

# Development of resins with very low formaldehyde emissions

*Nádia Tatiana Neto de Paiva*



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University of Porto

**Supervisors**  
Fernão Domingos de Magalhães  
Luísa Hora de Carvalho

**Enterprise coordinator**  
João Miguel Macias Ferra

**LEPABE – Laboratory for Process Engineering, Environment,  
Biotechnology and Energy**

Chemical Engineering Department

University of Porto – Faculty of Engineering

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Engenharia



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Coming together is a beginning.

Keeping together is progress.

Working together is success.

**-Henry Ford**



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## **ABSTRACT**

The present thesis is focused on the development of new formaldehyde-based resins with very low formaldehyde emissions during use as binders for wood-based panels. The industry associated to production of these materials represents an important sector in the national scene, with an annual production in 2013 of 1.7 million m<sup>3</sup>.

The adhesive system used in the production of wood based panels consists essentially in formaldehyde-based resins. Given the classification, by the International Agency for Research on Cancer (IARC) in 2006, of formaldehyde as "carcinogenic to humans", producers of wood-based panels, and therefore the producers of adhesives, were forced to reduce substantially the formaldehyde content of their products, driven by the increasingly demanding requirements of large clients such as IKEA.

In this study, the main objective was the development of three new resin formulations for different applications and purposes: i) a urea-formaldehyde resin (UF), or modified urea-formaldehyde resin, with low formaldehyde emission, for use in particleboard and medium density fibreboard; ii) a resin free of urea-formaldehyde bonds, for the same application, in order to achieve LEED certification; iii) a melamine-urea-formaldehyde resin with a water dilution capacity of at least 100%. These objectives correspond to the three central chapters of this thesis.

Regarding the development of a modified UF resin, the formulation was based on the strongly acid process, paying attention to the optimization of the process of melamine addition to the reaction mixture. It was also studied the influence of the formaldehyde/urea (F/U) molar ratio on the resin's

methylolation and condensation reactions evolution. Finally, it was studied the use of different catalysts in the production of wood-based panels with this new type of resin.

For developing a resin without urea-formaldehyde bonds, the synthesis process of a phenol-formaldehyde was studied in order to introduce innovative properties. Not only the traditional synthesis process had to be changed, but also the wood-based panel production process.

The strategy followed for the development of MUF resin with a high water dilution capacity was based on the addition of sodium metabissulphite during synthesis and the study of its effect on the structure of the resins produced.

The three major objectives outlined were successfully achieved, with five of the developed products being currently marketed by EuroResinas, the company that co-funded this PhD work.

## SUMÁRIO

A presente tese é focada no desenvolvimento de novas resinas à base de formaldeído com muito baixa emissão de formaldeído aquando da sua aplicação na produção de painéis de derivados de madeira. A indústria associada produtora destes materiais representa um sector importante no panorama nacional, sendo que em 2013 a produção anual foi de 1.7 milhões de m<sup>3</sup>.

O sistema adesivo utilizado na produção de painéis de derivados de madeira é constituído essencialmente por resinas à base de formaldeído. Desde a publicação por parte da *International Agency for Research an Cancer (IARC)*, em 2006, da classificação do formaldeído como “carcinogéneo para os humanos”, os produtores de painéis e por consequência os produtores de adesivos, viram-se obrigados a reduzir substancialmente o teor em formaldeído dos seus produtos, uma vez que a exigência de grandes clientes, como o IKEA, aumentou também consideravelmente.

Neste trabalho os objectivos foram essencialmente desenvolver três resinas para aplicações e finalidades diferentes: i) uma resina ureia-formaldeído (UF), ou ureia-formaldeído modificada, de baixa emissão de formaldeído, para aplicação em painéis de aglomerado de partículas de madeira e painéis de aglomerado de fibras de madeira de média densidade; ii) uma resina isenta de ligações ureia-formaldeído para a mesma aplicação, capaz de obter a certificação LEED; iii) uma resina melamina-ureia-formaldeído que permita a diluição em água a pelo menos 100 %. Estes três objetivos correspondem aos três capítulos centrais desta tese.

No que toca ao desenvolvimento de uma resina UF modificada, foi estudado essencialmente o processo fortemente ácido, efetuando-se a otimização da adição de melamina à mistura reaccional. Foi também estudada a influência da razão molar formaldeído/ureia (F/U) na evolução das reacções de metilolação e condensação das resinas. Por último, estudou-se a utilização de diferentes catalisadores na produção de painéis de aglomerados de madeira com esta nova tipologia de resina.

Para o desenvolvimento de uma resina isenta de ligações ureia-formaldeído, optou-se pelo estudo do processo de síntese de uma resina fenol-formaldeído com propriedades inovadoras. Foi necessário desenvolver várias alterações ao processo de síntese, bem como ao processo de produção de painéis de aglomerado de madeira.

A estratégia seguida para o desenvolvimento de uma resina MUF com elevada tolerância à água baseou-se na adição de metabissulfito de sódio durante a síntese, sendo estudado o seu efeito na estrutura das resinas produzidas.

Os três grandes objetivos delineados foram atingidos com sucesso, sendo que cinco dos produtos desenvolvidos são presentemente comercializados pela empresa EuroResinas, que co-financiou o trabalho de doutoramento.

## RÉSUMÉ

La présente thèse porte sur le développement des nouvelles résines à base de formaldéhyde avec une très faible émission de formaldéhyde, destinées à l'utilisation dans la production de panneaux à base de bois. L'industrie fabricant de panneaux à base de bois a un poids économique important dans la filière bois au Portugal, dont la production en 2013 a été de 1.7 millions de m<sup>3</sup>.

Le système adhésif utilisé dans la production de panneaux à base de bois est constitué essentiellement par des résines à base de formaldéhyde. À partir de la publication par *International Agency for Research on Cancer* (IARC), en 2006, de la classification du formaldéhyde comme du "cancérogène pour l'Homme", les producteurs de panneaux et par conséquent les producteurs d'adhésifs ont été obligés à réduire considérablement le teneur de formaldéhyde de ses produits, surtout depuis que l'exigence des grands clients, comme IKEA, a aussi augmentée.

Les objectifs de ce travail ont été le développement de trois résines pour usages différents: i) une résine urée-formaldéhyde (UF), ou urée-formaldéhyde modifiée de basse émission de formaldéhyde pour la fabrication de panneaux de particules et panneaux de fibres; ii) une résine sans liaisons urée-formaldéhyde pour la même usage, capable d'obtenir la certification LEED; iii) une résine mélamine-urée-formaldéhyde capable de permettre sa dilution en eau au moins 100 %. Ces trois objectifs correspondent aux trois chapitres centraux de cette thèse.

Dans ce qui concerne au développement d'une résine UF modifiée, le procédé fortement acide a été étudié, et l'optimisation de l'addition de mélamine à la mélange a été effectué. L'influence du rapport molaire formaldéhyde/urée

(F/U) dans l'évolution des réactions de méthylation et condensation des résines a été étudié. Finalement, l'utilisation des différents catalyseurs dans la production des panneaux de particules avec cette nouvelle typologie de résine a été étudiée.

Pour le développement d'une résine sans liaisons urée-formaldéhyde, on a choisi le procédé de synthèse d'une résine phénol-formaldéhyde avec des propriétés innovatrices. Il a été nécessaire développer plusieurs changements dans le procédé de synthèse, aussi bien que dans le procédé de production des panneaux de particules.

L'approche suivie pour le développement d'une résine MUF avec une grande tolérance à l'eau, a été basée sur l'addition de métabisulfite de sodium pendant la synthèse et son effet dans la structure des résines produites.

Les trois objectifs établis ont été atteints avec succès, dont cinq des produits développés dans le cadre de cette thèse sont maintenant commercialisés par l'entreprise EuroResinas, qui a co-financé le travail de doctorat.

# TABLE OF CONTENTS

## CHAPTER 1

1.	<u>Introduction</u> .....	3
1.1.	Formaldehyde-based Resins .....	3
1.1.1.	Urea-Formaldehyde and Melamine-Urea-Formaldehyde Resins .....	4
1.1.2.	Phenol-Formaldehyde Resins .....	16
1.1.3.	Resins Characterization.....	25
1.1.4.	Resins Applications.....	31
1.2.	Wood-based Panels Industry .....	35
1.2.1.	Raw materials for wood-based panels.....	36
1.2.2.	Particleboard Production .....	37
1.2.3.	Particleboard Characterization.....	39
1.2.4.	Wood-based Panels Market.....	40
1.2.5.	Formaldehyde Emissions .....	42
1.3.	Motivation and Outline.....	49
1.4.	References .....	51

## CHAPTER 2

2.	<u>Ultra Low Emitting Formaldehyde Resins</u> .....	65
2.1.	Production of a melamine fortified urea-formaldehyde resin with low formaldehyde emission .....	65
2.1.1.	Introduction.....	66
2.1.2.	Materials and Methods .....	70
2.1.3.	Results and Discussion.....	73
2.1.4.	Conclusions.....	80
2.2.	Study of the influence of synthesis conditions on the properties of melamine-urea-formaldehyde resins.....	82
2.2.1.	Introduction.....	83
2.2.2.	Materials and Methods .....	86

2.2.3.	Results and Discussion .....	91
2.2.4.	Conclusions.....	101
2.3.	Study of the cure of aminoresins with low formaldehyde emissions....	103
2.3.1.	Introduction.....	104
2.3.2.	Materials and Methods.....	106
2.3.3.	Results and Discussion .....	107
2.3.4.	Conclusions.....	113
2.4.	References .....	114

### CHAPTER 3

3.	<u>No Added Urea-Formaldehyde Resins</u> .....	119
3.1.	Development of a Phenol-Formaldehyde resin with low formaldehyde emissions that respects LEED® certification .....	119
3.1.1.	Introduction.....	120
3.1.2.	Materials and Methods.....	123
3.1.3.	Results and Discussion .....	126
3.1.4.	Conclusions.....	139
3.2.	References .....	140

### CHAPTER 4

4.	<u>Low Emitting Water Tolerant Formaldehyde Resins</u> .....	145
4.1.	Production of Water Tolerant Melamine-Urea-Formaldehyde Resin by Incorporation of Sodium Metabisulphite .....	145
	<i>Abstract</i> .....	145
4.1.1.	Introduction.....	146
4.1.2.	Materials and Methods.....	150
4.1.3.	Results and Discussion .....	153
4.1.4.	Conclusions.....	164
4.2.	References .....	165

## CHAPTER 5

5.	<u>General Conclusions and Future Work</u> .....	169
5.1.	General Conclusions .....	169
5.2.	Future Work .....	172



## LIST OF FIGURES

<b>Figure 1.1</b> Survey of industrial applications for formaldehyde and formaldehyde products (adapted from Salthammer et al. [6]) .....	4
<b>Figure 1.2</b> Formation of methylolureas (mono-, di- and tri) by the addition of formaldehyde to urea.....	11
<b>Figure 1.3</b> Influence of the pH on the rate constant for addition and condensation reactions of urea and formaldehyde (adapted from [38]).....	12
<b>Figure 1.4</b> Condensation of the methylolureas and methylolmelamines to form methylene-ether and methylene bridges .....	13
<b>Figure 1.5</b> Example of structure of a crosslinked UF resin.....	14
<b>Figure 1.6</b> Structure of Resol Resin (adapted from [65]).....	20
<b>Figure 1.7</b> Structure of Novolac Resin (adapted from [65]).....	21
<b>Figure 1.8</b> Formation of methylolphenols (mono-, di- and tri) by the addition of formaldehyde to phenol.....	22
<b>Figure 1.9</b> Methylolphenols condensation in order to create a phenol-formaldehyde network polymer.....	23
<b>Figure 1.10</b> Classification of wood-based panels by particle size, density and process type (adapted from [138]) .....	36
<b>Figure 1.11</b> Particleboard process diagram (adapted from [145]) .....	38
<b>Figure 1.12</b> Evolution of the production of wood-based panels in the world since 1961 to 2013.....	41
<b>Figure 1.13</b> Evolution of the production of wood-based panels in Portugal since 1961 to 2013.....	42
<b>Figure 1.14</b> A schematic diagram of linkage between the different chapters present in this thesis.....	51
<b>Figure 2.1</b> Formation of methylolureas and methylolmelamines (mono-, di- and tri) by the addition of formaldehyde to urea and to melamine.....	69
<b>Figure 2.2</b> Condensation of the methylolureas and methylolmelamines to form methylene-ether and methylene bridges.....	70
<b>Figure 2.3</b> Chromatograms of UF resins produced in fifth synthesis attempt .....	79
<b>Figure 2.4</b> Formation of methylolureas (mono-, di- and tri) by the addition of formaldehyde to urea.....	86
<b>Figure 2.5</b> Formation of methylolmelamines (mono-, di- and tri) by the addition of formaldehyde to melamine .....	87

<b>Figure 2.6</b> Condensation of the methylolureas and methylolmelamines to form methylene-ether and methylene bridges.....	88
<b>Figure 2.7</b> Normalized response of RI sensor for MUF resins produced in the first approach.....	93
<b>Figure 2.8</b> Normalized response of RI sensor for MUF resins produced in the second approach.....	95
<b>Figure 2.9</b> Reaction between two methylolureas in order to form a methylol derivate of methylene diurea (rate constants from [28]) .....	96
<b>Figure 2.10</b> Reaction between one methylolureas and one urea in order to form a methylene diurea (rate constants from [28]) .....	96
<b>Figure 2.11</b> Reaction between one methylolureas and one urea in order to form a methylene diurea (rate constants from [28]) .....	97
<b>Figure 2.12</b> Normalized response of RI sensor for MUF resins produced in the third approach.....	99
<b>Figure 2.13</b> Conceptual representation of the bond forming and test geometry (adapted from [35]).....	107
<b>Figure 2.14</b> Gel time variation according to the amount of hardener.....	108
<b>Figure 2.15</b> Experimental data obtained in the ABES tests with ammonium sulphate to different temperatures.....	109
<b>Figure 2.16</b> Experimental data obtained in the ABES tests with ammonium bisulphite to different temperatures.....	110
<b>Figure 2.17</b> Model fitting to the experimental data obtained in the ABES tests with ammonium sulphate for different temperatures.....	111
<b>Figure 2.18</b> Model fitting to the experimental data obtained in the ABES tests with ammonium bisulphite for different temperatures.....	111
<b>Figure 3.1</b> Structure of Novolac and Resol Resins.....	122
<b>Figure 3.2</b> Development of viscosity during the condensation reaction for Resins A and B Structure of Novolac and Resol Resins .....	129
<b>Figure 3.3</b> Resin viscosity evolution during 21 days (Resin A – 4 % alkaline content; Resin B – 8 % alkaline content) .....	130
<b>Figure 3.4</b> Development of viscosity during the condensation reaction for Resins B, C and D.....	132
<b>Figure 3.5</b> Resin viscosity evolution during 21 days ([Fa]: Resin B < Resin C < Resin D) .....	133
<b>Figure 3.6</b> Resin viscosity evolution during 21 days ([Fa]: Resin B < Resin C < Resin D) .....	136

<b>Figure 3.7</b> Development of viscosity during the condensation reaction for Resins B1, B2 and B3.....	137
<b>Figure 3.8</b> Resin B1, B2 and B3 viscosity evolution during one month.....	138
<b>Figure 4.1</b> Reactions between melamine and formaldehyde giving a methylolmelamine (a) and between methylolmelamine and sodium bisulphite (b) .....	148
<b>Figure 4.2</b> Evolution of viscosity during the condensation reaction, after addition of MTBS .....	155
<b>Figure 4.3</b> Resins viscosity evolution during 1 month of stability .....	156
<b>Figure 4.4</b> Resins water dilution capacity during 1 month of stability. Resin 4 is not shown in the figure, since it showed water dilution capacity above 100 in all measurements .....	157
<b>Figure 4.5</b> Chromatograms of MUF resins .....	158
<b>Figure 4.6</b> Chromatograms of samples taken from Resin 1 during the condensation step (1: 0 min, 2: 30 min, 3: 60 min, 4: 90 min, 5: 120 min and 6: 150 min).....	159
<b>Figure 4.7</b> Chromatograms of samples taken from Resin 4 during the condensation step (1 – 0 min, 2 – 30 min, 3 – 60 min, 4 – 90 min, 5 – 120 min and 6 – 150 min) ....	160
<b>Figure 4.8</b> Resin gel time evolution according to the amount of catalyst .....	161



## LIST OF TABLES

<b>Table 1.1</b> Standards and methods for determination of formaldehyde [155].....	44
<b>Table 1.2</b> Classification of particleboards panels according to the formaldehyde emission level.....	47
<b>Table 1.3</b> Relation between different existing methods and standards (Note*: Values obtained by correlations [159]).....	48
<b>Table 2.1</b> Operation conditions for the first four synthesis strategies .....	74
<b>Table 2.2</b> Particleboard properties obtained in the first four synthesis attempts .....	75
<b>Table 2.3</b> Properties of UF resins produced in fifth synthesis attempt .....	76
<b>Table 2.4</b> Particleboards properties obtained in fifth synthesis attempt .....	77
<b>Table 2.5</b> Particleboards properties produced with different UF resins.....	80
<b>Table 2.6</b> Properties of MUF resins produced in the first approach .....	92
<b>Table 2.7</b> Physico-mechanical properties of MUF resins produced in the first approach .....	94
<b>Table 2.8</b> Properties of MUF resins produced in the second approach.....	94
<b>Table 2.9</b> Physico-mechanical properties of MUF resins produced in the second approach.....	98
<b>Table 2.10</b> Properties of MUF resins produced in the third approach .....	99
<b>Table 2.11</b> Physico-mechanical properties of MUF resins produced in the second approach.....	100
<b>Table 2.12</b> Physico-mechanical properties of MUF resins produced in the second approach.....	101
<b>Table 2.13</b> Fitted parameters of the resin cure model ( $\tau_{max}$ : maximum shear strength; $t_0$ : resin gel time and $R^2$ : determination coefficient) .....	112
<b>Table 2.14</b> Gel time comparison between the two hardeners for the two methods..	113
<b>Table 3.1</b> Resins A and B final properties .....	127
<b>Table 3.2</b> Resins B, C and D final properties .....	132
<b>Table 3.3</b> Internal bond strength results for Resin A and B produced with different pressing times .....	134
<b>Table 3.4</b> Blending conditions for particleboard production optimization.....	135
<b>Table 3.5</b> Properties of the PF resins produced with 9 % of alkaline content.....	136

<b>Table 3.6</b> Resins B1, B2 and B3 particleboard properties produced with conditions C4 .....	139
<b>Table 4.1</b> Process variables and final properties of MUF resins .....	154
<b>Table 4.2</b> Particleboards Properties produced with MUF Resins.....	163
<b>Table 4.3</b> Particleboards properties produced with different MUF resins.....	164

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# ***CHAPTER 1***

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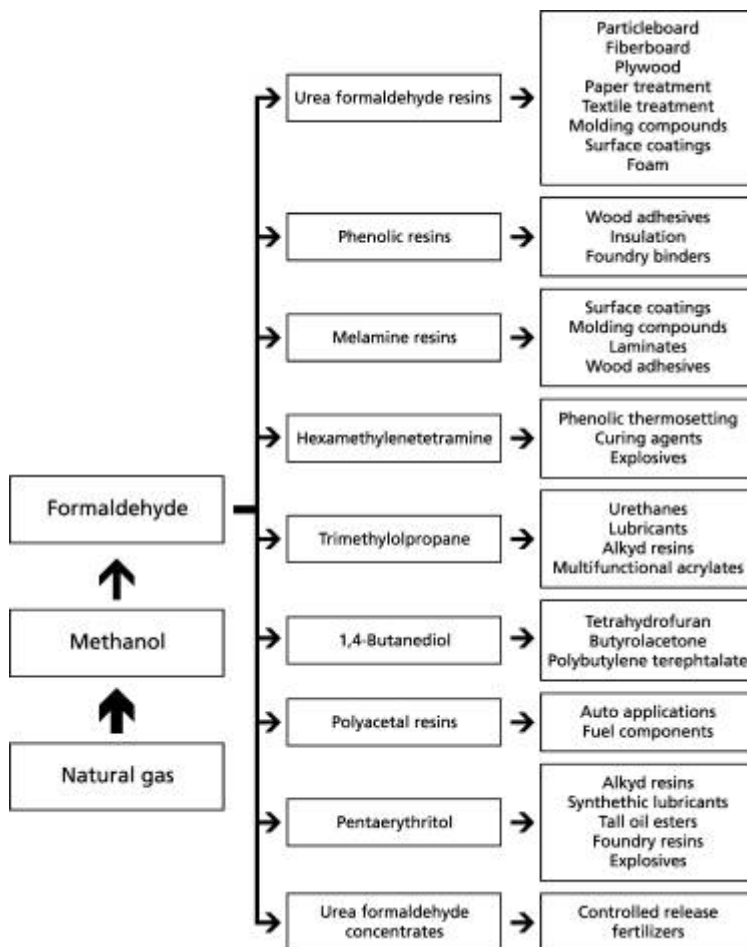
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## 1. Introduction

### 1.1. Formaldehyde-based Resins

Formaldehyde is an important chemical for the global economy, widely used in the production of thermosetting resins, as an intermediate raw material in the synthesis of several chemicals, and for preservation and disinfection [1, 2]. The global production capacity of formaldehyde surpassed the 46.4 million tonnes, in 2012. The Asian-Pacific region held a share of 56 % of the world's total formaldehyde capacity. It was followed by Europe and North America, accounting for 22 % and 15.83 % shares, respectively. China was an unrivalled leader in terms of formaldehyde capacity, accounting for over 51 % of the total capacity. In 2017, the global formaldehyde production is anticipated to exceed 52 million tonnes [3]. Urea-, phenol- and melamine-formaldehyde resins (UF, PF and MF resins) accounted for about 63 % of formaldehyde world consumption in 2011; other large applications include polyacetal resins, pentaerythritol, methylenebis(4-phenyl isocyanate) (MDI), 1,4-butanediol and hexamethylenetetramine [4]. In 2003, the value of sales of formaldehyde and derivatives products in United States and Canada reached approximately USD\$ 145 billion. The number of workers involved in related activities was reportedly 4.2 million, which represents nearly 3.4 % of employment in private, nonfarm establishments in North America [5]. Figure 1.1 summarizes the industrial uses of formaldehyde and related products.



**Figure 1.1** Survey of industrial applications for formaldehyde and formaldehyde products (adapted from Salthammer et al. [6])

### 1.1.1. Urea-Formaldehyde and Melamine-Urea-Formaldehyde Resins

Amino resins are polymeric products of aldehyde reaction with compounds carrying  $-NH_2$  and  $-NH$  groups. Such groups are mainly amide groups, such as those in urea and melamine. They constitute the most important members of this class of compounds, more so than the amine groups as in the case of aniline. Formaldehyde is the main aldehyde used. Other aldehydes, such as furfural, are generally not used for wood adhesives. The advantage of amino resin adhesives are their initial water solubility, hardness, non-flammability,

good thermal properties, absence of color in cured polymers and easy adaptability to a variety of curing conditions. Although many amidic and aminic compounds have been investigated for use in production of amino resins, only urea and melamine and, in rare cases aniline, are extensively used [7].

Amino resins are manufactured throughout the industrialized world to provide a wide variety of useful products. Adhesives, representing the largest single market, are largely used in the wood-based panels (WBP) industry [8]. Urea-formaldehyde (UF) resins are the most used type of amino resins adhesives. Worldwide, these resins represent 80 % of the total production in the aminoresins class [9]. The remaining 20 % correspond mainly to melamine-formaldehyde (MF) resins, with a small percentage of resins synthesized from other aldehydes and/or other amino compounds [10]. According to SRI Consulting [11], the global production of UF resins in 2008 was approximately 14 million ton. Their consumption increased 2.8 % in 2008, and is expected to grow an average 3.2 % per year from 2008 to 2013, and just under 2 % per year from 2013 to 2018. Urea-formaldehyde polymers have been for decades the most widely used adhesives in the manufacture of wood-based panels, such as particleboard (PB), medium density fibreboard (MDF) (both consuming 68 % of the world's UF resins productions) and plywood (consuming 23 %) [11, 12]. For example, the North America's production of formaldehyde-based resin in 1999 was 3.3 million tons, of which 56.6 % is UF resins and 40.3 % is PF resins [13]. On the other hand, the production of wood adhesive in European countries was 5.1 million tons in 2003, of which 69.6 % was UF resins [14]. In China, about 1.8 million tons of wood adhesives were produced, and about 63.4 % was UF resins in 2003 [15].

## ***History***

The first published studies about the reaction between urea and formaldehyde were the works by Tollens in 1884 [16]. The basic chemistry of amino resins was established around 1908 [17]. Carl Goldschmid published in 1986, a widely cited work that reported the formation of a precipitate as the result of the reaction between urea and formaldehyde under acidic conditions [18]. This precipitate was empirically identified as  $C_5H_{10}O_3N_4$  and later identified by Carlson as a cyclically structured condensation product (now called urons) [19].

The first patent disclosing production of the UF polymer is dated around 1918 and was issued to Hanns John [20], but the first commercial products were manufactured by E.C. Rossiter of British Cyanides Co. only in 1924. In 1925 this company developed moulding materials that are still use nowadays. A major step forward in the industrialization of amino resins became possible after the patent by A. Schmid and M. Himmelheber, in which the authors establish the basis for resin-bonded particleboard [21]. The industrial production of UF resins for the wood-working industry started in 1931 at the former IG-Farbenindustrie (now BASF) in Ludwigshafen, Germany. The main expansion for UF resins started with the development of particleboard as a new wood-based panel after World War II, with a tremendous increase in production rate up through the 1980s [22].

UF resin adhesive possesses some advantages such as fast curing, good performance in the panel, water solubility and lower price. Disadvantages of using the UF resins are the formaldehyde emission from the wood-based panels and lower resistance to water [23].

Free formaldehyde present in UF resin and hydrolytic degradation of UF resin under moisture condition has been known as responsible for the formaldehyde

emission from wood-based panels [24]. In other words, un-reacted formaldehyde in UF resin after its synthesis could be emitted from wood panels even after hot-pressing at high temperature. In addition, the reversibility of the aminomethylene link and its susceptibility to hydrolysis also explains lower resistance against the influences of water and moisture and, as consequence, the formaldehyde emission. This issue has been one of the most important aspects of UF resins studied in the last few decades [25-28].

Reduce or control of the formaldehyde emission from the UF resin bonded panels has been essentially studied in terms of resin technologies. Until the mid-sixties, most UF resins were synthesized by the two-step reaction process: methylation and condensation reactions [29]. This synthesis process was widely employed for UF resins preparations for a long time. In the early seventies, however, this method faced the serious problem of formaldehyde emissions. So, lowering the formaldehyde to urea mole ratio (F/U) for the synthesis of the UF resin was adopted as one of the approaches to reduce the formaldehyde emission from the wood based panels produced with UF resins [30]. Thus, lower F/U molar ratio, from 1.1 to 1.2, started to be used. This change had a great impact on the manufacturing process (implying higher press times and temperatures) and on the physical properties (lower bonding strength and moisture resistance) of the wood based panels [31]. The decreasing of F/U molar ratio leads to a decrease in the formaldehyde emission, but increases the thickness swelling and water absorption. [30]. In recent years, it was reported that resins with different F/U molar ratios have quite similar structures and performance, leading to the conclusion that this property is the most important factor in their synthesis [32].

Lower resistance to water limits the use of wood-based panels bonded with UF resins to interior applications. However, the formaldehyde emission from the

panels used for interior applications was one of the factors, affecting sick building syndrome in indoor environment [33]. This lower resistance to water is a consequence of the susceptibility of the aminomethylene linkage to hydrolysis and therefore this linkage is not stable at higher relative humidities, especially at elevated temperatures [23]. Water also causes degradation of the UF resin, the effect being more devastating the higher the water temperatures are. This different behaviour of wood based panels bonded with UF resins at various temperatures is the basis for standard testes and hence for the classification of bondlines, resins and wooden products. The incorporation of melamine and sometimes phenol improves the low resistance of UF bonds to the influence of humidity, water and weather. However, this changes the characteristics of the resins, especially concerning their reactivity. Additionally, the costs for these modified and fortified products are not comparable because of the much higher price of melamine when compared with urea. Therefore, the content of melamine in these resins is always as high as necessary but as low as possible, pure melamine-formaldehyde resins being in use only when mixed with UF resins. However, the advantage of higher hydrolysis resistance in pure MF resins is counteracted by their low storage stability in liquid form and their very high price [22].

With the incorporation of a small percentage of melamine in the UF resins, more stable bonds are obtained when a methylene carbon is linked to an amide group from a melamine ring, instead of a nitrogen from urea [23]. This is especially true at high temperatures due to the quasiaromatic ring structure of melamine. However, the addition the slower pH decrease in the bond line due to the buffer capacity of melamine could also explain the higher stability of the bonds in melamine-urea-formaldehyde resins (MUF). This behaviour is the

same if the melamine is added to the UF resin just before gelation or if it is incorporated chemically in any way during manufacture of the resin.

The wide range of formulations for MUF resins originates different properties, performances and stabilities [9, 10]. One can distinguish two particular cases: MUF resins, where the melamine content is above 5 %, and melamine-fortified UF resins, with melamine content below 5 %. In both cases the production can be performed in different ways: co-condensation of all monomers, melamine, urea and formaldehyde, in a multistep reaction; mixing of separately synthesized MF and UF resins; and post-addition of melamine, in various forms (pure melamine, MF/MUF powder resin or melamine acetates) to an UF resin during the preparation of the glue mix [10].

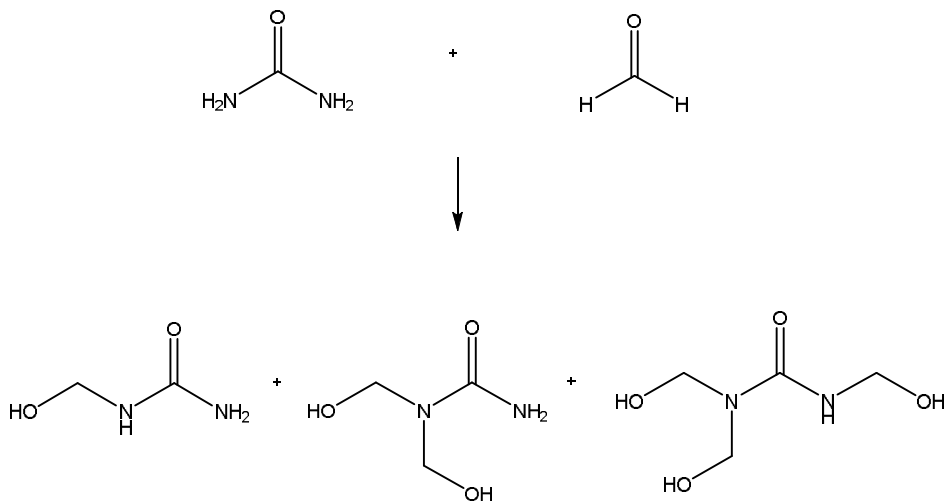
When added to the reaction mixture, melamine can enter in any of these steps: initial methylation step (before or after the addition of the first urea), condensation step (before or after the addition of the second urea), or final urea addition [34]. The studies by Shiau and Smith (1985), using an alkaline-acid process, showed that melamine addition is more effective in the methylation step. On the other hand, Hse studied melamine addition in a strongly acid process, and concluded that the best results were obtained for melamine addition during acidic condensation (pH between 4.5 and 6.5) [35]. This author essentially studied the melamine reaction with a UF pre-polymer formed in a strongly acid environment, the final MUF resin produced had an F/U molar ratio of 1.2, with 4.39 % (weight basis) maximum melamine content. MUF resins are produced and characterized according to the same procedures as UF resins.

### ***Synthesis Process – Chemical Reactions***

UF resins are based on only two main monomers, urea and formaldehyde, but they present a huge variety of possible reactions and structures [23]. Their basic characteristics can be explained at the molecular level by three main reasons: reactivity; water solubility, which renders them ideal for use in the woodworking industry; and reversibility of the aminomethylene link, which also explains the low resistance of UF resins against the influence of water and moisture, especially at higher temperatures. This last feature is also one of the reasons for their subsequent formaldehyde emission, when cured and in use [23].

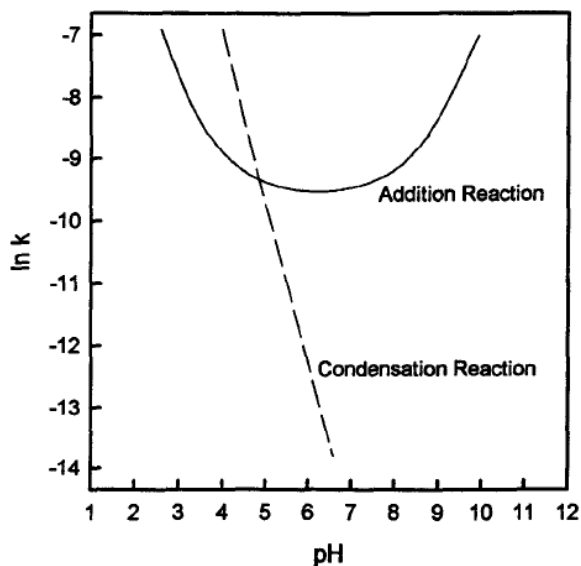
The use of different conditions of reaction and preparation could produce a broad variety of UF resins. The reaction of urea and formaldehyde is basically a two-step process: usually an alkaline methylation followed by an acid condensation. The combination of these two chemicals results in linear and/or branched as well as tridimensional network in the cured resin. [23] This is due to the functionality of four in urea (due to the four replaceable hydrogen atoms), and two in formaldehyde. The most important factors determining the properties of the reaction products are: the relative molar proportion of urea to formaldehyde, the reaction temperature and time, and the various pH values at which the condensation takes place [33].

In the first stage, methylation step, urea is hydroxymethylated by the addition of up to three (four in theory) molecules of the bifunctional formaldehyde to one molecule of urea to give the so-called methylolureas under basic conditions with a pH of 8-9 (Figure 1.2). This reaction is in reality a series of reactions that lead to the formation of mono-, di- and trimethylolureas.



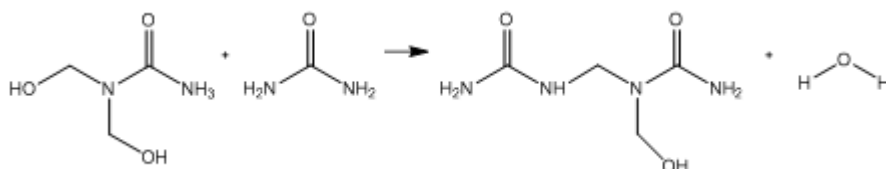
**Figure 1.2** Formation of methylolureas (mono-, di- and tri) by the addition of formaldehyde to urea

Each methylation step has its own rate constant for the forward and backward reactions. This reaction reversibility is one of the most important characteristics of the UF resins. This feature is the main responsible for the low resistance against hydrolysis caused by the presence of water or moisture and as consequence formaldehyde emission [23]. An important feature of these resins is the F/U molar ratio, which affects, the methylol groups produced during the methylation reaction, with higher molar ratios increasing the tendency to form highly methylolated species [36, 37]. Secondary products of the methylation reaction are acetals, hemiacetals and etherified products, with residual methanol always present in small amounts from the production of formaldehyde. The addition of formaldehyde to urea takes place over the entire pH range. The reaction rate is dependent on the pH (Figure 1.3). The rate for the addition of formaldehyde to successively form one, two and three methylol groups has been estimated to be in the ratio of 9:3:1, respectively [38]. The exact ratio is dependent on the reaction conditions employed in the addition reaction.



**Figure 1.3** Influence of the pH on the rate constant for addition and condensation reactions of urea and formaldehyde (adapted from [38])

The formation of UF or MUF polymer occurs during the acidic condensation where the methylols (mono-, di- and trimethylolureas or mono-, di- and trimethylolmelamines), free urea and formaldehyde still present in the system react to give linear to partly branched molecules with medium to high molar masses (Figure 1.4) [23]. The condensation mainly occurs in an acidic environment and the rate of the condensation reactions is very dependent on the value of pH that is used (Figure 1.3). The type of bond between the urea molecules depends on the conditions used. In the case of low temperatures and only slightly acidic pH the formation of methylene ether bridges ( $-\text{CH}_2\text{-OH-CH}_2-$ ) is favoured. On the other hand, higher temperatures and lower pH's lead to the more stable methylene bridges ( $-\text{CH}_2-$ ). Methylene ether bridges are more stable than ether bridges, due to the necessity of the presence of two formaldehyde molecules in the ether bond. So this last bond can be rearranged to methylene bridges by splitting off formaldehyde.



**Figure 1.4** Condensation of the methylolureas and methylolmelamines to form methylene-ether and methylene bridges

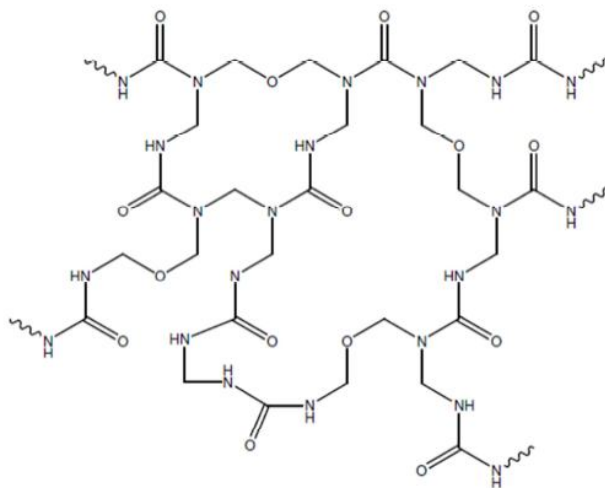
During manufacture, progress of synthesis reaction is followed by viscosity measurement; the reactions proceed until the desired viscosity is reached. At this point, the reactions are blocked by neutralization and cooling, resulting in a complex mixture of molecules with different sizes and different condensation degrees [10].

An alternative strategy is the strongly acid process [39-42]. In this case the initial reaction is carried out under strongly acidic environment, in which the methylation and condensation reactions occur simultaneously. The methylation step consists in the reaction between urea, melamine and formaldehyde to form the so called methylolureas. At this low pH, however, these species react almost instantly to form linear and/or branched polymers linked by methylene-ether and methylene bridges. The released heat is sufficient to drive the reaction to the desired condensation level, and can be controlled by a programmed addition of urea to the acidified formaldehyde solution. This process may reduce the reaction time by 30 % in relation to the alkaline-acid process, with much lower energy consumption. The reduced formaldehyde emission and increased hydrolytic stability have been attributed to the predominance of the more stable methylene linkages in the cured resin, unlike the alkaline-acid process which leads to a larger amount of methylene ether linkages in the cured resin. The disadvantage of this process lies in the difficulty in controlling the highly acid condensation step, due to its exothermic

character [40]. According to Hatjiissaak and Papadopoulou [43], this implies careful control, which may be difficult to achieve on the industrial scale, to prevent resin gelling in the reactor.

### **Cure**

During the UF resin synthesis, the polymer condensation is stopped by neutralization and cooling. In order to reactivate it and complete the crosslinking process, it is needed to add an acid catalyst and increase the temperature. In the curing process a more or less three-dimensional network is formed and this yields to an insoluble resin that is no longer thermoformable (Figure 1.5). The hardening is basically, the continuation of the acidic condensation reaction [23].



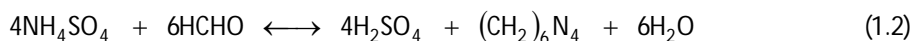
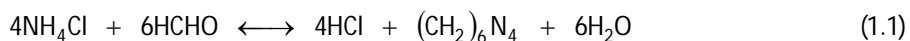
**Figure 1.5** Example of structure of a crosslinked UF resin

The acid conditions can be adjusted by the addition of a so-called latent hardener, or by the direct addition of acids (maleic acid, formic acid ,

phosphoric acid and others) or acid compounds which dissociate in water (ammonium chloride, ammonium sulphate and ammonium nitrate).

The curing of UF resins by direct addition of acids originates problems in equipments, wood degradation, and reduces considerably the pot life of the resin (stability time of the catalyzed resin) [23, 44-46].

On the other hand, the most common latent hardeners are ammonium sulphate and ammonium chloride. Use of ammonium chloride has been limited in some European PB and MDF mills, in countries such as Germany and Austria, for several years due to the formation of hydrochloric acid during combustion of wood-based panels, which results in corrosion problems and in the formation of dioxins (Equation 1.1) [23].



On the other hand, ammonium sulphate is the most used hardener in the PB and MDF plants. The product of its reaction with formaldehyde compound with formaldehyde is sulphuric acid, which decreases the pH of the medium (Equation 1.2). This, along with high pressing temperatures results in the gelling and hardening of the resin [23].

The reduction of the final F/U molar ratio from UF resins, due to formaldehyde emissions, originates a decrease in the performance of latent hardeners. This happens because these latent hardeners were originally selected to be used with resins with high levels of free formaldehyde. Several studies reported that the gel time and cure temperature increases with the decrease of the F/U molar ratio [47-50].

### **1.1.2. Phenol-Formaldehyde Resins**

Phenol-Formaldehyde (PF) resins are the polycondensation products of the reaction of phenol with formaldehyde, being the first true synthetic polymers to be developed commercially [51]. Since their first production in 1910, they have been developed enormously and remain one of the most important products of the plastic industry [52]. However, despite the fact that many studies have been made in order to understand the chemical structure of PF resins, this issue has not been yet fully clarified. This happens because the polymers derived from the reaction of phenol with formaldehyde are different from the ones found in other polycondensation products. In the case of PF resins the polyfunctional phenols can react with formaldehyde in ortho and para positions which will lead to condensation products with numerous positional isomerides for any chain length [51].

According with SRI Consulting [53] the global production and consumption of PF resins in 2008 were both approximately 3.25 million metric tons. Global capacity utilization was 62 % in 2008. PF resins consumption is estimated to have increased by 2.5 % in 2008, and is expected to average growth of 3.2 % per year from 2008 to 2013, with slower demand of around 2.7 % per year from 2013 to 2018.

The largest end use of PF resins is for the production of wood adhesives, accounting for around 35 % of total global consumption. Other applications include moulding compounds, insulation and laminates manufacture, abrasive papers and rigid foams. Phenolic resin consumption for moulding compounds (accounting for about 20 % of world consumption) will grow primarily in China and Other Asia as more moulding operations start up in the region. Laminates account for about 28 % of the world market [53].

PF resins show a very high resistance of the C-C-bonding between the aromatic nucleus and the methylolgroup or methylene bridge, and therefore are used for water and weather resistant glue lines and wood-based panels, like particleboards, OSB, MDF or plywood. Another advantage of the phenolic resins is the very low subsequent formaldehyde emission also due to the strong C-C-bonding [54].

### ***History***

Phenol reacts readily with formaldehyde under both acid and alkaline conditions to yield a wide array of products containing anywhere from one to great many phenolic nuclei [55]. The first report of the general reaction was made in 1872 by Bayer who found that phenol and acetaldehyde combined in the presence of an acid catalyst gives an unmanageable resinous mass [55]. In 1899, Arthur Smith filed a patent application where he described a method for a cast cured resin substitute for hard rubber [56].

In 1905, with a conviction that the reaction could be directed to give a commercially valuable product, Baekeland started to work with formaldehyde and phenol [57]. Controlling, the pressure and temperature applied to phenol and formaldehyde reactor, he was able to produce hard mouldable plastic: Bakelite. Bakelite is essentially a combination of phenol-formaldehyde resin with wood. Baekeland's process patent for making insoluble products of phenol and formaldehyde was filed in July 1907, and granted on December 7, 1909. By 1907 he had defined the differences between synthesis conditions, pH (acid or alkali) and molar ratio between formaldehyde and phenol, which permitted to manufacture a reproducibly thermosetting resin.

Between 1928 and 1931 phenolic resins gained increased importance through the treatment of resols with fatty oils to give air drying varnishes. The main

problem, an inadequate compatibility of phenolic resins with other varnish raw materials, was solved by using alkyl phenols or by etherification of the hydroxymethyl groups of resols with monohydric alcohols [58].

These varnish applications and the use of phenolic resins as thermosets and electrical insulating materials were the main application areas. However, other polycondensates and, above all, other polymers increasingly limited the market for phenolic resins from the mid 1930s onwards. Theoretical work on the constitution and mechanism of formation of phenolic resins was being carried out at that time by Von Euler, Hultsch, Megson [59], Ziegler, and others, which led to the development of new application areas for phenolic resins, such as adhesives, printing-ink binders, waterborne paints, temperature-resistant binders, and laminated plastics [58]. However, the rapid industrial development and increasingly extensive commercial applications of phenolic resins has been marked more by steady and continuous progress than outstanding landmarks [52].

### ***Synthesis Process - Principal Products***

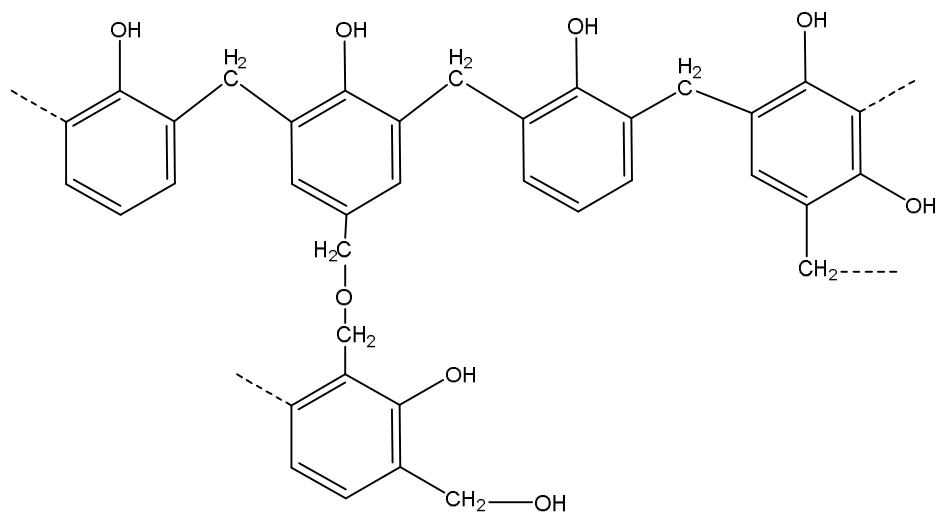
PF final properties are determined mainly by the molar ratio F/P [60], the concentration of two raw materials phenol and formaldehyde in the resin, the degree of condensation [61], the type and amount of the catalyst and the reaction conditions [54]. So, depending on these variables, the products of the condensation of a phenol with formaldehyde can be considered as thermosets, known as Resol, or as thermoplastics, known as Novolac.

Resol resins, which are highly branched, low molecular weight (150-1500) polymers with stoichiometric ratio formaldehyde-phenol between 1.2 to 3, formed at alkaline pH [62]. Characteristic functional groups of this class of resins are the hydroxymethyl group and the dimethylene ether bridge, both

reactive groups [58, 63]. Polycondensation reaction is stopped by cooling the reaction mixture. However, if the reaction mixture is reheated, the resol molecules are reactivated in order to react with each other and form larger molecules without hardener addition. The function of phenols as nucleophiles is improved by ionization of the phenol [51].

Due to the low yield of the phenol and formaldehyde condensation under the normal reaction conditions, a typical resol resin contains a high percentage of free monomers. These free monomers are volatile and highly toxic. Reducing the level of the free monomers in such resins, thus reducing their emissions into the environment during application processes, has been one of the most heavily researched areas by both phenolic resin producers and resin users for many years [64].

The structure of a resol resin depends not only on the choice of raw materials and their molar ratios, but also on the temperature of formation, concentration of raw materials, presence or absence of solvents, type of catalyst and concentration of catalyst [58]. A resol prepolymer differs from a novolac resin in that it contains not only methylene bridges but also reactive methylol groups and dimethylene ether bridges (Figure 1.6) [65].

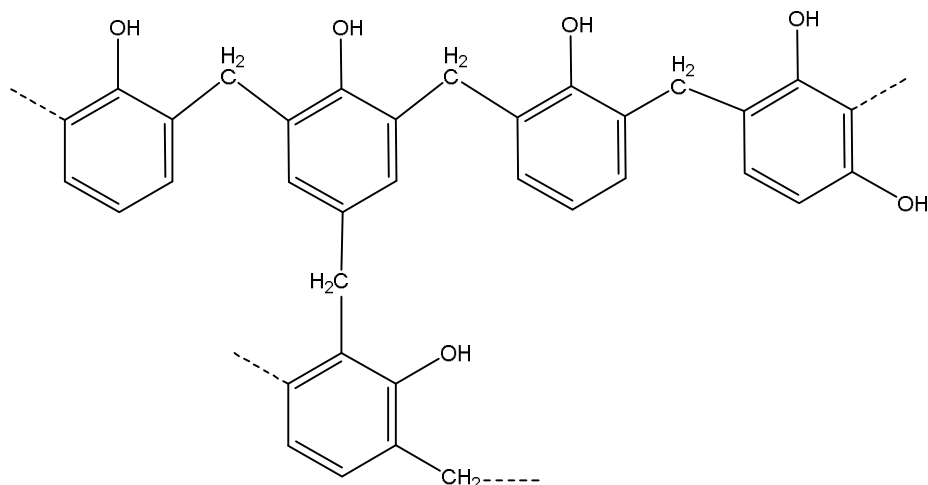


**Figure 1.6** Structure of Resol Resin (adapted from [65])

Novolacs, made at acid pH, with stoichiometric ratio formaldehyde-phenol between 0.5 and 0.8, which have a different and much less branched structure than resols. They are low molecular weight (500-5000) polymers [62]. Basically novolac resins are phenols that are linked by alkylidene (usually methide) bridges, without functional groups, apart from the phenolic hydroxyl groups, and cannot cure on their own. During their synthesis the hydroxymethyl compounds formed are unstable, due the acidic environment and are rapidly converted into compounds linked by methylene bridges (Figure 1.7) [51, 58, 63].

A curing agent, such as formaldehyde or hexamethylenetetramine, is added to cross-link the novolac resin in order to give an end product similar to a resol resin [51].

Novolac resins are sometimes used as chemically unmodified synthetic resins. Their main application is based, however, on their capability to undergo cross-linking with hexamethylenetetramine [58].

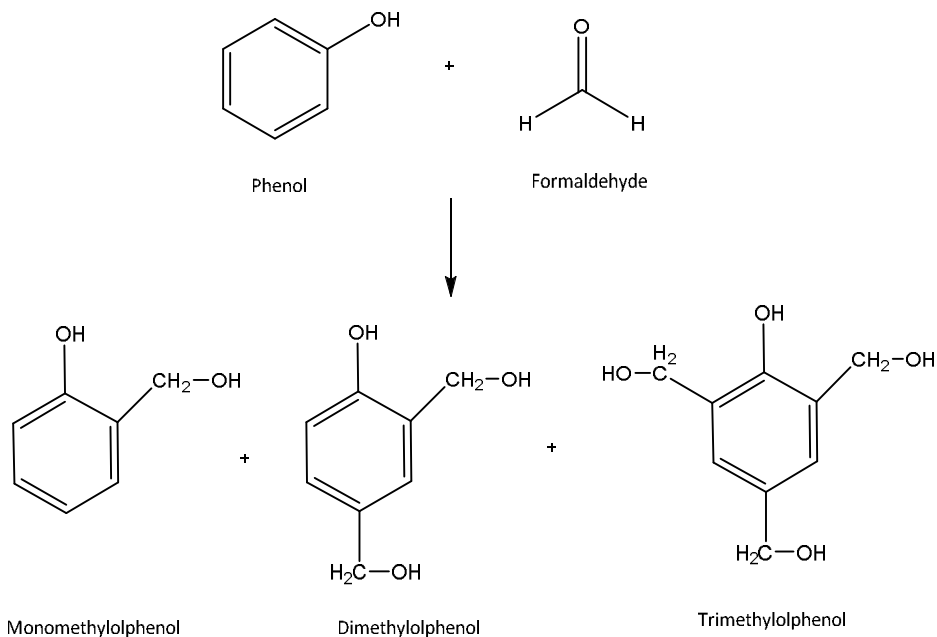


**Figure 1.7** Structure of Novolac Resin (adapted from [65])

The classification of phenolic resins into novolacs or resols is only strictly valid if phenols which are trifunctional towards formaldehyde are used as starting material, because resols from bifunctional phenols cannot crosslink by themselves. Nevertheless, the polycondensates, from substituted phenols are differentiated according to their characteristic groups as alkyl phenol novolac (alkylidene bridges) or alkyl phenol resols (hydroxymethyl group, dimethylene ether bridge) [58].

### ***Synthesis Process - Mechanism***

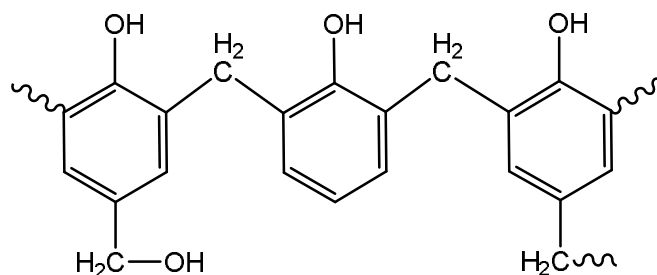
The first stage of the synthesis of a conventional product PF resin involves an electrophilic attack of the carbonyl compound (typically formaldehyde) in positions ortho or para of the phenol molecule. The product of this reaction may be either an ortho- or para-methylolphenol which can then further react with formaldehyde to form di- and trimethylolphenol (Figure 1.8) [51]. This reaction is strongly exothermic and includes the risk of an uncontrolled reaction, due for example to a high initial formaldehyde concentration [66].



**Figure 1.8** Formation of methylolphenols (mono-, di- and tri) by the addition of formaldehyde to phenol

The second stage of the reaction involves methylol groups with other available phenol or methylolphenol, leading first to the formation of linear polymers and then to the formation of hard-cured, highly branched structures (Figure 1.9) [67]. These structures present essentially methylene and ether linkages. However ether bridges are present in small amounts when the reaction is taken in high alkaline conditions. The reaction is stopped by cooling down the kettle, preventing gelation of the resin [54].

Resins are frequently worked up by distillation to give concentrated solutions or solid resins. At the end of their synthesis, PF resins contain oligomeric and polymeric chains as well as monomeric methylolphenols, free formaldehyde and unreacted phenol. The content of both monomers has to be minimized by the proper synthesis procedure [54]. Various synthesis processes are described in the chemical literature and in patents [68-72].



Phenol-Formaldehyde Network Polymer

**Figure 1.9** Methylolphenols condensation in order to create a phenol-formaldehyde network polymer

### **Cure**

The reaction of cure of a PF resin can be seen as the transformation of molecules of different size into a branching and crosslinking three-dimensional network, with a high molecular mass. This reaction rate depends highly on various parameters such as molar mass of the resin, molecular structures and P/F molar ratios as well as addition of catalysts and additive [54].

Alkaline PF-resins contain free reactive methylol groups in sufficient number and can harden even without any further addition of formaldehyde. Pizzi and Stephanou [73] investigated the dependence of the gel time from the pH of an alkaline PF-resin. Surprisingly they found an increase in the gel time in the region of very high pH-values (above 10); exactly such pH's, however, are given with the usual PF-resins with a content of NaOH of 5 to 10 % [73].

The cure process can be monitored using equipments such as Differential Scanning Calorimetry (DSC), Automated Bonding Evaluation System (ABES), or Dielectric Cure monitoring (DCM) or Dynamic Mechanical Analysis (DMA). 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 allowing the estimation of the degree of curing [74]. Mechanical curing in the sense of the increase in cohesive bond strength can be monitored by DMA and ABES [75]. The chemical hardening can be followed by means of solid state  $^{13}\text{C}$  Nuclear Magnetic Resonance (NMR), looking at the increase of methylene bridges based on the amount of aromatic rings, at the portion of 2, 4, 6- three substituted phenols or at the ratio between methylol groups and methylene bridges [76-79]. This degree of hardening however is not equal with the degree of hardening as monitored by DSC, because NMR gives us the chemical hardening while DSC gives the chemical degree of curing [54].

The acceleration of the cure reaction is possible by the increase of the degree of condensation during synthesis process as well as the addition of a propylene carbonate. However, the mechanism associate with the latter is not yet very clear. The acceleration can happen due to the presence of hydrogen carbonate ion, formed after the hydrolysis of the propylene carbonate [80] or due to the formation of hydroxybenzyl alcohol and aromatic carbonyl groups in the reaction of the propylene carbonate with the aromatic ring of the phenol [81]. As expected, the higher the addition of propylene carbonate, the lower the gel time obtained [82].

The differences between acid-catalyzed and base-catalyzed process are: rate of reaction between formaldehyde and phenol, methylolphenol condensation and the nature of the condensation products [51]. So the catalyst type influences the rate of the reaction of phenol and formaldehyde and consequently the final properties of the resins.

The catalytic action of acids on the condensation to produce novolacs is essentially a function of the hydrogen ion concentration. The nature of the

anion is less important but must be taken into account because of possible side reactions. Hydrochloric acid is the most interesting case of an acid catalyst as well as oxalic acid and phosphoric acid [51, 58]. Oxalic acid decomposes on heating above 180 °C and thus allows the production of catalyst-free novolacs [58].

For alkaline catalysis, sodium hydroxide [67, 73, 83] is the most common catalyst used and when this is used, the type of reaction mechanism is the one suggested by Caesar and Sachanen [83]. Besides sodium hydroxide, other basic catalysts can be used, such as  $\text{Ba}(\text{OH})_2$ ,  $\text{LiOH}$ ,  $\text{Na}_2(\text{OH})_3$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Al}_2\text{O}_3$ , ammonia or hexamine [76, 84-93].

### **1.1.3. Resins Characterization**

As mentioned formaldehyde based resins are very complex polymeric structures mostly because of the number of bonds that urea, melamine and phenol can originate (creating a high amount of different monomers, such as methylolureas, methylolmelamines and methylolphenols). On the other hand, the existence of reversible reactions (particularly in case of UF) and structural rearrangement during these resins synthesis and storage, requires close control of the synthesis and the final resins properties in order to obtain reproducible resins.

During their synthesis, the major variables controlled are the temperature and pH of the reaction as well as the viscosity obtained in the condensation step. Basic characterization of these products involves the determination of physical (solid content and viscosity) and chemical properties (reactivity and pH). However new characterization methods, such as chromatography and spectroscopic techniques, have been developed or updated in order to give a

more specific information of the structure and subsequent performance of the resins.

### ***Basic Characterization***

*Viscosity (mPa·s)* – Viscosity value gives a rough indication of the resin degree of polymerization. Usually the values of viscosity at 25 °C are comprised between 300 and 1000 mPa·s for resol resins and 150 to 400 mPa·s for UF and MUF resins.

*pH* – The pH measures the basicity of the resin. A certain basic pH should be preferably maintained for the resin to be free of precipitation and to have a high water tolerance.

*Water Tolerance (%)* – Distilled water at 25 °C is gradually added to 5 g resin until the resin solution turns hazy. The water tolerance of a resin is an indication of the miscibility of the resin with water. This method is mainly used in the PF and MF resins characterization.

*Free Phenol Content (%)* – The free phenol content is measured by gas chromatography. It is the amount of phenol in the resin at the end of synthesis. A lower number is preferred for increased resin efficiency and lower emissions. This method is mainly used in the PF resins characterization.

*Free Formaldehyde (%)* – The free formaldehyde content is measured commonly by the hydroxylamine titration method. This is the amount of formaldehyde left unreacted with phenol in the resin at end of synthesis. A lower number is preferred for higher resin use efficiency and lower emissions.

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

*Solid Content (%)* – The solid content measures the concentration of the phenolic resin which is not evaporable and is evaluated by oven drying. Usually values for these resins solid content ranges between 35 and 75 %, depending on the resin final application.

*Alkaline Content (%)* - The alkaline content is usually determined by potentiometric neutralization of a solution to a pH of 7, using a strong acid. This method is mainly used in the PF resins characterization.

*Buffer Capacity* – Evaluated by acid-base titration and measures the amount of acid (or base) needed to reduce (or increase) resin pH.

*Reactivity (s)* – Time needed for the resin gelification under similar conditions of the hot-pressing process (at 100 °C). This method is used to characterize UF and MUF resins and the usual values of gel time range between 50 and 100 s.

### ***Chromatographic Techniques***

**Size Exclusion Chromatography (SEC)** is usually used as a support technique for the characterization of the polymer essentially on the polymer structure and molecular weight distribution. This technique consists of an entropy controlled separation technique in which the molecules are separated based on their hydrodynamic volume and molecular size. With the use of a calibrated column together with a system of detectors (refractive index detector, viscosity and light scattering) can easily obtain the molecular weight distribution and average molecular weights in a given polymer. Its application for UF, MUF and PF is reported in several studies [94-97] but presenting some

difficulties, largely due to its low solubility. For this it is necessary to use solvents such as dimethylformamide (DMF) or dimethylsulfoxide (DMSO) to ensure complete solubility of the higher molecular weight fractions [96, 98, 99].

**High Performance Liquid Chromatography (HPLC)** is a chromatographic technique that allows separation of a mixture of different molecular weight compound. This technique is widely used in biochemistry and analytical chemistry in the identification, quantification and purification of individual components of a given mixture. In general the separation of components occurs by differential migration of sample components, when passing of the liquid mobile phase through the solid stationary phase. The use of this technique in the analysis of UF allows the separation and identification of unreacted urea, monomethylolurea and dimethylolurea [97, 100, 101]. Other monomers are also found but their quantification and identification due to the lack of standards in the market.

### ***Cure Evaluation Techniques***

There are several techniques useful for the evaluation of the curing process. For the evaluation of the behaviour during gelling and chemical curing techniques like Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) can be use. On the other hand, the determination and evaluation of the solidification of the adhesive in other to create a three-dimensional network is normally evaluated using methods such as Dynamic Mechanical Analysis (DMA), Thermal Mechanical Analysis (TMA) and Dielectric Cure Monitoring (DCM). The formation of the bond between two strips with resin can be followed by methods such as Automatic Bonding Evaluation System (ABES).

**Differential Thermal Analysis (DTA)** is a technique that measures the difference in temperature between two cells, both heated up according to a defined temperature program, whereby one of the cells has the sample in investigation [23, 48, 102]. On the other hand, **Differential Scanning Calorimetry (DSC)** measures the change of the difference in the heat flow rate between a sample and into the reference sample, while subjected to a certain controlled temperature program. For both techniques, usually one or two exothermic peaks can be found in a temperature scan. In the case of DSC, the samples are analyzed in sealed capsules, in order to decrease the intensity of the endothermic peak related to the evaporation of water, which would completely cover the exothermic peak of interest [23, 103, 104].

On the other hand, **Dynamic Mechanical Analysis (DMA)** is a technique that analyzes the response of a material subjected to a sinusoidal stress, which generates a corresponding sinusoidal strain [105]. On the other hand, **Thermal Mechanical Analysis (TMA)** involves the measurements of the dimensional modifications of a certain material under controlled conditions such as time, temperature and force. Basically this technique gives the average length of the polymer segments of the hardened adhesive network [23, 106].

**Dielectric Cure Monitoring (DCM)** is a process that involves measuring changes in the dielectric properties of the material by using an impedance analyzer over many decades of frequency. Some studies have been made in the wood industry and the results showed that this technique is suitable for curing characterization of formaldehyde based resins [107, 108].

The increased mechanical strength with time was followed by using the **Automated Bonding Evaluation System (ABES)** [75]. This is a system that allows performing bonding by hot pressing, followed by determining the

internal resistance of the adhesive joint. To perform a test using up two wooden sheets (117 x 20 x 0.5 mm) joined by a line of glue (study adhesive with addition of the appropriate catalyst) and fixed the ends of two strips. The overlapping portion of the two sheets (with an area of 100 mm<sup>2</sup>) is then pressed at a given temperature and predefined pressure for a given period of time. The end of this time the two sheets are pulled at a rate determined by its edges, and subsequently measuring the strength necessary to break the glue joint. This test is repeated for different time. This technique has been found useful for the determination of the bond strength for different adhesives types under different pressing parameters (temperature and time) and conditions (cooling effect) [109-112].

### ***Spectroscopic Techniques***

The determination of the chemical composition and structure of formaldehyde based resins can be done using several spectroscopic techniques, such as FTIR (Fourier Transform Infrared), FT-NIR (Fourier Transform Near-Infrared), NMR (Nuclear Molecular Resonance), Raman and MALDI-TOF (Matrix Assisted Laser-desorption Ionization Time of Flight). All of this methods allow to obtain correlations between different preparation strategies and resulting structures and properties of wood-based panels made with these resins [23].

**Fourier Transform Infrared (FTIR)** allows the detection of the functional groups by measuring the fundamental molecular vibrations in the wavelength between 4000-400 cm<sup>-1</sup>. Usually the most detect groups are the carbonyl groups, which mainly correspond to the amide bonds, due to their high molar absorptivity [113]. On the other hand, **Fourier Transform Near-Infrared (FT-NIR)** is a non-destructive, reliable, fast and versatile technique, which does not imply sample preparation [114]. Several studies concerning the application of

FT-NIR to formaldehyde based resins have been made in the recent years [115-117]. Most of them have been useful for the monitoring the consumption of  $\text{NH}_2$  groups during the early stage of the resin condensation reaction [114, 118].

From the many existing methods for **Nuclear Magnetic Resonance (NMR)**, the liquid-state  $^{13}\text{C}$  NMR is the most used. This provides the most complete information on the chemical structures present in formaldehyde based resins, enabling the identification and quantitative determination of many functional groups [119-122].

**Raman spectroscopy** is a technique that involves the study of the interaction of radiation with molecular vibrations. This method allows the analysis of the liquid resin, cured resin or the cured in wood based panels. This spectroscopy technique was used by Hill *et al.* [123] to determine the structure of cured UF resins and by Carvalho *et al.* [120] to study the UF oligomers and curing which permitted to obtain kinetic data as the basis for an empirical kinetic model.

Another technique used to determine to molar mass distribution and chemical composition distribution of formaldehyde based resins is **Matrix Assisted Laser-desorption Ionization Time of Flight (MALDI-TOF)** mass spectrometry [124]. In this technique the polymer is dispersed in a matrix, which consists of an UV absorber, and then bombarded by a laser. Some studies have been made by Zanetti *et al.* in order to analyze MUF resins [125].

#### **1.1.4. Resins Applications**

##### ***Urea-Formaldehyde and Melamine-Urea-Formaldehyde Resins***

UF and MUF are largely used in the manufacture of particleboard and plywood. However in some countries, an important application for UF cold-setting

adhesives is in the production of laminated timber for structural applications [126].

In the particleboard production, the UF glue mix is usually composed with four main compounds: a liquid UF resin, a certain amount of water added in order to decrease the resin viscosity and to facilitate resin spraying, small amounts of hardener that can be ammonium chloride or sulphate, and small quantities of wax emulsions. The amount of resin used is different for the core and surface particle. This value is based on the amount of dry wood and is around 6-8 % for the core layer and 10-11 % in the surface layer. After blending the glued particles have usually moisture contents between 7 % in the core particles and 10-12 % in the surface particles [10]. However, such proportions can be higher for the weaker low emission adhesives used today and depending for the application (PB and MDF production needed different amounts of resin) [127, 128]. Pressing temperatures and pressures used in the formation of the board are in the range of 150-200 °C and 2 to 35 kg·cm<sup>-2</sup>, respectively [10].

On the other hand, in the plywood production the UF resins used contain less than two moles of formaldehyde per mole of urea and their condensation reaction leads to a slightly viscous and water tolerant resin. The degree of condensation and as consequence the viscosity under comparable conditions of UF and MUF resins for plywood is generally higher than those of UF and MUF resins for PB. In this case is also used a small amount of acid as hardener and the pressing time and pressure are around 120 to 160 °C and 12 to 14 kg·cm<sup>-2</sup>, respectively. Usually the moisture content of the glued veneer is around 5 to 8 % [10].

Although PB, MDF and plywood are the major users of UF and MUF resins, two other applications, with much lower consuming of these resins, are also

important of note. The first is in the furniture and joinery industry, including the manufacture of hollow-core doors. The second application of note is in foundry applications as sand core binders and in this application UF resins compete with phenolic and furanic resins. Sometimes small amount of wax and corn flour are used to facilitate the mixing between resin and the sand (usually around 1 and 2.5 % resin on sand) [10, 126].

### ***Phenol-Formaldehyde Resins***

Phenol-formaldehyde resins are usually used as binders for exterior-grade plywood and particleboard, which need the superior water resistance provided by these resins. In the manufacture of plywood, the PF resin adhesive is usually applied to the wood veneers by roller or extrusion coating. The coated veneer is then cross-grained, stacked, and cured in a multidaylight press for 5 to 10 min 120 to 130 °C and at 11 to 16 kg·cm<sup>-2</sup>. In the manufacture of particleboard, PF resins are sprayed onto the wood chips by continuous blenders. The glued wood chips are formed into a mat and then pressed for 5 to 12 s·mm<sup>-1</sup>, according to thickness, press temperature and moisture content, at 190 to 230 °C and 25 to 35 kg·cm<sup>-2</sup> [51, 129].

The only type of PF resins used commercially for this application is resol-type. These are hardened by heating after the addition of small amounts of wax emulsion and preservative solution in the case of particleboard, and of vegetable or mineral fillers and tack agents in the case of plywood. Accelerators are sometimes added in both types of glue mixes. The pH of these resins varies between 10 and 13.5, usually between 12 and 12.5 [51].

Some studies have been made on the use of resol phenol-formaldehyde or resol modified phenol-formaldehyde resins to produce particleboards, where different resin preparation and particles moisture content [51, 129-131].

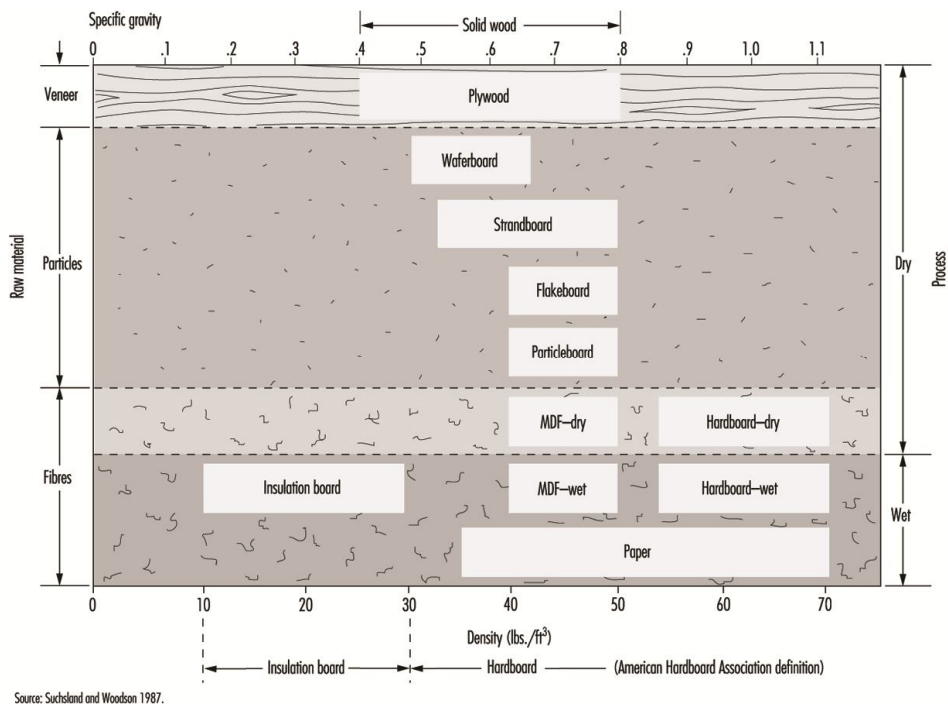
In the case of the application of PF resins to the manufacture of exterior-grade particleboard, the closest attention must be focused on the application of the resin rather than on its formulation [51]. Considerable variation in the properties of the final board can be obtained by varying the moisture contents of the surface and core layers and by using faster resins in the core layer and slower reacting resins in the surface layer. These variations intend to increase the board core density and to improve the density profile of the panel as a function of its thickness. Studies on the correlation of curing and bonding properties of particleboard glued with resol-type PF resins by DSC show that resols tend to reach two endothermic peaks: the first at 65 to 80 °C and the second at 150 to 170 °C. Resol-glued particleboard shows no bond formation at 120 °C, but at 130 °C panels show internal bond strength between 0.55 and 0.70 N·mm<sup>-2</sup>. The normal press platen temperatures for 12 to 13 mm thick board glued with PF adhesives are 170 to 230 °C. The pressing time is 18 to 12 s·mm<sup>-1</sup> for standard PF resins but PUF's [132], tannin-accelerated [133] and urea drowned PF resins [134] can reach pressing times as fast as 5 s·mm<sup>-1</sup> at 190 – 210 °C in industrial applications.

## **1.2. Wood-based Panels Industry**

Wood-based panels (WBP) are a general term for a variety of a different board product, which have an impressive range of engineering properties. While some panel types are relatively new on the market, others have been developed and successfully introduced during the last hundred years [135].

WBPs are manufactured from wood materials having different geometries (for example fibbers, particles, strands, flakes, veneers and lumber), combined with an adhesive system (resin, water, hardener and wax emulsion) and bonded in a press. The press applies heat (if needed) and pressure to activate the adhesive resin and bond the wood material into a solid panel having good mechanical and physical properties (strength, stiffness, form, dimensional stability, between others) [136].

The most used wood-based panels are particleboard (PB), medium density fibreboard (MDF), oriented strand board (OSB) and plywood (PL). Other examples of wood-based panels are hardboard, laminated veneer lumber (LVL), solid wood panels (SWP) and cement-bonded particleboard [136]. Plywood, made by gluing together several hardwood veneers or plies, was the first type of wood-based panels produced in the world. Only 60 years later particleboards panels were manufactured [137]. Figure 1.10 summarizes the classification of WBP according to particle size, density and process type.



**Figure 1.10** Classification of wood-based panels by particle size, density and process type (adapted from [138])

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

In the manufacture of wood-based panels, the raw material used has, besides the production process, an important influence on the final performance of the panel. Wood is the most important raw material in quantitative terms and as consequence the local availability of certain species, the competition introduced by the grant of wood as fuel and the use of recycled wood has increased fluctuations in timber supply in many European countries. The quality of wood may vary strongly depending in the regional differences and the assortment used, but also over time within the individual process [139]. Therefore, recycling of waste wood has become a common practice in several countries [140].

As the recycled wood is obtained from a variety of sources, its incorporation in the manufacture of wood-based boards has some limitations due to the size heterogeneity, and contamination [141]. In the particleboard industry, recycled wood has been already used in quite some time and more recently MDF manufacturers started to use recycled wood. The amount of recycled wood that is being used for the production of WBP has strongly increase during the recent years. Wood-based panels industry is clearly responding positively to the necessity of a sustained industrial development [142]. In Portugal, two major companies are implementing strategies for sustainable use of forest resources by recycling clean wood waste, but also industrial wood waste and packaging [143].

### **1.2.2. Particleboard Production**

Particleboard is used as a generic term for any panel product that is made with wood particles. There is a great range of particle shapes and size used to make particleboards. The type of particle is therefore used to define the type of particleboard product [135]. Particleboard is manufactured from wood chips, sawdust, waste materials and recycled woodchips [144]. Typically it is made in three layers, where the two external layers consist of finer particles and sawdust and the core layer is made of bigger wood material. The wood particles used for their production are blended by adding a synthetic adhesive and then pressed at high pressures and temperatures. A schematic example of a particleboard plant can be seen in Figure 1.11.

The manufacture of particleboard has five main steps: furnish preparation, resin application, mat formation, hot pressing and finishing. Furnish is prepared by refining the wood particles into smaller sizes follow by their drying to achieve a desired moisture content, between 2 and 3 % [144]. After these, the wood particles are blended with a mixture of resin with other additives

(hardener, hydrophobic agent, fire retardant agent, between others). The type of resin used in the particleboard depends on the characteristics desired, but normally urea-formaldehyde (UF) and melamine fortified urea-formaldehyde (MUF) resins are used. The resin/wood ratio, based on resin dry solids content and wood particle dry weight, is usually between 6 and 9 % [23, 144]. Moisture content is an important property of the blended particles and usually particles in the surface layer have higher moisture content than the core layer particles. After mechanically mixing the particles and the adhesive system, the material goes through a continuous mat-forming system and is then pressed in a hot press under pressures between 2 and 3 MPa and temperatures between 140 and 220 °C [23, 144]. After the press cycle is complete, the panel is transported to a board cooler, and then hot-stacked to wait sawing into finished panel sizes and sanding [136].

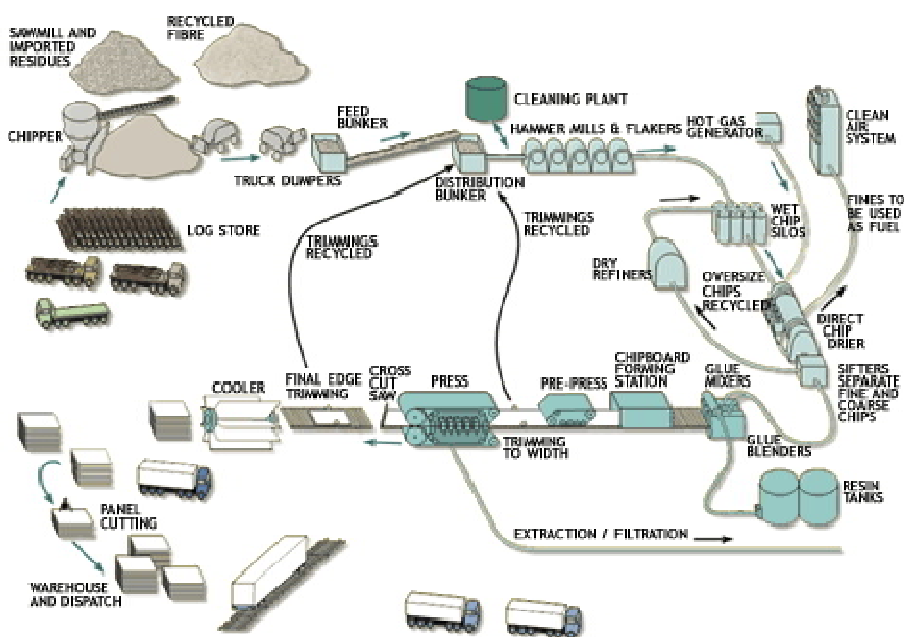


Figure 1.11 Particleboard process diagram (adapted from [145])

### **1.2.3. Particleboard Characterization**

Particleboards can be characterized by several methods and tests defined by recognize international organizations, such as Comité Européen de Normalisation (CEN), American Society for Testing and Materials (ASTM), Japanese Industrial Standards (JIS) and other regional standard organizations. Different tests or experimental conditions for evaluating similar properties, are usually, defined by each organization. In this work, all physico-chemical properties were evaluated according to the European Standards (EN).

#### ***Determination of Tensile Strength Perpendicular to the Plane of the Board***

The tensile strength perpendicular to the plane of the board (also denominated as internal bond – IB) is determined according to the Portuguese Standard NP EN 319. This test uses a 50 x 50 mm specimen, subjecting it to a tensile force perpendicular to the plane of the board, applied at a constant speed until rupture occurs. IB is determined by the ratio between the maximum load and the sample surface and is expressed in  $\text{N}\cdot\text{mm}^{-2}$ .

#### ***Determination of Density***

The density of the specimens of a wood-based panel was determined by the method described in Portuguese Standard NP EN 323 (2002). The principle of this standard is to determine the density as the ratio of mass to volume of each specimen, both measured with the same moisture and using these results to estimate the density of the entire boards. Specimens used for this test method shall be square with a side length of 50 mm. The density  $\rho$  of each sample is expressed in  $\text{kg}\cdot\text{m}^{-3}$ .

### ***Determination of Swelling in Thickness after Immersion in Water***

The thickness swelling of a particleboard is obtained by the method disclosed in the Portuguese Standard NP EN 317. The principle followed by the standard is the measurement of the thickness of the test piece with 50 x 50 mm of dimension, after complete immersion in water. Before immersion in water, the test pieces shall be conditioned at a temperature of  $(20 \pm 2)$  °C and a relative humidity of  $(65 \pm 5)$  %. The thickness swelling of each piece is expressed in percentage of the initial thickness.

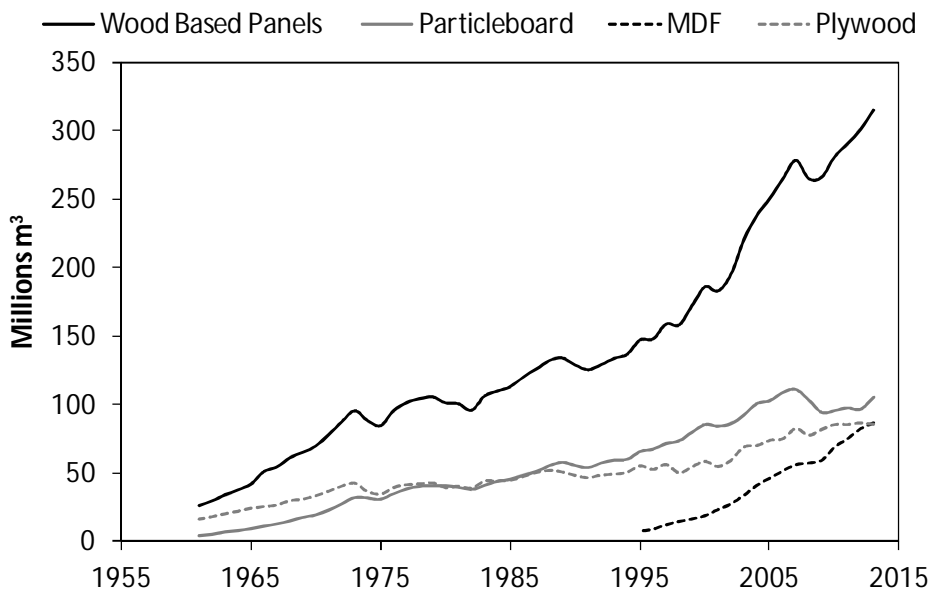
### ***Determination of Moisture Content***

The procedure for determining the moisture content of a wood based panel is described in Portuguese Standard NP EN 319 (2002). The moisture, determined by weighing, is calculated from the ratio between the weight loss of a sample dried at  $(103 \pm 2)$  °C to constant weight, and the mass of the final sample (after drying). The results are used to estimate the moisture of the whole board. In this type of analysis the sample shall have a minimum initial mass of 20 g, regardless of the shape and dimensions of the sample. The moisture content of each piece is expressed in percentage.

#### **1.2.4. Wood-based Panels Market**

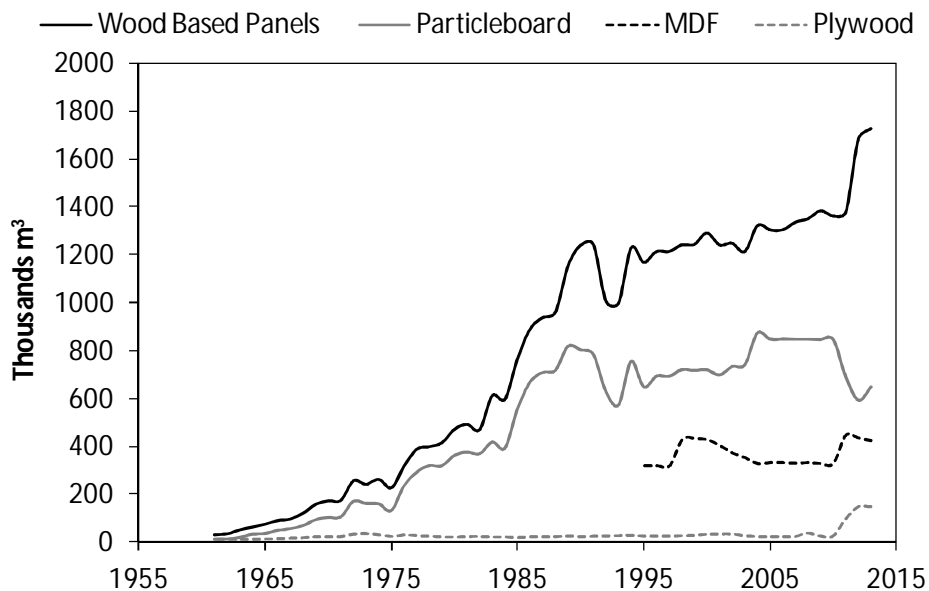
During the second half of the 20<sup>th</sup> century the development in the wood-based panels industry was huge, with a substantial increase of the relevance of particleboards on the wood-based panel's global production [146]. Currently, wood-based panels have changed completely. During the last years the production of panels has decreased greatly due to the global economic crisis that sits up to today. Thus the production of particleboards decreased about 1.5 % in 2011, 3.1 % in 2012 with a small increase of 0.6 % in 2013 [147, 148].

In 2013, Food and Agriculture Organization of the United States (FAO) stated that, approximately 360 million m<sup>3</sup> (40 % on China, 10 % on United States and 4 % on Russia) of wood-based panels were manufactured in the world [149]. In the Figure 1.12 it is possible to observe the evolution of the production of wood-based panels in the world between 1961 and 2013, as well as the values for the production of the particleboard, MDF and plywood.



**Figure 1.12** Evolution of the production of wood-based panels in the world since 1961 to 2013

The production of wood-based panels in Portugal has been approximately stable in the last decades. In 2013, the production volume was 1136 thousand m<sup>3</sup> (649 000 m<sup>3</sup> of particleboard, 421 000 m<sup>3</sup> of MDF and 31 000 m<sup>3</sup> of plywood) (Figure 1.13) [149]. The production of plywood is small due to the lack of some raw material such as veneers.



**Figure 1.13** Evolution of the production of wood-based panels in Portugal since 1961 to 2013

### 1.2.5. Formaldehyde Emissions

Formaldehyde, with chemical formula of  $\text{HCHO}$ , is a common organic compound used in various applications as a raw material, such as in the production of urea-formaldehyde resins, melamine-urea-formaldehyde, melamine-formaldehyde and phenol-formaldehyde. Despite the fact that the short-term health effects of formaldehyde exposure are well known, less is known about its potential long-term health effects. So in 1980, laboratory studies showed with experiences with rats, that long exposure to formaldehyde could cause nasal cancer [150]. In 1987, the US Environmental Protection Agency (EPA) has classified formaldehyde as a possibly human carcinogen, when subjected to unusual high or prolonged times of exposure. This distinction was based in several studies made with humans that have suggested that formaldehyde exposure is associated with certain types of cancer [151]. Formaldehyde will eventually be classified as "Possible carcinogenic to humans" by the World Health Organization (WHO) [152].

In 2004, the International Agency for Research on Cancer (IARC - International Agency for Research on Cancer) of WHO, recommended the reclassification of formaldehyde as "Carcinogenic to humans" [153]. Despite not having any legal effect, this classification led to rapid movements in various environmental protective bodies, industry associations and regulatory authorities. Despite the dismay of some associations and companies such as The Composite Panel Association and the EPF (European Panel Federation) in 2006 the recommendation of the IARC was finally taken into account. The statement published in 2006 says that "there is sufficient evidence in human and in experimental animals for the carcinogenicity of formaldehyde" [153]. Within European Union, formaldehyde is classified currently as 3-R40 substance ("limited evidence of carcinogenic effect"), but the classification has been reviewed under the new regulation for chemicals called REACH (Registration, Evaluation, Authorization and Restrictions of Chemicals). Most recently, in June 2011, the U.S. Department of Health and Human Services has listed formaldehyde as a known human carcinogen. Formaldehyde was also listed in the 12<sup>th</sup> Report on Carcinogens, compiled by the National Toxicology Program [154].

### **Emission Test Methods**

The emission of formaldehyde present in the wood-based panels is mainly due to the presence of residual formaldehyde after pressing, and the reversibility of urea-formaldehyde bridges caused by their low resistance to hydrolysis. In general it can be said that formaldehyde emission levels depend essentially on two different types of factors: internal and external. As internal factors it can be mentioned the quality of wood and of the resin used, as well as the pressing conditions and sizing of the sample. On the other hand, among the external factors it is possible to highlight the conditions of the panels storage location

after production such as temperature, relative humidity, air exchange rate and the total area of the panel relative to the storage area [155]. Methods for determining the formaldehyde content and emission should take into consideration the factors mentioned above in order to be reproducible, reliable and relatable to each other. These methods can be mainly divided into two types of groups: "emmittable potential" which considers the existing maximum formaldehyde in a panel issued under severe testing conditions and "measurable emission", which considers the amount of formaldehyde actually emitted under the test conditions [156]. In Table 1.1 is possible to observe some of the most important methods for the determination of formaldehyde used for analysis of wood-based panels.

**Table 1.1** Standards and methods for determination of formaldehyde [155]

Test Method	Standard, standard draft or method name
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	EN 717-3, method AWPA
Desiccator	ASTM D 5582, JIS A 1460, ISO 12460-4
Perforator	EN 120

### ***Perforator method***

Perforator method (EN 120) measures the formaldehyde emissions content of wood-based potentially emitted under forceful conditions. The principle of this method is that formaldehyde is extracted from test pieces by means of boiling toluene and then transferred into distilled or demineralized water. Consequently the formaldehyde content of this aqueous solution is

determined photometrically by the acetlyacetone method. This method is used daily as a factory production control due to this fast execution. The biggest disadvantage of this method is the toluene environmental impact.

### ***Desiccator method***

The more relevant desiccator method is defined in the Japanese standard JIS A 1460. It is one of the most economical methods, but it has a drawback. The test pieces shall be conditioned under standard conditions of temperature and humidity, until they reach constant mass, which can take one week. The principle of this test is that the emitted quantity of formaldehyde is obtained from the concentration of formaldehyde absorbed in distilled water or deionized water when the pieces of specified surface are placed in the desiccator. The principle for determination of concentration of formaldehyde is made using the acetlyacetone method.

### ***Gas analysis method***

Gas analysis method (EN 717-2) is a derived test used to determine formaldehyde released at accelerated conditions: a temperature of 60 °C and within a period of 4 hours. The principle is that a test piece of known surface area is placed in a closer chamber in which temperature, humidity, airflow and pressure are controlled to defined values. Formaldehyde released from the test piece mixes with the air in the chamber. This air is continually drawn from the chamber and passes through gas was bottles, containing water, which absorbs the released formaldehyde. At the end of the test, the formaldehyde concentration is determined photometrically, using the acetlyacetone method.

### ***Chamber method***

The evaluation of the real emission of formaldehyde from a product under typical indoor conditions in real-life, and over defined time scales requires the use of a climate-controlled chamber (EN 717-1) [136]. In this test the pieces of a known surface area, are placed in a chamber, in which the temperature, relative humidity, air velocity and exchange rate are controlled at defined values. Formaldehyde emitted from the test pieces mixes with the air in the chamber, which is periodically sampled. The formaldehyde concentration is determined by drawing air from the chamber through gas washing bottles containing water, which absorbs the formaldehyde.

### **Emission Regulations**

Particleboards panels are classified in terms of formaldehyde emissions, according to the analysis method used and the emission limit value as shown in Table 1.2.

There are, however, other classifications that have become standards for producers of wood-based panels, and they exert great influence on the whole market. For example, IKEA, in 2005, imposed on producers the obligation to produce boards with emission levels equivalent to the E1 class. Later, in 2009 they adopted the limits designated by the standard CARB, now requiring their suppliers to produce wood-based panels with maximum emission values of 4 mg/100 g oven dry board (usually known by E0). Thus, this decision led to almost no production of panels classified as E2. In the near future it may be expected that the level of demand IKEA is increasingly high (formaldehyde emissions smaller and smaller).

**Table 1.2** Classification of particleboards panels according to the formaldehyde emission level

Classification	Standard	Analysis Method	Region	Limit Value
E2	EN 13986	EN 717-1	Europe	$> 0.124 \text{ mg}\cdot\text{m}^{-3} \text{ air}$
		EN 717-2		$3.5 < \text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1} \leq 8$
		EN 120		$8 < \text{mg}/100 \text{ g oven dry board} \leq 30$
E1		EN 717-1		$\leq 0.124 \text{ mg}\cdot\text{m}^{-3} \text{ air}$
		EN 717-2		$\leq 3.5 \text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$
		EN 120		$\leq 8 \text{ mg}/100 \text{ g o. d. b.}$
F**	JIS A 5908 & 5905	JIS A 1460	Japan	$\leq 1.5 \text{ mg}\cdot\text{L}^{-1}$
F***				$\leq 1.0 \text{ mg}\cdot\text{L}^{-1}$
F****				$\leq 0.3 \text{ mg}\cdot\text{L}^{-1}$
CARB I	CARB	ASTM E1333	USA	0.18 ppm
CARB II				0.09 ppm

In the absence of a reference standard, plus the difficulty in relating the reference values between the different standards, relations were established that enable us to relate the main methods of formaldehyde determination. Due to the different operating conditions used in each method, it is not possible to obtain a relation, although approximate correlations are found in the literature [157, 158].

**Table 1.3** Relation between different existing methods and standards (Note\*: Values obtained by correlations [159])

Method	Japan		Europe	IKEA	USA	
	F***	F****	E1	E0.5	CARB I	CARB II
EN 120 [mg/100 g o.d.b.]	≤ 4.5*	≤ 2.7*	≤ 8.0	≤ 4.0	≤ 11.3*	≤ 5.6*
EN 717-1 [mg·m <sup>-3</sup> air]	≤ 0.054*	≤ 0.034*	≤ 0.124	≤ 0.050	≤ 0.176	≤ 0.088
ASTM E1333 [ppm]	≤ 0.055*	≤ 0.035*	≤ 0.127*	≤ 0.051*	≤ 0.180	≤ 0.090
JIS A 1460 [mg·L <sup>-1</sup> ]	≤ 0.5	≤ 0.3	≤ 0.9*	≤ 0.4*	≤ 1.3*	≤ 0.6*

Recently a new challenge was launched in the production of wood-based panel industry with the imposition of production boards with formaldehyde emissions to the natural wood level. A well-known company in this area conducted several comprehensive studies to define the emission limits and concluded that the natural wood has an average emission of 0.01 mg·m<sup>-3</sup>, as measured by the chamber method (EN 717-1). Thus, the purpose of the wood-based panels industry is focuses on obtaining a resin with a formaldehyde emission equal or below 0.01 mg·m<sup>-3</sup> (air).

### 1.2.6. LEED® Certification

The wood-based panels industry has achieved production of panels with very low formaldehyde emissions keeping a good overall physical-mechanical

performance, as a consequence of IARC's (International Agency for Research on Cancer) classification of formaldehyde as "carcinogenic to humans (Group 1)" [153]. However, a new important challenge has been recently imposed by LEED (Leadership in Energy and Environmental Design®) certification, implying the absence of adhesives with urea-formaldehyde chemical bonds in "Green Building" construction [160]. This restriction occurs essentially due to the reversibility of the urea-formaldehyde bonds upon its interaction with water or moisture, resulting in the subsequent emission of formaldehyde. The fact that melamine-formaldehyde and phenol-formaldehyde bonds present a much lower reversibility in the presence of water makes this typology of resins much more attractive for the application in the so-called "Green Buildings".

LEED certification is recognized standard for measuring building sustainability. The LEED green buildings rating system is designed to promote design and construction practices that increases profitability while reducing the construction practices that increase profitability while reducing the negative environmental impacts of buildings and improving occupant health and well-being. In our case the sector of LEED certification that is applied is the LEED for commercial interiors, which promotes the construction of sustainable buildings that meet a set environment preservation and human health quality goals. Minimizing indoor air contamination associated to substances that are odorous, irritating, and/or harmful to the comfort and well-being of installers and occupants is one of the objectives [160].

### **1.3. Motivation and Outline**

This PhD work started within the scope of the project entitled "E0 Formaldehyde - Conceção de sistemas *taylor-made* para o fabrico de painéis de madeira de baixa emissão de formaldeído" funded by Agência de Inovação in the context of the "QREN – I&D em Co-promoção" programme. This Project

involved two academic partners (FEUP and IPV) and an industrial promoter EuroResinas – Indústrias Químicas S.A. (Sines, Portugal). One main goal was the development and optimization of the resins that meet different formaldehyde emissions limits and provide improved characteristics to the wood-based panels.

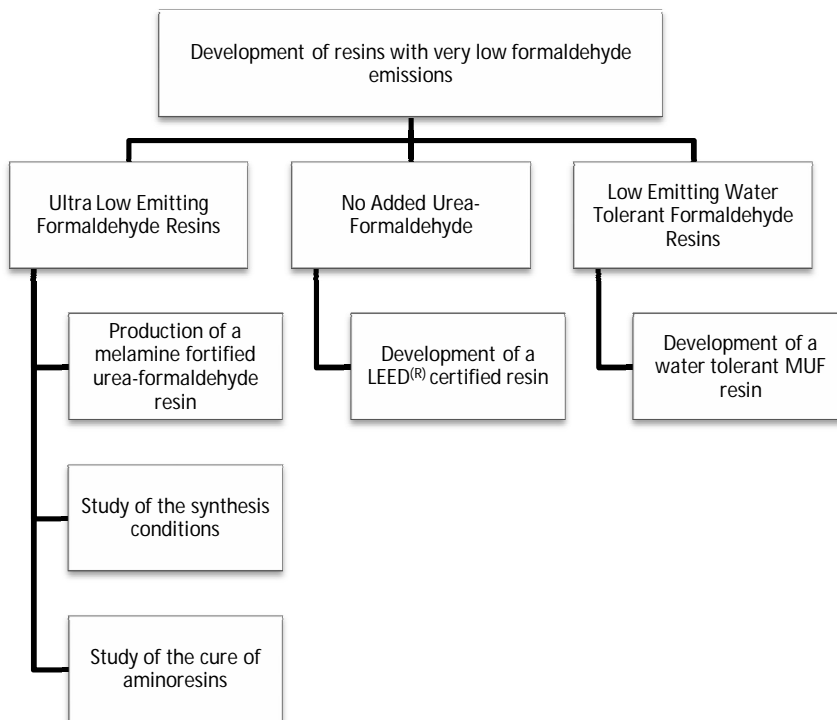
The present thesis is divided into five chapters, including this introduction. In Chapter 2, “Ultra Low Emitting Formaldehyde Resins”, the development and optimization of a UF modified resin is presented, as well as the study of the cure reaction during the particleboard production.

Chapter 3 “No Added Urea-Formaldehyde”, describes the development of a resin with no urea-formaldehyde bonds that respects LEED<sup>(R)</sup>.

Chapter 4, “Low Emitting Water Tolerant Formaldehyde Resins”, explores the development of MUF resins with high water dilution capacity by incorporation of a small amount sodium metabissulphite.

The main conclusions of this work and suggestions for future work that can be done in the future can be found in Chapter 5.

Figure 1.14 shows a schematic diagram of the structure of the present PhD thesis.



**Figure 1.14** A schematic diagram of linkage between the different chapters present in this thesis

#### 1.4. References

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## ***CHAPTER 2***

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## 2. Ultra Low Emitting Formaldehyde Resins

### 2.1. Production of a melamine fortified urea-formaldehyde resin with low formaldehyde emission<sup>1</sup>

#### **Abstract**

Melamine can be incorporated in the synthesis of urea-formaldehyde (UF) resins in order to improve performance in particleboards, mostly in terms of hydrolysis resistance and formaldehyde emission. In this work, melamine-fortified UF resins were synthesized using a strongly acid process. The best step for melamine addition and the effect of the reaction pH on the resin characteristics and performance were evaluated. Results showed that melamine incorporation is more effective when added on the initial acidic stage. The condensation reaction pH has a significant effect on the synthesis process. A pH below 3.0 results on a very fast reaction that is difficult to control. On the other hand, with pH values above 5.0, the condensation reaction becomes excessively slow. Particleboards panels produced with resins synthesized with a condensation pH between 4.5 and 4.7 showed good overall performance, both in terms of internal bond strength and formaldehyde emissions.

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<sup>1</sup> N. T. Paiva, A. Henriques, P. Cruz, J. M. Ferra, L. H. Carvalho and F. D. Magalhães, "Production of melamine fortified urea-formaldehyde resin with low formaldehyde emission", *Journal of Applied Polymer Science*, vol. 124, pp. 2311-2317, 2012.

### 2.1.1. Introduction

Urea-formaldehyde (UF) resins are the most used type of adhesives used in wood-based panels (WBP) industry [1]. Worldwide, these resins represent 80 % of the total production in the aminoresins class [2]. The remaining 20 % correspond mainly to melamine-formaldehyde (MF) resins, with a small percentage of resins synthesized from other aldehydes and/or other amino compounds [3]. According to SRI Consulting [4], the global production of UF resins in 2008 was approximately 14 million ton. Their consumption increased 2.8 % in 2008, and is expected to grow an average 3.2 % per year from 2008 to 2013, and just under 2 % per year from 2013 to 2018.

UF resins are thermosetting polymers that, before cure, consist of an aqueous solution/dispersion of unreacted monomers, linear or branched oligomeric and polymeric molecules [1]. They are condensation products of aldehydes with compounds containing amino groups. Their success on the market is mostly due to high reactivity, good performance and low cost. However, the hydrolytic degradation of UF polymers causes a significant weakening of resin bonds and is a source of formaldehyde emissions [5]. Another cause of formaldehyde emission from wood-based panels produced with these resins is the presence of free (unreacted) formaldehyde [1].

In 2006 the International Agency for Research on Cancer (IARC), has classified formaldehyde as "carcinogenic to humans"[6]. The new classification has led the industry to find strategies to limit formaldehyde emission levels from WBP. The most common approaches consist in: decreasing the F/U (formaldehyde/urea) molar ratio, incorporation of other co-monomers in the synthesis and adding formaldehyde scavengers to the particles/fibres before or after resin blending [7]. The F/U molar ratio has been slowly decreased over the years from its initially high value, but causes the manufacturing processes

to be more sensitive to perturbations in operating conditions and leads to particleboards with lower physical and mechanical properties [8].

The incorporation of a small percentage of melamine to UF resins improve moisture/water resistance and therefore decrease formaldehyde emissions. The aminomethylene bonds in UF resins are quite susceptible of hydrolytic attack. However, more stable bonds are obtained when a methylene carbon is linked to an amide group from a melamine ring, instead of nitrogen from urea. This is especially true at high temperatures, probably due to the quasiaromatic ring structure of the melamine. In addition, the slower pH decrease in the bond line due to the buffer capacity of melamine could also explain the higher stability of the bonds in melamine-urea-formaldehyde (MUF) resins [1]. However, this lower decrease in pH also causes an increase in gel time and consequently, higher pressing times.

The wide range of formulations for MUF resins originates different properties, performances and durabilities [2, 3]. One can distinguish two particular cases: MUF resins, where the melamine content is above 5 %, and melamine-fortified UF resins, with melamine content below 5 %. In both cases the production can be performed in different ways: co-condensation of all monomers, melamine, urea and formaldehyde, in a multistep reaction; mixing of separately synthesized MF and UF resins; and post-addition of melamine, in various forms (pure melamine, MF/MUF powder resin or melamine acetates) to an UF resin during the preparation of the glue mix [9].

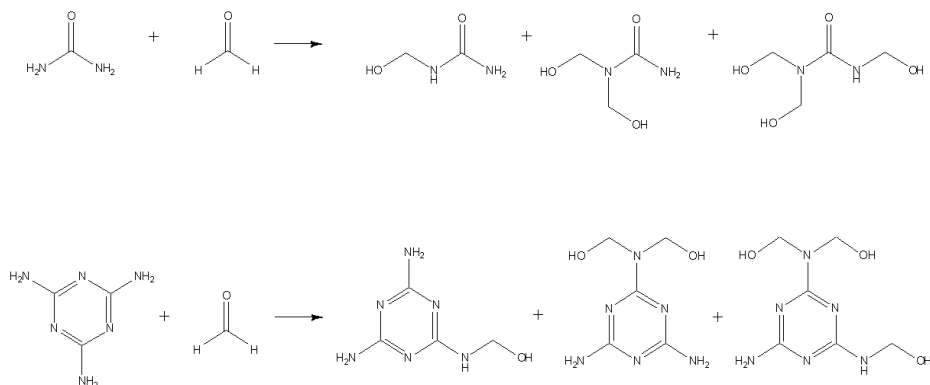
Melamine-fortified UF resins are now a conventional alternative to UF resins for application as adhesives in wood based panels (WBP), such as particleboard (PB) and medium density fibreboard (MDF). These allow reducing formaldehyde emissions and improving the physical properties of the panels.

However, the costs for these fortified products are higher due to the higher price of melamine compared to urea [1]. When added to the reaction mixture, melamine can enter in any of these steps: initial methylation step (before or after the addition of the first urea), condensation step (before or after the addition of the second urea), or final urea addition [5]. The best procedure depends on the particular process used. The studies by Shiao and Smith (1985), using an alkaline-acid process, showed that melamine addition is more effective in the methylation step. On the other hand, Hse studied melamine addition in a strongly acid process, and concluded that the best results were obtained for melamine addition during acidic condensation (pH between 4.5 and 6.5) [10]. This author essentially studied the melamine reaction with a UF pre-polymer formed in a strongly acid environment, the final MUF resin produced had a F/U molar ratio of 1.2, with 4.39 % (weight basis) maximum melamine content.

Previous studies have shown that the melamine content has a very significant effect on both the resin and particleboard properties. An increase in melamine content results in an increase in gel time, solid content and internal bond strength. On the other hand, there is a decrease in thickness swelling, water absorption and formaldehyde emission [11].

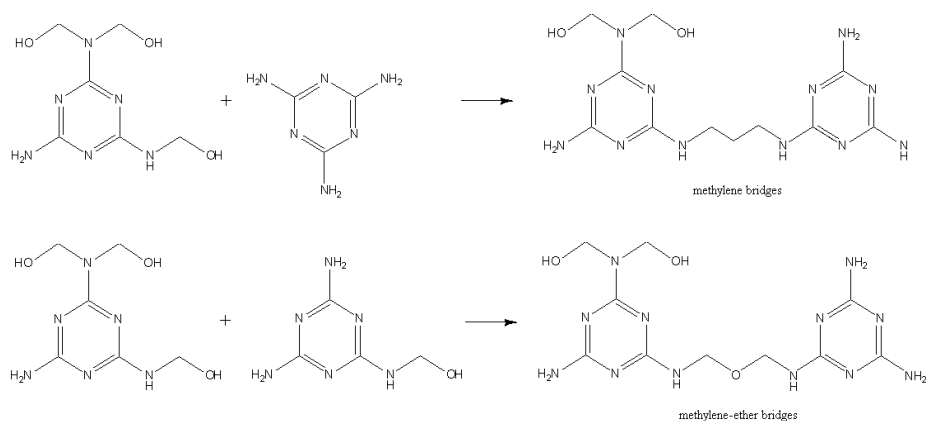
MUF resins are produced according to the same procedures as UF resins. The most common approach is the alkaline-acid process [9]. The process consists in an initial alkaline methylation (hydroxymethylation) step followed by an acidic condensation. An alternative strategy is the strongly acid process [8]. In this case the initial reaction is carried out under strongly acidic environment, in which the methylation and condensation reactions occur simultaneously. The methylation step consists in the reaction between urea, melamine and formaldehyde to form the so called methylolureas and methylolmelamines

(Figure 2.1). At this low pH, however, these species react almost instantly to form linear and/or branched polymers linked by methylene-ether and methylene bridges (Figure 2.2). The released heat is sufficient to drive the reaction to the desired condensation level, and can be controlled by a programmed addition of urea to the acidified formaldehyde solution. This process may reduce the reaction time by 30 % in relation to the alkaline-acid process, with much lower energy consumption. The disadvantage of this process lies in the difficulty in controlling the highly acid condensation step, due to its exothermic character [12].



**Figure 2.1** Formation of methylolureas and methylolmelamines (mono-, di- and tri) by the addition of formaldehyde to urea and to melamine

The present study investigates the best procedure for incorporation of melamine in the synthesis of UF resins, producing a MUF copolymer in the first reaction stages. The general goal is the production of a melamine fortified UF resin with a molar ratio F/U of 0.98, with good internal bond strength and low thickness swelling and formaldehyde emission.



**Figure 2.2** Condensation of the methylolureas and methylolmelamines to form methylene-ether and methylene bridges

### 2.1.2. Materials and Methods

#### *Resin Preparation*

All the resins were synthesized in the laboratory reactor. The synthesis was carried out in 2.5 and 5 L round bottom flasks, equipped with mechanical stirring and thermometer. Temperature control of the reactor is performed using a heating mantle. The resins were synthesized using the so-called strongly acid process, which is based on the occurrence of methylation and condensation reactions simultaneously [13].

The process begins with the methylation/condensation reaction between a 50 % formaldehyde solution and urea, at very low pH - between 0.5 and 2.5 - by adding an appropriate amount of a sulphuric acid. This reaction consists essentially in the addition of one to three formaldehyde molecules to a urea molecule, to form the so-called methylolureas. The UF polymer builds up when the methylolureas react with free urea and formaldehyde, producing linear and partly branched molecules with medium to high molecular weights [1]. Urea is added slowly, allowing the heat of reaction to raise the temperature

from the initial 60 °C to values between 80 and 90 °C. The amount of urea added to the formaldehyde solution during this initial step is sufficient to provide an F/U molar ratio of 3.5 to 3. If melamine is added in this step, the reaction then proceeds until a desired viscosity of 500 mPa·s is reached.

The second step consists in the methylation reaction of additional urea with free formaldehyde still present in the reaction mixture. To make sure that only this reaction takes place, and the condensation is inhibited, it is necessary to adjust the pH to a neutral or slightly basic value, by adding sodium hydroxide solution. The additional urea added in this step must be enough to provide an F/U molar ratio of 2.5 to 1.5. If melamine is to be added in this step, the gain in reaction mixture viscosity is expected to occur after this addition.

Afterwards, the reaction mixture is cooled during 30 min, until a temperature of 50 °C is attained. At this point, a final amount of urea is added to provide a final F/U molar ratio of 0.98. The reaction is terminated by cooling the mixture to a temperature of 25 °C.

Melamine can be added to the reaction mixture in any of three synthesis steps: in the initial methylation/condensation step (before or after the addition of the first urea), in the methylation step (before or after the addition of the second urea), or with the final urea. The first two alternatives were studied here. In all cases, the amount of melamine added was 3 % relative to final mass of resin.

### ***Resin Properties Determination***

Viscosity, pH, reactivity and solid content were determined at the end of each synthesis. Viscosity was measured with a Brookfield viscometer at a constant temperature of 25 °C. The resin pH was measured using a combined glass

electrode. The solid content was determined by evaporation of volatiles in 2 grams of resin for 3 hours at 120 °C. The resin reactivity was determined by measuring the gel time of a resin sample at 100 °C, after addition of a cure catalyst (ammonium sulphate or ammonium nitrate).

### ***GPC/SEC Analysis***

A GPC / SEC equipped with a Gilson Differential RI detector and a Rheodyne 7125 injector with a 20 µL was used. The columns used were PSS Proteema 100 and 300 5 µm, conditioned at 60 °C using an external oven. The flow rate was 1 mL·min<sup>-1</sup>. Samples for analyses were prepared by dissolving a small amount of resin in DMSO (dimethylsulfoxide), followed by vigorous stirring. Subsequently, the sample is left to rest, and then it is filtered through a filter of 0.45 µm [14].

### ***Particleboard Production***

The production of particleboards is essentially divided into four stages: preparation of raw materials, blending, mat formation and pressing. Wood particles were provided by a particleboard manufacturer (Sonae Indústria, Oliveira do Hospital). Standard mixtures were used for the core and face layers, which are composed of different proportions of pine, eucalyptus, pine sawdust and recycled wood. The moisture content of the standard mixtures was checked before blending, using an infrared balance. The average of the moisture content of the face and core layers particles was 2.5 % and 3.5 % respectively. Wood particles were then blended with the resin, catalyst and paraffin in a laboratory glue blender. The gluing factor was 6.3 % resin solids in the face and 6.9 % in the core, based on the oven-dry weight of wood particles. The resin was more catalyzed in the core layer (3 % solids based on oven-dry weight of resin) than in the face layer (1 % solids based on oven-dry weight of

resin). The paraffin level was 0.15 % solids (based on oven-dry weight of wood).

Three-layer particleboard was hand formed in an aluminium container with 220x220x80 mm. The total percentages of board mass were: 20 % for the upper face layer, 62 % for the core layer and for 18 % bottom face layer. The pressing of particleboard panels was carried out in a hot-press, controlled by computer and equipped with four thermocouples, a displacement sensor (LVDT), a load cell and a pressure transducer. Pressing cycle (stage duration, press closing time, platen temperature) was scheduled in order to simulate a typical particleboard continuous pressing operation. The glued particles were pressed at 190 °C with a pressing time of 150 s. The target thickness was 16 mm. The average density of the final boards was  $630 \pm 20 \text{ kg}\cdot\text{m}^{-3}$ . The thickness of the panels is measured in five points (center and each corner) after pressing.

### ***Physic-Mechanical Characterization of Particleboard***

After pressing, boards were stored in a conditioned room (20 °C, 65 % RH) and then tested accordingly to the European standards. The following physic-mechanical properties were evaluated: density (EN 323), moisture content (EN 322), internal bond strength (IB) (EN 319 – tensile strength perpendicular to the plane of the board) and thickness swelling (EN 317). For each experiment, four board replicates were obtained. Formaldehyde content was determined according to EN 120 (perforator method). Panels for the analysis of formaldehyde content were stored in sealed plastic bags.

#### **2.1.3. Results and Discussion**

This study essentially consisted in five distinct approaches for the synthesis strategy. The major difference between them consists essentially in the timing and pH for melamine addition.

### ***First four synthesis strategies***

For each attempts were made at least three resins and in Table 2.1 are listed the results obtained for one of these resins. For these formulations the solid content was about 63 % in all cases. It must be noted that there is a major difference between synthesis 1 and 3, which results in different ending viscosities. In the first one, the pH was increased to 7 after melamine addition, by adding sodium hydroxide solution, and then the second urea was added (second step). In resin UF 3, on the other hand, the base was not added after melamine addition, and there was only a waiting time for allowing the pH to increase until stabilizing. The final pH before the second step was therefore between 5 and 6.

In resin UF 2, melamine addition occurs in the second step (methylolation at neutral pH). It was observed that the resin did not gain viscosity after the addition, suggesting that the addition of melamine in a neutral to alkaline phase only promotes the formation of methylolmelamines.

Finally in resin UF 4 the melamine was added in the first step, after the addition of the first urea and at a pH between 5 and 7 (this value is obtained with the addition of an appropriated base).

**Table 2.1** Operation conditions for the first four synthesis strategies

Operation Conditions / Resin	UF 1	UF 2	UF 3	UF 4
Melamine addition step	1°	2°	1°	1°
pH before melamine addition	0.5-2	7-8	0.5-2	5-7
Final pH	8.83	7.81	8.90	8.82
Final viscosity (mPa-s)	60	140	210	65

Table 2.2 shows the results for the particleboard properties obtained with the first four resins. The results obtained for the resins 2 and 4 explain values out of specification with regard to IB strength (lower than  $0.35 \text{ N}\cdot\text{mm}^{-2}$ , the requirement for type P2 boards, according to EN 319) and thickness swelling, especially in procedure 2. Comparing the results for the UF resin 4 with the results for the UF resins 1 and 3 it is possible to observe that higher condensation pH results in the decrease of particleboard properties.

**Table 2.2** Particleboard properties obtained in the first four synthesis attempts

Properties / Resin	UF 1	UF 2	UF 3	UF 4
Density ( $\text{kg}\cdot\text{m}^{-3}$ )	666	642	633	627
Internal Bond Strength ( $\text{N}\cdot\text{mm}^{-2}$ )	0.38	0.18	0.43	0.28
Thickness Swelling (%)	28.1	38.1	28.6	33.2
Moisture Content (%)	6.3	6.1	4.7	6.0
Formaldehyde Content (mg/100 g oven dry board)	3.2	2.7	3.4	3.0

The panels produced with resins UF 1 and 3 present a high performance, namely high IB strength and low formaldehyde emission. However the synthesis processes were very unstable (the increase of the viscosity is too fast during the condensation step), making these strategies unviable for industrial use without rigorous on-line control of the degree of condensation.

#### ***Fifth synthesis strategies attempts***

In the ensuing approach, melamine was added to the initial formaldehyde solution at its normal pH (between 3 and 3.5), instead of decreasing it to 0.5 – 2.5 as before. After a 5 min stabilization period, pH was raised to 4.5 - 6, and only then the first urea was added. The second and third steps were then performed as previously described in synthesis described above. The major

difference between this approach and the previous is the initial formation of methylolmelamines, that posterior react with methylolureas and urea.

Table 2.3 summarizes the four syntheses that compose this fifth approach. The fundamental difference between them is the pH set for the addition of the first urea. For all the synthesis it was observed that lower pH implied faster viscosity increase (higher reaction rate). It possible to conclude that more acidic conditions favour the condensation of the methylolmelamines and methylolureas produced in the methylation reaction, instead of a methylation reaction between the unreacted urea and free formaldehyde.

**Table 2.3** Properties of UF resins produced in fifth synthesis attempt

Operation Conditions / Resin	UF 5.1	UF 5.2	UF 5.3	UF 5.4
pH before first urea addition	4.5	4.7	5.0	6.0
Final pH	8.21	7.78	9.18	8.80
Final viscosity (mPa·s)	430	100	140	95
Solid content (%)	63.4	62.3	63.4	64.1
Gel time (s)	75	68	110	48

The synthesis of UF 5.4 resin was slightly different. During the methylation/condensation reaction the resin did not gain the desired viscosity (500 mPa·s) after one and a half hours of reaction time. The temperature was therefore raised to 95 °C and the second urea was added immediately. In these conditions the reaction progressed and the viscosity increased. The reaction mixture was then cooled to 60 °C and the final urea was added. This synthesis was therefore different because both the first and second urea amounts were present in the methylation/condensation step.

In conclusion, it is possible to suggest that for this synthesis process, for pH higher than 5.5 the condensation reaction does not occur at low temperature and high F/U molar ratio.

Table 2.4 presents the physic-mechanical properties of the particleboard produced with the four resins. In general, the values are favourable for all features. Increasing the methylation/condensation reaction pH decreases the IB strength of the panels. However, all the IB strength values are higher than the minimum acceptable value of  $0.35 \text{ N}\cdot\text{mm}^{-2}$ . Regarding formaldehyde emissions, all resins are below the limit imposed by CARB II legislation corresponding to an equivalent of perforator value of  $\leq 5.6 \text{ mg}/100 \text{ g}$  oven dry board [15], all resins having emissions below  $3 \text{ mg}/100 \text{ g}$  oven dry board. The other properties are not sensitive to the reaction pH.

**Table 2.4** Particleboards properties obtained in fifth synthesis attempt

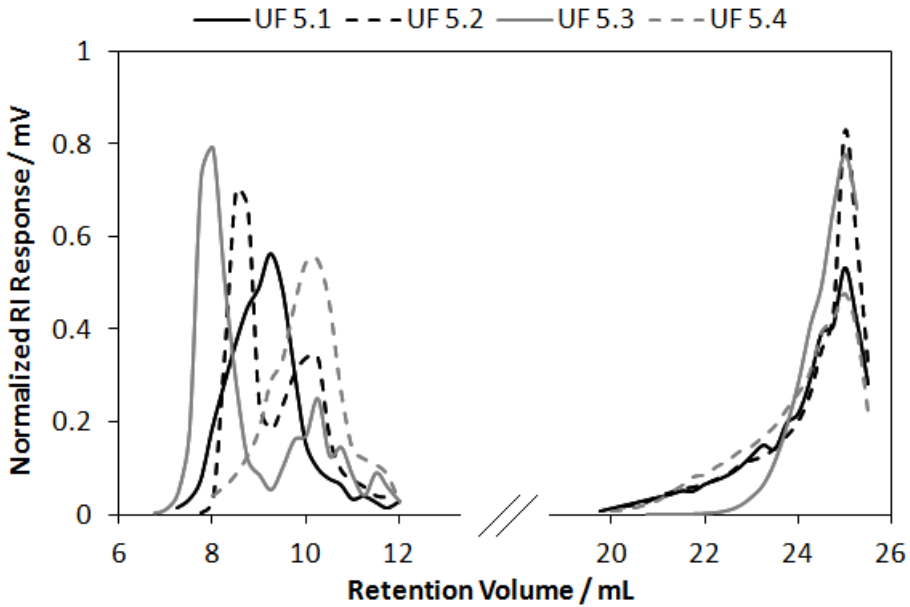
Properties / Resin	UF 5.1	UF 5.2	UF 5.3	UF 5.4
Density ( $\text{kg}\cdot\text{m}^{-3}$ )	637	622	634	641
Internal Bond Strength ( $\text{N}\cdot\text{mm}^{-2}$ )	044	0.44	0.35	0.36
Thickness Swelling (%)	28.9	30.9	29.6	29.9
Moisture Content (%)	5.4	4.7	5.0	5.1
Formaldehyde Content ( $\text{mg}/100 \text{ g}$ oven dry board)	2.7	2.8	2.5	2.7

All the resins produced in this fifth approach were analyzed by GPC/SEC in order to verify main differences between them and the results are present in the Figure 2.3. In this type of distribution the peaks with larger retention volume (retention volume between 20 and 26 mL) corresponds to free urea, methylolureas, methylolmelamines and oligomers (molecular weight  $< 3000$ ) and the peaks with lower retention volume (retention volume between 6-14

mL) correspond to polymer with high molecular weight (molecular weight > 12000). Considering the high molecular weight fraction of the chromatograms (retention volume between 7 and 12 mL), it can be seen that increasing pH leads to higher molecular weight polymer, for resins 5.1, 5.2 and 5.3. Resin 5.4 is an exception, since the synthesis process was modified as discussed above: the methylation/condensation step could only be carried after the addition of the second urea and increase of temperature. Since the F/U molar ratio is lower, the polymer condensation does not progress as much as for the other three resins. This occurs because the free formaldehyde reacts with the methylolureas and methylolmelamines, and also with this new urea.

In the lower molecular weight region (retention volume between 20 and 26 mL) it is noticeable that resin 5.3 shows a lower shoulder (21 to 23 mL), which may be related to the higher degree of condensation, obtained at the expense of oligomeric species.

The resin UF 5.4 present the lower reactivity (see Table 2.3), which is in agreement with the lower extension of the polymerization at the end of the reaction. The gel time values for resins UF 5.1 and UF 5.2 are very close and are essentially equivalent. Resin UF 5.3 shows the highest reactivity, which is once again relatable to the presence of higher molecular weight material.



**Figure 2.3** Chromatograms of UF resins produced in fifth synthesis attempt

### ***Comparison with other commercial resins***

In order to understand the impact of the development of this resin in relation to existing commercial products, Table 2.5 shows the results for physical-mechanical properties of panels produced with three resins produced by different processes and with different melamine contents. Resins 1 and 2 are produced by the alkaline-acid process, having a melamine incorporation of 0 and 0.3 % respectively. Resin 3 is produced by a basic process and has 3 % melamine. The panels and characterization procedures were performed in our lab in the same conditions as the previous ones.

The formaldehyde content for Resin UF 5.1 is significantly lower than for the other resins. Internal resistance is lower than for Resin 1, but still acceptable and similar to the values obtained for the other two resins. The other properties are also very similar for these four distinct resins.

**Table 2.5** Particleboards properties produced with different UF resins

Properties / Resin	R1	R2	R3	UF 5.1
Density ( $\text{kg}\cdot\text{m}^{-3}$ )	641	675	656	637
Internal Bond Strength ( $\text{N}\cdot\text{mm}^{-2}$ )	0.52	0.39	0.49	0.44
Thickness Swelling (%)	25.7	32.0	34.7	28.9
Moisture Content (%)	6.3	6.2	5.8	5.4
Formaldehyde Content (mg/100g oven dry board)	5.3	3.4	4.6	2.4

### 2.1.4. Conclusions

Resins UF fortified with melamine have been developed for upgrading the performance of UF bonded particleboards with low formaldehyde emissions. A strongly acid process was used for the resin synthesis. The addition of melamine was tested in the two main synthesis steps: acidic methylation/condensation and slightly basic methylation. Results indicated that the first step is the most appropriate for melamine addition. The effect of pH at this step was also studied. Very low or high pH values are not beneficial. Low pH (lower than 3) results in a very unstable reaction, as the resin gains viscosity very quickly. A high pH value (higher than 5) results in a very slow condensation reaction.

The particleboards produced with the several resins showed that an increase in the pH of the first reaction step results in lower values of IB strength. Regarding formaldehyde content, all the resins in this study showed very low formaldehyde emissions.

This work describes a new synthesis strategy for UF resins fortified with melamine. Moreover, this process yields resins with good mechanical performances in terms of IB strength and formaldehyde emissions. The novelty

of this approach lies on the melamine addition during the acidic step, promoting its reaction with formaldehyde prior to the introduction of urea. This yields a melamine-urea-formaldehyde copolymer with strong bonds, instead of only urea-formaldehyde and melamine-formaldehyde polymers.

## 2.2. Study of the influence of synthesis conditions on the properties of melamine-urea-formaldehyde resins<sup>2</sup>

### **Abstract**

The aim of this work is to assess the differences in the polymeric structure and performance of melamine-urea-formaldehyde (MUF) resins, when changing relevant synthesis variables: formaldehyde/amine groups ( $F/(NH_2)_2$ ) molar ratio (both in methylation and condensation steps) and feed rate of urea during the condensation step. This synthesis process differs from the traditional alkaline-acid process, since the  $F/(NH_2)_2$  molar ratio is different for the methylation and condensation steps. It was found that the  $F/(NH_2)_2$  molar ratio and urea feed rate in the condensation step are the most influential variables on the product characteristics. A relationship was established between polymeric structure of the resin and the physico-mechanical properties, as well as the levels of formaldehyde.

A resin formulation was obtained that exhibits formaldehyde content, evaluated both by perforator and desiccator methods, within the Japanese F\*\*\*\* requirements. This resin presents an overall performance better than the one obtained by two representatives commercial resins.

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<sup>2</sup> N. T. Paiva, J. Pereira, J. M. Ferra, P. Cruz, L. Carvalho and F. D. Magalhães, "Study of influence of synthesis conditions on properties of melamine-urea-formaldehyde resins", *International Wood Products Journal*, vol. 3, pp. 51-57, 2012

### 2.2.1. Introduction

The wood-based panels (WBP) industry relies heavily on the use of synthetic resins, such as urea-formaldehyde (UF), melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF) resins. UF resins are the most used, representing 80 % of the total production in the amino resins class [1]. Their commercial success is mostly due to their high reactivity, good performance and low cost. However, susceptibility to hydrolytic degradation causes a significant weakening of resin bonds and is a source of formaldehyde emissions [5]. Another cause of formaldehyde release from WBP produced with these resins is the presence of unreacted formaldehyde [1].

In 2004 the International Agency for Research on Cancer (IARC), has classified formaldehyde as "carcinogenic to humans" [6]. The new classification has led the industry to find strategies to limit formaldehyde emission levels from WPB. The most common approaches consist in: decreasing the F/U (formaldehyde/urea) molar ratio [16-18], incorporation of other co-monomers in the synthesis to change the polymeric structure of the final resins and consume more formaldehyde [10, 19] formaldehyde scavengers addition to the particles/fibres before or after resin blending [20, 21] and development of new synthesis processes [8, 12, 22].

The incorporation of a small percentage of melamine on UF resins improves moisture/water resistance and therefore contributes to decrease formaldehyde emissions [10, 19, 22]. The aminomethylene bonds in UF resins are quite susceptible of hydrolytic attack. However, more stable bonds are obtained, when a methylene carbon is linked to an amide group from a melamine ring, instead of nitrogen from urea. This is especially true at high temperatures, probably due to the quasaromatic ring structure of melamine. In addition, the slower pH decrease in the bond line due to the buffer capacity

of melamine could also explain the higher stability of the bonds in melamine-urea-formaldehyde (MUF) resins [1]. However, this lower decrease in pH also causes an increase in gel time and consequently, the need for higher pressing times.

The wide range of formulations for MUF resins originates different properties, performances and durabilities [2, 3]. One can distinguish two particular cases: MUF resins, where melamine content is above 5 %, and melamine-fortified UF resins, with melamine content below 5 %. In both cases the production can be performed in different ways: co-condensation of all monomers, melamine, urea and formaldehyde, in a multistep reaction; mixing of separately synthesized MF and UF resins; and post-addition of melamine in various forms (pure melamine, MF/MUF powder resin or melamine acetates) to an UF resin during the preparation of the glue mix [23, 24].

Previous studies have shown that the melamine content has a very significant effect on both the resin and particleboard properties. An increase in melamine content results in an increase in gel time, solid content and internal bond strength. On the other hand, there is a decrease in thickness swelling, water absorption and formaldehyde emission [11]. Production of MUF resins is carried out mostly using the alkaline-acid synthesis process. It is not yet clear what is the effect of changes in some process variables on the performance of these resins [1].

In this study the synthesis process used was slightly different from the traditional approach, in which the methylation and condensation steps have the same  $F/(NH_2)_2$  molar ratio [9, 25]. In this study the  $F/(NH_2)_2$  molar ratio in the methylation and condensation steps is different. The key idea was to

increase the quantity of urea introduced in these two steps in order to allow a higher incorporation in the polymeric matrix, and analyse its consequences.

Size exclusion chromatography (SEC) is often used in order to understand the influence of changes in a synthesis process on polymer structure and molecular weight distribution (MWD) [14]. The mechanical and bonding properties of an adhesive are strongly dependent on its MWD [9, 24, 26]. This technique is an entropically controlled separation technique in which molecules are separated on the basis of hydrodynamic molecular volume and size. With proper column calibration or by use of molecular-weight-sensitive detectors, such as light scattering, viscometry or mass spectrometry, the molecular weight distribution and the statistical molecular weight averages can be obtained readily. Thus, SEC is the premier technique for determining these properties of both synthetic polymers and biopolymers [26].

Its application to UF and MUF resins is reported in several studies [27], but presents some difficulties, largely due to the limited solubility of these resins, which are surmountable only after a correct choice of solvent and mobile phase [14]. It is necessary to use solvents such as DMSO (dimethylsulfoxide) and DMF (dimethylformamide) to ensure complete dissolution of high molecular weight polymer. Another problem is related to the complexity of the polymer structure, and the presence of linear and branched fractions. Thus the calibration becomes a difficult task, with no commercial standards available [14].

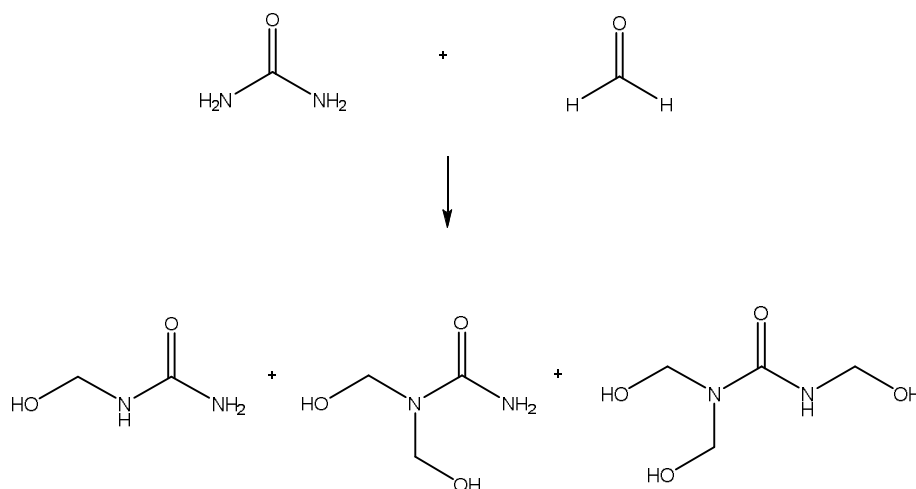
The main objective of this study is to understand the influence of key process variables on physico-chemical and physico-mechanical properties of MUF resins.

## 2.2.2. Materials and Methods

### *Resin Preparation*

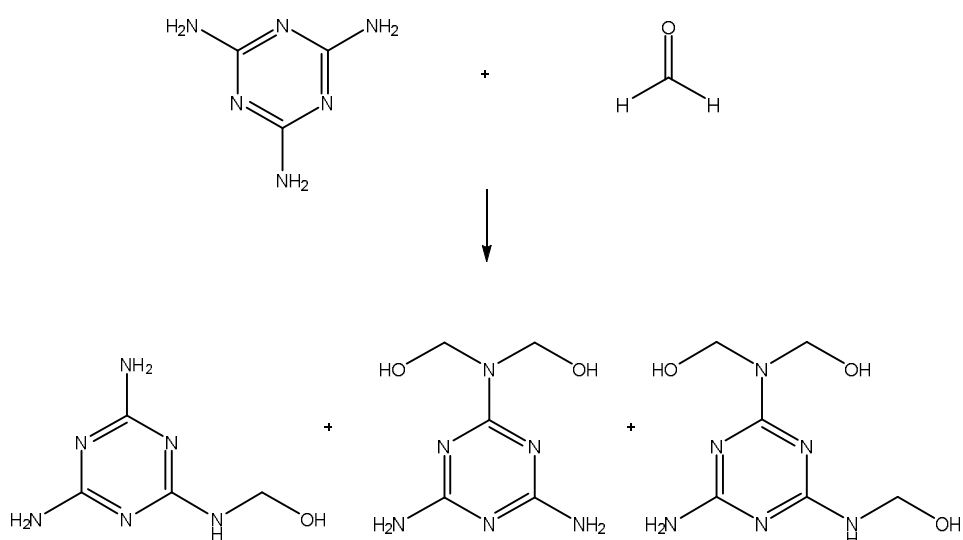
All resins were synthesized in round bottom flasks with volumes 2.5 or 5 L, equipped with mechanical stirring and a thermometer. Temperature control was accomplished by means of a heating blanket. pH and viscosity measurements are performed off-line, on samples taken from the reaction mixture. The resins were synthesized according to the so-called alkaline-acid process, which consists of three steps: a methylation step at alkaline conditions, a condensation step at acidic conditions, and an addition of the so-called final urea [12].

The synthesis process starts with the methylation reaction between 50% formaldehyde solution, urea and melamine, at a basic pH (usually between 7.5 and 9), obtained by adding an appropriate amount of base. In this reaction the addition of one to three molecules of formaldehyde to one molecule of urea forms methylolureas (Figure 2.4).



**Figure 2.4** Formation of methylolureas (mono-, di- and tri) by the addition of formaldehyde to urea

Simultaneously, the reaction of one to six molecules of formaldehyde with one molecule of melamine produces methylolmelamines (Figure 2.5). Urea is added gradually, allowing the heat of reaction to raise temperature from the initial 60 °C to values between 80 and 90 °C. The amount of urea and melamine added to the formaldehyde solution during this initial step is sufficient to provide a formaldehyde/amine groups molar ratio ( $F/(NH_2)_2$ ) of 3.5 to 2.5.

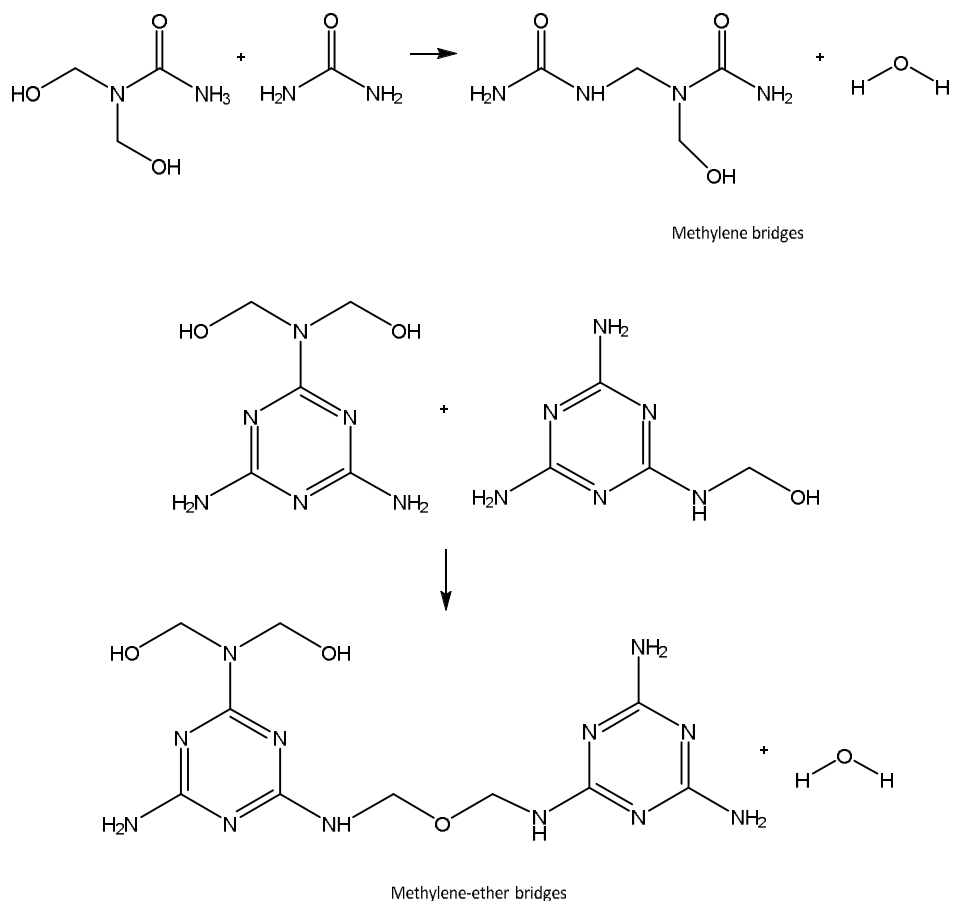


**Figure 2.5** Formation of methylolmelamines (mono-, di- and tri) by the addition of formaldehyde to melamine

In the second step, the MUF polymer builds up when the methylolureas and methylolmelamines react with free urea and formaldehyde, producing linear and partly branched molecules with medium to high molecular weights [1] (Figure 2.6).

Additional urea is added at the beginning of this step, for 20 min, in 20 equal portions, at a pH between 4.8 and 5.3. The  $F/(NH_2)_2$  molar ratio at the end of this step is between 2.4 and 1.4, depending on the amount of urea added. The

condensation reaction continues until a desired viscosity is attained, between 400 and 600 mPa·s, and is terminated by neutralization of the resin to a slightly basic pH and then cooling to a temperature of 50 °C. At this point a given final amount of urea is added in order to decrease the  $F/(NH_2)_2$  molar ratio to a value of 0.85, which was the same for all productions. The reaction is terminated by cooling the reaction mixture to a temperature of 25 °C.



**Figure 2.6** Condensation of the methylolureas and methylolmelamines to form methylene-ether and methylene bridges

### ***Resin Properties Determination***

Viscosity, pH, reactivity and solid content were determined at the end of each synthesis. Viscosity was measured with a Brookfield viscometer at 25 °C. The resin pH was measured using a combined glass electrode. The solid content was determined by evaporation of volatiles in 2 g of resin for 3 h at 120 °C. The resin reactivity was determined by measuring the gel time of a resin sample at 100 °C, after addition of cure catalyst (ammonium sulphate or ammonium nitrate).

### ***Commercial Resins***

The two commercial resins analysed in this study were supplied by EuroResinas (Sonae Indústria, Portugal). Both resins are produced according to the alkaline-acid synthesis process. Resin A is a UF resin with a final F/U molar ratio of 1.07, and Resin B is a melamine-fortified UF resin with a final F/U molar ratio of 0.98 and a percentage of melamine of 3 %. According to manufacturer's information, both resins have a final viscosity between 150 and 300 mPa·s, a final pH between 8.0 and 9.5 and a solid content around 64 %. Resin A has a reactivity of 60 s and Resin B has a reactivity of 80 s.

### ***GPC/SEC Analysis***

A GPC / SEC equipped with a Knauer RI detector 2300 and a Knauer injector with a 20 µL was used. The columns used were PSS Proteema 100 and 300 5 µm, conditioned at 60 °C using an external oven. The flow rate was 1 mL·min<sup>-1</sup> and DMF was used as the mobile phase. Samples for analyses were prepared by dissolving a small amount of resin in DMSO (dimethylsulfoxide), followed by vigorous stirring. Subsequently, the sample is left to rest, and then it is filtered through a 0.45 µm filter [14].

### ***Particleboard Production***

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 gluing factor was 7 % resin solids in the face and 7 % in the core, based on the oven-dry weight of wood particles. 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 (220x220x80 mm). 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 boards 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 glued particles were pressed at 190 °C for 150 s to produce panels with a target density of 650 kg·m<sup>-3</sup> and thickness of 17 mm.

### ***Determination of Internal Bond Strength and Formaldehyde Content***

After pressing, boards were stored in a conditioned room (20 °C, 65 % relative humidity) and then tested according to European standards. The internal bond strength (IB) was determined according to EN 319 (tensile strength perpendicular to the plane of the board) and formaldehyde content was determined according to EN120 (perforator method) and to JIS 1460-2001

(desiccator method). Panels for formaldehyde content analysis were stored in sealed plastic bags.

### **2.2.3. Results and Discussion**

In this study, a set of resins was synthesized according to the same process, only with small changes in three relevant process variables:  $F/(NH_2)_2$  molar ratio at the end of the methylation step (designated as  $F/(NH_2)_2_{I}$ ),  $F/(NH_2)_2$  molar ratio at the end of the condensation step ( $F/(NH_2)_2_{II}$ ), and feed rate of urea during the condensation step. The other variables are the same for the nine resins synthesized in this study. The final  $F/(NH_2)_2$  molar ratio is 0.85 and is equal for all resins. The amount of final urea added is adjusted in order to obtain this final molar ratio. The amount and process of melamine addition is also identical for all resins. This is done in the beginning of the synthesis, before the addition of the first urea.

GPC/SEC analyses were performed for all resins. A typical chromatogram for this type of resins (see for example Figure 2.3) presents two distinct regions: one corresponding to larger retention volumes (RV between 20 and 26 mL) can be assigned to free urea, methylolureas, methylolmelamines, oligomers and polymer with an intermediate molecular weight (molecular weight < 3000), and another presenting lower retention volumes (RV between 6-14 mL) corresponds to polymer with high molecular weight (molecular weight >12000) [22].

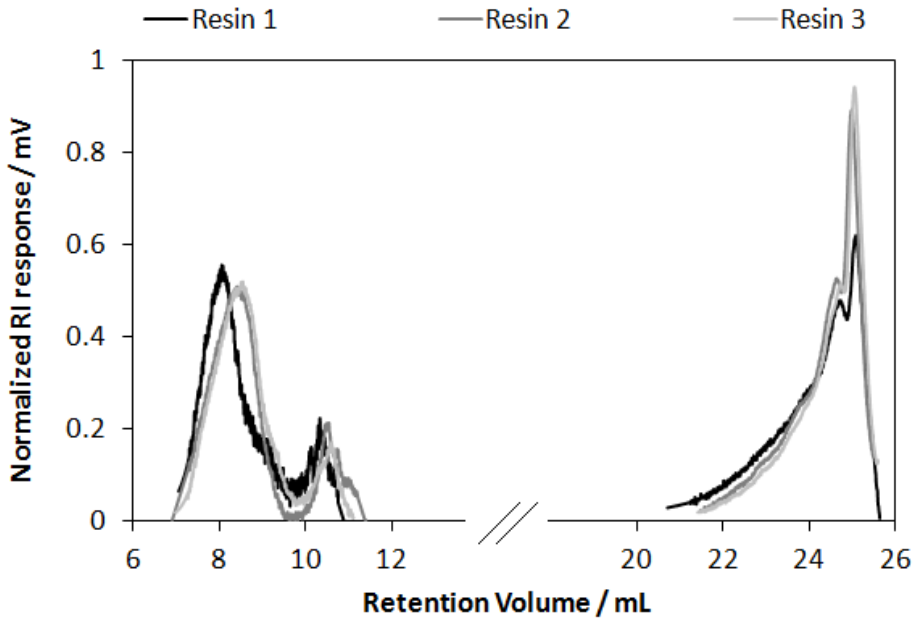
**Effect of  $F/(NH_2)_2$  I Molar Ratio**

Initially three resins with different molar ratios in the methylation step (between 3.5 and 2.5) were synthesized. The molar ratios are related in the following way: Resin 1 > Resin 2 > Resin 3. The other process variables were identical for the three resins. As seen in Table 2.6 the three resins presented similar characteristics.

**Table 2.6** Properties of MUF resins produced in the first approach

Properties / Resin	Resin 1	Resin 2	Resin 3
Final pH	8.7	9.1	9.3
Final viscosity (mPa·s)	150	160	150
Solid content (%)	63.5	63.4	65.0
Gel time (s)	89	77	82

Figure 2.4 shows the normalized response of RI sensor for the three MUF resins synthesized, being the three resins very similar. Resin 1, with the higher  $F/(NH_2)_2$  I molar ratio, shows a small difference in the higher molecular weight area (RV between 7 and 11 mL) when compared with Resins 2 and 3. However, the key difference occurs for low molecular weights (RV between 24 e 26 mL). This range corresponds mostly to unreacted urea. The presence of high molecular weight polymer may indicate that the degree of condensation was higher on Resin 1, leading to more urea and formaldehyde being consumed.



**Figure 2.7** Normalized response of RI sensor for MUF resins produced in the first approach

Table 2.7 presents the internal bond strength and formaldehyde content of particleboard panels produced with resins 1, 2 and 3. Resin 1 shows lower values of formaldehyde content and internal bond strength, which is in agreement with the previously discussed lower amount of available formaldehyde. Resins 2 and 3 are very similar in terms of bond strength. All resins present internal bond strength values higher than the acceptable minimum of  $0.35 \text{ N}\cdot\text{mm}^{-2}$  (the requirement for type P2 boards according to EN 319 standard). The formaldehyde content is also below the maximum acceptable value of  $2.7 \text{ mg}/100 \text{ g}$  oven dry board specified by the Japanese F\*\*\*\* legislation [15].

**Table 2.7** Physico-mechanical properties of MUF resins produced in the first approach

Properties / Resin	Resin 1	Resin 2	Resin 3
Internal Bond Strength (N·mm <sup>-2</sup> )	0.36	0.43	0.45
Formaldehyde Content (mg/100g oven dry board)	2.2	2.6	2.6

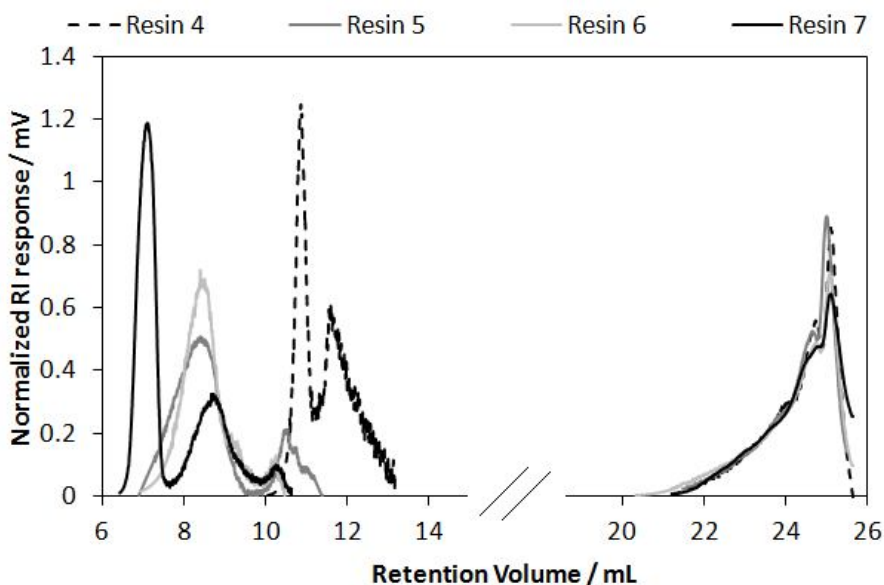
### ***Effect of F/(NH<sub>2</sub>)<sub>2</sub>\_II Molar Ratio***

On the subsequent approach, four resins with different F/(NH<sub>2</sub>)<sub>2</sub>\_II molar ratio (between 2.4 and 1.4) were synthesized. Resin 4 had the highest molar ratio: Resin 4 > Resin 5 > Resin 6 > Resin 7. Higher values of F/(NH<sub>2</sub>)<sub>2</sub>\_II imply that less urea was added during the condensation step. More exactly, urea was added at a lower rate along a period of 20 min (kept constant for all resins).

Table 2.8 shows the properties of MUF resins produced. Solids content, gel time and pH are again very similar for the three resins. The slight difference in final viscosities is associated to the different amounts of final urea added. Resin 4, with the higher F/(NH<sub>2</sub>)<sub>2</sub>\_II molar ratio, takes the largest amount of final urea, implying the lowest final viscosity. Note that all resins ended the condensation step with very similar viscosities.

**Table 2.8** Properties of MUF resins produced in the second approach

Properties / Resin	Resin 4	Resin 5	Resin 6	Resin 7
Final pH	8.9	9.2	8.7	8.8
Final viscosity (mPa·s)	110	160	170	210
Solid content (%)	63.4	63.4	63.9	64.0
Gel time (s)	86	77	87	89

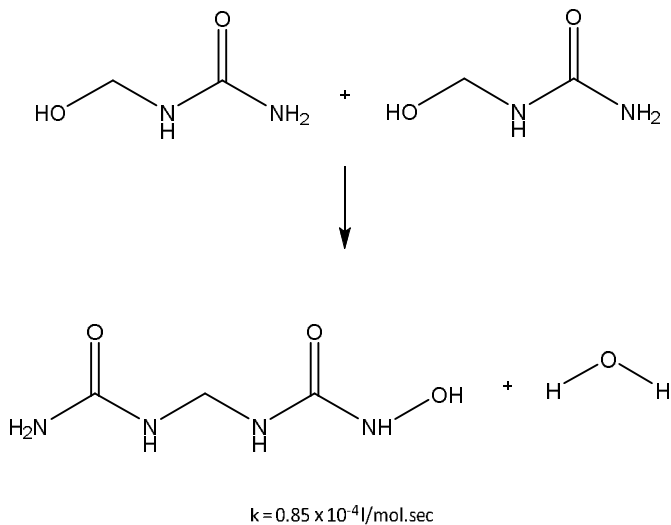


**Figure 2.8** Normalized response of RI sensor for MUF resins produced in the second approach

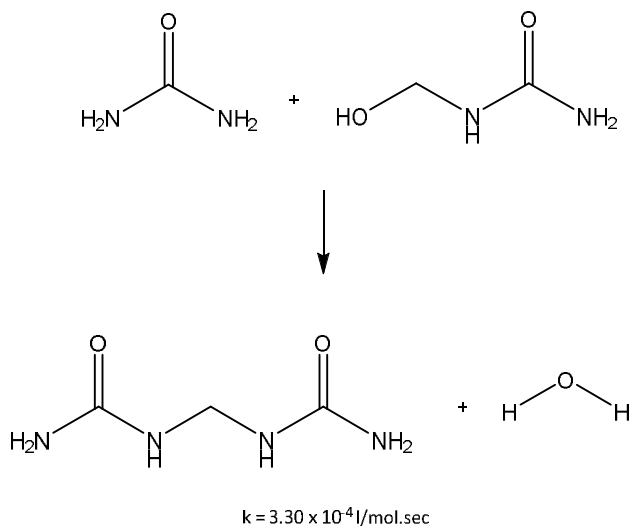
Figure 2.8 shows the normalized response of RI sensor for the four MUF resins synthesized. The differences between the chromatograms are quite noticeable, especially in the higher molecular weight range. Resin 7 has the higher amount of urea added in the condensation step. This may lead to formation of higher molecular weight polymer and/or more linear chains, by promoting the reaction between oligomers intermediated by urea molecules.

It rationale for expecting that in these conditions more linear polymer will be formed is based on the different reactivities of the chemical species present. The reactivity of the amine group in monomethylolurea is about 50 % of the reactivity of an unsubstituted amide group in urea, and the reactivity of a methylol group in a dimethylolurea is about 1/3 of the reactivity of a methylol group in a monomethylolurea [28]. Therefore the presence of a higher amount of urea will probably promote reaction of urea with methylolureas, instead of reaction between methylolureas. Additionally, the rate constant of reaction between two monomethylolurea molecules (Figure 2.9) is lower than the rate

constant of the reaction between one monomethylurea and one urea (Figure 2.10) [28].

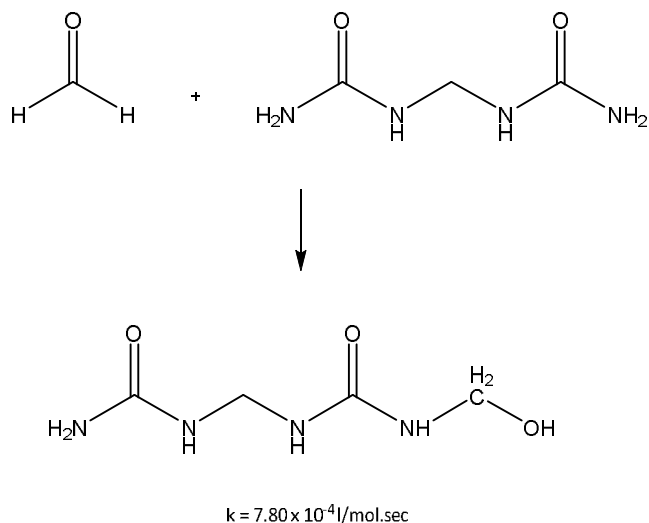


**Figure 2.9** Reaction between two methylolureas in order to form a methylene diurea (rate constants from [28])



**Figure 2.10** Reaction between one methylolureas and one urea in order to form a methylene diurea (rate constants from [28])

The product of this last reaction is methylene diurea, which reacts preferably with formaldehyde and urea (Figure 2.11) [29].



**Figure 2.11** Reaction between one methylene diurea and formaldehyde (rate constants from [28])

Another important aspect is that the rate constant of the reaction between urea and methylolureas decreases with the methylolureas degree of substitution. For the reaction of a urea with dimethylolurea the rate constant is considerably lower when compared with the reaction between urea and a monomethylolurea [29]. The type of polymer created probably will be more linear and as a consequence will have higher hydrodynamic radius and thus present lower retention volume. The reaction between methylolureas and methylolmelamines also occurs, but in lower extent, which may explain the lower peaks present in the high molecular weight range of the chromatogram.

On the other hand, in Resin 4, with the higher  $F/(\text{NH}_2)_2$  molar ratio, the amount of urea added is lower during the condensation reaction. This will promote reaction between methylolureas and reaction between methylolureas and methylolmelamines. This results in a polymer with lower

molecular weight and/or higher degree of branching. Resin 5 and 6 chromatograms correspond to an intermediate situation between the previous two resins.

In the lower molecular weight region, the chromatograms for the four resins are very similar. The difference lies in the amount of unreacted urea, which is larger for resins with higher  $F/(NH_2)_2$  molar ratio, since the quantity of urea added in the final step is higher.

**Table 2.9** Physico-mechanical properties of MUF resins produced in the second approach

Properties / Resin	Resin 4	Resin 5	Resin 6	Resin 7
Internal Bond Strength ( $N \cdot mm^{-2}$ )	0.36	0.43	0.35	0.40
Formaldehyde Content (mg/100 g oven dry board)	2.3	2.6	2.4	1.6

As we can see in Table 2.9, the resin with lowest  $F/(NH_2)_2$  molar ratio (Resin 7) presents the lowest formaldehyde content. This can be expected since formaldehyde was consumed by the excess urea (and methylene diurea) present in the condensation step. The other three values are similar. These values are quite good, especially the result for Resin 7. Regarding internal bond strength, the values are slightly different between the four resins, but are all higher or equal to the acceptable minimum for this type of boards.

### ***Effect of Urea Feed Rate on the Condensation Step***

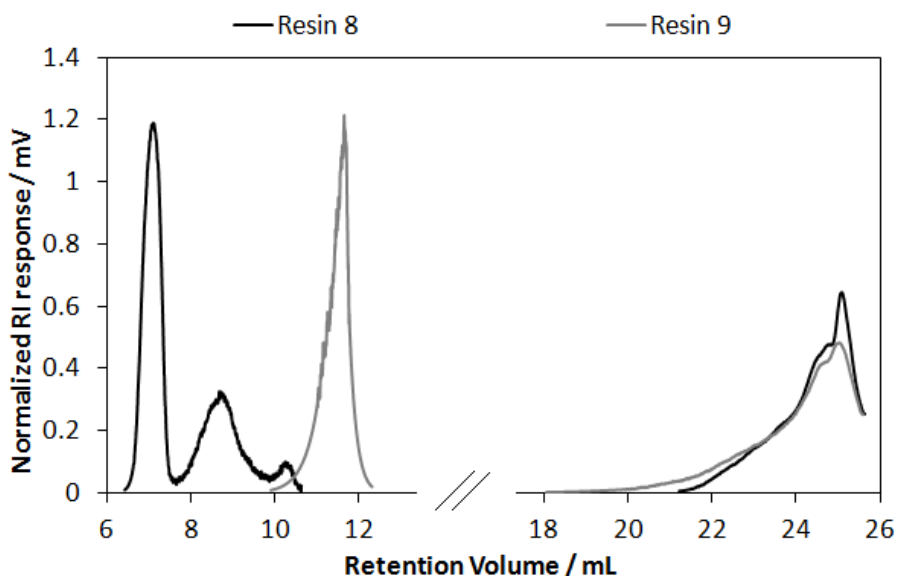
On a final approach two resins were synthesized with different urea feed rate in the condensation step (but identical  $F/(NH_2)_2$  molar ratio) were synthesized. For Resin 8 urea was added during 20 min and for Resin 9 during 60 minutes. The total duration of the condensation step was about 90 min in

both cases. Table 2.10 shows the properties of MUF resins produced in this approach. The values of the four properties are similar for both resins.

**Table 2.10** Properties of MUF resins produced in the third approach

Properties / Resin	Resin 8	Resin 9
Final pH	8.8	8.9
Final viscosity (mPa·s)	210	170
Solid content (%)	64.0	63.4
Gel time (s)	89	88

Figure 2.12 shows the normalized response of RI detector for Resins 8 and 9. In this case it is possible to observe large differences between the two resins on both higher and lower molecular weights regions.



**Figure 2.12** Normalized response of RI sensor for MUF resins produced in the third approach

The differences observed in the high molecular weight range can be explained in the same terms as before, considering that for Resin 8 more urea is present

at the beginning of the condensation step. This excess of urea will preferably promote the reaction between urea and methylolureas, instead of the reaction between the methylolureas and methylolmelamines, resulting in a more linear polymer, which will elute at a lower retention volume. On the other hand, Resin 9 has a slower rate of urea addition, promoting reaction between methylolureas and reaction between methylolureas and methylolmelamines, resulting in lower molecular weight or higher degree of branching. Another effect of the slower urea addition is the formation of moderate molecular weight species (retention volume between 18 and 21 mL).

Table 2.11 shows the results for the internal bond and formaldehyde content for these two resins. It is possible to observe that the internal bond results are very similar. On the other hand, formaldehyde content is lower for Resin 8. Faster addition of urea favours the formation of methylene diurea, which is highly reactive towards formaldehyde [29].

**Table 2.11** Physico-mechanical properties of MUF resins produced in the second approach

Properties / Resin	Resin 8	Resin 9
Internal Bond Strength (N·mm <sup>-2</sup> )	0.40	0.37
Formaldehyde Content (mg/100 g oven dry board)	1.6	2.2

### ***Comparison with Other Commercial Resins***

Resin 7, which showed the best performance in this study, was compared to representative commercial resins produced by the same alkaline-acid process. Resin A is an UF resin with final F/U molar ratio of 1.07. Resin B is a melamine-fortified UF resin (3 %) with final F/U molar ratio of 0.98. Table 2.12 presents internal bond strength and formaldehyde content results for panels produced with the three resins. In this case the formaldehyde content was measured by

both the perforator method (EN 120) and the desiccator method (JIS 1460) in order to better validate the results.

**Table 2.12** Physico-mechanical properties of MUF resins produced in the second approach

Properties / Resin	Resin A	Resin B	Resin 7
Internal Bond Strength ( $\text{N}\cdot\text{mm}^{-2}$ )	0.60	0.52	0.40
Formaldehyde Content (mg/100 g oven dry board)*	4.8	3.0	1.6
Formaldehyde Content ( $\text{mg}\cdot\text{L}^{-1}$ )**	0.85	0.40	0.22

\*Formaldehyde content determined by perforator method (EN120)

\*\*Formaldehyde content determined by desiccator method (JIS1460)

Resin 7 shows lower internal bond strength than resins A and B, but this value is still higher than the minimum acceptable of  $0.35 \text{ N}\cdot\text{mm}^{-2}$  specified by EN 319. Resin 7 is the only one of the three that can reach the Japanese F\*\*\*\* legislation, which simultaneously requires formaldehyde contents below 2.7 by the perforator method and below 0.3 by the desiccator method [15]. With this resin it is therefore possible to obtain particleboards with a better overall result than with the other two commercial resins.

#### 2.2.4. Conclusions

With this study it was possible to conclude that small variations in some process variables of MUF synthesis may result in significant differences in the final resin properties. Among the three variables studied,  $\text{F}/(\text{NH}_2)_2\text{I}$  molar ratio,  $\text{F}/(\text{NH}_2)_2\text{II}$  molar ratio and feed rate of second urea, the last two, which affect the condensation step, are the most influential in terms of the product's polymeric structure and mechanical performance.

The use of lower  $\text{F}/(\text{NH}_2)_2$  molar ratios and faster rates of urea addition in the condensation step results in particleboards with lower formaldehyde content, without significantly affecting the internal bond strength. This was associated

to the formation of the more stable bonds between methylene diurea and formaldehyde, promoted when more urea is added of urea in the condensation step, particularly in the initial stages.

The best performing resin obtained in this study compared favourably to two representative commercial resins. Even though bond strength is not as good, but is still within acceptable values, formaldehyde emissions are significantly lower, verifying the Japanese F\*\*\*\* requirements.

### 2.3. Study of the cure of aminoresins with low formaldehyde emissions<sup>3</sup>

#### **Abstract**

The main objective of this work was to study the influence of temperature and hardener on melamine-urea-formaldehyde (MUF) resin curing as well as the development of a mathematical model to describe the adhesive bond strength. The effect of two different compounds as resin hardeners (ammonium sulphate and ammonium bisulphite) was assessed, as well as the possibility of using ABES equipment for the resin gel time determination.

The results of the curing studies of MUF resin with low formaldehyde emissions performed with ABES technique are presented. Comparing the two hardeners in study it is possible to say that despite the fact that ammonium bisulphite is essentially a formaldehyde scavenger, this compound can also be used as hardener for this type of resins. Between the two hardeners used in this study, the results are very similar, but the best gel time results are obtained for the ammonium sulphate. A comparison between the results for the resin gel time obtained using ABES and conventional methods is also presented which allowed to conclude that ABES can be used as gel time determination equipment for MUF resins.

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<sup>3</sup> N. T. Paiva, J. Ferrá, P. Cruz, J. Martins, F. D. Magalhães and L.H. Carvalho, "Study of the cure of aminoresins with low formaldehyde emissions", *Towards forest products and processes with lower environmental impact (E-book)*, Editions University Fernando Pessoa, pp. 281-288, 2014.

### 2.3.1. Introduction

Aminoresins are the most widely used adhesives for wood-based panels (WBP). These are thermosetting polymers that, before curing, are made of an aqueous solution/dispersion of unreacted monomers, linear or branched oligomeric and polymeric molecules [1]. They are obtained by condensation of aldehydes with compounds containing amino groups and their commercial success is mostly due to high reactivity, good performance and low cost. However, hydrolytic degradation of covalent bonds in the cured resin causes a significant weakening of mechanical strength and is a source of formaldehyde emissions. The main strategy to reduce the formaldehyde emission of aminoresins has been the change on its formulation by decreasing the molar ratio of formaldehyde to urea. However the reduction weakens the mechanical properties of particleboard and moreover it increases the time required for hardening under the action of current hardeners (latent acids) [9]. Hence, it is necessary to optimize the synthesis of urea-formaldehyde (UF) and melamine-urea-formaldehyde (MUF) resins, by changing their synthesis process. There are, in the literature, several possibilities to optimize the UF/MUF resins production described by several researchers. New processes for the synthesis of these resins have been studied and developed in order to produce resin with better physico-mechanical properties and lower formaldehyde emissions [8, 22]. These can be summarized into two main classes: the strongly acid and the alkaline-acid processes. The details of these processes pathways have been described elsewhere by Ferrá et al. [12]. The understanding of adhesive curing behaviour and its dependence on temperature and chemical conversion is an important starting point for the establishment of new ways for the board production and prediction of the properties of cured bondlines [30]. So, one of the most important aspects is the study of the resin gel time, which influences the pressing time and hence the productivity.

In industry, the methods used for determining resin gel time are not representative of reality, since they are very inaccurate and operator-sensitive. Other advanced characterization equipment, such as Differential Scanning Calorimetry (DSC) allows the identification of the onset temperature, curing rate, heat of reaction and kinetic parameters. However, it does not assess the strength of bonds formed within the resin, neither its interaction with wood. While DSC monitors the “chemical cure”, ABES (Automatic Bonding Evaluation System) [31], TMA (Thermo Mechanical Analysis) and DMTA (Dynamic Mechanical Thermal Analysis) allow for the evaluation of the bonding strength development [23].

ABES equipment, developed by Philip Humphrey, was designed to allow studying the dynamic cure process in wood-based panels production [32]. This technique enables the characterization of different catalysts, adhesives and their affinity for wood, as well as the effects of the different cure temperatures and pressing times on bond shear strength. This equipment can be used with different supports such as wood, paper or cork [30, 31, 33]. For all the ABES analysis the most important parameters to take into account are the platen temperatures, resin spread rate and pressing time. The maximum force required to cause the failure of the system (adhesive + support) is measured. For different times it is possible to measure the adhesive shear strength and then the characteristic curve of the resin can be obtained for different temperatures plotting the shear strength as a function of time.

In this work, two different chemicals, ammonium sulphate and ammonium bisulphite, are used for the resin cure and tested with ABES equipment. In order to simplify the analysis a mathematical model was developed and fitted to all the experimental data. This model allows the characterization of the performance of new hardeners.

### **2.3.2. Materials and Methods**

#### **Materials**

Formaldehyde (55 wt.% solution), urea and melamine for the production of UF resins were provided by EuroResinas – Indústrias Químicas, S.A. (Sines, Portugal). Beech veneer strips for ABES tests were supplied by Sonae Indústria PCDM, S. A. (Mangualde, Portugal). Wood particles, paraffin and ammonium sulphate were supplied by Sonae Indústria PCDM (Oliveira do Hospital, Portugal) for the production of the particleboard production.

#### **Methods**

##### ***Resin Preparation***

Resins were synthesized according to the so-called alkaline-acid process, which consists of three steps: a methylation step at alkaline conditions, a condensation step at acidic conditions, and an addition of the so-called final urea [34]. The addition of melamine was made in the methylation step.

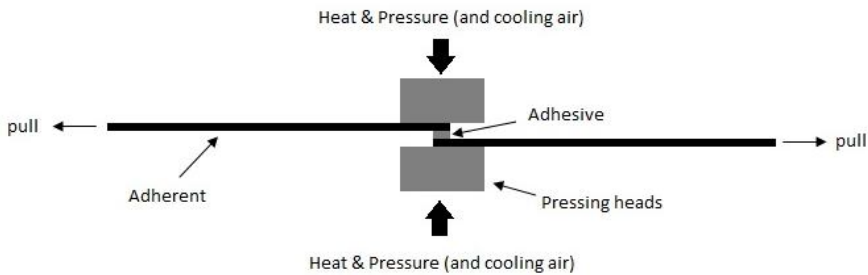
##### ***Gel time determination***

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 and a 70 wt.% ammonium bisulphite solutions were used as catalyst.

##### ***ABES Analysis***

Beech veneers were previously conditioned at given relative humidity (RH) and temperature conditions (20 °C, 65 % RH), in order to stabilize them and attain equilibrium moisture content (EMC) between 8 and 11 % (dry basis). Subsequently, the veneers were cut into strips using a pneumatically driven

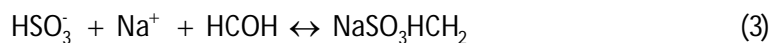
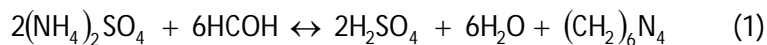
precision sample-cutting device supplied by Adhesive Evaluation System Inc (Corvallis, Oregon) [32]. Each veneer strip had 0.5 mm thickness, 20 mm wide and 117 mm in length. Adherent pairs were mounted in the system (Figure 2.13) with an overlapping area of 100 mm<sup>2</sup> (20 x 5 mm). The amount of adhesive system used for each test was 15 µL. Three different temperatures (85, 95 and 105 °C) were considered with press times between 25 and 400 seconds. For each temperature it was possible to obtain the characteristic curve by plotting the shear strength in function of time.



**Figure 2.13** Conceptual representation of the bond forming and test geometry (adapted from [35])

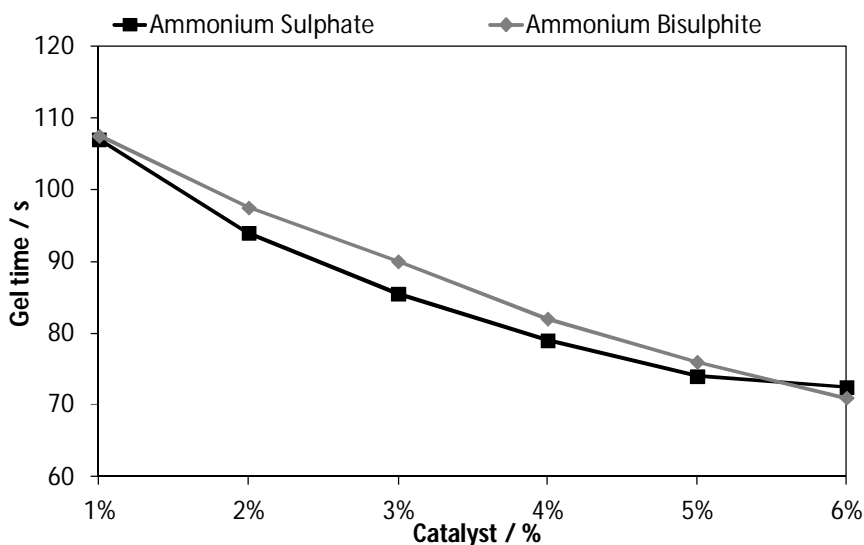
### 2.3.3. Results and Discussion

In this study, a MUF resin with low formaldehyde emissions was used to test two different hardeners for UF/MUF resins: ammonium sulphate and ammonium bisulphite. Ammonium sulphate, which is a latent hardener usually used in the adhesive preparation for the board production, reacts with formaldehyde forming sulphuric acid promoting an acidic environment, essential for the cure reaction (Equation 1) [23]. On the other hand, ammonium bisulphite, which is usually used as a formaldehyde scavenger, dissociates in to ammonium and sulphite ions (Equation 2). The sulphite ion will react with sodium ion, decreasing the pH of the solution creating an acidic environment crucial for resin cure (Equation 3).



### ***Gel-time of the adhesive***

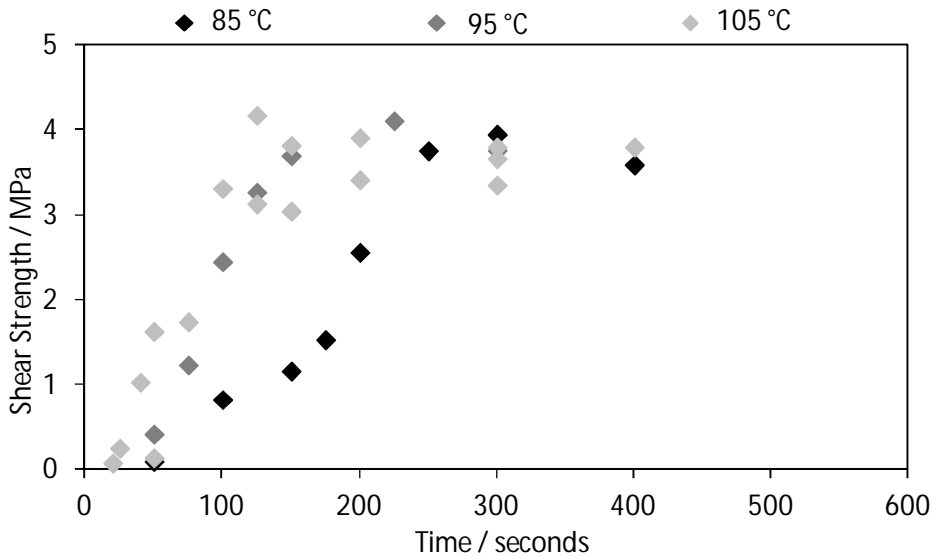
To determine the ideal amount of hardener used in resin cure, gel time tests were carried out using hardener dosages between 1 and 6 % (Figure 2.14). The expected gel time values of this type of resins with low formaldehyde emission are usually between 75 and 90 seconds.



**Figure 2.14** Gel time variation according to the amount of hardener

Taking into account that increasing the amount of hardener used results in an increased production cost of wood-based panels, it was established that the amount of hardener to be used, in the ABES analysis, would be 3 %. Therefore, for all the ABES tests, the following conditions were used: 3 % of hardener, glue joint area of 100 mm<sup>2</sup>, pressing time between 25 and 400 seconds and

test temperature between 85 and 105 °C. Figure 2.15 and Figure 2.16 show the results obtained with ABES for the different hardeners at different temperatures. In the horizontal axis it is represented the curing time, while in the vertical axis it is represented the shear strength of the glue joint after curing.

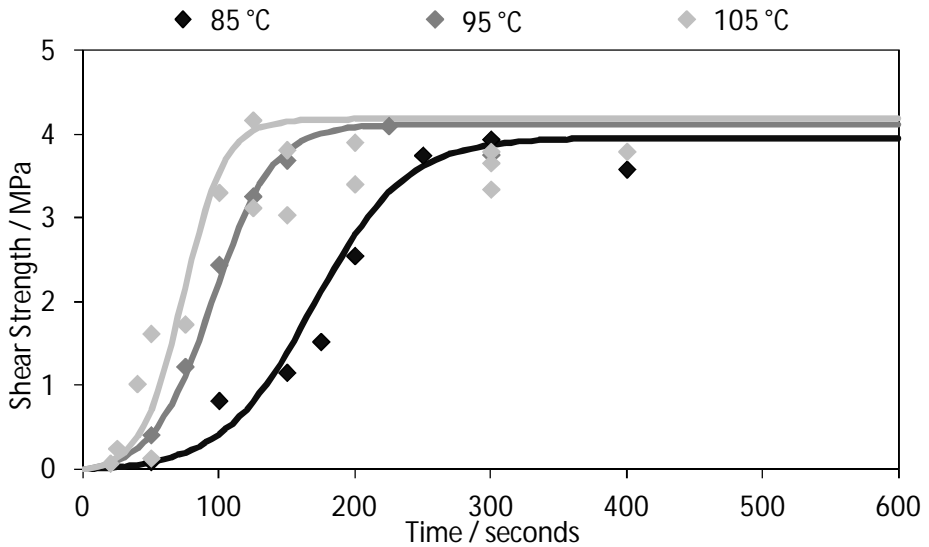


**Figure 2.15** Experimental data obtained in the ABES tests with ammonium sulphate to different temperatures

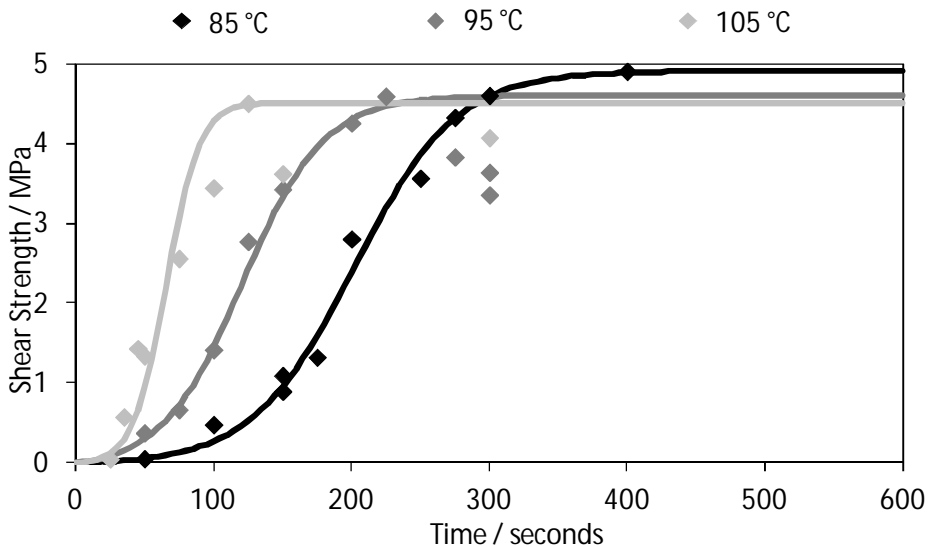
From these figures it is possible to identify two distinct phases in the experimental results. Initially, resin cure progresses leading to an increase in shear strength along the pressing time. In a second phase, the shear strength value stabilizes at values close to 4 or 5 MPa. For higher pressing times there is a decrease in the maximum shear strength, which can be associated to thermal degradation of the glue joint and/or degradation of wood itself.



the temperatures tested. Ammonium sulphate shows a higher curing rate when compared with ammonium bisulphite, for the same temperature, except for 85 °C where the cure is faster using ammonium bisulphite as hardener.



**Figure 2.17** Model fitting to the experimental data obtained in the ABES tests with ammonium sulphate for different temperatures



**Figure 2.18** Model fitting to the experimental data obtained in the ABES tests with ammonium bisulphite for different temperatures

Table 2.13 shows the parameter values of the resin cure model,  $\tau_{max}$  and  $t_o$ , as well as the determination coefficient for the different hardeners and temperatures.

**Table 2.13** Fitted parameters of the resin cure model ( $\tau_{max}$ : maximum shear strength;  $t_o$ : resin gel time and  $R^2$ : determination coefficient)

Hardener	Ammonium Sulphate			Ammonium Bisulphite		
	85	95	105	85	95	105
Temperature	85	95	105	85	95	105
$\tau_{max}$	3.968	4.128	4.193	4.921	4.610	4.521
$t_o$	169.9	95.6	73.7	201.9	121.5	65.8
$R^2$	0.970	0.998	0.965	0.990	0.995	0.941

$\tau_{max}$  is independent of temperature but the results show that it is slightly higher for the tests made with ammonium bisulphite. On the other hand,  $t_o$  is a function of the temperature and catalyst used. As expected, the resin gel time decreases with temperature increase and is higher for the test made with ammonium bisulphite, except for the trial carried out at 85 °C.

The resin gel times at 100 °C computed from the ABES model were compared to the values obtained by the conventional procedure (described in the Materials and Methods section).

Table 2.14 presents these results which are very similar for both methods and hardeners, but the best gel time results are obtained for the ammonium sulphate.

**Table 2.14** Gel time comparison between the two hardeners for the two methods

Hardener /Method	Conventional Method	ABES Method
Ammonium Sulphate	86	86
Ammonium Bisulphite	90	89

Comparing the two hardeners in study we can say that, despite the fact that ammonium bisulphate is essentially used as a formaldehyde scavenger, this compound can be used as hardener for this type of resins.

#### 2.3.4. Conclusions

With this work it was possible to show that ABES (Automatic Bonding Evaluation System) is a technique useful for the evaluation of the joint glued with UF and MUF and it is possible to use simple mathematical models for this evaluation. With ABES analysis it was possible to conclude that this technique allows the curing characterization of adhesives with different hardeners and different temperatures (ammonium sulphate and ammonium bisulphite). Despite the fact that ammonium bisulphite is essentially used as a formaldehyde scavenger, this chemical shows a good performance as hardener for this type of resins. Between the two hardeners used in this study, the results are very similar, but the best gel time results are obtained for the ammonium sulphate.

A mathematical model with three parameters ( $\tau_{max}$ : maximum shear strength;  $t_0$ : resin gel time and  $\lambda$ : model time constant) was developed to describe the results. Different test temperatures, between 85 and 105 °C, and curing times, between 25 and 400 seconds, were considered and, for all the temperatures, higher determination coefficients were obtained. The values, for the resin gel

time, obtained by ABES equipment are similar to the ones obtained with the conventional method.

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## ***CHAPTER 3***

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### **3. No Added Urea-Formaldehyde Resins**

#### **3.1. Development of a Phenol-Formaldehyde resin with low formaldehyde emissions that respects LEED® certification<sup>4</sup>**

##### ***Abstract***

In the last years, production of particleboards with good overall performance and very low formaldehyde emission has been a challenge to wood based panels (WBP) industry, mainly since the re-classification of formaldehyde by the IARC (International Agency for Research on Cancer) as 'carcinogenic to humans (Group 1)'. Moreover, a new important limitation to the use of formaldehyde-based resins has been recently imposed by the LEED (Leadership in Energy and Environmental Design) certification for 'Green Building' construction: 'wood composites must contain no added urea-formaldehyde resins'. In this context, the main purpose of this study is to develop a PF resin for particleboard production that fulfils formaldehyde emission restrictions and LEED criteria, while presenting appropriate reactivity and bond strength. The mechanical performance and formaldehyde emissions of particleboards were optimized, changing both the resin synthesis and board production procedures. The synthesis process of these resins was carried out under an alkaline environment, and with an excess of formaldehyde towards phenol, in order to produce resol-type PF resins. The effect of changing the amount of added sodium hydroxide was studied. The particleboard production parameters were also changed, both in terms of blending conditions (amount of hardener and resin) and hot-pressing conditions (pressing time). A PF resin with very good internal bond strength, low formaldehyde strength and reasonable board pressing times was obtained using the following conditions:

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<sup>4</sup> N. T. Paiva, J. Pereira, J. M. Ferra, J. Martins, L. Carvalho and F. D. Magalhães, "Development of phenol-formaldehyde resin with low formaldehyde emissions that respects LEED<sup>(R)</sup> certification", *International Wood Products Journal*, vol.5, pp. 161-167

sodium hydroxide amount of 9% during the synthesis process, and 10% hardener (based on oven-dry weight of resin) together with gluing factor between 4.5 and 5 % on the core layer during particleboard production. The best performing resin obtained demonstrated to be appropriate for use in the so called 'Green Building' construction.

### **3.1.1. Introduction**

The wood-based panels industry has achieved production of panels with very low formaldehyde emissions keeping a good overall physical-mechanical performance, in response to the IARC's (International Agency for Research on Cancer) classification of formaldehyde as "carcinogenic to humans (Group 1)" [1]. Most recently, in June 2011, the U.S. Department of Health and Human Services has listed formaldehyde as a known human carcinogen. Formaldehyde was also listed in the 12<sup>th</sup> Report on Carcinogens, compiled by the National Toxicology Program [2]. However, a new important challenge has been recently imposed by LEED (Leadership in Energy and Environmental Design®) certification, implying the absence of adhesives with urea-formaldehyde chemical bonds in "Green Building" construction [3].

LEED certification is the recognized standard for measuring building sustainability. Achieving LEED certification is the best way to demonstrate that a building project is truly "green". The LEED green buildings rating system is designed to promote design and construction practices that increase profitability while reducing the negative environmental impacts of buildings and improving occupant health and well-being. In our case the sector of LEED certification that is applied is the LEED for commercial interiors, which promotes the construction of sustainable buildings that meet a set of environment preservation and human health quality goals. Minimizing indoor air contamination associated to substances that are odorous, irritating, and/or

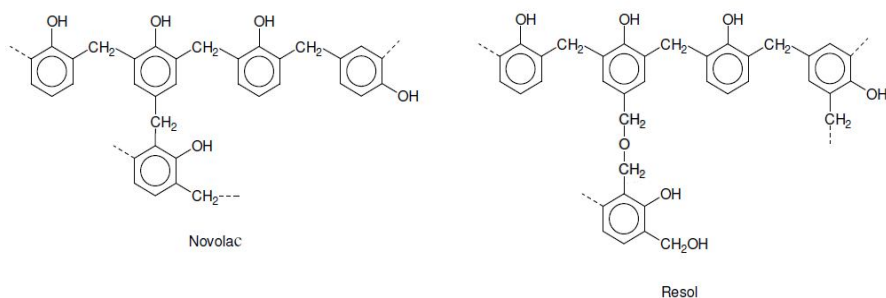
harmful to the comfort and well-being of installers and occupants is one of the objectives [3].

In this context possible alternatives to urea-formaldehyde (UF) resins are melamine-formaldehyde (MF), melamine-phenol-formaldehyde (MPF) and phenol-formaldehyde (PF) resins. So the last group of resins was the one used in this study.

PF resins are the polycondensation products of the reaction of phenol with formaldehyde and they were the first true synthetic polymers to be developed commercially [4]. Since their first production in 1910 they have been developed enormously and they remain one of the more important products of the plastic industry [5]. Global phenol-formaldehyde resin consumption grew at an average annual rate of less than 1 % during 2007–2010 (but fell during 2007–2009). The overall weak global economy had a large negative impact on total phenol-formaldehyde resin consumption during 2007–2009, hitting the construction industry particularly hard in 2008 and 2009. However, the industry had started its road to recovery by year-end 2009, and in 2010 made a significant comeback as the world economy improved [6].

Depending on the F/P molar ratio and the pH used during the condensation step, the final phenol condensation products can be resol or novolac resins. Resols are obtained as a result of alkaline catalysis and an excess of formaldehyde, which means that F/P greater than 1 (Figure 3.1). Heating causes the reactive methylol groups present in resol resins to condense to form larger molecules, a result achieved without the addition of a substance containing reactive methylene (or substituted methylene) groups [4, 7]. On the other hand, Novolac resins are produced with an acidic catalyst and with a deficiency in formaldehyde, which means that F/P is lower than 1 (Figure 3.1).

This type of resins has no reactive methylol groups and therefore incapable of condensing with other novolac molecules on heating without the addition of hardening agents [4, 7].



**Figure 3.1** Structure of Novolac and Resol Resins

The biggest differences between acid and alkaline catalysis present in the PF synthesis process are: rate of reaction between formaldehyde and phenol, methylolphenol condensation and the nature of the condensation products [4]. Hydrochloric acid is the most interesting case of acid catalyst, as well as oxalic acid and phosphoric acid. For alkaline catalysis, sodium hydroxide [8], ammonia and hexamine [9, 10] can be used. The catalyst concentration is important in the case of acidic catalysis, mostly affecting the reaction rate.

Phenol-formaldehyde resins are used to make a variety of products including consolidated wood products such as plywood, engineered lumber, hard board, fibreboard and oriented strand board for exterior applications. Other products include fibreglass insulation, laminates, abrasive coatings, friction binders, foams, foundry binders and petroleum recovery binders [11]. Wood adhesives will continue to have the largest share (about 33 %) of the world market for phenolic resins and will drive phenolic resin consumption on a global scale. The developing regions of Central and South America and Central and Eastern Europe will experience the largest growth in this application. Phenolic resin

consumption for moulding compounds (accounting for about 20 % of world consumption) will grow primarily in China and Other Asia as more moulding operations start up in the region. Laminates account for about 28 % of the world market [6].

In this work, the purpose is to produce particleboard for interior applications with this type of resins, more properly with PF resol resins. Some studies have been made on the use of resol phenol-formaldehyde or resol modified phenol-formaldehyde resins to produce particleboards, where different resin preparation and particles moisture content [4, 12-14]. In these studies were used hot platen press with a pressing factor between 5 and 12 s·mm<sup>-1</sup>, depending on the pressing time used and the desired moisture panel [4]. Usually the platen temperature used is between 180 and 220 °C, pressures in the 25 and 35 kg·cm<sup>-2</sup> and pressing time are between 8 and 12 min [4, 13].

The main purpose of this study is to develop a PF resin for wood-based panel's production with good physic-mechanical performance that satisfies formaldehyde emission restrictions and LEED criteria, by changing some process variables during the synthesis process, as well as some changes on the resin formulation for the particleboard production.

### **3.1.2. Materials and Methods**

#### ***Preparation of PF resins***

All resins were synthesized in round bottom flasks with 5 L volume, equipped with mechanical stirring and a thermometer. Temperature control was accomplished by means of a heating blanket. pH and viscosity measurements are performed off-line, on samples taken from the reaction mixture. The resins

were synthesized according to the conventional process in which the methylation and condensation step both occurs at alkaline conditions.

The process begins with the methylation/condensation reaction between a formaldehyde solution (30-50 %) and a 90 % phenol solution, at an alkaline pH – between 9 and 10 – by adding an appropriate amount of sodium hydroxide. In the methylation step, the initial attack may be at the 2-, 4- and 6- position of the phenolic ring. The formaldehyde solution is added gradually, allowing the heat of reaction to raise temperature from the initial 60 °C to values between 95 and 100 °C. The amount of formaldehyde solution added to the phenol solution is sufficient to provide a formaldehyde/phenol molar ratio (F/P) of 1.8.

The condensation step involves the reaction of the methylol groups with other available phenol or methylolphenol, leading first to the formation of linear polymers and then to the formation of hard-cured, highly branched structures. This reaction proceeds until a desired viscosity is attained, between 400 and 600 mPa·s, and is terminated by cooling the resin to a temperature of 50 °C. At this temperature a determined amount of sodium hydroxide is added to guaranty that the final resin pH is between 11 and 12. The reaction is finally terminated by cooling the reaction mixture to a temperature of 25 °C.

### ***Resin Properties Determination***

Viscosity, pH, alkaline content, water tolerance, free phenol and solid content were determined at the end of each synthesis. Viscosity was measured with a Brookfield viscometer at 25 °C and expressed in mPa·s. The resin pH was measured at 25 °C using a combined glass electrode. The solid content was determined by evaporation of volatiles in 2 g of resin for 2 h at 135 °C and expressed in %. The alkaline content was determined by potentiometric

neutralization of a solution to a pH of 7, using a strong acid. The free phenol content was determined with gas chromatography and is expressed in %. The water tolerance (express in %) was determined by the amount of water that is possible to add to a 5 g of resin until this solution turns hazy.

### ***Particleboard production***

The production of particleboards is essentially divided into four stages: preparation of raw materials, blending, mat formation and pressing. Wood particles were provided by Sonae Indústria, Oliveira do Hospital. Standard particle mixtures were used for the core and face layers, which are composed of different proportions of pine, eucalypt, pine sawdust and recycled wood. The moisture content of the standard mixtures was checked before blending. The average moisture content of the face and core layers particles was 2.5 % and 3.5 % respectively. Wood particles were then blended with resin, catalyst and paraffin in a laboratory glue blender. The gluing factor was 7 % resin solids in the face and between 4 and 6 % in the core, based on the oven-dry weight of wood particles. The catalyst content, potassium carbonate, in the core layer was higher (between 5 and 10 % solids based on oven-dry weight of resin) than in the face layer (1 % solids based on oven-dry weight of resin). The paraffin level was 0.1 % solids (based on oven-dry weight of wood).

Three-layer particleboard was hand formed in an aluminium container with 220x220x80 mm. The total percentages of board mass were: 20 % for the upper face layer, 62 % for the core layer and for 18 % bottom face layer. Boards were pressed in a laboratory scale hot-press, controlled by a computer and equipped with a displacement sensor (LVDT), thermocouples and pressure transducers. The glued particles were pressed at 190 °C with pressing times

between 150 and 300 s to produce panels with a target density of  $650 \text{ kg}\cdot\text{m}^{-3}$  and thickness of 17 mm.

### ***Determination of internal bond strength and formaldehyde content***

After pressing, boards were stored in a conditioned room (20 °C, 65 % relative humidity) and then tested accordingly to the European standards. The internal bond strength (IB) was determined according to EN 319 (tensile strength perpendicular to the plane of the board) and the formaldehyde content was determined according to EN120 (perforator method). Panels for the formaldehyde content analysis were stored in sealed plastic bags.

### **3.1.3. Results and Discussion**

#### **Resin Synthesis Process**

The main purpose of this work was to produce a resol PF resin for particleboard production, with low formaldehyde emission and for interior use in the so called “Green Building”. With this in mind, the final resin must meet the following characteristics: a viscosity between 400-600 mPa·s (in order to avoid high penetration of the resin on the wood chips during the particleboard production), a high water tolerance (an indication of the miscibility of the resin with water) and lower phenol content (at least lower than 0.50).

#### ***Effect of alkaline content***

Initially two resins with different alkaline content (amount of sodium hydroxide added) were synthesized. In Resin A, 4 % sodium hydroxide was added, while in Resin B the added amount was 9 % (both values based on the total weight of the resins). The remaining process variables were the same for both resins, and their final F/P molar ratio was 1.8. Table 3.1 shows the physico-chemical properties of the two resins. The biggest difference between these

resins is the free phenol content, which is highly related with the amount of sodium hydroxide added in each. The final pH and water tolerance are also different for both resins due to the different amounts of sodium hydroxide added.

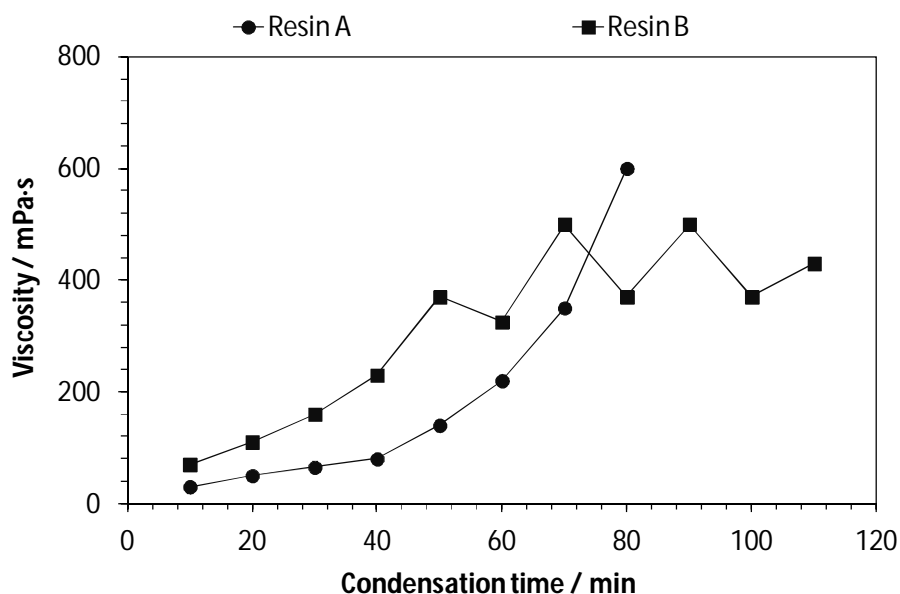
**Table 3.1** Resins A and B final properties

Properties / Resin	A	B
Solids content (%)	50.02	49.90
Alkaline content (%)	3.6	8.8
Final pH	10.52	12.21
Final viscosity (mPa·s)	500	430
Free phenol (%)	1.02	0.22
Water tolerance (%)	500	>2000

In both resins the total amount of sodium hydroxide added was divided between the beginning and ending of the synthesis. The amount added in the beginning is essentially to promote the reaction of the formaldehyde and phenol in an alkaline environment (between 8 and 9). On the other hand, the amount of sodium hydroxide added at the end of the synthesis allows resin stabilization in terms of molecular weight, viscosity, and water tolerance. This stabilization promoted by sodium hydroxide addition is a consequence of the high solubility of this type of resins in strong alkali solutions [4]. However, in this case, the quantity of base added is only enough to promote the dissolution of the high molecular weight polymer and to increase the water tolerance of the final resin. So an important relationship is here present between water tolerance and molecular weight: lower molecular weight translates into higher water tolerance [11].

For both resins the amount of sodium hydroxide added in the beginning of the synthesis is the same, so the differences are found on the final addition. In the case of Resin A, the final sodium hydroxide was added all at once when the resin reached a viscosity between 400 and 700 mPa·s, during the condensation reaction. However, in case of Resin B, the final amount of sodium hydroxide was added stepwise and started when the resin viscosity was around  $300 \pm 50$  mPa·s. Since the final amount of sodium hydroxide was higher for Resin B, this approach has avoided a substantial decrease in viscosity and has allowed a higher consumption of phenol and formaldehyde in the condensation reaction, without formation of high molecular weight polymer, since the water tolerance was always higher than 500 % along the condensation reaction.

Figure 3.2 shows the viscosity evolution during the condensation reaction for both resins. For Resin A the viscosity increases continuously during the condensation reaction, after the initial sodium hydroxide addition. On the other hand, during condensation reaction of Resin B, the sodium hydroxide additions (at 20 minute intervals) have originated a decrease in viscosity, followed by a rise as the reaction proceeds. It is also possible to see that this modification on the synthesis process results in an increase in 30 minutes on the duration of the condensation reaction.

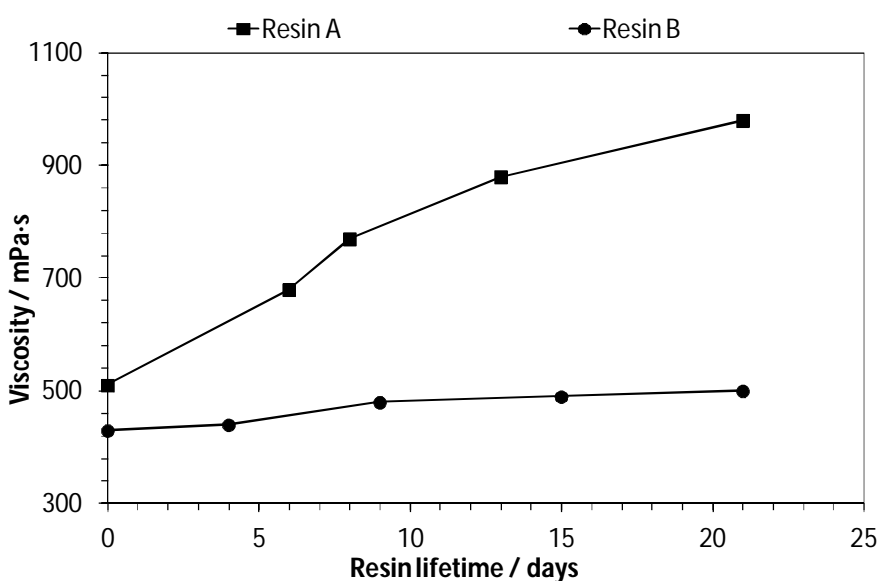


**Figure 3.2** Development of viscosity during the condensation reaction for Resins A and B

So, according to the results obtained for the final characteristics of the resins (especially in terms of the final viscosity and phenol content) and the progress of the synthesis was possible to conclude that the best amount of sodium hydroxide used was 9 %. However, one of most important PF resins characteristics is their low stability along time. In order to evaluate the stability, these resins were stored at 25 °C during 21 days, with weekly measurements of viscosity and pH. The viscosity evolution along time is present in Figure 3.3.

It is possible to see that Resin B, with the higher final alkaline content, presents more stability than Resin A, which viscosity increased from around 500 to 1000 mPa·s in just 21 days. On the other hand, viscosity of Resin B only increased 70 mPa·s during the same amount of time. This fact can be explained by the different water tolerance of both resins, which indicates a difference in their molecular weight. It is known that the higher the molecular weight of a resin,

the lower is its water tolerance and storage stability [4, 11]. Since Resin B has a value of water tolerance at least four times higher than the value present in Resin A, it was expected that it would have better stability. With regard to pH, it remains constant during the stability period. On the other hand, it was possible to observe a colour change from a light-red (obtained at the end of the synthesis) to dark-brown (obtain at the end of the stability period), this being more evident in the Resin A.



**Figure 3.3** Resin viscosity evolution during 21 days (Resin A – 4 % alkaline content; Resin B – 8 % alkaline content)

### ***Effect of formaldehyde concentration***

In this case, resins were synthesized with different formaldehyde concentration. The idea of was to raise the resin solid content in order to improve the particleboard production. During the particleboard manufacture the amount of water present in the core layer must be as low as possible in order to promote a more effective reaction between the resin and wood, with the purpose of achieving reasonable values for internal bond strength. As

higher is the amount of water in the core layer (sum of the water from the wood and resin), higher is the time needed for the optimal cure reaction because during the pressing process initially occurs the evaporation of the water and then the cure reaction takes place in a more effective way. To produce PF resins with high solid content is already possible in industry using an extraction system. However, depending on the target solids content, this process can take many hours, becoming very expensive.

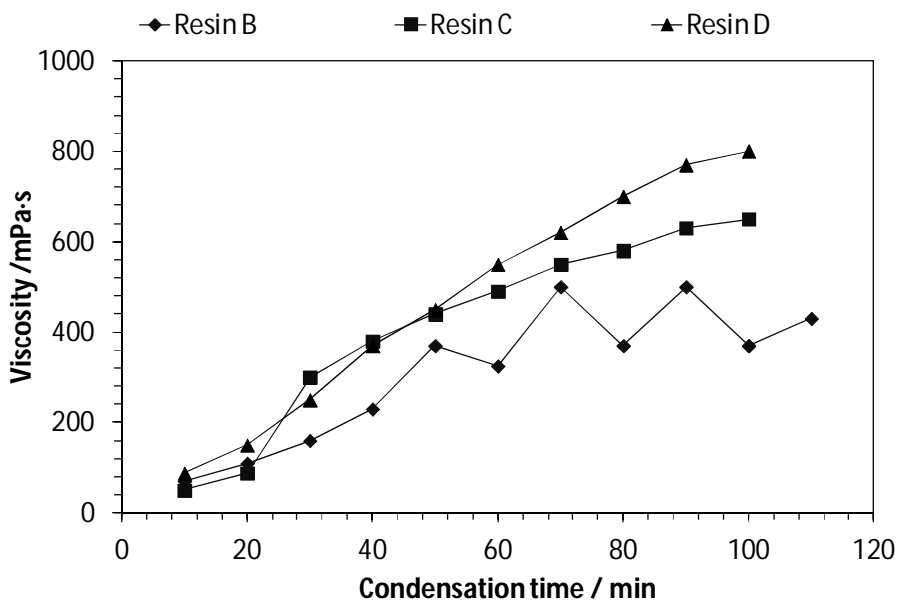
With all of this in mind, three resins were produced having formaldehyde concentrations between 30 and 50 % and they are related in the following way: Resin B < Resin C < Resin D. The alkaline content used on this case was 9 % and the other process variables were identical for the three resins.

In terms of synthesis process the initial formaldehyde concentration variation affects essentially the exothermicity of the reaction between formaldehyde and phenol. As said before, formaldehyde was added in a stepwise mode in order to promote the raise of the temperature from 50 to 90°C with the help of the heat of the reaction. In Resin B this happened perfectly and the temperature has raised to a value around 80 °C. However, for Resins C and D the formaldehyde addition has resulted in a sudden temperature increase to values higher than 100 °C, especially on Resin D. So it was necessary to cool down the reaction mixture quicker in order to avoid a faster polymerization reaction as well as a possible explosion of the glass reactor due to high temperatures.

As we can see in the Table 3.2 this synthesis behaviour results in resins with higher viscosity (comparing with value obtain in Resin B) and lower phenol content. On the other hand, and as expect, increasing the formaldehyde concentration results in resins with higher solids content.

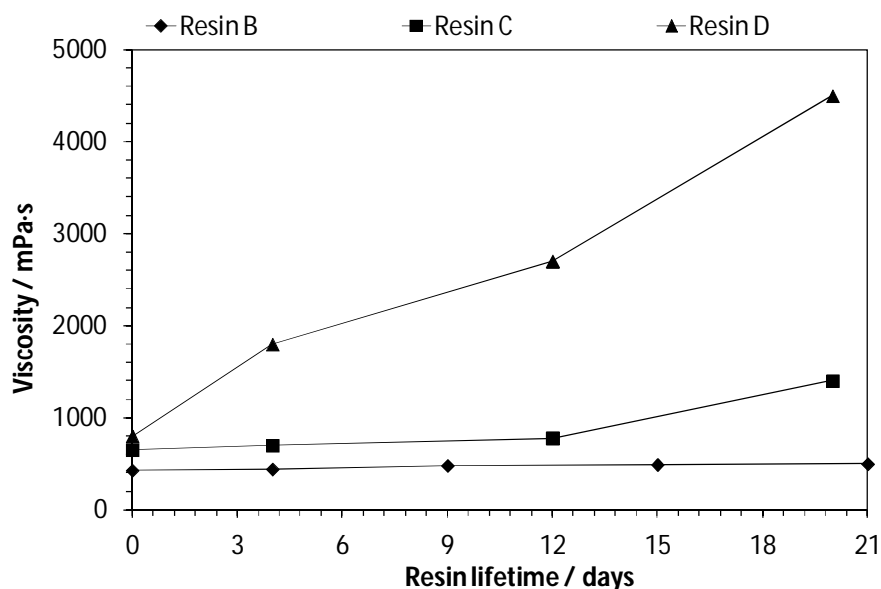
**Table 3.2** Resins B, C and D final properties

Properties / Resin	B	C	D
Solids content (%)	49.90	57.85	63.26
Alkaline content (%)	8.8	8.0	7.9
Final pH	12.21	11.63	11.64
Final viscosity (mPa·s)	430	650	800
Free phenol (%)	0.22	0.08	0.14
Water tolerance (%)	>2000	>2000	>2000

**Figure 3.4** Development of viscosity during the condensation reaction for Resins B, C and D

In addition to the control of the initial reaction, another important aspect in this synthesis is the monitoring of the condensation reaction during the addition of sodium hydroxide (Figure 3.4).

In the case of resins with higher formaldehyde concentrations (Resins C and D), a stepwise addition of sodium hydroxide has resulted only in a small slowing of the polymerization reaction with a continuous increase in viscosity (Figure 3.4). However, comparing the viscosity evolution of the Resins C and D with Resin A (where there no stepwise addition of sodium hydroxide), it is possible to observe that unlike what happened with Resin A, where the viscosity evolution showed a exponential performance, in the case of Resin C and D there is a tendency to viscosity stabilization all over this step.



**Figure 3.5** Resin viscosity evolution during 21 days ([Fa]: Resin B < Resin C < Resin D)

In terms of stability, as it is possible to see in Figure 3.5, as higher was the formaldehyde concentration, lower was the resin lifetime. With an increase on the viscosity around 100 % in the first 4 days, Resin D is the worst in terms of stability.

Taking into account the problems of the synthesis process (due to the higher exothermicity of the reaction between formaldehyde and phenol) and the

worst stability (comparing with the Resin B), it was possible to conclude that raise the formaldehyde concentration was not a viable solution to improve the particleboard production.

### **Particleboard Evaluation**

For the particleboard production only Resin A and B were used. Initially a series of particleboard panels were produced with these resins using different pressing times (between 150 and 300 s). The amount of resin used in the core layer was 4.5 % (based on the oven-dry weight of wood particles) and the amount of catalyst was 5 % (based on the oven-dry weight of the resin). The catalyst used was a 50 % solution of potassium carbonate.

The results, present on the Table 3.3, are very clear and show that the presence of a higher value of alkaline content is better for the physic-mechanical properties. All boards made with Resin A present very low values of internal bond strength. However, the boards made with Resin B show values between 0 and 0.50 N·mm<sup>-2</sup>.

**Table 3.3** Internal bond strength results for Resin A and B produced with different pressing times

Pressing time (s)	Resin A	Resin B
150	0.00	0.00
210	0.01	0.10
240	0.03	0.18
300	0.14	0.47

### ***Effect of amount of catalyst and resin***

In order to identify the best conditions for blending and pressing of the wood particles, a series of particleboards panels were produced with Resin B using

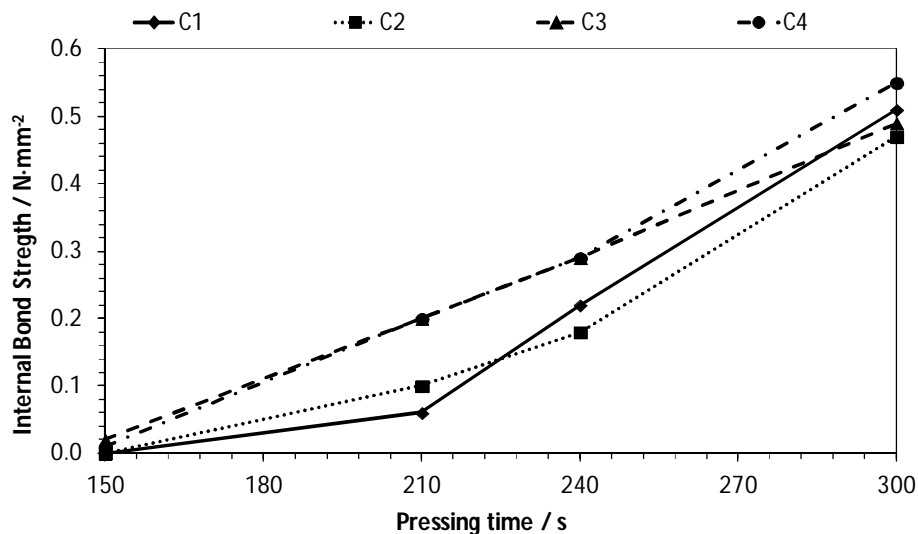
different amounts of resin and catalyst in the core layer particles. It was used different pressing times too.

Table 3.4 shows the four different conditions used. The amount of resin is based on the oven-dry weight of wood particles and the amount of catalyst is based on the oven-dry weight of resin.

**Table 3.4** Blending conditions for particleboard production optimization

Condition	Amount of resin (%)	Amount of catalyst (%)
C1	4.5	5
C2	5.0	5
C3	4.5	10
C4	5.0	10

Figure 3.6 shows the results for the internal bond strength for different pressing times. As shown in this figure, for all conditions, lower pressing time values result in lower internal bond strength values. Better results are found for the two series of boards that were produced with a higher amount of catalyst, but the best value is the one with simultaneously the highest amount of resin and catalyst. Since the main objective is to produce boards with the minimum acceptable value of  $0.35 \text{ N}\cdot\text{mm}^{-2}$  (the requirement for type P2 boards according to EN 312 standard), it is possible to claim that, under these conditions, a pressing time between 270 and 300 s is needed to obtain boards with good quality.



**Figure 3.6** Resin viscosity evolution during 21 days ([Fa]: Resin B < Resin C < Resin D)

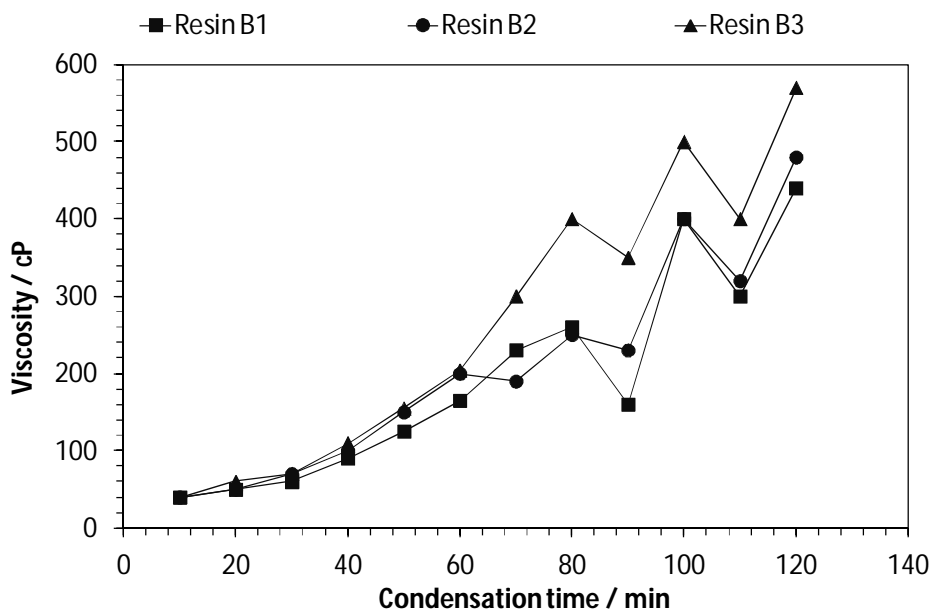
### Resin B Synthesis Process Reproducibility

In order to prove the reproducibility of the Resin B synthesis process, three new resins were synthesized. Table 3.5 shows the results for the physico-chemical properties of these three resins. As it is possible to see, all resins are very similar and the difference in the final viscosity is acceptable (the objective was to obtain a resin with a viscosity between 400 and 600 mPa·s).

**Table 3.5** Properties of the PF resins produced with 9 % of alkaline content

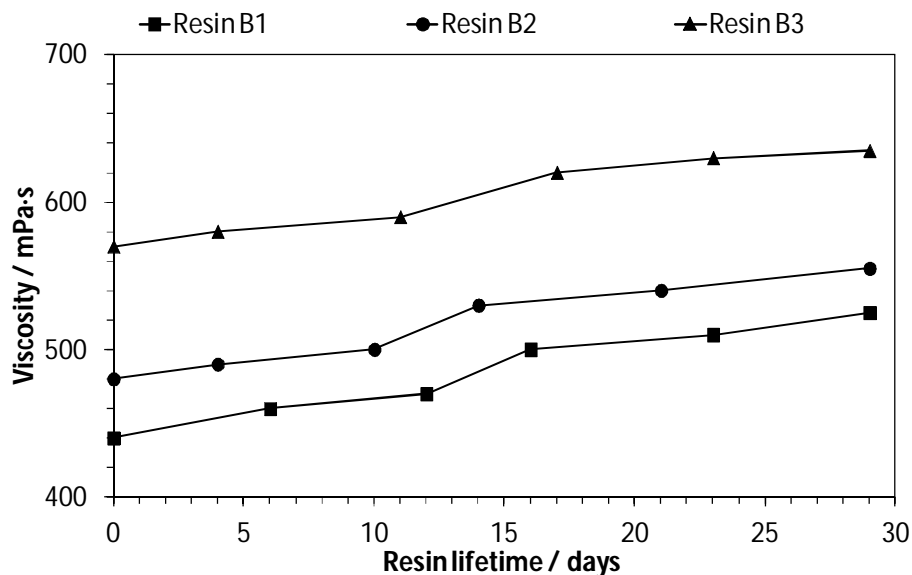
Properties / Resin	B1	B2	B3
Solids content (%)	49.95	49.88	50.12
Alkaline content (%)	8.0	7.8	7.5
Final pH	12.20	11.96	11.75
Final viscosity (mPa·s)	440	480	570
Free phenol (%)	0.40	0.28	0.30
Water tolerance (%)	>2000	>2000	>2000

In terms of synthesis process all resins had a similar behaviour, either during the initial reaction, as well as during the stepwise addition of sodium hydroxide, as it is possible to see in the Figure 3.7.



**Figure 3.7** Development of viscosity during the condensation reaction for Resins B1, B2 and B3

Regarding the stability of these resins (Figure 3.8), this was followed throughout 1 month and it was found small increases in viscosity, behaviour similar in all aspects to the one observed in the Resin B.



**Figure 3.8** Resin B1, B2 and B3 viscosity evolution during one month

For particleboard production with these three resins, the conditions C4 (5 % of resin and 10 % of catalyst) and pressing time between 210 and 300 s were chosen. For the formaldehyde determination it was used the panels produced with pressing times of 300 s. The physico-mechanical properties of these three resins are present in Table 3.6. As we can see the three resins are very similar for both properties and it can be said that the synthesis process is reproducible. Resin B2 and B3 presents values higher than the acceptable minimum of  $0.35 \text{ N}\cdot\text{mm}^{-2}$  for the panels produced with pressing time of 270 s. For a pressing time of 300 s this minimum is also achieved. The values of formaldehyde content are also below the maximum acceptable of 2.7 mg/100 g oven dry board specified by the Japanese F\*\*\*\* legislation [15]. These lower values of formaldehyde content can be easily related to the lower phenol content, since they were both highly consumed during the sodium hydroxide addition on the condensation reaction.

**Table 3.6** Resins B1, B2 and B3 particleboard properties produced with conditions C4

Properties / Resin	Pressing time (s)	Resin B1	Resin B2	Resin B3
Internal Bond Strength (N·mm <sup>-2</sup> )	210	0.04	0.22	0.11
	240	0.19	0.25	0.20
	270	0.24	0.46	0.42
	300	0.43	0.54	0.50
Formaldehyde Content (mg/100 g oven dry board)	300	1.9	1.1	1.5

#### 3.1.4. Conclusions

Concerning synthesis process, it was possible to conclude that the presence of a higher amount of base in the final resin results in more stable resin, with much better physic-mechanical properties. On the other hand, base addition results in a resin with low content of phenol due to its higher consumption during the condensation step.

Taking into account the problems encountered during synthesis process (due to the higher exothermicity of the reaction between formaldehyde and phenol) and the worst stability, it was verified that raise the formaldehyde concentration was not a viable solution to improve the particleboard production.

Regarding particleboard production it was also possible to infer that for achieving simultaneously good internal bond strength and reasonable board pressing times, the following conditions should be used: 10 % of hardener (based on oven-dry weight of resin) and a gluing factor between 4.5-5 % on the core layer during particleboard production.

The best performing resin obtained Resin B, showed very good values for internal bond strength and formaldehyde content, allowing its use of in the so-called "Green Building" construction.

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## ***CHAPTER 4***

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## **4. Low Emitting Water Tolerant Formaldehyde Resins**

### **4.1. Production of Water Tolerant Melamine-Urea-Formaldehyde Resin by Incorporation of Sodium Metabisulphite <sup>5</sup>**

#### ***Abstract***

The aim of this work was the development of a new MUF resin formulation with high tolerance towards water dilution, and a good overall performance in terms of physico-mechanical properties and formaldehyde emissions. For this purpose, sodium metabisulphite (MTBS) was added during melamine condensation reaction, therefore decreasing its extent by blocking amino groups. It was found that higher added amounts of MTBS resulted in resins with higher water dilution capacity (a percentage of 6 % of MTBS resulted in a resin with a water tolerance four times higher than the one present in a resin without MTBS incorporation). The molecular weight distribution showed that the resins produced with MTBS have a different polymeric structure. Regarding particleboard production and evaluation, it was possible to conclude that larger addition of MTBS, leads to lower internal bond strength and formaldehyde emissions. However, for a percentage of 6 % it was possible to obtain a resin with internal bond strength higher than the acceptable minimum ( $0.45 \text{ N}\cdot\text{mm}^{-2}$ ), with a pressing time of 150 s. When compared with commercial MUF resins, the formulation developed in this work presents lower values of formaldehyde emissions, verifying CARB II regulation, even though with somewhat inferior physico-mechanical performance.

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<sup>5</sup> Submitted to Bioresources Journal

#### 4.1.1. Introduction

Formaldehyde-based resins are the most commonly used adhesive system in industrial production of wood-based panels. Urea-formaldehyde resins (UF) are predominant, followed by phenol-formaldehyde (PF), melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF). Other synthetic and natural adhesives are employed, but in a significantly lower scale [14, 15]. Formaldehyde-based resins are mostly used in the production of a wide range of board's types such as particleboard (PB), medium density fiberboard (MDF), oriented strand board (OSB) and plywood (PL)[16].

The success of UF resins is due to their high reactivity and good mechanical performance, combined with low cost. However, they have an important disadvantage: low water resistance caused by chemical reversibility of aminomethylene bonds, leading to release of formaldehyde [17]. MF resins have much higher resistance to water, which is their main advantage when compared with UF resin. However, the higher cost and slightly lower reactivity make MF resins acceptable only for high value-added products. Melamine-based resins are among the most used adhesives for exterior and protected exterior wood-based panels and for the production and bonding of low- and high-pressure decorative laminates and overlay sheets [5].

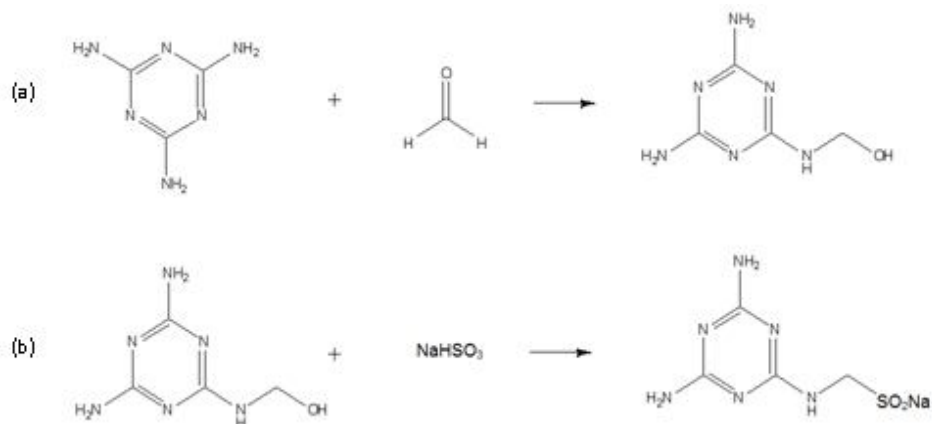
In order to reduce cost, melamine-urea-formaldehyde (MUF) resins are often used as an alternative to MF, despite the decrease in performance of the final product. MUF resins obtained by copolymerization of the three monomers are superior in performance to those prepared by mixing pre-polymerized UF and MF resins [5]. The relative mass ratios of melamine to urea used in the synthesis are generally in the range between 50:50 and 30:70 [18].

Melamine resins, particularly MUF resins, while useful to produce moisture resistant particleboard, have very poor dilutability in water and therefore are inconvenient to handle in PB and MDF mills [18]. This limitation, which does not occur with UF resins, is a consequence of the methylation and condensation reactions of formaldehyde with melamine. Formaldehyde first attacks the amino groups of melamine, forming methylol groups. However, this addition occurs in a larger extension than when formaldehyde is reacted with urea. The amino group in melamine accepts easily up to two molecules of formaldehyde and thus the complete methylation of melamine is possible, which is not the case with urea. Due to melamine's functionality, up to six molecules of formaldehyde can be attached to one molecule and the methylation step can lead to a series of methylolated compounds. As a consequence, highly hydrophobic compounds are formed early in the reaction [5]. These are responsible for the lower water compatibility of melamine-based resins.

The ability of sodium sulphites to react with aldehydes is well known. Sodium metabisulphite (MTBS), in particular, has actually been described in some studies as an effective formaldehyde scavenger [19, 20]. MTBS, with molecular formula of  $\text{Na}_2\text{S}_2\text{O}_5$ , forms sodium bisulphite after contact with water (equation 1)[19].



The addition of MTBS in the production of MF and MUF resins reduces the production of the hydrophobic compounds, due to the reaction between sodium bisulphite and methylolmelamines (Figure 4.1) [5] producing a sodium salt of bisulphite adduct [21]. This reaction is called sulfonation.



**Figure 4.1** Reactions between melamine and formaldehyde giving a methylolmelamine (a) and between methylolmelamine and sodium bisulphite (b)

Su et al. studied which factors affect sulfonation and condensation of highly-sulfonated melamine-formaldehyde (sodium metabisulphite/melamine, MTBS/M, molar ratio = 1.5) production and concluded that to achieve resins with good water solubility was necessary to extend the condensation reaction for 24 hours [22]. Gourdarzian and Rabiee used paraformaldehyde for the preparation of sulfonated melamine-formaldehyde and studied the effect of different degrees of sulfonation with several ratios of MTBS/M (0.6-1.2) [23]. The results show that the resins produced with lower values of S/M ratios are more viscous. Decreasing the MTBS/M molar ratio, results in an increase in the viscosity of the final resins [23]. At lower degree of sulfonation, where MTBS/M molar ratio is 0.6, the viscosity of the final solution decreases with a decreasing F/M ratio until gelation takes place at much higher F/M ratios [23]. Both works were directed towards MF application as concrete plasticizer.

Considering MF resins for thermal insulation, Tutin studied addition of MTBS to MF synthesis in proportions between 0.15-0.25 (in terms of MTBS/M molar ratio) with an incorporation of a polyhydroxy compound such as sucrose or sorbitol [24]. Despite the good water dilution capacity observed, in all these

studies the resins produced had low solid contents (between 30 and 45 %) and synthesis process times (7 to 10 hours) were excessively high, increasing the cost of the final product.

The incorporation of MTBS on the production of melamine-urea-formaldehyde resins was also studied by Dopico and co-workers in proportions of 0.1 to 0.3 (in terms of MTBS/M molar ratio), along with the incorporation of a urea-formaldehyde prepolymer (UFP) in proportions between 0.1-1 (in terms of M/UFP) [19]. The synthesis process used was divided in two different steps: first reaction between formaldehyde, MTBS, urea-formaldehyde prepolymer and melamine, and then a new amount of melamine was added along with the formaldehyde. The copolymerization of melamine, urea and formaldehyde therefore occurred only in the first step, along with urea-formaldehyde prepolymer. The resins produced had water dilution capacity (WCD) higher than 20:1 (water/resin). However, this study did not test the incorporation of MTBS alone, and very long reaction times were used.

The main purpose of the current work is to develop a new MUF formulation with high water dilution capacity and good overall performance in terms of physico-mechanical properties and formaldehyde emissions. The addition of MTBS during condensation stage is tested (MTBS/M molar ratio between 0.15 and 0.50). An alkaline synthesis process is adopted in order to promote the copolymerization of melamine, urea and formaldehyde.

## 4.1.2. Materials and Methods

### Materials

#### *Raw Materials*

Formaldehyde (55 wt.% solution), urea, melamine and sodium metabisulphite 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 the particleboard production.

#### *Commercial Resins*

The three commercial resins analyzed in this study were supplied by EuroResinas – Indústrias Químicas, S.A. (Sines, Portugal). Both are melamine-urea-formaldehyde resins with percentages of melamine between 8 and 16 % (CR3 < CR2 < CR1). According to manufacturer's information, both resins CR1 and CR2 have a final viscosity between 150 and 300 mPa·s, a final pH between 8.5 and 10.0, a solid content around 64 % and a gel time of 80 seconds. By other side resin CR3 has a final viscosity between 100 and 200 mPa·s, a final pH around 9.0, a solid content between 61 and 65 % and a gel time of 110 seconds. All the commercial resins have low water capacity dilution stability, with acceptable values for only 1 to 3 days.

### Methods

#### *Resin Preparation*

Resins were synthesized in a round bottom glass flask with a volume of 2 L equipped with mechanical stirring and a thermometer. pH and viscosity measurements were performed off-line, on samples taken from the reaction mixture while temperature control was accomplished with a heating blanket.

The resins were synthesized according to the so-called alkaline process, which consists in methylation and condensation reaction at an alkaline environment followed by a final addition of urea [5].

The synthesis process begins with the methylation reaction between 50 % formaldehyde solution, urea and melamine, at a basic pH (usually between 7.5 and 9.0), obtained by adding an appropriate amount of base. Urea is added slowly, allowing the heat of reaction to raise the temperature from the initial 60 °C to values between 80 and 90 °C. The amount of urea and melamine added in this step is sufficient to provide a formaldehyde/amine groups molar ratio ( $F/(NH_2)_2$ ) of 4 to 3.5.

The condensation reaction can be divided in two different steps: initially the reaction proceeds until a viscosity of around 100 mPa·s is obtained. At this point, a second amount of melamine is added in order to provide a  $F/(NH_2)_2$  molar ratio of 3.0 to 2.5. Then the condensation reaction continues until a desired viscosity is attained, between 350 and 400 mPa·s, and is terminated by cooling the reaction mixture to a temperature of 60 °C. Hereupon, a given amount of urea is added in order to decrease the  $F/(NH_2)_2$  molar ratio to a value between 1.15 and 1.05, which was the same for all productions. The reaction is terminated by cooling the mixture to a temperature of 25 °C.

The major difference between all the produced resins is the amount of sodium metabisulphite added to the reaction mixture. This addition was carried out during the condensation reaction

### ***Resin Properties Determination***

At the end of each synthesis properties like viscosity, pH, reactivity, solid content and water dilution capacity were determined. Viscosity was measured with a Brookfield viscometer at 25 °C and it is expressed in mPa·s. The resin pH was measured using a combined glass electrode. The solid content was determined by evaporation of volatiles in 2 g of resin for 3 h at 120 °C and it is expressed in percentage. The resin gel time (expressed in seconds) was determined by measuring the gel time of a resin sample at 100 °C, after addition of cure catalyst (ammonium sulphate or ammonium nitrate). Water dilution capacity (WDC) (expressed in %) was determined by the amount of water that is possible to add to 5 g of resin until this solution turns hazy and present phase separation.

### ***GPC / SEC Analysis***

A GPC/SEC equipped with a Knauer RI detector 2300 and a Knauer injector with a 20 µL was used. The columns used were PSS Proteoma 100 and 300 5 µm, conditioned at 60 °C using an external oven. The flow rate was 1 mL·min<sup>-1</sup> and DMF was used as the mobile phase. Samples for analyses were prepared by dissolving a small amount of resin in DMSO (dimethylsulfoxide), followed by vigorous stirring. Subsequently, the sample was left to rest, and then filtered through a 0.45 µm filter [7, 12].

### ***Particleboard Production***

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 millimeters). Wood amount was determined in order to obtain boards with target densities of  $650 \pm 20 \text{ kg}\cdot\text{m}^{-3}$ . 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. Pressing cycle (stage duration, press closing time, platen temperature) was scheduled in order to simulate a typical particleboard continuous pressing operation. Five boards were produced for each synthesized resin.

### ***Physic-Mechanical Characterization of Particleboard***

After pressing, boards were stored in a conditioned room (20 °C, 65 % RH) and then tested accordingly to the European standards. The following physico-mechanical properties were evaluated: density (EN 323), moisture content (EN 322), internal bond strength (IB) (EN 319 – tensile strength perpendicular to the plane of the board) and thickness swelling (EN 317). For each experiment, four board replicates were obtained. Formaldehyde content was determined according to EN 120 (perforator method) and formaldehyde emission was determined according JIS A 1460 (desiccator method). Panels for the analysis of formaldehyde content and emission were stored in sealed plastic bags.

## **4.1.3. Results and Discussion**

### ***Synthesis***

A set of resins was synthesized according to the same process, varying only the amount of MTBS added during the condensation step. The amount of MTBS was varied between 0 (resin 1) and 6 wt. % (resin 4). Table 4.1 presents the final properties of the MUF resins produced.

**Table 4.1** Process variables and final properties of MUF resins

Properties / Resin	Resin 1	Resin 2	Resin 3	Resin 4
% MTBS	0.0	2.0	3.0	6.0
RM MTBS/M	0.00	0.15	0.25	0.50
Solids content (%)	64.7	65.1	65.6	67.1
Final pH	9.51	9.45	9.85	9.80
Final viscosity (mPa·s)	160	180	190	170
Gel time (s)	55	58	64	65
Density (kg·m <sup>-3</sup> )	1.290	1.296	1.310	1.330

Concerning the final pH and viscosity, the results are very similar for the four resins. The slight increases in solid content and density occur because an extra compound was added without adjusting the concentration of the other reactants. Gel time tends to increase (*i.e.* reactivity decreases) with MTBS addition because of the premature consumption of a significant amount of free formaldehyde, which is not available for the final cure reaction. This free formaldehyde reacts with sodium bisulphite producing a sodium salt of the bisulphite adduct [26].



The viscosity of the resins was followed during the condensation step, after addition of MTBS. The results are shown in Figure 4.2 The amount of MTBS added does not affect the reaction progress and all resins presented a condensation time of approximately 75 minutes. The last point in the graph corresponds to the viscosity after 30 minutes of cooling down to a temperature of 60 °C.

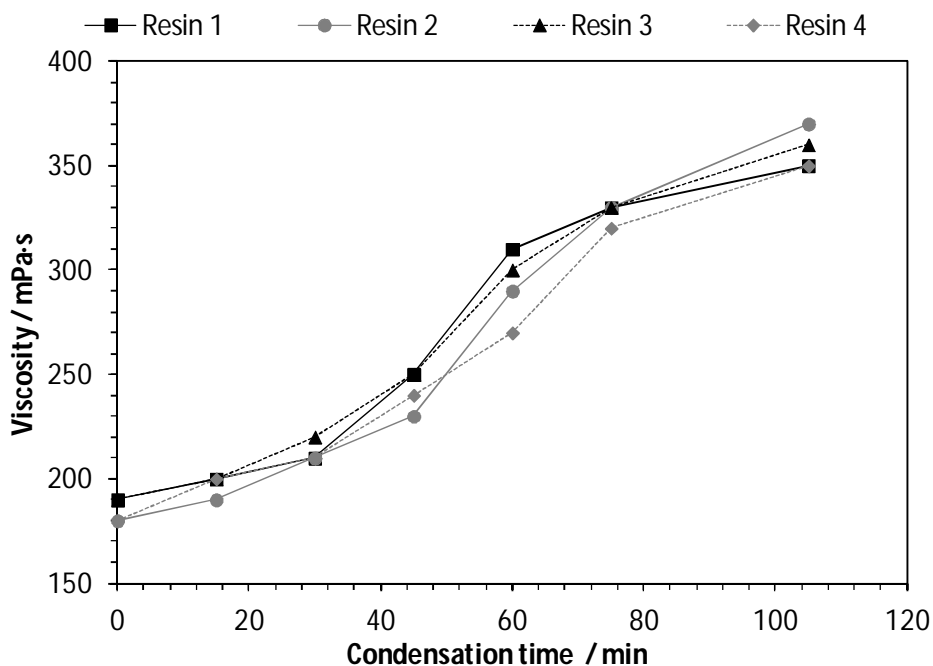
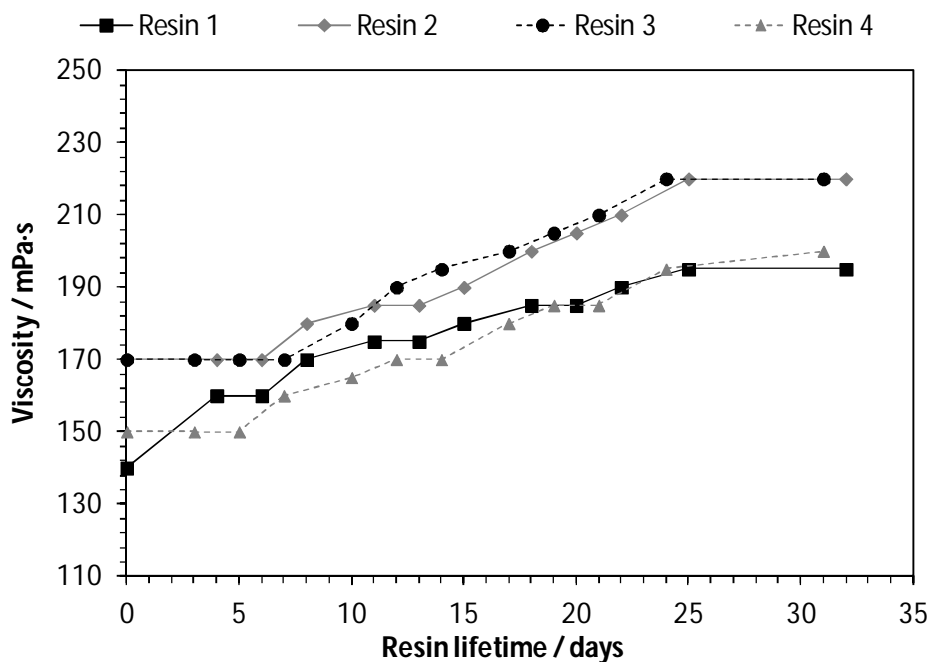


Figure 4.2 Evolution of viscosity during the condensation reaction, after addition of MTBS

### ***Resins Stability***

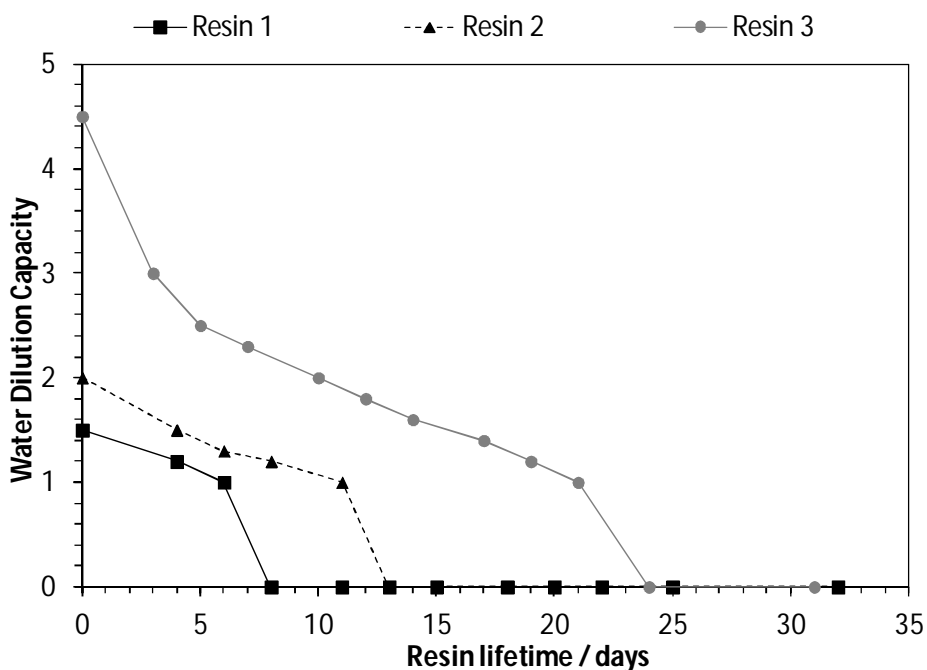
The stability of the four resins was evaluated along storage for one month at 25 °C. Viscosity, pH and water dilution capacity were measured weekly. The evolution of pH in this period, not shown here, was very similar for all resins and showed a decrease from 10.0 to 8.0. Viscosity and water dilution capacity as function of storage time are presented in Figure 4.3 and Figure 4.4, respectively. The change of viscosity with time is analogous for all resins, increasing by about 50 mPa·s after one month. Resins 1 and 4 maintain viscosities lower than the other two, but within the acceptable variability range for this synthesis process.



**Figure 4.3** Resins viscosity evolution during 1 month of stability

Regarding water dilution capacity, Figure 4.4 shows that increasing the amount of sodium metabisulphite results in a significant increase in water dilution capacity (WDC) right after synthesis. This translates into longer storage times until reaching WDC lower than 1. The best result was obtained for resin 4, with 6 % of MTBS added, which consistently exhibited WDC above 100 along the entire one month storage period.

As previously discussed, the increase of the resin's WDC with addition of sodium metabisulphite is related to a higher sulfonation of methylolmelamines by MTBS. Addition of this compound along with the second melamine addition minimizes condensation of methylolmelamines into hydrophobic products and thus reduces the tendency for precipitation upon water dilution.



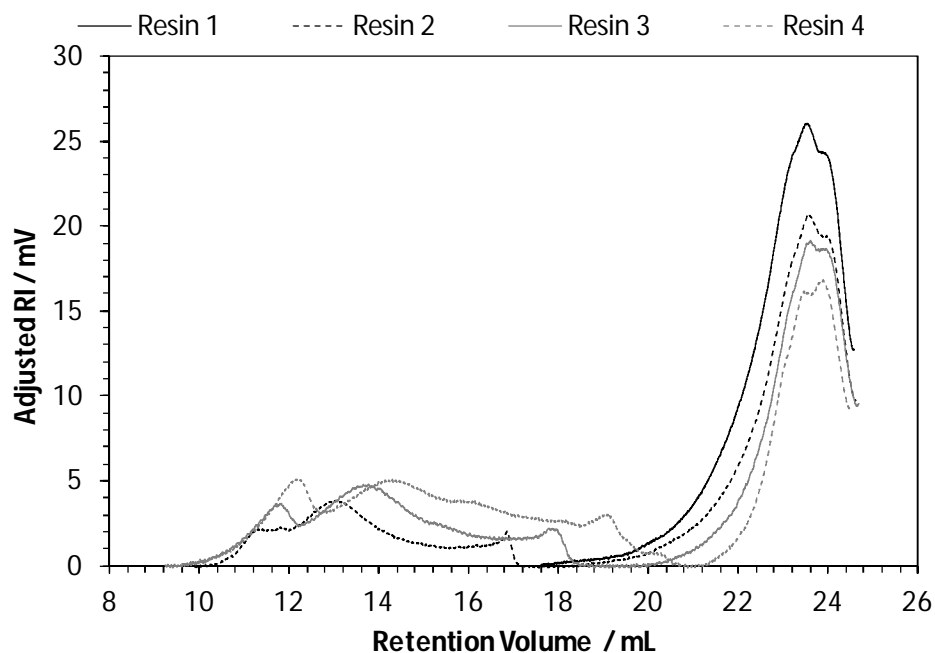
**Figure 4.4** Resins water dilution capacity during 1 month of stability. Resin 4 is not shown in the figure, since it showed water dilution capacity above 100 in all measurements

The decrease in the resins WDC during the storage period is a consequence of the progressive reaction between methylolmelamines, methylolureas and free melamine, urea and formaldehyde along time. This leads to formation of insoluble colloidal aggregates, originating the observed viscosity increase, and reducing the water dilution capacity [26].

### **GPC/SEC Characterization**

Figure 4.5 shows the results for the GPC chromatograms for the four MUF resins synthesized in this study. The first thing that can be noticed is that the resin without MTBS incorporation (resin 1) presents only one peak, for larger retention volumes (RV between 20 and 26 mL). This RV range corresponds to lower molecular weights, and can be assigned to free urea, methylolureas, methylolmelamines, oligomers and polymer with intermediate molecular

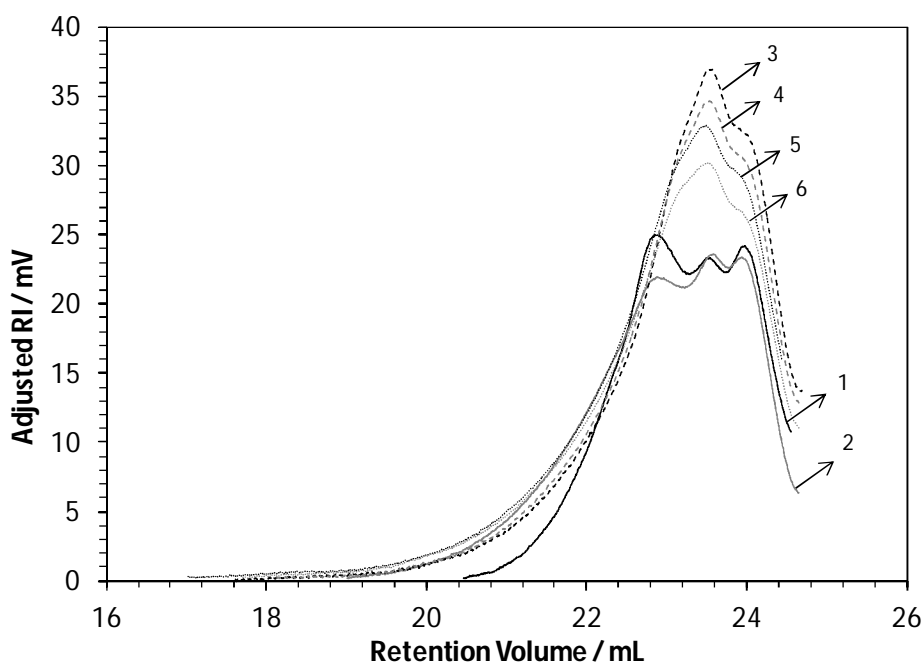
weight ( $< 3000$ ) [12]. The chromatograms for the other three resins are more complex, showing peaks at lower retention volumes (RV between 6-20 mL), which corresponds to the presence of polymer with high molecular weight ( $>12000$ ).[13] This difference can be explained considering that the higher molecular weight fraction present in resin 1 does not actually enter the GPC column. This fraction, produced during the condensation reaction, is known to form molecular aggregates that can be retained in the micro porous filter with  $0.45 \mu\text{m}$  during sample preparation [7].



**Figure 4.5** Chromatograms of MUF resins

In the case of resins 2 to 4, the addition of MTBS reduces the formation of these aggregates, allowing the detection of polymer with higher and intermediate molecular weights (RV between 9 and 20 mL), as seen in Figure 4.5. The higher the quantity MTBS of incorporated higher is the amount of intermediate molecular weight polymer produced, which promotes the

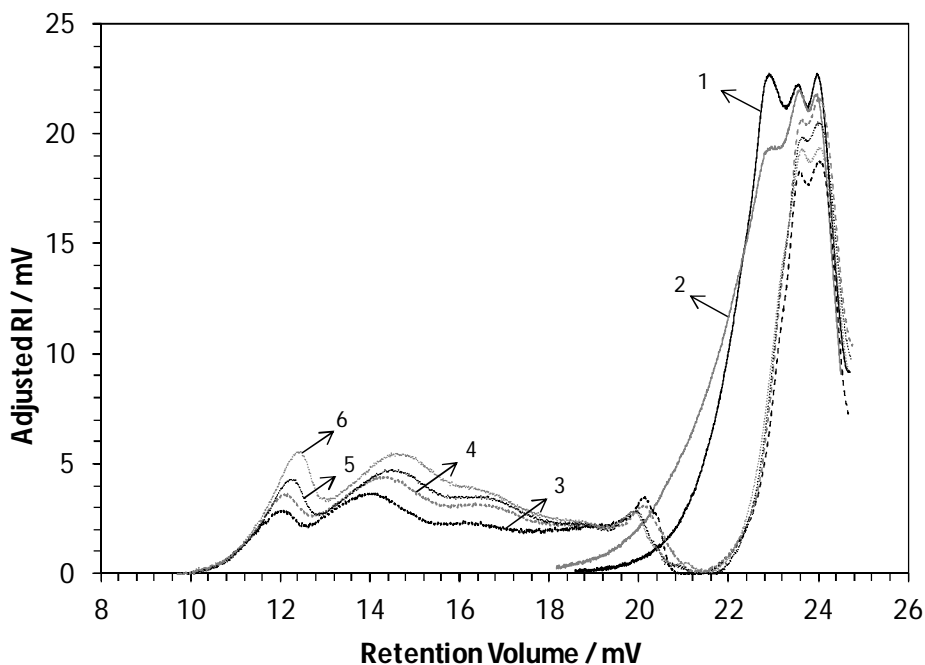
displacement to the right of the peak between RV 6 and 20 ml. In order to understand the evolution of the condensation reaction, samples were taken and analyzed during the synthesis of resins 1 and 4. Figure 4.6 and Figure 4.7 show the evolution of the GPC/SEC chromatograms during the condensation step, in 30 minutes intervals.



**Figure 4.6** Chromatograms of samples taken from Resin 1 during the condensation step (1: 0 min, 2: 30 min, 3: 60 min, 4: 90 min, 5: 120 min and 6: 150 min)

Figure 4.6, in which the molecular weight distribution evolution for resin 1 (resin without any MTBS incorporation) is present, has only one peak on the lower molecular weight for all samples taken during the condensation. The first two samples were taken before the melamine addition. After that, the peak corresponding to urea and methylolureas (RV between 23 and 24 mL) suddenly increases (resin 3). As the condensation time proceeds (resins 4 and 5), this peak decreases, accompanied by an increase in polymer with

intermediate molecular weight (RV between 17 and 21). Concerning the higher molecular weight polymer, as it was explained earlier, this was not detected due to their retention on the filter during sample preparation.



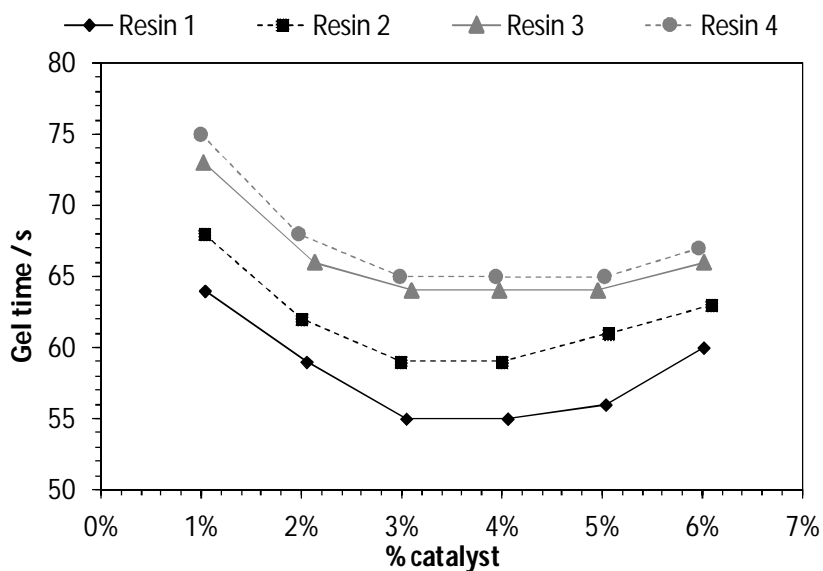
**Figure 4.7** Chromatograms of samples taken from Resin 4 during the condensation step (1 – 0 min, 2 – 30 min, 3 – 60 min, 4 – 90 min, 5 – 120 min and 6 – 150 min)

Figure 4.7 presents the evolution in resin 4, with 6 % of MTBS. In this case the samples 1 and 2 were taken before MTBS addition, which explains the difference in the intensity of these two samples when compared with the other 4. It is possible to see that as the reaction proceeds, the intensity of the peak between of 20 and 23 mL of RV decreases together with an increase of the peak corresponding to the higher and intermediate molecular weight (RV between 10 and 20 mL). In this case, the peak corresponding to the higher and intermediate molecular weight is detected, with an increase on the intensity of

this peak with the condensation time due to the growth of the polymer during this step.

### **Particleboard Evaluation**

To determine the ideal amount of hardener (ammonium sulphate) to use in resin cure, gel time tests were carried out using hardener dosages between 1 and 6 % (Figure 4.8). The expected gel time values of for this type of resins, without addition of external agents, are usually around 55 to 60 seconds. Addition of MTBS results in a significant increase in gel time: about 10 seconds from resin 1 to resin 4. Since the lowest values were obtained for percentages between 3 and 4 %, it was established that the amount of hardener to be used in particleboard production would be 3%.



**Figure 4.8** Resin gel time evolution according to the amount of catalyst

Table 4.2 presents the physico-mechanical properties of particleboards produced with the four MUF resins. The pressing times used were 120 and 150 seconds. In the first case, the values found for density and water content are

very similar for all resins. Concerning internal bond strength, most values are higher than the minimum acceptable value of  $0.45 \text{ N}\cdot\text{mm}^{-2}$ , the requirement for type P3 (non load-bearing boards for use in humid conditions) and P5 (load-bearing for use in humid conditions) boards, according to EN 312, except the one produced with Resin 4. On the other hand, regarding formaldehyde content, all the resins are below the limit imposed by CARB II legislation corresponding to an equivalent of perforator value  $\leq 5.6 \text{ mg}/100 \text{ g}$  oven dry board [27]. The formaldehyde emissions for all the resins are below the limit imposed by CARB I legislation, corresponding to an equivalent desiccator test value  $\leq 1.3 \text{ mg}\cdot\text{L}^{-1}$  [27]. For all the formaldehyde results it is possible to observe that increasing the amount of MTBS added to the resin during synthesis decreases the formaldehyde emission and content of the particleboards.

As expected, increasing pressing time to 150 seconds results in better properties mainly for the particleboards produced with resins 3 and 4. With resin 4 it is possible to obtain values of internal bond strength higher than the minimum acceptable of  $0.45 \text{ N}\cdot\text{mm}^{-2}$ . In terms of formaldehyde emissions and content, the values are lower than the ones found with shorter pressing times, and both respect the limit imposed by CARB II (in terms of formaldehyde content) and CARB I (formaldehyde emission).

**Table 4.2** Particleboards Properties produced with MUF Resins

Properties / Resin	Pressing time (s)	Resin 1	Resin 2	Resin 3	Resin 4
Density ( $\text{kg}\cdot\text{m}^{-3}$ )		670	680	674	659
Internal Bond Strength ( $\text{N}\cdot\text{mm}^{-2}$ )		0.84	0.77	0.58	0.32
Thickness Swelling (%)		20.7	24.6	27.0	36.3
Moisture Content (%)	120	5.6	5.2	5.2	5.1
Formaldehyde Content (mg/100 g oven dry board)		5.0	4.6	4.2	4.0
Formaldehyde Emission ( $\text{mg}\cdot\text{L}^{-1}$ )		1.20	1.11	1.05	0.93
Density ( $\text{kg}\cdot\text{m}^{-3}$ )		681	706	686	674
Internal Bond Strength ( $\text{N}\cdot\text{mm}^{-2}$ )		0.84	0.84	0.70	0.53
Thickness Swelling (%)		22.9	24.4	28.3	33.8
Moisture Content (%)	150	4.9	4.8	4.9	4.6
Formaldehyde Content (mg/100 g oven dry board)		4.2	3.7	3.4	3.3
Formaldehyde Emission ( $\text{mg}\cdot\text{L}^{-1}$ )		1.04	1.02	0.87	0.84

### ***Comparison with other commercial resins***

Table 4.3 shows the physico-mechanical properties of the particleboards produced with resin 4 and three MUF commercial resins with melamine contents varying between 8 and 22 % ( $\text{CR3} < \text{CR1} < \text{CR2}$ ).

Despite the fact that the resin 4 has the lowest values of internal bond strength and the highest values of thickness swelling, it is the only one with formaldehyde content values below the limit imposed by CARB II legislation, corresponding to an equivalent of perforator value  $\leq 5.6$  mg/100 g oven dry board, both with pressing times of 120 and 150 seconds.

Comparing these four resins in terms of water dilution capacity (Figure 4.4) and physico-mechanical properties, it is possible to conclude that resin 4 provides the best overall performance.

**Table 4.3** Particleboards properties produced with different MUF resins

Properties / Resin	PT (s)	Resin 4	CR 1	CR 2	CR 3
Density ( $\text{kg}\cdot\text{m}^{-3}$ )		659	666	706	674
Internal Bond Strength ( $\text{N}\cdot\text{mm}^{-2}$ )		0.32	0.63	0.73	0.64
Thickness Swelling (%)	120	36.3	18.6	19.0	21.3
Moisture Content (%)		5.1	7.2	6.9	7.2
Formaldehyde Content (mg/100 g oven dry board)		4.0	8.0	-	7.2
Density ( $\text{kg}\cdot\text{m}^{-3}$ )		674	692	708	681
Internal Bond Strength ( $\text{N}\cdot\text{mm}^{-2}$ )		0.53	0.81	0.81	0.89
Thickness Swelling (%)	150	33.8	20.8	15.1	13.3
Moisture Content (%)		4.6	6.6	6.9	7.6
Formaldehyde Content (mg/100 g oven dry board)		3.3	6.5	8.1	5.7

#### 4.1.4. Conclusions

This work studied the effect of MTBS addition during MUF synthesis, with the purpose of developing resins tolerant to dilution in water. MTBS was added during the condensation reaction.

Water dilution capacity was observed to increase significantly with MTBS incorporation. This was attributed to the presence of MTBS minimizing the condensation of methylolmelamines into hydrophobic products. On the other hand, the resin reactivity decreased, due to premature formaldehyde consumption. GPC/SEC results showed that the resins produced with MTBS

incorporation present lower molecular weight when compared with the one without MTBS.

Regarding particleboard production and evaluation, MTBS addition lead to lower values of internal bond strength. However, for a percentage of 6 % it was possible to obtain a resin with internal bond strength above the acceptable minimum ( $0.45 \text{ N}\cdot\text{mm}^{-2}$ ), using a pressing time of 150 s. When compared with other commercial MUF resins, the formulations containing MTBS present lower values of formaldehyde emissions, verifying CARB II criteria, and much higher water tolerance.

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## ***CHAPTER 5***

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## 5. General Conclusions and Future Work

### 5.1. General Conclusions

The objective of this PhD thesis was the development of formaldehyde-based resins with very low formaldehyde emissions, for use in the production of wood-based-panels. This work was co-funded and developed in close cooperation with the Portuguese company EuroResinas – Indústrias Químicas S.A., a major producer of formaldehyde-based resins.

The first studies made in this thesis were focused on the development of a UF or modified UF resin with very low formaldehyde emission using the strongly acid synthesis process. The main conclusions of this work were:

- ✓ A small amount of melamine added during the UF resin synthesis results in resins with good overall performance, both in terms of internal bond strength and formaldehyde emissions, when compared with UF resins;
- ✓ Using the strongly acid process, the best performance is obtained when melamine is added during the initial acidic stage;
- ✓  $F/(NH_2)_2$  molar ratio and feed rate of second urea, which affect the condensation step, are the most influential in terms of the product's polymeric structure and mechanical performance;
- ✓ The use of lower  $F/(NH_2)_2$  molar ratios and faster rates of urea addition in the condensation step results in particleboards with lower formaldehyde content, without significantly affecting the internal bond strength;

- ✓ ABES is a useful technique for the evaluation of the rate of strength development of UF and MUF resins as they cure. It is possible to use simple mathematical models to describe the evolution of the bond's shear strength along curing time;
- ✓ Despite the fact that ammonium bisulphite is mostly used as a formaldehyde scavenger, this chemical shows a good performance as hardener for this type of resins.

Another goal was the development of a PF resin for particleboard production that fulfils formaldehyde emission restrictions and LEED criteria, while presenting appropriate reactivity and bond strength. The principal conclusions are:

- ✓ The presence of a higher amount of base in the final resin results in a more stable resin, with much better physic-mechanical properties. On the other hand, base addition also results in a resin with low content of phenol due to its higher consumption during the condensation step;
- ✓ To achieve simultaneously good internal bond strength and reasonable board pressing times it is necessary to use 10 % hardener relative to oven-dry weight of resin, and a gluing factor between 4.5-5 % on the core layer during particleboard production.

The development of a new MUF resin formulation with high tolerance towards water dilution, and a good overall performance in terms of physico-mechanical properties and formaldehyde emissions, lead to the following main conclusions that:

- ✓ Water dilution capacity increases significantly with MTBS incorporation, with a consequent decrease in resin reactivity, due to the premature formaldehyde consumption;
- ✓ MTBS addition leads to lower values of internal bond strength, but for a percentage of 6 % it was possible to obtain a resin with internal bond strength above the acceptable minimum ( $0.45 \text{ N}\cdot\text{mm}^{-2}$ , the requirement for PB type P3-non load-bearing boards for use in humid conditions according EN 312) using a pressing time of 150 s;
- ✓ When compared with other commercial MUF resins, the formulations containing MTBS present lower values of formaldehyde emissions, verifying CARB II criteria, and much higher water tolerance.

The major difficulty encountered during this work was the lack of information concerning the effective production of wood-based panels (mainly particleboard) with very low formaldehyde emission. The studies found in the literature do report several trials to produce resins with low formaldehyde emissions, but most of them show a decrease on the resin reactivity and, as a consequence, a significant decrease in the performance of the resins when applied to wood-based panel's production. This doctoral work brought relevant practical knowledge concerning this issue. However, this work was mainly focused on competitive solutions that could be directly introduced on the market. This work allowed the development of five new resin formulations (two UF modified resins, one PF resin and two MUF resins) that are currently marketed by EuroResinas, the company that co-funded the PhD grant.

## **5.2. Future Work**

Despite the fact that the use of formaldehyde-based resins in the wood-based panels industry has been questioned in the last years, mostly due to the concerns towards formaldehyde emissions, these products are not expected to be replaced by another kind of adhesive in the immediate future. These resins have unique advantages in terms of availability of raw materials, production costs, and performance, which are still very important to this industry.

With the formaldehyde emission legislation becoming stricter, demands for new adhesive systems arise again. One strategy may involve incorporation of biopolymers in the resins synthesis process, by partial substitution of urea or melamine by the new compound. An alternative is incorporation before particleboard production, by incorporating the bio compound in the final adhesive system.

Regarding the synthesis processes, further studies should be performed on the strongly acid synthesis process, once the advantages reported in the literature have not been confirmed in the tests carry out during this work.

