s.



Wood particles were blended with resin, paraffin and catalyst in a laboratory glue blender. Face and core layers of wood particles were blended separately. The amount of ammonium sulphate was 1 % (based in solid resin) in face layer and 3 % (based in solid resin) in core layer. The amount of paraffin was 2 % (based in solid resin) in face and core layer.

Three layer particleboards were hand formed in a square section aluminium mould (220 x 220 x 80 mm<sup>3</sup>). The wood mass distribution was as follows: 20 % for the upper face layer, 62 % for the core layer and 18 % in the bottom face layer. The pressing cycle conditions (stage duration, press closing time and platen temperature) were set in accordance to typical industrial practices. The press schedule of an industrial continuous process (for 16 mm boards) was transposed to a batch cycle. The mats were then pressed in a laboratory scale, computer controlled, batch hot-press, equipped with a LVDT sensor (linear variable displacement transducer), pressure transducer and thermocouples.

The boards were hermetically conditioned until being tested. The evaluated physico-mechanical properties, and the corresponding standard measurement methods, were: density (D) (EN 323), internal bond (IB) (EN 319), moisture content (MC) (EN 322) and thickness swelling (TS) (EN 317). For each experiment, four board samples were produced. For formaldehyde content (FC) analysis, according to EN 120, one of the four panels of each series was selected randomly. One of the panels of each series was stored at lab conditions during 120 days. Then, part of the panel was cut to evaluate the internal bond. The other part was stored at controlled temperature (54 °C) and relative humidity (75 %) during 90 days. Internal bond and formaldehyde content were evaluated after this storage period.

### 3.1.3. Results and discussion

#### *Reactivity of the adhesive*

Figure 3.1.1 presents the pH and reactivity values of the UF resin for different amounts of orthophosphoric acid. The target was to obtain a reactivity of about 60 s. This reactivity was obtained for about 5.2 g of solid acid per kg of solid resin, corresponding to a pH  $\approx$  5.

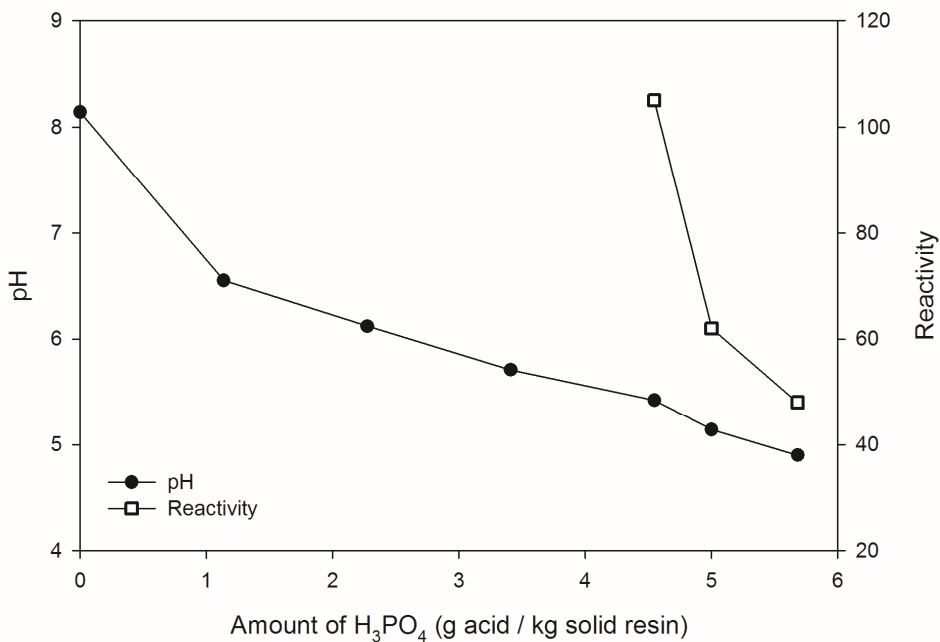


Figure 3.1.1 – pH and reactivity of UF resin titrated with orthophosphoric acid

#### *Evaluation of pot-life*

The pot-life of the resin/catalyst mixture has a special interest in industrial applications. The blending of adhesive with wood particles occurs often at temperatures around 40 °C (exit temperature of the wood particle dryer). When operational problems occur, a delay of more than

30 min can occur until panel pressing. It is therefore desirable that the pot-life of the adhesive be longer than one hour. Figure 3.1.2 shows the evolution of the resin viscosity already containing catalyst at 40 °C. When orthophosphoric acid is used, the pot-life is around 40 min, while ammonium sulphate leads to a value of 120 min. This difference in pot-life was expected. Orthophosphoric acid immediately acidifies the liquid medium inducing the cure. On the other hand, ammonium sulphate is a latent catalyst and its reaction with formaldehyde to produce sulphuric acid (equation 1.3) is slow at 40 °C. The fact that ammonium sulphate only induces rapid curing under hot-pressing conditions is a major advantage in industrial operation, since it avoids resin pre-cure problems. The short pot-life of orthophosphoric acid is a limitation common to all acid catalysts, but could be, in principle, overcome by resorting to encapsulation.

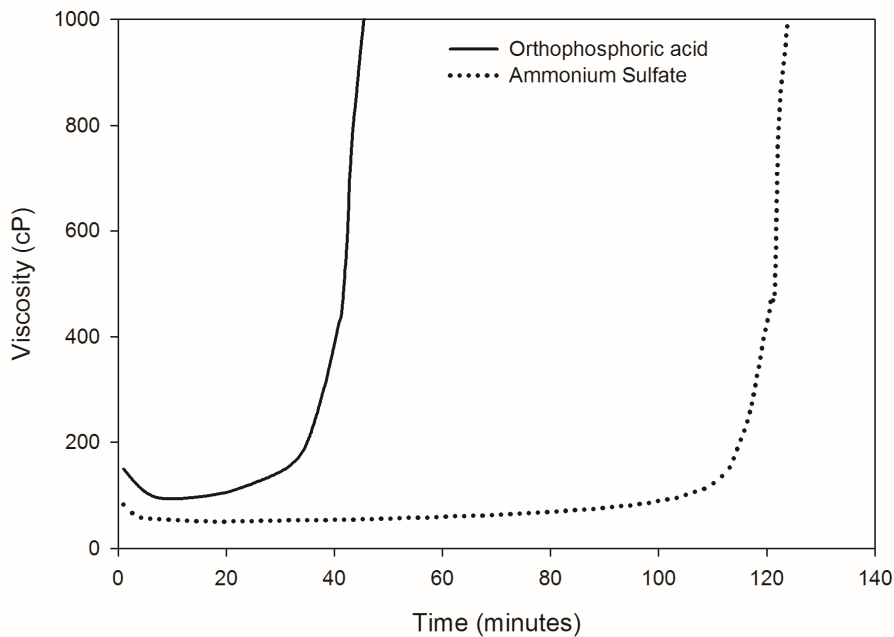


Figure 3.1.2 – Pot-life of UF resin with catalysts ammonium sulphate and orthophosphoric acid

The effect of pressing time and temperature was assessed for both catalysts with the ABES apparatus. The shear strength results for ammonium sulphate are shown in Figure 3.1.3 and for orthophosphoric acid in Figure 3.1.4.

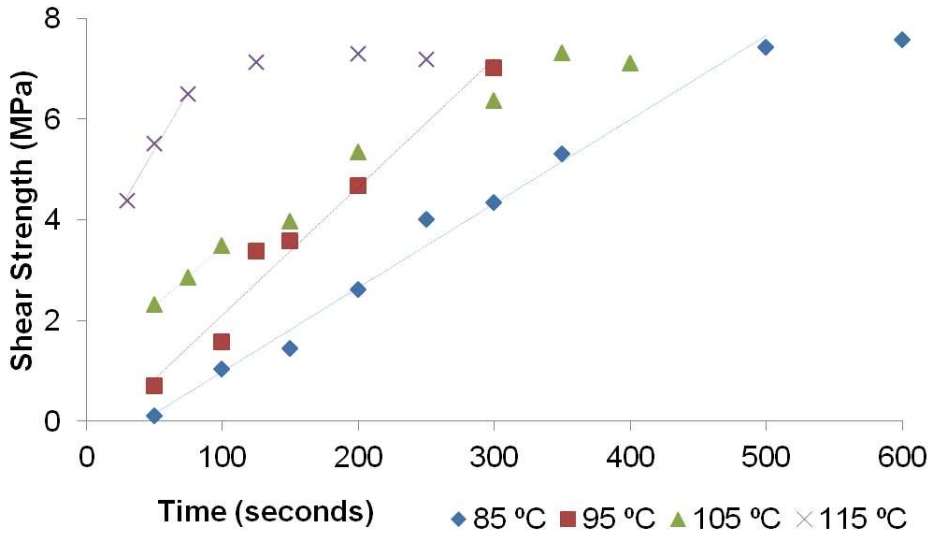


Figure 3.1.3 – Shear strength history for resin containing catalyst ammonium sulphate for curing temperatures between 85 and 115 °C (indicated in the legend)

For all temperatures, UF resin presents a faster cure when using ammonium sulphate. This denotes that ammonium sulphate provides better conditions for curing, as it promotes a lower pH than orthophosphoric acid. At 105 °C, the data for ammonium sulphate presents an irregular behaviour, which may be caused by water vaporization interfering with resin cure. This may be the cause of the inconsistent slope for ammonium sulphate at 105 °C. The maximum shear strength value is the same for both catalysts and all temperatures, corresponding to the limiting strength of the 0.5 mm beech strips.

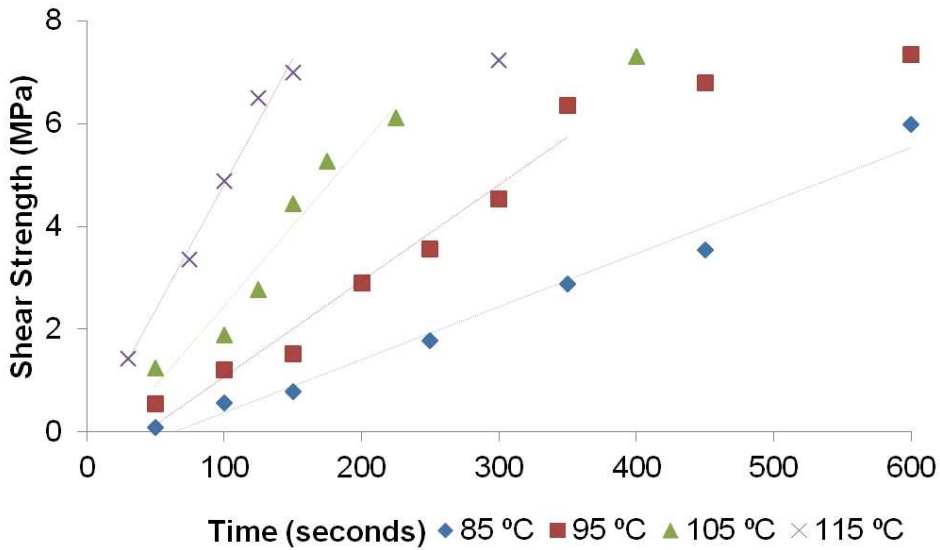


Figure 3.1.4 – Shear strength history for resin containing catalyst orthophosphoric acid for curing temperatures between 85 and 115 °C (indicated in the legend)

The slope of the regression lines in Figure 3.1.3 and Figure 3.1.4 reflects the reactivity of the adhesive. The reactivity index ( $R_i$ ) describes the bonding kinetics of the adhesive system [19, 20] and is given by equation 3.1:

$$R_i = -T \times \ln(k) \quad (3.1)$$

where  $T$  is the absolute Temperature (K) and  $k$  is the rate of the bond strength development ( $\text{kPa}\cdot\text{s}^{-1}$ ). As shown by Heinemann [19], the linearity of the data (Figure 3.1.5) suggests that bond strength development rate can be described by a first order chemical reaction. To obtain the activation energy values, the reactivity index was multiplied by the universal gas constant ( $R$ ). The reactivity index and activation energy values obtained with ammonium sulphate were 4.73 and 39.28  $\text{kJ}\cdot\text{mol}^{-1}$ , and with orthophosphoric acid were 7.22 and 60.04  $\text{kJ}\cdot\text{mol}^{-1}$ . The higher

values of activation energy for orthophosphoric acid indicate that with this catalyst resin cure is more sensitive to temperature.

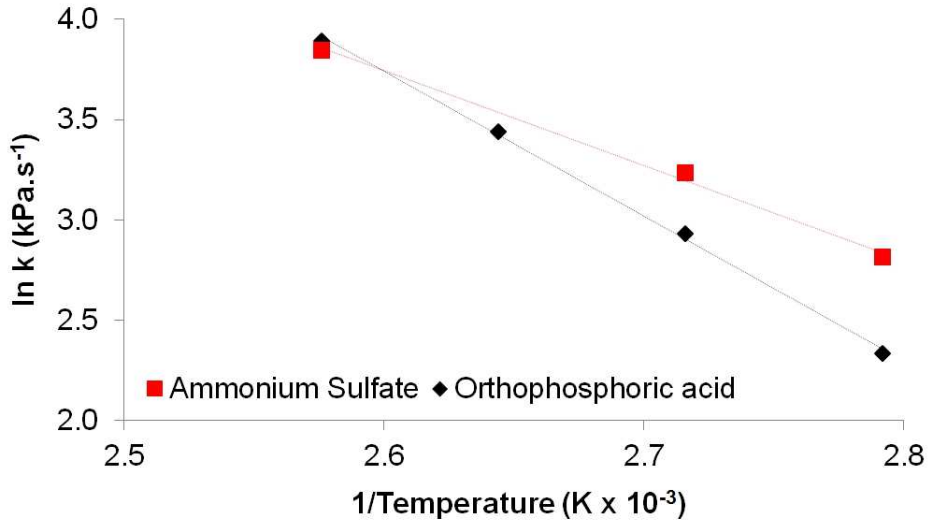


Figure 3.1.5 – ABES-derived Arrhenius plot for both catalysts

### *Production of particleboards*

To further evaluate the performance of orthophosphoric acid in relation to ammonium sulphate, a series of particleboards with the same catalyst amount as before was prepared and tested. The amount of resin used was 6.9 g of solid resin per 100 g of dry wood in core layer and 6.3 in face layer was applied in both cases. For each series, 5 boards were made. One of the boards, randomly selected, was used for measuring formaldehyde content, 3 were used for evaluating density, thickness swelling, moisture content and internal bond and one board was stored at room temperature for 120 days. After storage, the board was cut, and part was used for evaluating internal bond and the other part was stored at controlled temperature (54 °C) and relative humidity (75 %) during more 90 days. Then internal bond and formaldehyde content were measured.

The results of physic-mechanical properties are presented in Table 3.1.1 and Table 3.1.2 and formaldehyde content and moisture content of corresponding boards are presented in Table 3.1.3.

Table 3.1.1 – Results of physical and mechanical tests for boards produced with both catalysts

Catalyst	Density ( $\text{kg}\cdot\text{m}^{-3}$ )	Thickness swelling (%)	Moisture content (%)
Ammonium sulphate	633	27.5	6.6
Orthophosphoric acid	634	25.3	6.5

Table 3.1.2 – Internal bond and standard deviation of boards produced with both catalysts (results are expressed in  $\text{N}\cdot\text{mm}^{-2}$ )

Catalyst	Internal bond after production	Internal bond after conditioning – 120 days	Internal bond after forceful conditions – 210 days
Ammonium sulphate	$0.35 \pm 0.02$	$0.39 \pm 0.05$	$0.19 \pm 0.02$
Orthophosphoric acid	$0.29 \pm 0.01$	$0.30 \pm 0.02$	$0.19 \pm 0.04$

Table 3.1.3 – Results of moisture (MC) and formaldehyde content (FC) for boards produced with both catalysts (formaldehyde content is expressed in  $\text{mg}/100$  g of oven dry board)

Catalyst	Moisture content (%)	Formaldehyde content	Moisture content (210 days) (%)	Formaldehyde content (210 days)
Ammonium sulphate	6.6	5.8	13.1	6.6
Orthophosphoric acid	6.5	10.9	13.1	5.6

As seen in Table 3.1.1 and Table 3.1.2, thickness swelling is similar for both catalysts, but internal bond is higher for ammonium sulphate. This could be associated to pH during cure being lower with ammonium sulphate, as previously discussed. The internal bond of boards stored during 120 days increased for panels cured with ammonium sulphate and stayed constant for orthophosphoric acid. The stability of the internal bond during storage at room conditions shows that the amount of acid used is not sufficient to cause wood deterioration and reduction of internal cohesion. When stored for more 90 days under forceful conditions, internal bond decreased substantially in both cases, but more so for ammonium sulphate catalysed panels (about 50 %).

Table 3.1.3 presents the results for moisture and formaldehyde content. According to Pizzi [9], the measured formaldehyde content comes from different sources: unreacted formaldehyde, hydrolysis of methylene-ether bridges and hydrolysis of hexamine. The formaldehyde content evaluated after board production is lower for the resin catalysed by ammonium sulphate, due to the capability of ammonia to react with free formaldehyde, therefore acting also as a scavenger. Free formaldehyde is released during the days subsequent to production of boards.

Formaldehyde content after storage at forceful conditions is higher for ammonium sulphate catalysed boards. This may be related to formaldehyde released from hydrolysis of methylene-ether bridges or decomposition of hexamine formed during cure [11] (equation 1.3 and equation 1.4).

The lower values of formaldehyde content for boards with acid-catalysed resin encourage the study of catalysts that do not produce hexamine as by-product. The presence of hexamine as formaldehyde release agent could be a problem for production of boards with low formaldehyde emission, close to natural wood values. The limitation of the reduced pot-life might be overcome by encapsulating the active agent with a material that melts or bursts during board pressing.



### 3.1.4. Conclusions

Experiments with ABES proved that orthophosphoric acid is able to effectively catalyse the cure of UF resins, although ammonium sulphate presents faster bond development. In addition, resin combined with orthophosphoric acid presents a shorter pot-life than ammonium sulphate.

Particleboards with both catalysts present reasonable internal bond values, which increase slightly after 120 days of storage. Under forceful conditions (high temperature and relative humidity), both present a decrease in internal bond. When orthophosphoric acid is used, formaldehyde content after panel production is significantly higher when compared with ammonium sulphate. However, after free formaldehyde was released during storage, the board cured with orthophosphoric acid presented the lowest formaldehyde content. This may indicate that hexamine produced during cure with ammonium sulphate is a potential formaldehyde release agent in wood based panels.

### 3.2. EMISSION IN WOOD-BASED PANELS: EFFECT OF CURING REACTIONS<sup>4</sup>

#### *Abstract*

The influence of hexamine formed as by-product during the UF cure was ignored in the past. However, with the increasing interest on low formaldehyde emission boards, this issue became pertinent. Formaldehyde release from hexamine degradation is extensive and could limit the success of the development of low formaldehyde emission adhesives if the conventional latent catalysts continue in use.

In this study, formaldehyde released from recycled wood, hexamine and cured UF resin was assessed. Citric and oxalic acid, in solid form, were used as catalysts for UF resin in production of particleboard. Mat with solid acids are less susceptible to resin pre-cure than with latent catalyst.

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<sup>4</sup> On-going, to be submitted

### 3.2.1. Introduction

UF resins are acid catalysed, meaning that needs an acidic environment to cure. Usually, it used ammonium sulphate as a latent catalyst (sometimes called hardener to avoid misunderstood). Despite not being an acid, ammonium sulphate, under heat reacts with formaldehyde forming sulphuric acid, water and hexamine as by-product. However, under acidic conditions and heat, hexamine formed may decompose releasing formaldehyde [10]. Hexamine may also react slowly with water, forming ammonia and formaldehyde. Both mechanisms may lead to formaldehyde emission during the lifetime of the panel.

Costa *et al.* [21] showed that using phosphoric acid as catalyst, besides good performance of internal bond, when particleboards were stored under forceful conditions of moisture and temperature formaldehyde content in panels with phosphoric acid was lower 1 mg per 100 g oven dry board than boards with ammonium sulphate. After 7 month of storage, formaldehyde content of boards with UF resin catalysed by acid decreased around 50 % while formaldehyde content of boards with ammonium sulphate increased around 15 %. Higher formaldehyde content with phosphoric acid, after pressing, can be related with unreacted cure of resin and inability of phosphoric acid to consume formaldehyde while the higher formaldehyde content of boards with ammonium sulphate can be related with the decomposition of hexamine formed during the cure reaction, supporting that hexamine act also as a formaldehyde release agent during the lifetime of boards. However, when mixed with resin, phosphoric acid reduces the pot-life of adhesive, even at moderated temperatures (40 °C), which is a usual temperature of wood during blending operation.

In this work it was measured the formaldehyde content of recycled wood collected in a Portuguese particleboard plant and was also assessed the contribution from hexamine and cure UF resin to formaldehyde content using the perforator method (EN 120). Particleboards were produced using oxalic and citric acid as catalysts and their performance compared

with ammonium sulphate. Different concentrations of acid were tested as well as the influence of mat pot life was also assessed.

### **3.2.2. Material and methods**

#### ***Materials***

Recycled wood was supplied by Sonae Indústria PCDM (Oliveira do Hospital – Portugal). UF resins, urea, hexamine and ammonium sulphate were provided by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal). Analytical grade oxalic and citric acid were purchased from VWR Portugal.

#### ***Methods***

Wood particles were blended with resin, paraffin, and catalyst in a laboratory glue blender. Acids in solid state were hand distributed after adhesive (mixture of resin, paraffin and water to adjust moisture content) blending. Resin load in all trial was 7 wt.% (solid based per oven dry wood). Three-layers particleboards were hand formed in a square aluminium deformable container with 220 x 220 x 80 mm<sup>3</sup>. Wood mass distribution was 20 % in the upper face layer, 62 % in the core layer, and 18 % in the bottom face layer with a density target of 650 kg·m<sup>-3</sup>. The pressing schedule of an industrial continuous process (16 mm boards) was adapted to a batch cycle in a laboratory scale press with computer controlled equipped with a linear variable displacement transducer (LVDT) and equipped with a pressure transducer and thermocouples.

The boards were tested according to the European standards for internal bond (IB) (EN 319). Despite not showed, density (D) (EN 323), moisture content (MC) (EN 322) and thickness swelling (EN 317) were also evaluated to assure quality control. For each series, one board was randomly selected for the analysis of formaldehyde content (FC) according to EN120 (perforator method).

### 3.2.3. Results and discussion

#### *Hexamine as formaldehyde release agent*

Formaldehyde content of the potential release agents present in particleboards were assessed by perforator method (based on EN120 standard procedure). Hexamine powder evaluation was performed placing it in testing flask with recycled wood from same lot (1.0 wt.% hexamine). Standard UF resin (E1) was cured at 60 °C during 24 hours in an oven and then placed in a testing flask. Table 3.2.1 shows formaldehyde content obtained in the tests.

Table 3.2.1 – Formaldehyde content of recycled wood, hexamine and cured UF resin by perforator method

	<b>Formaldehyde content (mg/100 g)</b>
Recycled wood	2.9
Recycled wood + 1% hexamine	13.3
Long-time cured UF resin	0.7

As expected, formaldehyde content of recycled wood is considerably high. These results are according to those obtained by Martins *et al.* [22]. It is important to note that formaldehyde content from recycled wood is closely dependent on the type of wood used.

Standard particleboards are produced with 7 wt.% of UF resin (solid based) and ammonium sulphate is used as catalyst (3 wt.% solid content based on solid resin). 100 g of oven dry board contains 7 g of UF resin and 0.21 g (1.6 mmol) of ammonium sulphate. According to equation 1.3 and considering total consumption of catalyst, 111 mg (0.8 mmol) of hexamine will be formed. Data from Table 3.2.1 shows that 1 g of hexamine releases 10.4 mg of formaldehyde in perforator method, which corresponds to 1.2 mg of formaldehyde released from the hexamine formed during cure. A long-time cured UF resin, which can be considered as completely reacted, presents 0.7 mg of formaldehyde per

100 g of resin. Resin load in particleboard production is around 7 %, which means less than 0.05 mg per 100 g of oven dry board. Therefore, in particleboards produced with this recycled wood and this resin, the minimum formaldehyde content that would be possible to attain is 4.1 mg per 100 g of oven dry board (adding the contributions from recycled wood, hexamine and fully cured resin). However, boards are nowadays produced with emission values well below 4.0 mg per 100 g of oven dry board, despite using recycled wood with high formaldehyde content. As discussed in previous works, UF resins actually may act as formaldehyde scavengers due to the presence of excess unreacted urea [23]. However, this is not an efficient approach, because the amount of urea needed to reduce formaldehyde content reduces drastically resin reactivity, and thickness swelling is considerably increased [24].

### *Solid acids as catalyst for UF resins*

#### **Standard E1 UF resin**

The performance of acids in solid form (oxalic and citric acid) as catalysts was evaluated and the results compared with a latent catalyst (ammonium sulphate). Pot life of mat was also evaluated.

Five series of particleboards were produced using different catalysts and concentrations. Oxalic acid (OA) and citric acid (CA) were added in solid state after resin blending in concentrations of 0.6 and 1.0 wt.% (acid based in oven dry wood). Ammonium sulphate (AS) was used as reference at 3.0 wt.% (based in solid resin). After blending, the mat was formed and each series was distributed for three different storing conditions: “standard” (mats were pressed immediately after forming), “4 h” (mats were stored at room temperature during 4 hours before pressing) and “4 h 40 °C” (mats were conditioned in an oven during 4 hours at 40 °C before pressing). Figure 3.2.1 shows the results of internal bond for the panels produced.

Boards produced with ammonium sulphate present higher internal bond when pressed under standard conditions. When acids are used as catalyst, in the same conditions, oxalic acid presents better internal bond than citric acid, this being more evident when a lower concentration is used. However, oxalic acid performance is lower than ammonium sulphate. This better performance of the latent catalyst is due to being directly added to the liquid resin, improving homogeneity of distribution on wood particle surfaces and increasing accessibility for reacting with formaldehyde and starting the cure reaction. When solid acids are used, direct addition to resin is not possible, since this would originate resin pre-cure. These catalysts must therefore be mixed with wood particles in the powder form, leading to a less homogeneous distribution. Direct addition of acid catalysts to the resin could be achieved by encapsulation.

Storage at room temperature does not present significant variations in internal bond in boards produced with ammonium sulphate. When acids in solid form are used, a slight reduction in internal bond is observed, mainly when higher concentrations are used. However, the internal bond obtained is still above  $0.35 \text{ N}\cdot\text{mm}^{-2}$ , which is the minimal requirement for standard particleboards (type P2 according to EN 312).

Storage at  $40 \text{ }^\circ\text{C}$  shows the opposite effect: internal bond of boards with ammonium sulphate decreases substantially, while boards with acids maintain the same internal bond. This reduction is caused by resin pre-cure during mat storage. These early formed bonds are destroyed during the pressing stage. Note that a standard E1 UF resin with 3 wt.% of ammonium sulphate has a pot life of 2 hours [21]. When solid acids were used, on the other hand, resin pre-cure does not occur, since the catalyst remains in solid powder form in the mat, therefore not contacting the resin. During the pressing stage, water vapour formed dissolves the solid acid, promoting acidification of the medium and resin cure.

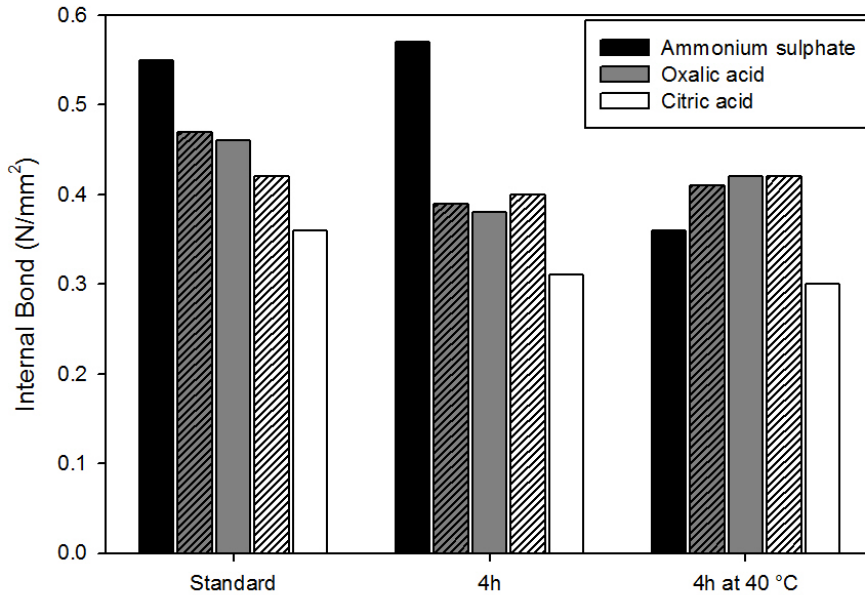


Figure 3.2.1 – Internal bond of boards produced with a standard E1 UF resin catalysed by different hardeners (pattern bars correspond to an amount of acid of 1.0 wt.% and unpattern bars to 0.6 wt.%)

Table 3.2.2 shows the formaldehyde content of particleboards produced under standard conditions. As expected, ammonium sulphate presents lower formaldehyde content due to its scavenging ability. Formaldehyde content in boards produced with solid acids is similar, Boards with higher amount of acid added present slightly higher formaldehyde content, possibly due to some wood degradation caused by the excess of acid. However, in service, boards produced with resins catalysed by acids will present lower formaldehyde content, during their life time, due to the absence of hexamine [21]. Formaldehyde content values of boards produced with latent and acid catalysts are according to previously published results.



Table 3.2.2 – Formaldehyde content of boards produced with a standard E1 UF resin catalysed by different hardeners

<b>Catalyst</b>	<b>AS</b>	<b>OA (0.6 %)</b>	<b>OA (1.0 %)</b>	<b>CA (0.6 %)</b>	<b>CA (1.0 %)</b>
Formaldehyde content (mg/100 g oven dry board)	5.2	8.2	8.4	8.1	8.5

### 3.2.4. Conclusions

This work has shown that hexamine is a formaldehyde release agent in wood-based panels. Formaldehyde content in recycled wood is significantly higher than in a completely cured UF resin.

Acids in solid form can catalyse UF resins during pressing stage, and the internal bond of produced boards is still above minimal standard requirements. Moreover, when solid acids are used, the mat is less susceptible to pre-cure than when using a latent catalyst, when stored during 4 hours at 40 °C. Using a standard UF resin, the formaldehyde content in the produced boards reach the upper limit of E1 emission class.

These results reinforces the importance of new catalytic systems for UF resins without formation of hexamine as by-product and supports that the use of acids should not be discarded as an effective alternative

### 3.3. REFERENCES

1. Dongbin, F., L. Jianzhang, and M. An, Curing Characteristics of Low Molar Ratio Urea-Formaldehyde Resin. *Journal of Adhesion and Interface*, 2006. 7(4): p. 45-52.
2. Eom, Y.-G., et al., Reduction of Formaldehyde Emission from Particleboards by Bio-Scavengers. *Mokchae Konghak*, 2006. 34: p. 29-41.

3. Ferra, J.M., et al., Optimization of the Synthesis of Urea-Formaldehyde Resins using Response Surface Methodology. *Journal of Adhesion Science and Technology*, 2010. 24(8-10): p. 1455-1472.
4. Pereira, J., et al., Production of Environmentally Compatible Particleboard With a High Recycled Content, in *Ecwood*. 2008. p. 97-104.
5. Despres, A., et al., Formaldehyde-free aminoresin wood adhesives based on dimethoxyethanal. *Journal of Applied Polymer Science*, 2008. 110(6): p. 3908-3916.
6. Myers, G.E., How Mole Ratio of Uf Resin Affects Formaldehyde Emission and Other Properties - a Literature Critique. *Forest Products Journal*, 1984. 34(5): p. 35-41.
7. Lehmann, W.F., Method and Composition for Reduction of Formaldehyde Emission in Wood Composite Panels. 1983, United States Patent 4397756.
8. Dunky, M., The Chemistry of Adhesives, in *COST Action E13: Wood Adhesion and Glued Products, State of the art Report*, M.E. Dunky, Editor. 2001.
9. Pizzi, A. and K.L. Mittal, *Handbook of adhesive technology*. 1994: Marcel Dekker Inc.
10. Walker, J.F., *Formaldehyde*. American Chemical Society Monograph Series. 1944, New York: Waverly Press, Inc.
11. Dreyfors, J.M., S.B. Jones, and Y. Sayed, Hexamethylenetetramine - a Review. *American Industrial Hygiene Association Journal*, 1989. 50(11): p. 579-585.
12. Pizzi, A., *Wood adhesives: chemistry and technology*. Vol. 2. 1989: Marcel Dekker Inc. New York
13. Gunnells, D. and K. Griffin. *Catalyst Systems*. in *Resin & Blending Seminar Proceedings*. 1998. Portland, Oregon and Charlotte, North Carolina: Forest Products Society.
14. Atkins, P. and L. Jones, *Chemical principles: the quest for insight*. Third Edition ed. 2005, New York: W. H. Freeman and Company.
15. Lebow, P.K. and J.E. Winandy, Verification of a kinetics-based model for long-term effects of fire retardants on bending strength at elevated temperatures. *Wood and Fiber Science*, 1999. 31(1): p. 49-61.
16. LeVan, S.L., R.J. Ross, and J.E. Winandy, Effect of Fire Retardant Chemicals on the bending Properties of Wood at Elevated Temperatures, in *Forest Product Laboratory*. 1990.
17. Levan, S.L. and J.E. Winandy, Effects of Fire Retardant Treatments on Wood Strength - a Review. *Wood and Fiber Science*, 1990. 22(1): p. 113-131.
18. Ayrlimis, N., Effect of fire retardants on internal bond strength and bond durability of structural fiberboard. *Building and Environment*, 2007. 42(3): p. 1200-1206.

19. Heinemann, C., R. Lehnert, and P.E. Humphrey. Kinetic response of thermosetting adhesive systems to heat: Physico-chemical versus mechanical responses. in Sixth Pacific Rim Bio-Based Composites Symposium. 2002. Oregon State University, Corvallis.
20. Humphrey, P. and S. Ren, Bonding kinetics of thermosetting adhesive systems used in wood-based composites: the combined effect of temperature and moisture content. *Journal of Adhesion Science and Technology*, 1989. 3(1): p. 397-413.
21. Costa, N., et al., Alternative to latent catalysts for curing UF resins used in the production of low formaldehyde emission wood-based panels. *International Journal of Adhesion and Adhesives*, 2012. 33: p. 56-60.
22. Martins, J., et al. Effect of recycled wood on formaldehyde release of particleboard. in COST Action E49 Conference "Measurement and Control of VOC Emission from Wood-Based Panels. 2007. Braunschweig, Germany.
23. Paiva, N.T., et al., Production of melamine fortified urea-formaldehyde resins with low formaldehyde emission. *Journal of Applied Polymer Science*, 2012. 124(3): p. 2311-2317.
24. Costa, N., et al., Innovative Catalysts for Urea-formaldehyde Resins, in *Minimizing the Environmental Impact of the Forest Products Industries*, F. Caldeira, Editor. 2011, University Fernando Pessoa: Porto.



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## ***CHAPTER 4***

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## CHAPTER 4 – FORMALDEHYDE ISSUES

### 4.1. SODIUM METABISULPHITE AS A SCAVENGER OF AIR POLLUTANTS FOR WOOD-BASED BUILDING MATERIALS<sup>5</sup>

#### *Abstract*

This paper reports on different applications of sodium metabisulphite as a formaldehyde scavenger. The reduction of formaldehyde emission and the effect on physico-mechanical properties of particleboards was studied. The scavenger was mixed with urea-formaldehyde (UF) resins with different formaldehyde to urea (F/U) molar ratios and added separately in the production of particleboards. Several differences between the formaldehyde content and physico-mechanical properties of boards were found. When applied to melamine-formaldehyde (MF) resins the changes in formaldehyde emission were less significant, probably due to the incorporation of sodium bisulphite in polymeric matrix. The type of formaldehyde based resin and the form of scavenger addition are the majors factors affecting formaldehyde scavenging efficiency.

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<sup>5</sup> N. A. Costa, J. Pereira, J. Ferra, P. Cruz, J. Martins, F.D. Magalhães, A. Mendes and L. H. Carvalho, *International Wood Products Journal*, 2013. 4(4): 242-247

### 4.1.1. Introduction

Formaldehyde based resins are the most used in wood based panels industry. The most predominant are urea-formaldehyde (UF) resins, followed by phenol-formaldehyde (PF), melamine-urea-formaldehyde (MUF) and melamine-formaldehyde (MF). Other synthetic binders are used, but in lower scale. These resins are employed in production of a wide range of board types, namely particleboards (PB), medium density fibreboard (MDF), plywood (PW), and oriented strand board (OSB) [1, 2]. MF resins are less susceptible to hydrolysis than UF resins, but their higher price and lower reactivity makes this product acceptable only for high value products [3].

LEED (Leadership in Energy and Environmental Design) is an internationally-recognized building certification that encourages the global adoption of sustainable green building, promoting a whole-building approach to sustainability by recognizing performance in different key areas of human and environment health like materials selection and indoor environmental quality [4]. According to this regulation, the use of UF resins, or adhesives with urea-formaldehyde bonds, is banned due to susceptibility to hydrolysis, which leads to release of formaldehyde during the life time of panels. MF resins are accepted due to the higher hydrolysis resistance [5].

Since the reclassification of formaldehyde as “carcinogenic to humans” by International Agency for Research on Cancer (IARC) in 2004 and published in 2006 [6], several efforts have been made by industry to reduce formaldehyde in wood-based panels. New product classes based on formaldehyde emission emerged. However, each world region established its own classifications, reference methods and standards. In USA, especially in California, formaldehyde emission needs to fulfil the California Air Resources Board (CARB) requirements, being the highest emission standards of 0.09 ppm for particleboards since 2011. In Japan, despite not mandatory, the classification of F\*\*\*\*\* is the most restrictive. In Europe, all the members of European Panel Federation (EPF) agreed to only produce E1 class, which is the more stringent classification



among formaldehyde emission standards in Europe. Nevertheless, driven by IKEA (IOSMAT 0003), a class with half of E1 formaldehyde emission limits has been introduced: the so-called E0 (or E0.5), which was not officially recognized by European Committee for Standardization (CEN) [2]. A new class, E1plus, is currently under discussion by CEN.

In recent years, several studies have been published on the use different formaldehyde scavengers for formaldehyde-based resins. Porous materials like pozzolan [7] and charcoal [8, 9] provide some scavenging ability, but reduce the bending strength on the finished panels. Tannins have been reported to reduce formaldehyde emissions and also improve panel internal bond, due to the presence hydroxyl groups [8, 9]. The scavenging activity of paper pulp was studied by Migneault *et al.* [10] who proposed that proteins present in the sludge plays an important role in the reduction of formaldehyde emission. It was also noted that the physico-mechanical properties are severely penalized [10]. Chemical compounds like amine compounds [11] or urea solution and urea-formaldehyde pre-polymer [12] were also studied, but bond strength was always negatively affected. Hematabadi *et al.* [13] reported on the positive effect of urea pre-treatment on the reduction of formaldehyde emission without reducing the physico-mechanical properties of particleboards.

The ability of sodium sulphites to react with aldehydes is well known [14-16]. There are some commercial formaldehyde scavengers available on the market. These are usually amino compounds, polyalcohols and other compounds with good affinity to formaldehyde. But they are usually expensive and penalize physico-mechanical properties, namely internal bond and thickness swelling. Sodium metabisulphite has been described in some patents as formaldehyde scavenger [17-19], but no other published studies deal with this subject.

Sodium metabisulphite is an inorganic compound with molecular formula of  $\text{Na}_2\text{S}_2\text{O}_5$ , forming, in water, sodium bisulphite [16] (equation 4.1):



Reaction of aldehydes with sodium bisulphite produces a sodium salt of the bisulphite adduct [20]. This is a stable compound, with potential use as formaldehyde scavenger in wood based panels. Addition of sodium metabisulphite to an UF resin forms sodium bisulphite that reacts with free formaldehyde (equation 4.2):



Recently, new formaldehyde-free resins have been reported in the literature, but have not yet convinced industrial wood-based panel producers, due to difficulty in application [21] and/or low reactivity, which would lead to higher pressing times and lower productivity [22, 23]. Other synthetic resins are commercialized but, despite having acceptable reactivity, the higher price and the use of peroxides, which cause corrosion on industrial equipment, are disadvantages that also impair acceptance by industry [24].

In this paper, sodium metabisulphite was tested as formaldehyde scavenger. Incorporation was performed in different forms: during adhesive synthesis and during particleboard production. The scavenging performance was tested with UF and MF resins. Formaldehyde content and several physico-mechanical properties of particleboards produced were evaluated by test methods defined in European standards.

#### **4.1.2. Material and methods**

##### ***Materials***

Commercial last generation UF and MF resins were provided by Euroresinas – Industrias Químicas, S. A. (Sines, Portugal). Wood particles, paraffin and ammonium sulphate were supplied by Sonae Indústria PCDM (Oliveira do Hospital, Portugal) for the production of

particleboards. Analytical grade sodium metabisulphite were purchased from Vaz Pereira, S. A. (Lisboa, Portugal).

### *Methods*

#### **Resin analysis**

The gel time of the resins was measured in a laboratory test tube ( $\phi = 18$  mm) immersed in boiling water corresponding to the time necessary to attain the onset of gelification, observed visually on tube walls when dragged by a glass rod ( $\phi = 6$  mm). 250  $\mu$ L of adhesive mixed with 3 % of ammonium sulphate (solid based) was used as catalyst.

A 20 wt.% ammonium sulphate solution was used as catalyst. The amount of catalyst used was the same for particleboard production, 3 wt.% solid catalyst based in solid resin. Resins with a gel time higher than 120 seconds were considered as having very low reactivity and so the times were not recorded.

#### **Particleboards production**

The adhesive system consisted of UF resin, paraffin (2 wt.%), catalyst (3 wt.%) and water (for adjusting the mat moisture content). In all series, the amount of solid resin was 7 wt.% based in mass of oven dry wood. Scavenger (when used) was 10 wt.% based in solid resin (except for resin B2, where it was 20 wt.%). Wood particles were blended with adhesive in a laboratory glue blender. Scavenger was added in two ways: mixed with the liquid resin after synthesis, or mixed in powder form with the wood particles, after glue blending.

Three layer particleboards were hand formed in a square aluminium deformable container with 220 x 220 x 80 cubic millimetres. Particleboards were designed to obtain density between 600 to 650  $\text{kg}\cdot\text{m}^{-3}$  and 16 mm thickness. Wood mass distribution was 20 % in upper face layer, 62 % for the core layer and 18 % in the bottom layer.

Core and face layers differ in the moisture content and size distribution of particles. Moisture content of mat was 11 wt.% in face layer and 6.5 % in core layer. The pressing program of a continuous industrial process was adapted to a batch cycle in a computer controlled laboratory scale press, equipped with a linear variable displacement transducer (LVDT), a pressure transducer and thermocouples. For all series, 5 boards were produced with a pressing factor of  $9.5 \text{ s} \cdot \text{mm}^{-1}$ .

After pressing, boards were stabilized in air until reaching room temperature. Then the boards were stored in an air-tight container until testing. Three samples of each board were tested according to the European standards for density (D) (EN 323), internal bond (IB) (EN 319), moisture content (MC) (EN 322) and thickness swelling (TS) (EN 317). For each series, one board was randomly selected for analysis of formaldehyde content (FC) based on EN 120 (perforator method).

### **4.1.3. Results and discussion**

#### *UF resins*

##### **No scavenger added**

A sample of an industrial resin batch was taken before addition of final urea [25-27]. The formaldehyde to amino groups ( $F/(\text{NH}_2)_2$ ) molar ratio in the collected product was 1.30. From this industrial sample (sample A), two new resins were obtained in laboratory by addition of urea until reaching a  $F/(\text{NH}_2)_2$  molar ratios of 1.10 and 0.90 (samples B and C, respectively).

Five particleboard panels were produced with each resin, according to the protocol described before. The resulting properties are shown in Table 4.1.1.

As expected, particleboards produced with resin A present higher internal bond and lower thickness swelling due to the excess of free formaldehyde (unreacted during synthesis), leading to high degree of crosslinking

during cure. However, the formaldehyde content in resin A exceeds the limit specified by E1 class according to EN 312. With addition of final urea, (resins B and C) formaldehyde content decreased, so that resin B falls within E1 class, and resin C, fulfils the unofficial class E0.

Table 4.1.1 – Properties of particleboards produced with UF resins with different final F/(NH<sub>2</sub>)<sub>2</sub> molar ratios (standard deviation measurements on at least three boards is presented between parenthesis)

<b>Resin</b>	<b>A</b>	<b>B</b>	<b>C</b>
F/(NH <sub>2</sub> ) <sub>2</sub> MR	1.30	1.10	0.90
IB (N·mm <sup>-2</sup> )	0.72 (0.01)	0.62 (0.08)	0.49 (0.07)
D (kg·m <sup>-3</sup> )	622 (6)	617 (13)	619 (8)
TS (%)	17.5 (0.1)	17.9 (1.2)	27.5 (2.3)
MC (%)	6.1 (0.1)	5.9 (0.2)	6.1 (0.2)
FC (mg/100 g oven dry board)	11.9	6.0	3.8

### Scavenger added to resins after synthesis

The amount of sodium metabisulphite added to resins A, B and C was 10 wt.% (resins A1, B1, C1). An amount of 20 wt.% was also added to resin B (resin B2). Figure 4.1.1 shows the measured values of gel time for these resins. As expected, the addition of final urea (reduction of F/(NH<sub>2</sub>)<sub>2</sub> molar ratio) increased the gel time of the resin due to consumption of free formaldehyde in cure process. The addition of sodium metabisulphite to the resins increased significantly the gel time of the resins, also indicating premature consumption of a significant amount of free formaldehyde.

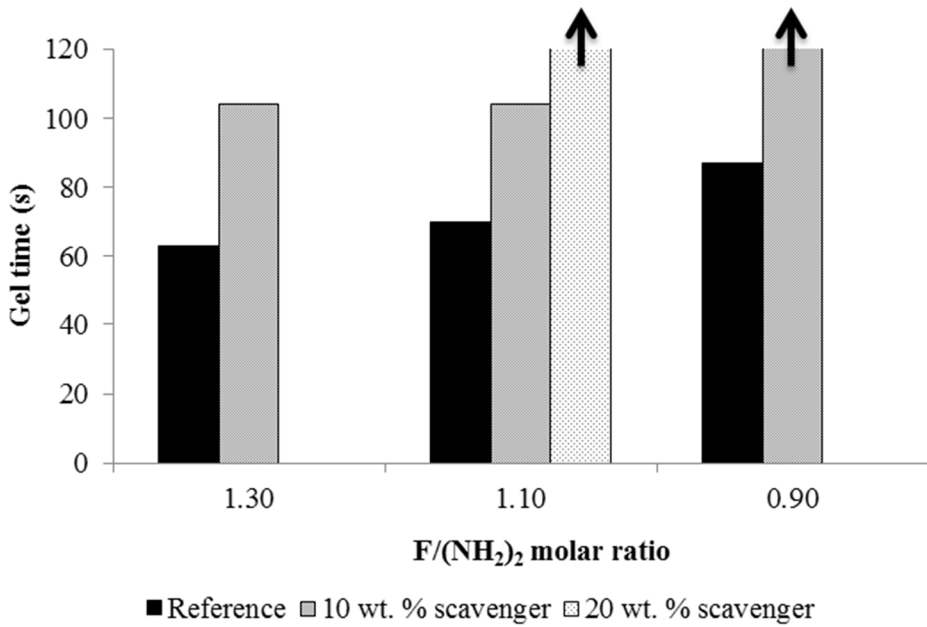


Figure 4.1.1 – Comparison between gel time of different resins produced (resins with 0.90 F/(NH<sub>2</sub>)<sub>2</sub> molar ratio with 10 wt.% of scavenger and resin with 1.10 F/(NH<sub>2</sub>)<sub>2</sub> molar ratio and 20 wt.% present gel time higher than 120 seconds)

Table 4.1.2 presents the properties of particleboards produced with UF resins with sodium metabisulphite. As expected, formaldehyde content was reduced in all cases when compared to the references without scavenger (resins A, B and C in Table 4.1.1), although penalizing the physico-mechanical properties. Particleboards produced with resins B2 and C1 were unable to be submitted to perforator test to determine the formaldehyde content, due to the low cohesion of material. Low material cohesion results from low concentration of free formaldehyde on adhesive required for curing. Although the test was not performed, very low formaldehyde content would be expected.

Table 4.1.2 – Properties of particleboards produced with UF resin with different F/(NH<sub>2</sub>)<sub>2</sub> molar ratio with sodium metabisulphite (\* test unable to be performed due to the low cohesion of board) (standard deviation measurements on at least three boards is presented between parenthesis)

Resin	A1	B1	B2	C1
F/(NH <sub>2</sub> ) <sub>2</sub> MR	1.30	1.10	1.10	0.90
IB (N·mm <sup>-2</sup> )	0.42 (0.05)	0.24 (0.01)	0.01 (0.00)	0.04 (0.02)
D (kg·m <sup>-3</sup> )	597 (2)	589 (5)	538 (19)	570 (1)
TS (%)	27.5 (1.9)	36.4 (2.9)	64.1 (11.0)	58.6 (1.3)
MC (%)	6.2 (0.1)	5.9 (0.1)	6.4 (0.1)	5.9 (0.1)
FC (mg/100 g oven dry board)	8.8	3.4	*	*

The reduction in adhesive reactivity and internal bond supports the occurrence of reaction between formaldehyde and sodium bisulphite before hot-pressing. This effect is more significant in resins with lower formaldehyde to amino groups molar ratio, where free formaldehyde is already present in low concentration. This issue is relevant not only in the context of formaldehyde scavenger systems. Free formaldehyde is also consumed in the activation reaction with latent catalyst (ammonium sulphate), which motivates studies on new catalyst systems what do not imply reaction with formaldehyde.

### Scavenger added to wood particles

Particleboards were produced using resins A, B and C with sodium metabisulphite being added after resin addition to wood particles. The amount of scavenger added was 10 wt.% relative to solid resin. Table 4.1.3 shows the properties of the particleboards produced. This form of addition avoids premature reaction between formaldehyde and sodium bisulphite. Comparing the results in Table 4.1.2 and Table 4.1.3, and taking as reference the values in Table 4.1.1, it is observed that the scavenging performance is similar for both addition procedures, as seen

more detail in Figure 4.1.2. However, the mechanical properties are less penalized when the scavenger is added directly to the wood particles, possibly because premature consumption of formaldehyde is substantially reduced.

Table 4.1.3 – Properties of particleboards produced with UF resin and sodium metabisulphite added during the blending operation (standard deviation measurements on at least three boards is presented between parenthesis)

Resin	A	B	C
MR F/(NH <sub>2</sub> ) <sub>2</sub>	1.30	1.10	0.90
IB (N·mm <sup>-2</sup> )	0.54 (0.04)	0.55 (0.03)	0.31 (0.01)
D (kg·m <sup>-3</sup> )	631 (5)	640 (11)	612 (8)
TS (%)	20.2 (0.5)	23.3 (1.7)	31.6 (2.2)
MC (%)	5.9 (0.1)	5.8 (0.1)	6.2 (0.1)
FC (mg/100 g oven dry board)	9.1	2.9	1.4

The better performance obtained when sodium metabisulphite is added to glued wood particles, is a consequence of reduced interaction between scavenger and resin, due to lack of a continuous liquid phase surrounding the particles, which minimizes premature formaldehyde consumption. During hot pressing, formaldehyde carried by water vapour contacts the scavenger, forming an adduct compound (equations 4.1 and 4.2).

Application of sodium metabisulphite in solid form to the blended particles will cause liberation of dust particles into the air. The use of protective mask is recommended, in order to protect the respiratory tract from contact with sodium metabisulphite. Water present in the gastrointestinal tract will dissolve sodium metabisulphite, forming sodium bisulphite that will oxidize to sulphate in vivo causing irritation [16]. This is a major restriction to the use of sulphites in industrial applications. An interesting alternative would be to encapsulate the scavenger, as long as exposure upon hot pressing can be guaranteed.



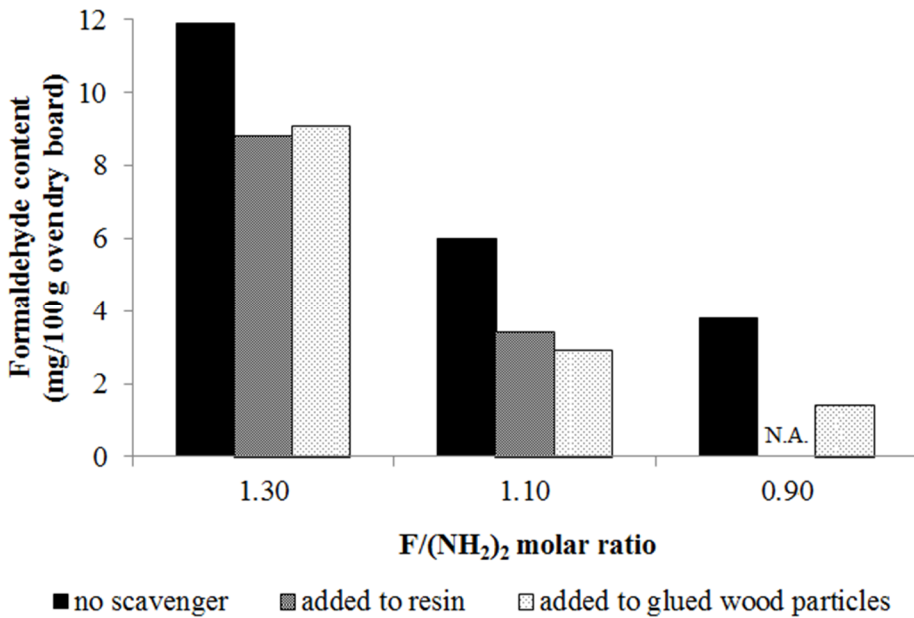


Figure 4.1.2 – Formaldehyde content of particleboards produced without scavenger, with scavenger added to the resin, and with scavenger added to glued wood particles (N.A.: not available)

### MF resins

Wood particles were blended with a commercial MF resin according to the previous protocol and the same procedure was applied for the incorporation of sodium metabisulphite during board production, after resin blending. Table 4.1.4 presents the properties of the produced particleboards.

Table 4.1.4 – Properties of particleboards produced with MF resin and sodium metabisulphite added separately (standard deviation measurements on at least three boards is presented between parenthesis)

Resin	D	D
MR F/(NH <sub>2</sub> ) <sub>2</sub>	1.10	1.10
Scavenger	No	Yes
IB (N·mm <sup>-2</sup> )	0.45 (0.04)	0.52 (0.03)
D (kg·m <sup>-3</sup> )	655 (10)	647 (8)
TS (%)	19.2 (1.1)	19.9 (1.4)
MC (%)	7.0 (0.1)	6.8 (0.1)
FC (mg/100 g oven dry board)	8.0	6.5

Contrary to UF resins, the addition of sodium metabisulphite to MF resins increased the internal bond, but the reduction of formaldehyde content was lower than expected. Figure 4.1.3 shows a relation between the percentage of reduction of formaldehyde content (% *R*) on particleboards with scavenger ( $FC_{Scavenger}$ ) and formaldehyde content on reference particleboards ( $FC_{Reference}$ ) (equation 4.3).

$$\% R = (FC_{Reference} - FC_{Scavenger}) / FC_{Reference} \quad (4.3)$$

A linear correlation ( $r^2 = 0.9996$ ) was found, and a linear relationship between the formaldehyde content of the reference board and the percentage of reduction can be estimated by equation 4.4:

$$\% R = -0.049 \cdot FC_{Reference} + 0.81 \quad (4.4)$$

Using this equation to estimate the percentage of reduction in boards produced with MF resins, a reduction of 42 % on formaldehyde content would be expected. Hence, from equation 4.3, boards produced with sodium metabisulphite should present formaldehyde content of 4.6 mg/100 g of oven dry board. However, the measured FC was 6.5, meaning that the reduction of FC was only 19 %, less than a half of the

expected reduction Figure 4.1.3. This indicates that a significant fraction of sodium metabisulphite is probably consumed in other parallel reactions. Reaction of sodium bisulphite with methylol melamines (sulfonation) [28, 29] could justify this lower performance in terms of formaldehyde scavenging (Figure 4.1.4).

Contrarily to the observed with UF resin, addition of sodium metabisulphite to MF resin increases internal bond. Methylolated urea compounds, namely mono and di-methylol urea, despite being highly reactive, are also less stable, so the compounds involved in formaldehyde scavenging reaction will be readily decomposed. Methylolated melamine compounds are known to be stable (that is the reason why UF resins doped with melamine present lower formaldehyde emission).

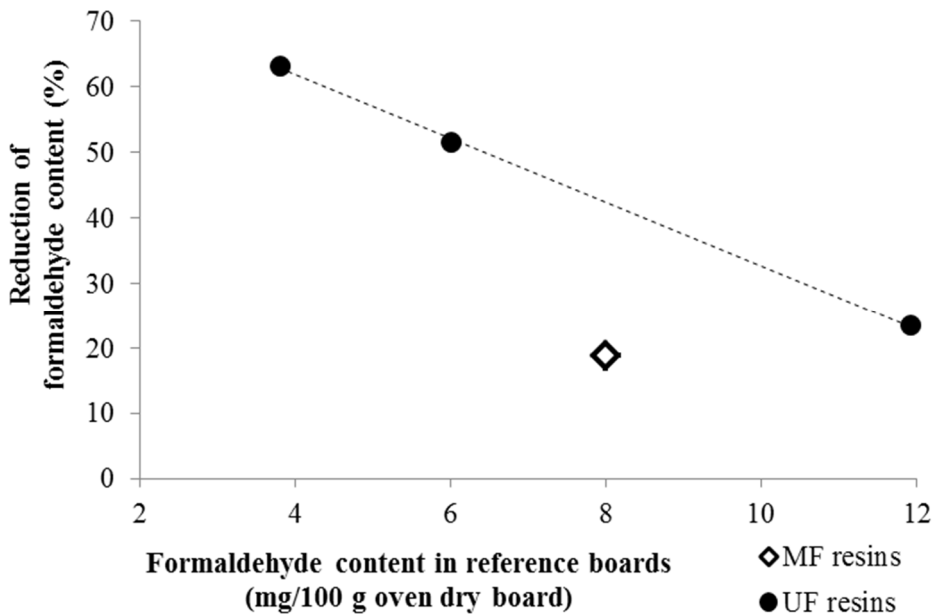


Figure 4.1.3 – Relation between formaldehyde content in reference boards, and reduction in formaldehyde content achieved by scavenger addition

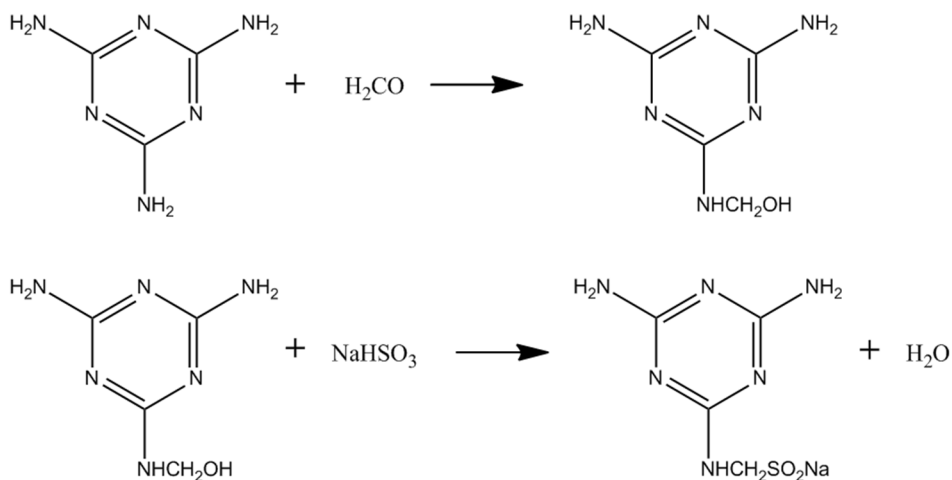


Figure 4.1.4 – Reaction between melamine and sodium bisulphite

#### 4.1.4. Conclusions

Sodium metabisulphite is an effective formaldehyde scavenger for wood based panels. The observed decrease in mechanical performance is still within acceptable values. The addition procedure affects significantly the scavenging action and the particleboard performance. The addition of sodium metabisulphite mixed with UF resin penalizes internal bond and thickness swelling of the boards produced. Even so, the reduction in formaldehyde content was significant. When sodium metabisulphite was applied in powder form to wood particles after the gluing operation, the internal bond and thickness swelling were not damaged while formaldehyde content was still reduced. When the same procedure was applied to melamine-formaldehyde resins, the scavenging performance was lower, but internal bond increased, supporting the interest in more studies using sodium metabisulphite as additive for MF resins in order to obtain low formaldehyde emission boards with LEED certification.

## 4.2. SCAVENGERS FOR ACHIEVING ZERO FORMALDEHYDE EMISSION ON WOOD-BASED PANELS<sup>6</sup>

### *Abstract*

This work studies the performance of three formaldehyde scavengers in wood-based panels. Sodium metabisulphite, ammonium bisulphite and urea were applied in different physical forms during particleboards production, and the resulting physico-mechanical properties (internal bond strength, thickness swelling, density and moisture content) and formaldehyde emission levels were compared. Formaldehyde content was measured using the perforator method and formaldehyde emission was evaluated both by desiccator and gas analysis methods.

The chemical reactions involved in each formaldehyde scavenging process are proposed and discussed. The scavengers tested showed distinct performances under the different emission testing conditions, which was interpreted in terms of the stability of the chemical compounds formed upon formaldehyde capture.

Sodium metabisulphite proved to be an excellent scavenger in all formaldehyde methods, allowing the production of particleboard panels with zero formaldehyde emission.

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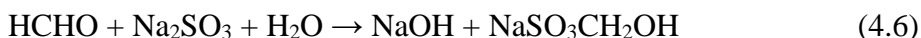
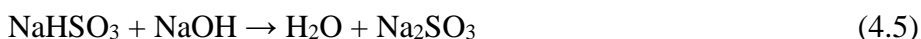
<sup>6</sup> N. A. Costa, J. Pereira, J. Ferra, P. Cruz, J. Martins, F. D. Magalhães, A. Mendes and L. H. Carvalho, *Wood and Science Technology*, 2012. 47(6):1261-1272

### 4.2.1. Introduction

Reduction of F/U molar ratio has been a strategy adopted in the last decades to decrease formaldehyde emission [30]. However, this reduction decreases the reactivity of UF resins. Currently, reactivity of industrial UF adhesives is near the minimum limit accepted for industrial panel production [31].

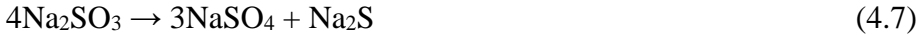
Substitution of UF resins by other formaldehyde-free adhesives does not convince industrial producers, due to their higher price or lower reactivity [22-24]. In order to increase the degree of cure and reduce free formaldehyde at the end of cure, new catalysts were studied, but reactivity is still too low [32].

The use of scavengers, such as natural or bio-based scavengers [7-9] or other compounds with good affinity to capture formaldehyde [11, 12], to reduce formaldehyde emission from wood-based panels is commonly adopted. In section 4.1 is studied the use of sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) as formaldehyde scavenger in particleboards produced with UF and melamine-formaldehyde (MF) resins, with good results. The reaction of sodium metabisulphite with water forms sodium bisulphite, also called sodium hydrogen sulphite (equation 4.1). The reaction between formaldehyde and sodium bisulphite forms a bisulphite adduct (equation 4.2) [14, 16]. When neutralized with sodium hydroxide, sodium bisulphite forms sodium sulphite ( $\text{Na}_2\text{SO}_3$ ), as seen in equation 4.5. Sodium sulphite is used to quantify formaldehyde by titration of the sodium hydroxide formed as by-product (equation 4.6) [14].

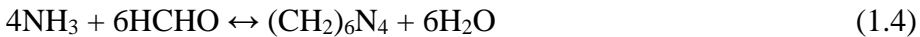


When strongly heated, sodium sulphite decomposes into sodium sulphate and sodium sulphide (equation 4.7) [33]. In the pulp and paper industry sodium sulphide combined with sodium hydroxide are used in Kraft process, an alkaline chemical process used for treating wood chips in

order to break the bonds between lignin and cellulose and separate the fibres [34].



Ammonium and sulphite ions are in equilibrium in ammonium sulphite aqueous solution (equation 4.8). In the presence of sodium ions (existent in the UF resin) and formaldehyde, the sulphite ions react forming an adduct (equation 4.2). Ammonia in aqueous solution reacts with formaldehyde forming hexamine (hexamethylenetetramine) (equation 4.9 and equation 4.11) [14, 35].



There are several methods for the determination of formaldehyde emission on wood based-panels. They can be divided in two main groups: emittable potential and measurable emission of formaldehyde. The first type measures the formaldehyde content, without establishing whether it will actually emitted, or in which time this emission may occur. The second type determines the actual emitted formaldehyde amount under the test conditions [36].

Emittable potential is evaluated by perforator method (EN 120), whereas actual emitted formaldehyde can be evaluated by several methods: chamber method (EN 717-1, ASTM E 1333 or ASTM D 6007), gas analysis (EN 717-2) and desiccator method (JIS A 1460). Many authors have tried to relate formaldehyde emissions measured by different methods [37-40], but the relations are influenced by other variables, such as resin type, type of wood-based panels, thickness or manufacturing

conditions. Salem *et al.* [41] and Kim and Kim [42] studied formaldehyde emission from different types of formaldehyde based resins. Salem *et al.* [43] showed that the manufacturing variables interfere significantly with formaldehyde emissions and the correlations between methods to assess different products were not possible.

The present work studies the performance of sodium and ammonium bisulphite and urea as formaldehyde scavengers in particleboards production. Formaldehyde emissions evaluated by perforator, desiccator and gas analysis methods are compared and discussed.

### **4.2.2. Material and methods**

#### ***Materials***

Last generation commercial UF resins (0.94 F/(NH<sub>2</sub>)<sub>2</sub> molar ratio) and urea were provided by EuroResinas – Indústrias Químicas, S.A. (Sines Portugal). Wood particles, paraffin and ammonium sulphate for the production of particleboard were supplied by Sonae Indústria PCDM (Oliveira do Hospital, Portugal). Analytical grade sodium metabisulphite and ammonium bisulphite solution (70 wt.%) were used.

#### ***Methods***

##### **Particleboard production**

The adhesive system is composed by UF resin, paraffin, catalyst (ammonium sulphate 30 wt.% solution) and water for adjusting the mat moisture content. Wood particles were blended with the adhesive in a laboratory glue blender. The solid resin load was 7 wt.% based in oven dry wood. Scavengers, when applied in liquid form, were added to wood particles at the beginning of the blending operation, prior to resin blend. Scavengers applied in solid form were dispersed by hand on wood particles after resin blending.



Three particle layer mats were hand formed in a square aluminium deformable container with 220 x 220 x 80 mm<sup>3</sup>. Wood mass distribution was 20 % in upper face layer, 62 % for the core layer and 18 % in the bottom face layer. Core and face layers differ in moisture content (11 % in face layer and 8 % in core layer) and size distribution of particles (smaller particles in face layer and larger in core layers, as used in industrial productions). Particleboards were designed to obtain a target density between 650 and 700 kg·m<sup>-3</sup>.

The pressing schedule of an industrial continuous process was adapted to a batch cycle in a computer controlled laboratory scale hot-press equipped with a linear variable displacement transducer (LVDT), a pressure transducer and thermocouples.

For all series, 6 boards with 16 mm of thickness were produced with a pressing factor of 9.5 s·mm<sup>-1</sup>. Control series were produced using the same operating conditions as the other series.

### **Particleboard analysis**

All boards were hermetically conditioned until tested. The boards were tested according to European standards for density (D) (EN 323), internal bond (IB) (EN 319), moisture content (MC) (EN 322) and thickness swelling (TS) (EN 317). For each series, one board was randomly selected for formaldehyde content (FC) analysis according to EN 120 (perforator method) (the formaldehyde content was adjusted to 6.5 % of moisture content according to EN 312). Three boards were used for the desiccator method (JIS A 1460). In the second part of this work, one panel of each series was submitted to the gas analysis method (EN 717-2) for determination of formaldehyde emission.

### 4.2.3. Results and discussion

#### *Evaluation of performance of different formaldehyde scavengers*

Table 4.2.1 presents the properties of the particleboards produced with 5 wt.% scavenger (solid content based in solid resin) added in three different forms: a) solid sodium metabisulphite (SMBS), b) sodium bisulphite aqueous solution (40 wt.% sodium metabisulphite in water) (SB40) and c) SB40 partially neutralized with sodium hydroxide to pH = 5.8 (SB\_NaOH).

Table 4.2.1 – Properties of particleboards produced with sodium metabisulphite and bisulphite

	Control	SMBS	SB40	SB_NaOH
Internal Bond (N·mm <sup>-2</sup> )	0.58	0.57	0.41	0.45
Density (kg·m <sup>-3</sup> )	690	696	690	679
Thickness Swelling (%)	33.3	33.5	38.2	32.9
Moisture Content (%)	7.3	7.3	7.8	7.3
Formaldehyde content (mg/100 g oven dry board)	2.2	1.8	1.7	2.6
Formaldehyde emission (mg·L <sup>-1</sup> )	0.45	0.13	0.30	0.43

As reported in section 4.1, small amounts of sodium metabisulphite reduce substantially the formaldehyde content of particleboards. Table 4.2.1 supports these results and shows that formaldehyde emission is lower when solid sodium metabisulphite is used.

The release of small particles of sodium metabisulphite into air causes respiratory tract irritation [16], which can be avoided if the scavenger is applied in liquid solution. However, dissolution of sodium metabisulphite in water forms sodium bisulphite. Due to its proton donor ability, it presents acidic characteristics, which can cause resin pre-cure in blending operation. The sodium bisulphite solution, prepared with 40 wt.% of

sodium metabisulphite, has a pH of 3.7. Internal bond decrease and thickness swelling increase – Table 4.2.1 – can be related to pre-cure of the resin at this low pH, or to premature consumption of formaldehyde due to higher mobility/dispersability of the scavenger in liquid form. The formaldehyde content obtained is similar using either metabisulphite in solid form or in solution (Table 4.2.1). However, formaldehyde emissions are higher in the second case, although still below the control (without scavenger). The lower effectiveness in reducing formaldehyde emission can be related to migration of sodium bisulphite towards the core layer of the mat, dissolved in the vapour phase formed during hot-pressing [44]. Scavenger depletion in the external layers reduces effectiveness in formaldehyde capture in emission testing (desiccator method). Formaldehyde content measurements (perforator method) are not affected by scavenger distribution, since this test evaluates all formaldehyde present in the sample.

The purpose of the trial performed with sodium bisulphite solution neutralized with sodium hydroxide was to avoid resin pre-cure due to low pH, as discussed above. However, as seen in Table 4.2.1, this led to similar emission as the control and slightly higher formaldehyde content. Internal bond has decreased. Sodium bisulphite reacts with sodium hydroxide forming sodium sulphite (equation 4.5). During cure, sodium sulphite reacts with formaldehyde forming sodium hydroxide (equation 4.6) and increasing pH, thus unfavoring the cure reaction. In addition, under high temperatures (190 °C), decomposition of sodium sulphite into sodium sulphide (equation 4.7) can possibly cause some degradation of wood components, which supports the reduction on physico-mechanical properties of boards [35].

Table 4.2.2 shows the properties of particleboards produced with ammonium bisulphite solutions (70 wt.%, pH = 5.0) with two different incorporations: 5 % (ABS\_5) and 10 % (ABS\_10) based in solid resin. As observed with sodium bisulphite, the application of scavenger in liquid form reduces formaldehyde emission but affects negatively particleboard physico-mechanical properties.

Table 4.2.2 – Properties of particleboards produced with ammonium bisulphite

	<b>Control</b>	<b>ABS_5</b>	<b>ABS_10</b>
Internal Bond (N·mm <sup>-2</sup> )	0.54	0.33	0.12
Density (kg·m <sup>-3</sup> )	669	684	643
Thickness Swelling (%)	30.8	36.3	51.3
Moisture Content (%)	7.9	7.9	8.6
Formaldehyde content (mg/100 g oven dry board)	2.5	1.6	0.9
Formaldehyde emission (mg·L <sup>-1</sup> )	0.47	0.37	0.22

### *Comparison between different formaldehyde emission methods*

In the previous part of this work was shown that sodium metabisulphite presents higher formaldehyde scavenging ability when applied in solid form. Ammonium bisulphite also presented good performance, but affects negatively the internal bond and thickness swelling. Another effective scavenger is urea, which has been widely used in industry due to its good performance and low price [12, 45, 46].

In this section, the scavenging performance of sodium metabisulphite in solid form, ammonium bisulphite in liquid solution, and urea is evaluated using three different formaldehyde evaluation standard methods: perforator, desiccator and gas analysis.

Urea was applied in solution (30 wt.%) in the face layer to avoid the “blistering effect” noted when a decorative paper is pressed over a urea prill. In the core layer urea was applied in solid form (prills) to avoid an increase in internal moisture content that inhibits heat transfer [44]. The amount of scavengers added was 5 wt.%, 10 wt.% and 15 wt.% (solid scavenger based in solid resin). Physico-mechanical (internal bond and thickness swelling) and formaldehyde content (perforator method) and emission (desiccator and gas analysis method) were evaluated for each series of particleboards and the results are presented below. A control

series was produced with the same resin and operating conditions, but without scavenger addition.

All particleboards were produced with the same resin and using the same pressing conditions (16 mm of thickness, 150 seconds of pressing at 190 °C). Figure 4.2.1 shows the internal bond and thickness swelling of particleboards produced. As previously concluded, particleboards produced with sodium metabisulphite do not present a significant reduction in internal bond, neither suffer substantial penalty in thickness swelling. Urea presents similar behaviour. Ammonium bisulphite presents higher penalty in internal bond and thickness swelling.

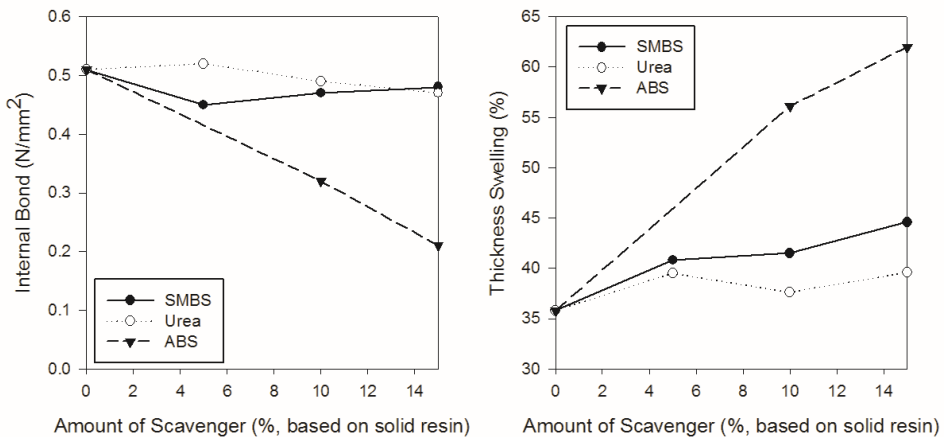


Figure 4.2.1 – Comparison between internal bond and thickness swelling with different amount of formaldehyde scavengers (SMBS: sodium metabisulphite, ABS: ammonium bisulphite)

Figure 4.2.2 presents the formaldehyde content of particleboards produced with different scavengers. Urea presents the lowest ability for scavenging formaldehyde. This result supports the idea that urea is no longer a preferred formaldehyde scavenger to produce ultra-low emission wood-based panels. Sodium metabisulphite and ammonium bisulphite present similar results using the perforator method. Boards produced with

15 wt.% sodium metabisulphite show formaldehyde content near values typical of solid wood [47].

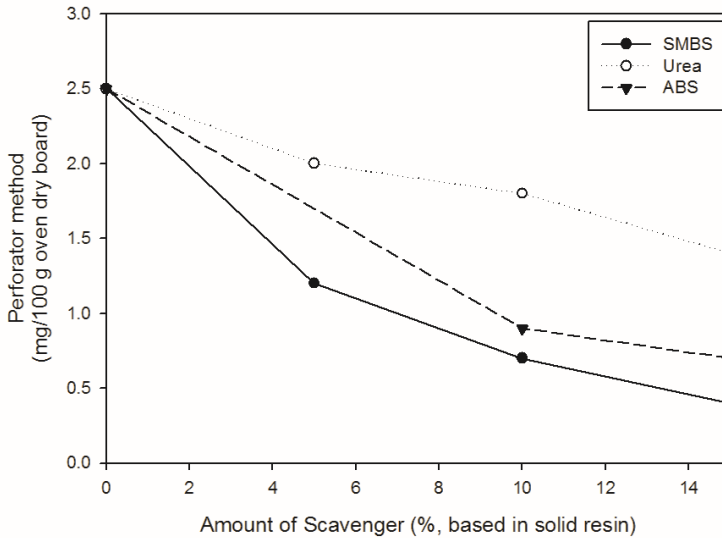


Figure 4.2.2 – Formaldehyde content by perforator method (EN 120) of particleboards produced with different formaldehyde scavengers

Figure 4.2.3 shows formaldehyde emission of particleboards analysed by desiccator method. Sodium metabisulphite presents zero formaldehyde emission when incorporated at 15 wt.%, while ammonium bisulphite and urea present a significant reduction in formaldehyde emission. Figure 4.2.4 shows formaldehyde emissions by the gas analysis method. The test performed with ammonium bisulphite at 15 wt.% is not shown due to experimental errors during analysis.

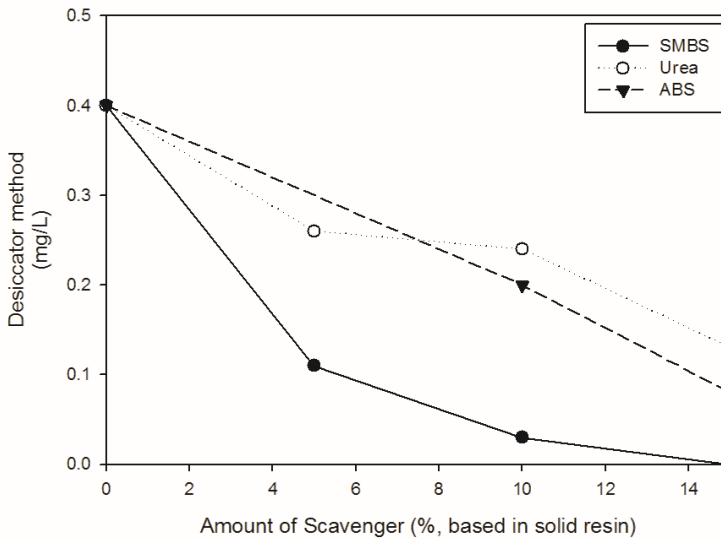


Figure 4.2.3 – Formaldehyde emission by desiccator method (JIS A 1460) of particleboards produced with different formaldehyde

The better performance of sodium metabisulphite in desiccator method can be related to higher hydrolysis resistance of the adduct formed in the reaction with formaldehyde. The addition reaction between formaldehyde and urea used as scavenger forms methylolureas, which tends to undergo hydrolysis in the presence of moisture, releasing formaldehyde [48, 49]. This explains the poor performance of urea addition in the desiccator method, since test pieces are subjected to a high relative humidity. Ammonium bisulphite presents similar behaviour, indicating that the compound formed by reaction with formaldehyde also has low moisture resistance.

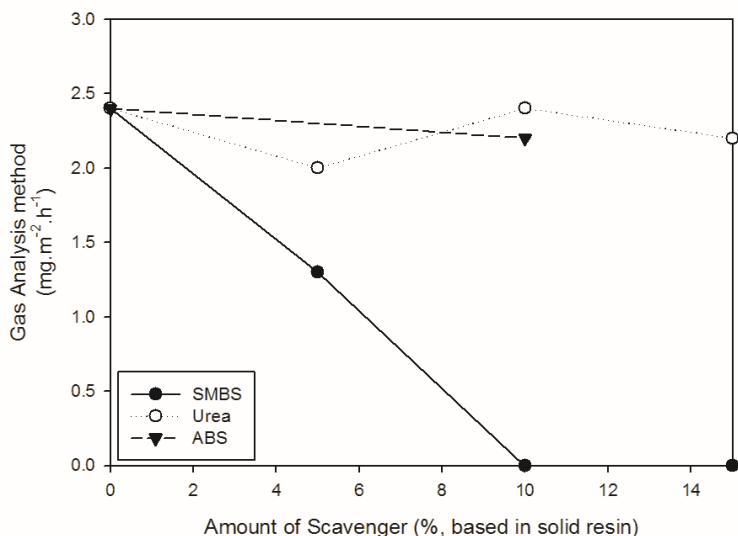


Figure 4.2.4 – Formaldehyde emission by gas analysis method (EN 717-2) of particleboards produced with different formaldehyde scavengers

In the gas analysis method, urea does not show scavenging ability. This may be related to the low thermal stability of the oligomeric species formed by reaction of urea scavenger with formaldehyde, even at a relatively low temperature of 60 °C. Ammonium bisulphite presents a similar trend. Compounds formed between ammonium bisulphite and formaldehyde do not present the same stability as those formed with sodium metabisulphite. The product formed in the presence of ammonium ions is probably less stable than the sodium salt adduct described in equation 4.5. The higher temperature (60 °C) of the test can also reverse some of the scavenging reactions.

Figure 4.2.5 shows the relation between formaldehyde emission obtained by the desiccator method and formaldehyde content measured by the perforator method. Sodium metabisulphite and urea exhibit a similar linear trend, unlike ammonium bisulphite. Park *et al.* [39] have compared both methods for particleboards within the range between 2.9 and



16.2 mg per 100 g of oven dry board and 0.3 and 3.0 mg·L<sup>-1</sup>, for perforator and desiccator values, respectively. No scavengers were used in this case. Our data shows a similar slope as these authors, but covers lower emission values, including zero emission (Figure 4.2.5). Risholm-Sundman *et al.* [37] present a relation between both methods, also without scavenger addition, for formaldehyde contents between 1.0 and 8.0 mg per 100 g (o.d.b.) and emissions between 0.16 and 0.74 mg·L<sup>-1</sup>. In this case, the linear relation obtained is different from our work.

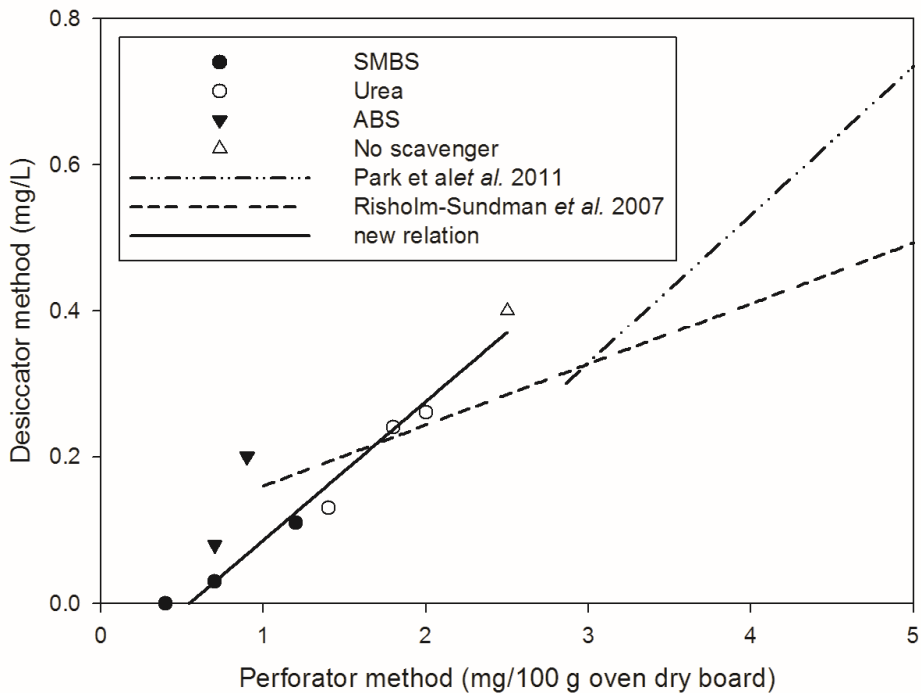


Figure 4.2.5 – Comparison between formaldehyde content by perforator method (EN 120) and formaldehyde emission by desiccator method (JIS A 1460) of particleboards produced with different scavengers

#### 4.2.4. Conclusions

In this work, different formaldehyde scavengers were studied: powder sodium metabisulphite, aqueous solutions of sodium, and ammonium bisulphite and urea, either in aqueous solution or particulated. The formaldehyde emission of particleboards was evaluated using three standard methods: perforator (EN 120), desiccator (JIS A 1460) and gas analysis (EN 717-2). Boards produced with sodium metabisulphite exhibited formaldehyde content (perforator value) near solid wood levels and zero formaldehyde emissions (desiccator method). The other scavengers tested yielded much lower performances.

The scavenging performance of each scavenger is strongly dependent on the formaldehyde analysis method. The test conditions, such as temperature, relative humidity or air exchange, may interfere in different ways on the stability of the chemical compounds formed in the scavenging reactions with formaldehyde. This study supports that the comparisons between different formaldehyde emission standard methods should be carefully analysed.

Sodium metabisulphite showed the best formaldehyde scavenging performance in all methods, even in the gas analysis method, where the other additives did not display scavenging ability. Boards with higher content of sodium metabisulphite showed zero emission without deteriorating physico-mechanical properties.

A relation between desiccator and perforator method values was given but it was not possible to establish a correlation between gas analysis and the other methods, because this relation is strongly dependent on the type of scavenger used.

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### 4.3. REFERENCES

1. Anonymous, Wood handbook: Wood as an engineering material. General Technical Report FPL-GTR-190. General Technical Report FPL-GTR-190. 2010, Madison, WI: U.S.: Forest Products Laboratory. Department of Agriculture, Forest Service, Forest Products Laboratory.
2. Carvalho, L., F. Magalhães, and J. Ferra, Formaldehyde Emissions from Wood-Based Panels -Testing Methods and Industrial Perspectives, in Chemistry, Applications and Role in Polymerization, C.B. Cheng and F.H. Ln, Editors. 2012, Nova Science Publishers, Inc.: Hauppauge, NY
3. Shumigin, D., Ammonium Nitrate Based Catalysts for the Production of Particleboards. 2010: Lambert Academic Publishing.
4. Unite States Green Building Council. Available from: <http://www.usgbc.org/>, accessed on January 2012
5. Unite States Green Building Council. LEED 2009 for Commercial Interiors. Available from: <http://new.usgbc.org/Docs/Archive/General/Docs5543.pdf>, accessed on January 2012.
6. IARC, Monographs on the Evaluation of Carcinogenic Risk to Humans. 2006, World Health Organization - International Agency For Research On Cancer.
7. Kim, S., The reduction of indoor air pollutant from wood-based composite by adding pozzolan for building materials. Construction and Building Materials, 2009. 23(6): p. 2319-2323.
8. Eom, Y.-G., et al., Reduction of Formaldehyde Emission from Particleboards by Bio-Scavengers. Mokchae Konghak, 2006. 34: p. 29-41.
9. Kim, S., et al., Effect of bio-savengers on the curing behavior and bonding properties of melamine-formaldehyde resins. Macromolecular Materials and Engineering, 2006. 291(9): p. 1027-1034.
10. Migneault, S., et al., Potential of pulp and paper sludge as a formaldehyde scavenger agent in MDF resins. Holzforschung, 2011. 65(3): p. 403-409.
11. Boran, S., M. Usta, and E. Gümüşkaya, Decreasing formaldehyde emission from medium density fiberboard panels produced by adding different amine compounds to urea formaldehyde resin. International Journal of Adhesion and Adhesives, 2011. 31(7): p. 674-678.
12. Park, B.D., E.C. Kang, and J.Y. Park, Thermal curing behavior of modified urea-formaldehyde resin adhesives with two formaldehyde scavengers and their influence on adhesion performance. Journal of Applied Polymer Science, 2008. 110(3): p. 1573-1580.

13. Hematabadi, H., et al., The reduction of indoor air formaldehyde from wood based composites using urea treatment for building materials. *Construction and Building Materials*, 2012. 28(1): p. 743-746.
14. Walker, J.F., Formaldehyde. American Chemical Society Monograph Series. 1944, New York: Waverly Press, Inc.
15. National Research Council, Committee on Aldehydes. Formaldehyde and other aldehydes. 1981: National Academy Press.
16. Barberá, J.J., A. Metzger, and M. Wolf, Sulfites, Thiosulfates, and Dithionites. *Ullmann's Encyclopedia of Industrial Chemistry*. 2000: Wiley-VCH Verlag GmbH & Co. KGaA.
17. Boyer, P., K. Tutin, and R. Srinivasan, Reducing Formaldehyde Emissions from Fiberglass Insulations. 2008: US.
18. Tutin, K., et al., Fibrous Having reduced formaldehyde emission. 2008.
19. Ishimoto, K., et al., Scavenger for aldehyde(s) and a manufacturing method of a woody panel using the same. 2009. United States Patent 2009/0130474 A1
20. Caron, S., *Practical Synthetic Organic Chemistry: Reactions, Principles, and Techniques*. 2011: John Wiley & Sons.
21. Prasittisopin, L. and K. Li, A new method of making particleboard with a formaldehyde-free soy-based adhesive. *Composites Part A: Applied Science and Manufacturing*, 2010. 41(10): p. 1447-1453.
22. Despres, A., et al., Colourless formaldehyde-free urea resin adhesives for wood panels. *European Journal of Wood and Wood Products*, 2010. 68(1): p. 13-20.
23. Tang, L., et al., The preparation and application of a new formaldehyde-free adhesive for plywood. *International Journal of Adhesion and Adhesives*, 2011. 31(6): p. 507-512.
24. Amazio, P., et al., Low formaldehyde emission particleboard panels realized through a new acrylic binder. *Journal of Applied Polymer Science*, 2011. 122(4): p. 2779-2788.
25. Costa, N.A., et al., The role of sucrose in amino polymers synthesized by the strongly acid process. *Journal of Adhesion Science and Technology*, 2012. DOI: 10.1080/01694243.2012.727150
26. Ferrá, J.M.M., et al., Comparison of UF synthesis by alkaline-acid and strongly acid processes. *Journal of Applied Polymer Science*, 2012. 123(3): p. 1764-1772.
27. Paiva, N.T., et al., Production of melamine fortified urea-formaldehyde resins with low formaldehyde emission. *Journal of Applied Polymer Science*, 2012. 124(3): p. 2311-2317.
28. Ramachandran, V.S., *Concrete admixtures handbook: properties, science, and technology*. 1995: Noyes Publications.
29. Goudarjian, N., A. Rabiee, and H. Hamidi, Effect of Reactant Ratios on Gel Point of Sulphonated Melamine-Formaldehyde Superplasticizer. *Indian Polymer Journal*, 1996. 5(1): p. 24-29.

30. Myers, G.E., How Mole Ratio of Uf Resin Affects Formaldehyde Emission and Other Properties - a Literature Critique. *Forest Products Journal*, 1984. 34(5): p. 35-41.
31. Dongbin, F., L. Jianzhang, and M. An, Curing Characteristics of Low Molar Ratio Urea-Formaldehyde Resin. *Journal of Adhesion and Interface*, 2006. 7(4): p. 45-52.
32. Gunnells, D. and K. Griffin. Catalyst Systems. in *Resin & Blending Seminar Proceedings*. 1998. Portland, Oregon and Charlotte, North Carolina: Forest Products Society.
33. Gerrans, G.C., P. Hartmann-Petersen and R. Hartmann-Petersen, *Encyclopaedia of science & technology*. 2004: New Africa Education.
34. Miller, F.P., A.F. Vandome, and J. McBrewster, *Kraft Process*. 2009: VDM Publishing House Ltd.
35. Dreyfors, J.M., S.B. Jones, and Y. Sayed, Hexamethylenetetramine - a Review. *American Industrial Hygiene Association Journal*, 1989. 50(11): p. 579-585.
36. Dunky, M., *The Chemistry of Adhesives*, in *COST Action E13: Wood Adhesion and Glued Products*, State of the art Report, M.E. Dunky, Editor. 2001.
37. Risholm-Sundman, M., et al., Formaldehyde emission—Comparison of different standard methods. *Atmospheric Environment*, 2007. 41(15): p. 3193-3202.
38. Que, Z. and T. Furuno, Formaldehyde emission from wood products: relationship between the values by the chamber method and those by the desiccator test. *Wood Science and Technology*, 2007. 41(3): p. 267-279.
39. Park, B.-D., et al., Empirical correlations between test methods of measuring formaldehyde emission of plywood, particleboard and medium density fiberboard. *European Journal of Wood and Wood Products*, 2011. 69(2): p. 311-316.
40. Salem, M.Z.M., et al., Evaluation of formaldehyde emission from different types of wood-based panels and flooring materials using different standard test methods. *Building and Environment*, 2012. 49(0): p. 86-96.
41. Salem, M.Z.M., et al., Formaldehyde Emission from Wood-Based Panels Bonded with Different Formaldehyde-Based Resins. *Drvna Industrija*, 2011. 62(3): p. 177-183.
42. Kim, S. and H.J. Kim, Comparison of standard methods and gas chromatography method in determination of formaldehyde emission from MDF bonded with formaldehyde-based resins. *Bioresource Technology*, 2005. 96(13): p. 1457-1464.
43. Salem, M.Z.M., et al., Effect of some manufacturing variables on formaldehyde release from particleboard: Relationship between

- different test methods. *Building and Environment*, 2011. 46(10): p. 1946-1953.
44. Carvalho, L., J. Martins, and C. Costa, Transport Phenomena, in *Wood-based Panels: An Introduction for Specialists*, H. Thoemen, M. Irle, and M. Sernek, Editors. 2010, Brunel University Press: London. p. 123-176.
  45. Lehmann, W.F., Method and Composition for Reduction of Formaldehyde Emission in Wood Composite Panels. 1983, United States Patent 4397756.
  46. Costa, N., et al., Alternative to latent catalysts for curing UF resins used in the production of low formaldehyde emission wood-based panels. *International Journal of Adhesion and Adhesives*, 2012. 33: p. 56-60.
  47. Meyer, B. and C. Boehme, Formaldehyde emission from solid wood. *Forest Products Journal*, 1997. 47(5): p. 45-48.
  48. Dunky, M., Urea-formaldehyde (UF) adhesive resins for wood. *International Journal of Adhesion and Adhesives*, 1998. 18(2): p. 95-107.
  49. Pizzi, A. and K.L. Mittal, *Handbook of adhesive technology*. 1994: Marcel Dekker Inc.

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## ***CHAPTER 5***

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## CHAPTER 5 – VOCs ISSUES

### 5.1. THE PERFORMANCE OF SCAVENGERS ON VOCs EMISSION IN PARTICLEBOARDS MADE FROM PINE AND POPLAR<sup>7</sup>

#### ***Abstract***

This paper studies the performance of scavengers on VOCs (Volatile Organic Compounds) emission from wood-based composites. Particleboards made from maritime pine (*Pinus pinaster*) and European poplar (*Populus* spp.) were produced with a UF resin doped with melamine and two scavengers, sodium metabisulphite and urea, were used. VOCs emission was measured according to ISO 16000. Particleboards made from pine present much higher TVOCs (total VOCs) emission than boards made from poplar. Pine emits a higher amount of terpenes, but also aldehydes, acids and terpenoids, while Poplar emits mainly acetic acid.

Sodium metabisulphite showed an excellent ability to reduce aldehydes emission, which represents near 50 % of total emission of particleboards made from pine. When sodium metabisulphite was applied to particleboards made from poplar, reduction on TVOCs was not significant due to the low contribution of aldehydes to TVOCs. Urea presents a diminished reduction on TVOCs for both wood species.

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<sup>7</sup> N. A. Costa, M. Ohlmeyer, J. Ferra, F. D. Magalhães, A. Mendes and L. H. Carvalho, *European Journal of Wood and Wood Products*, 2013, doi:10.1007/s00107-013-0761-9

### 5.1.1. Introduction

Wood trees can be divided into two broad classes: hardwood and softwoods. Despite their botanical differences, anatomically, hardwoods are porous, containing vessel elements, set above another, forming a continuous tube which serves as a conduit for transporting water or sap in the tree. Softwoods are usually cone-bearing plants with needles or scale-like evergreen leaves [1]. *Pinus pinaster* is one of the most softwoods common in Portugal, corresponding to more than 75 % of the total consumption of the sawmill industry [2] and also widely used in the production of particleboards (usually combined with other wood types, mainly eucalypt (*Eucalyptus globulus*) and recycled wood) [3]. Poplar is well known for its ability to adapt to different environments and for its integration and synergy with agriculture. In Europe, poplar plantations are 4 % of the total plantations; reaching more than 14 % in France, more than 18 % in Croatia and 19 % in Italy [4]. In natural stands the genus *Populus* is generally represented by several species, where *Populus nigra* and *Populus alba* are the most common in Iberia Peninsula [5].

In the last decades, there is an increasing concern about indoor air quality. Wood and wood-based panels release a low, but still detectable, amount of volatile organic compounds (VOCs) [6, 7]. The frequent use of wood-based panels in the house construction can often lead to elevated VOCs concentration, mainly due to terpenes and aldehydes [8]. VOCs emission from wood-based panels depends on production parameters, such as pressing time and temperatures, surface structure and storage conditions [9, 10].

VOCs release is usually measured in test chambers with 1 m<sup>3</sup>, however, studies carried by Makowski and Ohlmeyer [11] showed that minimal differences can be found in VOCs emission between tests carried in the large (1 m<sup>3</sup>) and small (23.5 L) chambers.

Wood contains several free compounds in its interlinked main cell wall constituents. Softwoods are usually rich in extractives and therefore can release substantial amounts of VOCs, mainly terpenes and aldehydes [12]. Terpenes and acids are strongly dependent on wood species, while

formaldehyde is related to the adhesive. Other aldehydes are formed under certain conditions, by autoxidative splitting of free unsaturated fatty acids and triglycerides [9, 13, 14]. Makowski and co-workers [9, 15] observed an increase in aldehydes emission during the first days, followed by a decrease in the last week. Terpenes are essential components for defence against insects and fungi and occur naturally in softwood oleoresin. Due to their relatively high vapour pressure at ambient temperatures terpenes are volatile and contribute to the characteristic odour of different wood species [12, 15]. Hardwoods release mainly a high amount of acetic and formic acid and less terpene compounds [16].

In the last years, the emission issues have been focused on VOCs. Germany and France were pioneers on VOCs regulations. In Germany, the health impact of VOCs is under evaluation by AgBB (Ausschuss zur gesundheitlichen Bewertung von Bauprodukten). Currently, German requirements are valid only for flooring products and define limits to emissions after 3 and 28 days for test pieces stored in a test chamber according to ISO 16000. AgBB establishes limits for carcinogen compounds, for each VOC as well as for total volatile organic compounds (TVOCs). French authorities established a mandatory labelling of construction products (covering wood products) according to the emission classes. Products labelling are marked as C, B, A and A+, being the last the tighter and the C class non-restrictive. No mandatory upper limits are established yet.

This paper evaluates the performance of formaldehyde scavengers (urea and sodium metabisulphite) on VOCs emission from particleboards made from two different wood species (pine and poplar). VOCs were collected in Tenax tubes, measured according to ISO 16000-6, during 28 days in a 23.5 L chamber and evaluated using a GC-MS. It must be noted that Tenax does not adsorb formaldehyde. Therefore this analysis does not account for formaldehyde emission from the resin. Only larger aldehydes and other VOCs, coming solely from the wood species, are quantified.

### 5.1.2. Material and methods

#### *Materials*

A last generation commercial UF resin was provided by EuroResinas – Indústrias Químicas, S. A. (Sines, Portugal). Maritime pine (*Pinus pinaster* Ait.) particles were supplied by Sonae Indústria PCDM, S. A. (Oliveira do Hospital, Portugal) and poplar (*Populus* spp.) particles were supplied by Sonae Indústria Tradema S.L. (Linares). Scavengers were provided by EuroResinas (urea) and purchased from Vaz Pereira, S. A. (Lisbon, Portugal) (sodium metabisulphite).

#### *Methods*

##### **Particleboard production**

Wood particles were blended with resin, paraffin and catalyst (ammonium nitrate) in a laboratory glue blender. For all trials, the resin load was kept constant (8 % based on oven dry wood). Face and core layer differ in the final moisture content (11 % and 8 %, respectively) and catalyst content (1 % and 3 %, respectively, based on solid resin). Sodium metabisulphite in powder form was spread after the blending operation. Solid urea (prills) used in core layer was spread after the blending operation while in face layer a 30 % solution was added prior to blending operation. Particleboards were hand formed in a square shape with 50 cm by side achieving a wood mass distribution of 20 % in the upper face layer, 60 % in the core layer and 20 % in the bottom layer. Boards were pressed at 190 °C during 160 seconds.

##### **VOCs evaluation**

Equipment, sampling as well as analytical procedures were according to ISO 16000 part 6 (2011) and part 9 (2006). Glass desiccators (23.5 L) were used as emission test chamber. Air exchange rate of 3.1 h<sup>-1</sup> was kept constant as well as temperature and relative humidity (23 °C and 50 %).

Sample area related to chamber volume was  $3.1 \text{ m}^2 \text{ m}^{-3}$ . Air samples (2 to 4 L) were pumped at the 1<sup>st</sup>, 3<sup>rd</sup>, 7<sup>th</sup>, 21<sup>st</sup> and 28<sup>th</sup> days from the test chambers. VOCs were collected in metallic tubes filled with Tenax TA. Compounds identification and quantification was performed in a gas chromatograph (Agilent 6895), coupled with a thermal desorption unit (Markes, UK) and a mass spectrometer (Agilent 5973N). Limit of quantification considered was  $5 \mu\text{g}\cdot\text{m}^{-3}$  as defined at AgBB. Emission results are expressed as concentration C of compounds in chamber air ( $\mu\text{g}\cdot\text{m}^{-3}$ ). Due to the selected loading factor and air exchange rate, as well as the relatively slow decay of the concentration over time, the results can also be read directly as area-specific emission rates (emission factors, SERa in  $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ), according to ECA report no. 18 (1997). TVOCs means total VOCs emission in the air sample. It is calculated by adding the concentrations of all single compounds detected in that air sample.

### 5.1.3. Results and discussion

Figure 5.1.1 shows emission from particleboards made from pine. It can be observed that aldehydes emission increased with time, presenting a small reduction after 28 days. This behaviour was already reported by Makowski and Ohlmeyer [9, 15] and could be related to oxidation of fatty acids. A small reduction of aldehydes emission is visible when urea is used. However, after 28 days this difference is negligible. Aldehydes released are mainly hexanal, but pentanal, nonal, octanal and heptanal are also found. When sodium metabisulphite is used, the reduction is substantial, showing the excellent ability of sodium metabisulphite to scavenge a wide range of aldehydes. The amount of acids (acetic) release was kept stable during the testing period and no significant differences on acid emission can be found when scavengers were used.

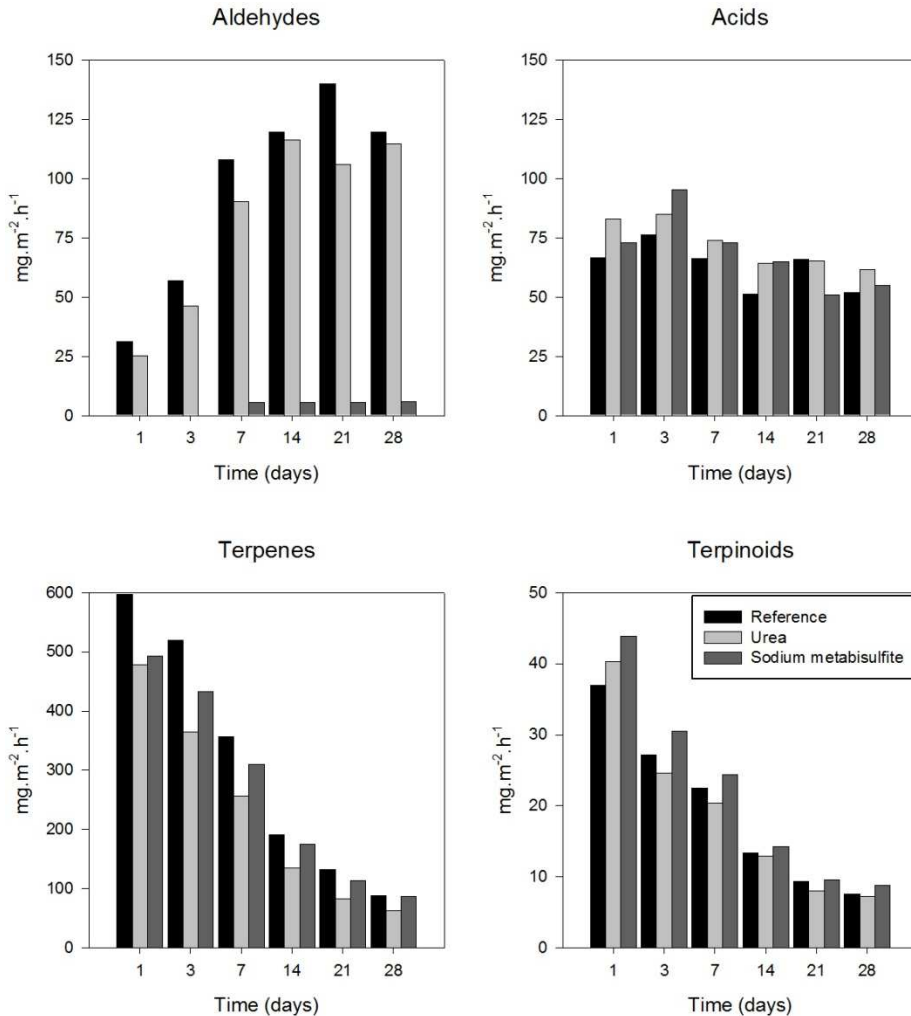


Figure 5.1.1 – Amount of VOCs (aldehydes, acids, terpenes and terpinoids) emissions from boards made from Maritime pine (*Pinus pinaster* Ait.)

Terpenes are the main source of VOCs from the particleboard made from pine, being these extractives responsible for its characteristic odour [15]. Terpenes from pine are mainly longifolene,  $\alpha$ -pinene and caryophyllene, corresponding to more than 90 % of the terpene emission after the 7<sup>th</sup> day. In the first days, emission of  $\beta$ -pinene, limonene and terpinolene can

also be found. Terpenoids emission is mainly terpineol, despite some camphor release can be found in the first day. No significant differences can be found when using different scavengers. Other compounds were also released in the first week, such as alcohols, ketones and hydrocarbons (fatty acids and waxes), and no significant differences were found between boards (not shown, but considered in TVOCs).

Figure 5.1.2 shows the VOCs release from particleboards made from poplar. VOCs emission is mainly acetic acid, but a small amount of aldehydes (hexanal) was also found. In the first week, it was also found some release of ketones, alcohols and hydrocarbons (not shown, but considered in TVOCs). No significant differences were found in particleboards with scavenger, except the total absence of aldehydes when sodium metabisulphite was used.

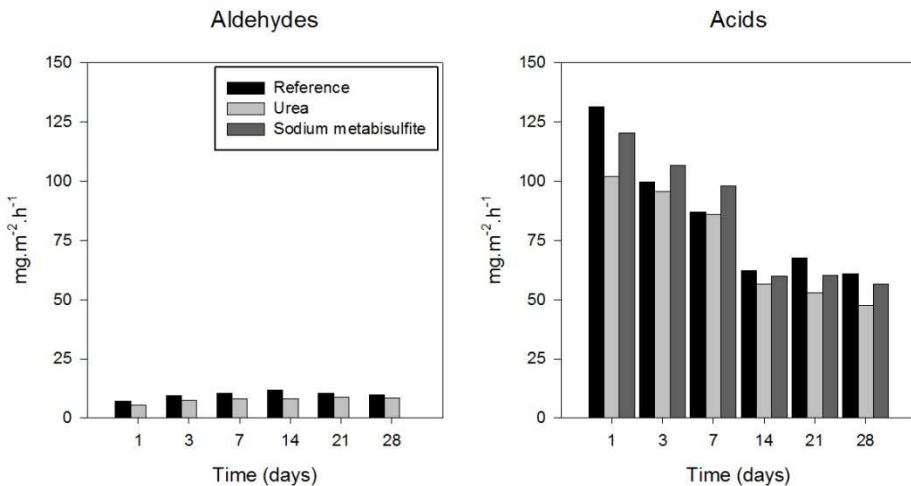


Figure 5.1.2 – Amount of VOCs (aldehydes and acids) emission from boards made from poplar

Small amount of longifolene (a terpene) emission was found during the first days in particleboards made from poplar. As stated in the literature, terpenes are not usual in hardwoods, being sesquiterpenes characteristics

from softwoods. In these special case, longifolene (a sesquiterpene) is typical from pine and spruce species [12], indicating that the presence of these compound could be related to some cross contamination, probably during the collection of wood particles in the industrial plant.

Figure 5.1.3 shows the TVOCs emitted from produced particleboards. Differences between boards made from pine and poplar can be clearly observed. Poplar boards present much lower VOCs emission than boards made from pine. Despite some reduction on TVOCs induced by urea during the test period, after 28 days, differences in total emission can be neglected. However, when sodium metabisulphite is used, a substantial reduction on total emission is found. This reduction is caused mainly due to the excellent ability of sodium metabisulphite to scavenge aldehydes. After 28 days, reduction induced by sodium metabisulphite is more than 40 % while reduction by the addition of urea is lower than 10 %. When poplar is used as wood raw material, no significant differences are found in TVOC emission during the whole testing period. This might be related to the reduced presence of aldehydes.

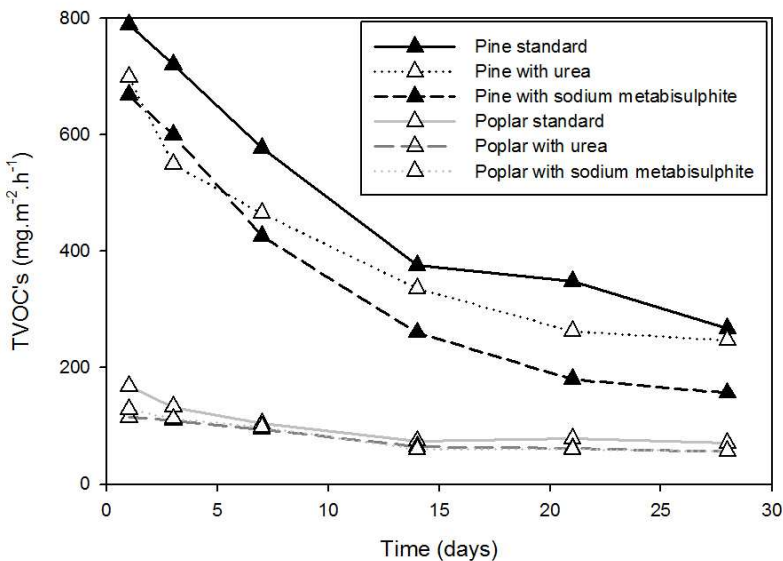


Figure 5.1.3 – TVOCs (total volatile organic compounds) emitted from the boards produced



#### 5.1.4. Conclusions

VOC scavenging ability of two formaldehyde catchers (sodium metabisulphite and urea) was tested using two different wood species: maritime pine (*Pinus pinaster*) and poplar (*Populus* spp.). Particleboards were produced using a low formaldehyde emission UF resin and were characterised according to the ISO 16000.

TVOCs emission from particleboards made from poplar is 25 % of the emission from pine. Boards made from pine emits higher amount of terpenes, acids as well as aldehydes while boards made from poplar emits mainly acetic acid. Addition of urea did not affect TVOCs, while sodium metabisulphite reduced more than 40 % of total emission of boards made from pine. When applied to boards made from poplar, reduction was negligible due to the lower emission of aldehydes. Sodium metabisulphite is an excellent aldehyde scavenger and is able to reduce substantially TVOCs from wood-based panels, when softwoods are used as raw-materials.

## 5.2. REFERENCES

1. Anonymous, Wood handbook: Wood as an engineering material. General Technical Report FPL-GTR-190. General Technical Report FPL-GTR-190. 2010, Madison, WI: U.S.: Forest Products Laboratory. Department of Agriculture, Forest Service, Forest Products Laboratory.
2. Associação das Indústrias de Madeira e Mobiliário de Portugal. Aplicações Industriais do Pinheiro Bravo. Available from: <http://www.aimmp.pt>, accessed on January 2013.
3. Martins, J., et al. Effect of recycled wood on formaldehyde release of particleboard. in COST Action E49 Conference "Measurement and Control of VOC Emission from Wood-Based Panels. 2007. Braunschweig, Germany.
4. Coaloa, D. and G. Nervo, Poplar wood production in Europe on account of market criticalities and agricultural, forestry and energy policy, in Third International Congress of Salicaceae. 2011: Neuquén, Argentina.
5. Carvalho, A., Madeiras Portuguesas, Vol II. 1997: Direção Geral das Florestas.

6. United States Environmental Protection Agency, Office of Air and Radiation. Report to Congress on Indoor Air Quality, Volume II: Assessment and Control of Indoor Air Pollution 1989.7. Roffael, E., Volatile organic compounds and formaldehyde in nature, wood and wood based panels. *Holz als Roh- und Werkstoff*, 2006. 64(2): p. 144-149.
8. Hodgson, A.T., D. Beal, and J.E.R. McIlvaine, Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house. *Indoor Air*, 2002. 12(4): p. 235-242.
9. Makowski, M. and M. Ohlmeyer, Influences of hot pressing temperature and surface structure on VOC emissions from OSB made of Scots pine. *Holzforschung*, 2006. 60(5): p. 533-538.
10. Ohlmeyer, M., et al., Influence of panel thickness on the release of volatile organic compounds from OSB made of *Pinus sylvestris* L. *Forest Products Journal*, 2008. 58(1-2): p. 65-70.
11. Makowski, M. and M. Ohlmeyer, Comparison of a small and a large environmental test chamber for measuring VOC emissions from OSB made of Scots pine (*Pinus sylvestris* L.). *Holz Als Roh-Und Werkstoff*, 2006. 64(6): p. 469-472.
12. Fengel, D. and G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*. 1989: Walter De Gruyter Incorporated.
13. Fischer, M. and K. Aehlig, Emission of VOC from wood and wood products – two case studies, in COST Action E49 Conference "Measurement and Control of VOC Emissions from Wood-Based Panels". 2007: Braunschweig.
14. Steckel, V., W. J., and M. Ohlmeyer, Emissions of volatile organic compounds from convection dried Norway spruce timber, in COST Action E53 Conference "The Future of Quality Control for Wood & Wood Products". 2010: Edinburgh.
15. Makowski, M. and M. Ohlmeyer. Influences on VOC Emissions of Wood-Based Panels. in 9th European Panel Products Symposium. 2005. Llandudno, Wales, UK.
16. Risholm-Sundman, M., et al., Emissions of acetic acid and other volatile organic compounds from different species of solid wood. *Holz als Roh- und Werkstoff*, 1998. 56(2): p. 125-129.

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## ***CHAPTER 6***

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## CHAPTER 6 – GENERAL CONCLUSIONS AND FUTURE WORK

### 6.1. GENERAL CONCLUSIONS

The objective of this thesis was to study the production of wood-based panels using urea-formaldehyde (UF) resins with low formaldehyde emission. This work was funded and developed in close cooperation with EuroResinas – Indústrias Químicas, S.A., a major Portuguese producer of formaldehyde based resins.

The first studies of this thesis are focused on the strongly acid process for UF resin synthesis. This synthesis process is not studied in depth and the resulting polymeric structure is not fully understood. However, presents some competitive advantages, but the resulting resins are less reactive due to the cyclic structures formed during the synthesis. During the strongly acid process study, the production of urons was minimized. The best pH and condensation temperatures were identified in order to optimize the particleboards properties, namely higher internal bond and lower formaldehyde content. The addition of sucrose (hydroxyl groups containing compound) was studied, investigating the effect of concentration and pH during addition. Sucrose addition under alkaline environment promotes premature consumption of formaldehyde that is essential to the cure reaction, originating boards with low formaldehyde content but with impaired physico-mechanical properties. On the other hand, addition of sucrose under strongly acid environment promotes sucrose dissociation into monosaccharides and favours their reaction with urea. These compounds continue to polymerise, becoming part of the UF polymer. The resin development originates particleboard with improved mechanical properties. Formation of cyclic structures was confirmed by Nuclear Magnetic Resonance (NMR) and reaction of sucrose with urea was supported by Raman spectroscopy and Gel Permeation Chromatography. Adhesive performance was assessed over produced boards.

Alternative catalysts for UF resins cure were tested in liquid and solid form. Phosphoric acid, in liquid state, was mixed directly to resin. Adhesive pot-life obtained was acceptable for industrial application without presenting problems related to pre-cure. Despite formaldehyde content of these particleboards, determined immediately after production, being higher than when using latent catalysts, after storage under forceful conditions, the formaldehyde content of the phosphoric acid catalysed particleboards was lower than when latent catalysts are used. These results were interpreted in terms of formation of hexamine by-product in latent catalysts. Complementary work was done to confirm this hypothesis and the contribution of hexamine to formaldehyde release in the perforator method was validated. Additional work was done using citric and oxalic acids: particleboards were produced with acceptable internal bond showing that these acids could be considered to produce low formaldehyde emission particleboards. Resin pre-cure was less significant when these catalysts in solid form were used.

In the fourth part of the thesis, formaldehyde scavengers were studied. Different application procedures were tested, and their performance was evaluated according to the most relevant methods for determining formaldehyde content and emission in wood-based panels, namely: perforator, gas analysis and desiccator methods. It should be emphasised that the validity of relationships between different methods is questionable, especially when very low formaldehyde emissions are considered. Particleboards with “zero formaldehyde emission” were produced using sodium metabisulphite.

In the fifth part of this thesis, VOCs emission from two wood species, *Pinus pinaster* Ait. (softwood) and *Populus* spp. (hardwood), was assessed, as well as VOCs reduction using the most promising formaldehyde scavengers. It was concluded that sodium metabisulphite presents an excellent ability to capture aldehydes, but has no effect on the reduction of terpenes, terpenoids, acids and even other volatile compounds. Urea has no effect on VOCs reduction.

A major challenge found during this work was the lack of scientific information concerning the effective production of wood-based panels with very low formaldehyde emission. Studies found in the scientific literature do not report efficient solutions, such as resins with an acceptable reactivity and suitable resin loads. The majority of solutions found increase considerably the final cost, being impracticable for standard products. Similar limitations are found in new formaldehyde-free adhesives. Despite the importance of these studies and innovative developments, this work was mainly focused on competitive solutions that could be directly introduced on the market. This work provides an important scientific contribution towards formaldehyde-based adhesives understanding as well as in the production of low emission wood-based panels.

## 6.2. FUTURE WORK

The use of urea-formaldehyde resins in wood-based panels industry has been questioned in the last years, mostly due to the concerns related to formaldehyde emissions. However, these adhesives are not expected to be replaced in an immediate future. Their advantages in terms of raw materials, production costs and performance are still very relevant for the industry. The recent developments in the reduction of formaldehyde emission, either by the optimization of resin synthesis and additives incorporation, as well as the combination with scavengers, brought an additional trump to formaldehyde-based resins.

In order to improve the adhesive performance, new additives should be studied and their role in the resin fully understood, as well as the interaction of the adhesive with wood structure, which is still under controversy. Bio-based additives and substitutes have shown good performance and further studies should be encouraged.

Concerning the catalysts for urea-formaldehyde adhesives, the lower performance of the latent catalysts was already reported but no effective alternatives were implemented. Solid-state citric and oxalic acids seem to have good performance on resin cure. However, these improvements still not convince when compared with latent catalyst. One way to improve the effectiveness of these catalysts is to assure that resin and catalysts meet each other in the early stages of pressing. This could be achieved by encapsulation of these catalysts, which would allow mixing with the liquid resin prior to the blending operation. These capsules should release the catalyst during the pressing operation.

Regarding formaldehyde scavengers, a similar approach should be considered. Encapsulation will allow the direct mixture to the resin, avoiding the premature consumption of formaldehyde. Furthermore, other scavengers should be studied, namely bio-based additives.

Beyond resin synthesis protocol optimization and the study of innovative scavengers, the study of wood as raw-material should not be discarded.



Drying operation conditions (such as temperature, contact time, etc.) should be studied in order to minimize formaldehyde (and other VOCs) emission contribution to the overall emission of the final product.

Until now, no limit values for the upper limit concentration of Volatile Organic Compounds (VOCs) emitted from wood-based panels has been indicated by official regulation in Europe. This circumstance led to focusing the efforts mostly on formaldehyde emission reduction. However, recently France and Germany defined new regulations concerning VOC emissions. Existing studies mainly concern raw materials and product characterization. Lately, new studies focusing on optimization of pressing operation parameters were published. Nevertheless, additional studies concerning the effect of the raw materials heat-treatments on the VOCs emissions of the final products, as well as the study and development of new VOCs scavengers are needed.



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***ANNEX I***

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ANNEX I – STANDARDS REFERRED IN THIS THESIS

- ANSI A 208.1-2009 – Particleboard Standard
- ANSI A 208.2-2009 – Medium Density Fiberboard Standard
- AS/NZS 4266-16 – Reconstituted wood-based panels – Methods of test.  
Method 16: Formaldehyde emission – Desiccator method
- ASTM A 1333-10 – Standard Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Chamber
- ASTM D 5582-00(2006) – Standard Test Method for Determining Formaldehyde Levels from Wood Products Using a Desiccator
- ASTM D 6007 - 02(2008) – Standard Test Method for Determining Formaldehyde Concentration in Air from Wood Products Using a Small Scale Chamber
- EN 120:1992 – Wood based panels - Determination of formaldehyde content - Extraction method called the perforator method
- EN 309:2005 – Particleboards - Definition and classification
- EN 310:1993 – Wood-based panels - Determination of modulus of elasticity in bending and of bending strength
- EN 312:2010 – Particleboards – Specifications
- EN 317:1993 – Particleboards and fibreboards - Determination of swelling in thickness after immersion in water
- EN 319:1993 – Particleboards and fibreboards - Determination of tensile strength perpendicular to the plane of the board
- EN 322:1993 – Wood-based panels - Determination of moisture content
- EN 323:1993 – Wood-based panels - Determination of density
- EN 717-1:2004 – Wood-based panels - Determination of formaldehyde release - Part 1: Formaldehyde emission by the chamber method
- EN 717-2:1994/AC:2002 – Wood-based panels - Determination of formaldehyde release - Part 2: Formaldehyde release by the gas analysis method
- EN 717-3:1996 – Wood-based panels - Determination of formaldehyde release - Part 3: Formaldehyde release by the flask method

- EN 13986:2004 - Wood-based panels for use in construction - Characteristics, evaluation of conformity and marking
- IOS-MAT 0003 (2009) – IKEA Specification - Formaldehyde requirements of wood-based materials and products
- ISO 12460-1:2007 – Wood-based panels - Determination of formaldehyde release - Part 1: Formaldehyde emission by the 1 cubic-metre chamber method
- ISO 12460-2:2006 – Wood-based panels - Determination of formaldehyde release - Part 2: Small-scale chamber method
- ISO 12460-3:2008 – Wood-based panels - Determination of formaldehyde release - Part 3: Gas analysis method
- ISO 12460-4:2008/Amd 1:2011 – Wood-based panels - Determination of formaldehyde release - Part 4: Desiccator method
- ISO 12460-5:2011 – Wood-based panels - Determination of formaldehyde release - Part 5: Extraction method (called the perforator method)
- ISO 16000-6:2011 – Indoor air - Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID
- ISO 16000-9:2006 – Indoor air - Part 9: Determination of the emission of volatile organic compounds from building products and furnishing - Emission test chamber method
- JAS 233:2003 – Plywood
- JAS MAFF 235:2003 – Structural Glued Laminated Timber
- JIS A 1460:2001 - Building boards Determination of formaldehyde emission - Desiccator method
- JIS A 1901:2009 – Determination of the emission of volatile organic compounds and aldehydes for building products - Small chamber method
- JIS A 1911:2006 – Determination of the emission of formaldehyde for building materials and building related products - Large chamber method
- JIS A 5905:2003 – Fibreboards
- JIS A 5908:2003 – Particleboards