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DEVELOPMENT OF NEW RESINS AND CHARACTERIZATION TECHNIQUES FOR LAMINATES

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Development of new resins and characterization techniques for laminates

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To my grandparents Benjamim and Belmiro

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My love, I don’t have words!

“Someone in the crowd
Could be the one you need to know
The one to fin'lly lift you off the ground “

ABSTRACT

High-pressure laminates are added-value products with an expected worldwide market size of 10.7 billion m^2 for 2018. Their versatility in commercial and residential areas encompasses many applications, such as furniture, flooring, façades or kitchen and vanity tops.

Nowadays, the market is focused on pleasing the customer, being important to create and show products with new and improved characteristics. On the other hand, the industry searches for new technologies that are able to improve the quality of the products and reduce costs.

The work of this thesis is focused on the development of new impregnation resins with improved storage stability, and of resin formulations for achieving high-pressure laminates with differentiated surface properties. In addition, near infrared (NIR) spectroscopy was studied as an approach for efficient estimation of quality parameters in high-pressure laminates industry.

It is well-known that, during storage, unmodified melamine-formaldehyde resins tend to be unstable, leading to poor physicochemical properties after cure. As a possible mitigation to this situation, benzoguanamine was tested as partial substitute for melamine (up to 15 % substitution). Accordingly, upon addition of this molecule late in the reaction process, the ensuing resins exhibited improved storage stability (of at least 4 days *vs.* 1 day in pristine melamine-formaldehyde resin). As a result, the high-pressure laminates produced with décor paper impregnated with the benzoguanamine containing resins revealed excellent surface properties.

As a product, high-pressure laminates are largely used as design and decoration materials in furniture and construction industries. However, one of their main handicaps is the tendency for staining by fingerprints. Such issue can be minimized by increasing both the hydrophobicity and oleophobicity of the surface. Modification of the chemical composition of the resin used for impregnation of the decorative paper on laminate’s top layer was studied as a strategy for increasing hydrophobicity. More specifically, a melamine-benzoguanamine-formaldehyde resin was selected as a starting point, and caprinoguanamine was then included as a

comonomer in different stages of the synthesis. The inclusion at the end of the synthesis process showed to be the most promising solution to tune hydrophobicity. As a result, a water contact angle of 91.2° was achieved, which highly contrasts with the value of 58° found in commercial laminates impregnated with standard melamine-formaldehyde resins.

In turn, several commercial additives were tested for increasing oleophobicity, where a fluorocarbon based additive was concluded to be the most interesting option. With that inclusion, contact angles of 114° and 76° were obtained for water and an artificial fingerprint-simulating liquid, respectively. It must be noted that, for the latter liquid, the contact angle on standard laminates is of 27.3°. In addition, it was noticed that fingerprints were easier to clean on the modified laminate’s surface while, at the same time, other relevant surface properties (resistance to boiling water, water vapour, impact, dry heat, scratch and staining) remained practically unchanged when compared with the reference commercial impregnation resin.

Finally, NIR spectroscopy was explored as tool for the determination of moisture and resin content on papers (of different colours and grammages) impregnated with melamine-formaldehyde resins, devoted to high-pressure laminates production. While NIR analysis covered wavelengths ranging from 12000 cm^{-1} to 4000 cm^{-1}, several multivariate calibration procedures and pre-processing techniques were tested, including iPLS, fiPLS and siPLS, to select the best spectral interval. Finally, the performance of the calibration models was evaluated in terms of the root mean squared error of cross-validations (RMSECV) and the coefficient of determination (R^2). In addition, an external validation procedure was accomplished using different decorative papers (red, pearl, yellow, violet and pale green). The models’ performance was checked using RMSEP (root mean square error of prediction) as the statistical criterion. The validation confirmed that the developed models can be applied in the determination of resin content independently of the grammage and colour of the papers. However, for the volatile content indicator, the models seem to be affected by external factors such as the presence of dyes and pigments. As a result, for this indicator, the model is only applicable if the studied papers have similar spectra to those used in the calibration model.

SUMÁRIO

Os laminados de alta pressão (HPL) são um produto de alto valor acrescentado, com um mercado global de 10.7 mil milhões de m^2 em 2018. A sua versatilidade em áreas comerciais e residenciais abrange várias aplicações, como: mobiliário, pavimento, fachadas, cozinhas e tampos.

Atualmente, o mercado é focado no cliente e nas suas necessidades, sendo importante criar e lançar produtos com novas e melhoradas propriedades. Por outro lado, a indústria procura novas tecnologias que sejam capazes de melhorar a qualidade final dos produtos e reduzir custos durante o processo industrial.

O trabalho desta tese é focado no desenvolvimento de novas resinas de impregnação com um maior tempo de estabilidade durante o armazenamento, e no desenvolvimento de formulações de impregnação que resultem em laminados de alta pressão com propriedades diferenciadoras. Para além disso, a espectroscopia do infravermelho próximo (NIR) foi estudada de forma a verificar-se o seu potencial na determinação de parâmetros de qualidade na indústria dos HPL.

É sabido que durante o tempo de armazenamento, as resinas melamínicas inalteradas têm tendência a ser instáveis, o que resulta num fraco desempenho físico químico das mesmas após a cura. De forma a atenuar esta situação, a benzoguanamina foi testada como um substituto parcial da melamina (até um máximo de 15% de substituição). A adição desta molécula nas fases finais do processo de síntese, resulta em resinas que demonstram uma estabilidade melhorada (4 dias ou mais de estabilidade *vs* 1 dia de estabilidade em resinas não modificadas). Para além disso, os laminados de alta pressão produzidos com papel decorativo impregnado com as resinas estáveis desenvolvidas demonstram excelentes propriedades superficiais.

Como produto, os laminados de alta pressão são altamente usados em materiais de decoração e de design na indústria do mobiliário e da construção. Contudo, uma das suas maiores desvantagens é a sua tendência em sujar-se com dedadas. Este problema pode ser minimizado pelo aumento da hidrofobicidade e oleofobicidade da superfície.

A modificação da composição química da resina usada na impregnação do papel decorativo foi estudada como estratégia para aumentar a

hidrofobicidade. Para tal, foi usado como ponto de partida uma resina melamina-benzoguanamina-formaldeído, sendo que posteriormente foi incluída a caprinoguanamina como comonómero em diferentes etapas de síntese. A inclusão deste comonómero na fase final da etapa de síntese resultou numa solução promissora para melhorar a hidrofobicidade.

Como resultado, foi atingido um ângulo de contato para a água de 91,2, que contrasta consideravelmente com o valor de 58° encontrado no laminado comercial impregnado com uma resina melaminica padrão. Por sua vez, vários aditivos comerciais foram testados para aumentar a oleofobicidade, tendo sido um aditivo à base de fluorcarbono o mais promissor. Esta adição, resulta em ângulos de contato de 114° e 76° para a água e para um líquido artificial que simula a dedada, respetivamente. Deve ser notado, que no caso de um HPL padrão a utilização do líquido artificial que simula a dedada resulta num ângulo de contato de 27,3°. Para além disso, foi verificado que as dedadas eram fáceis de limpar, enquanto que as outras propriedades da superfície (resistência ao vapor de água, água em ebulição, calor seco, risco e nódoa) permanecem praticamente inalteradas.

Por último, a espectroscopia do infravermelho próximo foi explorada como ferramenta de determinação do teor de resina e teor de voláteis em papéis (de diferentes cores e gramagens) impregnados com resina melamina-formaldeído, utilizada na produção de HPL. De forma a determinar a gama espetral de interesse entre 12000 cm^{-1} e 4000 cm^{-1}, vários procedimentos de calibração multivariada que incluem o iPLS, fiPLS e siPLS foram utilizados assim como várias técnicas de pré-processamento.

A performance dos modelos de calibração foi avaliada através do RMSECV (raiz quadrada de erro quadrático médio da validação cruzada) e do coeficiente de determinação (R^2). Para além disso, uma validação externa foi realizada tendo sido usados vários papéis decorativos (vermelho, pérola, amarelo, violeta e verde claro). A performance dos modelos foi verificada tendo sido usado o RMSEP (raiz quadrada do erro quadrático médio de previsão) como critério estatístico. A validação confirmou, que os modelos desenvolvidos podem ser aplicados na determinação do teor de resina independentemente da gramagem e da cor dos papéis. Contudo, para o teor de voláteis, os modelos parecem ser afetados por fatores externos como a presença de pigmentos e corantes. Para este parâmetro o modelo é apenas aplicado em papéis com um espetro idêntico aos usados no modelo de calibração.

RÉSUMÉ

Les stratifiés décoratifs haute pression sont des produits à haute valeur ajouté avec un marché globale estimé à 10.7 milliards de m^2 en 2018. Sa versatilité d’usage en zones commerciales et résidentielles englobe les applications suivants: ameublement, revêtements de sol, façades, cuisines et plans.

Actuellement, le marché est axé sur le client et ses besoins, et donc il est important de créer et lancer des produits avec des propriétés nouvelles et améliorées. Par contre, l’industrie cherche des nouvelles technologies capables d’améliorer la qualité finale des produits et réduire les coûts pendant le processus industriel.

Ce travail porte sur le développement de nouvelles résines d’imprégnation avec un temps de stabilité plus long pendant le stockage et sur le développement de formulations d’imprégnation qui se traduisent par des stratifiés de haut pression avec des propriétés remarquables. En plus, la spectroscopie proche infrarouge a été étudié de forme à vérifier son potentiel pour la détermination des paramètres de qualité dans l’industrie des HPL.

On sait que pendant le stockage, les résines mélamines inchangées ont la tendance à être instables, ce que résulte dans une faible performance du point de vue physico-chimique après la réticulation. Pour surmonter cette situation, la benzoguanamine a été testé comme substitut partiel de la mélamine (jusqu’á un maximum de 15% de substitution). L’ajout de cette molécule dans les étapes finales du processus de synthèse conduit à des résines que démontrent avoir une stabilité améliorée (4 jours de stabilité vs 1 jour de stabilité en résines non modifiées).

En outre, les stratifiés haut pression produits avec du papier décoratif imprégné avec des résines stables développées ont démontrées des propriétés superficielles excellents.

Comme produit, les stratifiés décoratifs haute pression sont utilisés comme matériaux de décorations et de design dans l’industrie de l’ameublement et du bâtiment. Cependant, la tendance à se salir avec des empreintes digitales est une de ces plus grands désavantages. Ce problème peut être minimisé par l'augmentation de l’hydrophobicité et de l’oleophobicité de la surface.

La modification de la composition chimique de la résine utilisée dans l’imprégnation du papier décoratif a été étudiée comme stratégie pour augmenter l’hydrophobicité. Pour cela, une résine mélamine-benzoguanamine-formaldéhyde a été utilisé comme point de départ, et ensuite caprinoguanamine a été ajouté comme co-monomère en différents étapes de la synthèse. L’inclusion de ce co-monomère dans l´étape finale de la synthèse a conduit à une solution prometteuse pour améliorer l’hydrophobicité.

À la suite, un angle de contact de l’eau de 91,2º a été obtenu, ce qui contraste considérablement avec un valeur de 58° obtenu dans le stratifié imprégné avec la résine standard.

À son tour, plusieurs aditifs commerciaux ont été testé pour augmenter l’oleophobicité, et le résultat plus prometteur a été obtenu avec un aditif à base de fluorcarbone. L’usage de ce produit a résulté en angles de contact de 114° et 76° pour l’eau et pour un liquide artificiel qui simule l’empreinte digitale, respectivement.

Il doit être souligné que dans le cas d’un HPL standard, l’utilisation d’un liquide artificiel qui simule l’ empreinte digitale correspond à un angle de contact de 27,3°. En outre, il a été vérifié que les impressions digitales ont été faciles de nettoyer, tandis que les autres propriétés de la surface (résistance à la vapeur d'eau, eau en ébullition, chaleur sèche, rayure et taches) ont resté pratiquement inchangé.

Finalement, la spectroscopie proche infrarouge a été explorée comme outil pour évaluer la teneur en résine et en volatiles en papiers (de différents couleurs et grammages) imprégnés avec de la résine mélamine-formaldéhyde utilisé dans la production de HPL. De façon à trouver la gamme spéctrale d’intérêt entre 12000 cm^{-1} et 4000 cm^{-1}, des plusieurs procédés d’étalonnage multivariée qui inclus iPLS, fiPLS et siPLS ont été utilisé, ainsi que des différents techniques de pré-traitements.

La performance des modèles d’étalonnage a été évaluée par le calcul de RMSECV (racine carrée de l'erreur quadratique moyenne de validation croisé) et du coefficient de détermination (R^2).

De plus, une validation externe a été accompli et plusieurs papiers décoratifs ont été utilisés (rouge, perle, jaune, violette et vert clair). La performance de ces modèles a été vérifiée à travers du calcul de RMSEP (racine carrée de l'erreur quadratique moyenne de prévision) comme critère statistique. La validation a confirmé que les modèles développés peuvent être appliqués dans la détermination du teneur de résine indépendamment du grammage et de la couleur des papiers. Cependant, pour la teneur en volatiles, les modèles semblent être affectés pour des facteurs externes, comme la présence de pigments et colorants. Pour ce paramètre, le modèle est seulement appliqué en papiers avec un spectre identique aux utilisés dans le modèle d´étalonnage.

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CHAPTER 1 – INTRODUCTION

1.1. MOTIVATION

Sonae Arauco is one of the largest wood based panels producers in the world. The products range includes particleboard, MDF (Medium Density Fibreboard), Hardboard, OSB (Oriented Strand Board), production of impregnated papers and also production of chemical products (formaldehyde and formaldehyde-based resins).

EuroResinas, is part of Sonae Arauco. It is located in Sines, and is devoted to the production and commercialization of synthetic resins and formaldehyde. In addition, EuroResinas also produces decorative paper impregnated with melamine resins and *kraft* paper impregnated with phenolic resins. These papers are used for the production of high-pressure laminates (HPL), being the major clients SIR (Portugal) and Glunz AG (Germany).

Nowadays, the dynamics of the global market, through a continuous changing trend mechanism involving also end user expectations, fosters the development of new and improved features for wood-based products. In order to go along with such trend, it is important for companies to introduce in their portfolio products with innovative and improved characteristics.

This thesis tries to answer some of those topics, which were considered to be particularly relevant by the company. The following goals have been therefore defined for this work:

- Development of paper impregnation resins with improved storage stability;
- Development of HPL with dirt repellency surface properties.

Besides, Euroresinas has also proposed an additional challenge, focused in the improvement of the control quality methodology of HPL production process. An additional goal was therefore established:

- Development of an expeditious method for the estimation of moisture and resin content in impregnated paper using near infrared spectroscopy.

1.2. OUTLINE

The thesis begins with a general introduction to the high-pressure laminates (HPL) subject (Section 2.1), where aspects such raw-materials, paper impregnation, storage, pressing process and standards, among others, are overviewed. This is followed by an introduction to melamine-formaldehyde resins (Section 2.2), including their synthesis and characterization procedures. Finally, the current challenges concerning development of new functionalities in melamine resins (Section 2.3) and in HPL (Section 2.4) are addressed. From these, the topics on resin storage stability (Section 2.3.3) and dirt repellent HPL (Section 2.4.4) are the ones further researched in this thesis work.

In Chapter 3, the state of the art on use of near-infrared (NIR) spectroscopy in wood-based products industry (including HPL and melamine resins production) are highlighted. The following topics are covered: fundamentals (Section 3.2), chemometrics (Section (3.3), industrial applications (Section 3.4), monitoring industrial processes (Section 3.5), forest products applications (Section 3.6), current use of NIR spectroscopy in formaldehyde-based resins production (Section 3.7), and the future perspectives of use of this technique in this industrial sector (Section 3.8). From all these, the application of NIR spectroscopy to the impregnation process with melamine resins (in the HPL industry) is the one investigated in more detail in this thesis.

The fourth chapter concerns the study of the addition of benzoguanamine as a partial substitute of melamine during the synthesis of melamine-formaldehyde resin, at four different stages of the synthesis. The effect of benzoguanamine in the final polymer was assessed and the resin performance on high-pressure laminates was also evaluated.

The fifth chapter is devoted to the demonstration of improved hydrophobic and oleophobic performance of high-pressure laminates through the introduction of caprinoguanamine in a melamine-benzoguanamine-formaldehyde resin, combined with a fluorinated additive in the impregnation bath.

It is followed by a chapter describing the use of NIR spectroscopy as a tool for the determination of moisture and resin content on papers impregnated with melamine-formaldehyde resins for high-pressure laminate production.

Finally, in the seventh chapter, general conclusions based on the knowledge produced during this thesis are provided, which open the way to future research opportunities.

CHAPTER 2

CHAPTER 2 – HIGH-PRESSURE LAMINATES AND IMPREGNATION RESINS [1]

2.1. HIGH-PRESSURE LAMINATES (HPL)

According to the European Standard EN 438-2 [1] a high-pressure laminate (Figure 2.1.1) consists of layers of cellulosic fibrous material (normally paper) impregnated with thermosetting resins and bonded together. Production involves the simultaneous application of heat (temperature ≥ 120 °C) and high specific pressure (≥ 5 MPa), to provide homogeneous flow and subsequent curing of the thermosetting resins, to obtain a homogeneous non-porous material with increased density (≥ 1.35 g/cm^3) and with the required surface finish.

Figure 2.1.1 – High-pressure laminates (courtesy of SIR-Sonae Indústria de Revestimentos)

Decorative HPL are available in a wide range of colours and patterns combined with different textures and gloss levels. In this kind of material excellent reproductions of natural materials such as textiles, fabrics,

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[1] Henriques A, Coelho C, Ferra JM, Martins J, Magalhães FD and Carvalho L. Introduction of advanced functionalities in laminates for wood-based panels:surface quality evaluation. In: Davim JP and Aguilera A (ed) *Wood Composites: Materials Manufacturing and Engineering*. Berlin: De Gruyter, 2017.

exotic wood, veneers and stone can be achieved. On the other hand, different printing technologies e.g. digital, screen and offset printing can be used to produce customized designs. Offered in various sizes they allow large areas to be covered without seams [2].

The history of HPL began back in 1886, when Leo Baekeland combined phenol and formaldehyde to obtain a resin product that could be converted into an insoluble polymer, adding a fine sawdust filler, he obtained a very dark coloured plastic material, the Bakelite. The “precursor” of today’s HPL was born. After that, in 1906 Leibich was focusing his research on the reaction of melamine-formaldehyde. It was discovered that these resins, mixed with cellulose and subjected to a polymerisation process, produced a solid material with excellent mechanical properties. Then in ‘40s, the development of decorative papers that were highly absorbent made it possible to pay attention to the appearance [3] .

Nowadays, the industry offers various grades of standardized HPL with specific characteristics for used in a wide variety of applications: HPL-Standard, HPL-Postforming, HPL-Fire Retardant and HPL-Compact. The mentioned grades are further subdivided into several performance categories, e.g. horizontal and vertical applications as well as qualities which are suited for interior or exterior uses [2].

Looking at economic aspects, the global demand for decorative laminates is expected to rise 5.6 % per year to 10.7 billion m^2 in 2018 [4]. The increasing of the available income, the constant economic growth, the rising of standards of living and the increased demand for housing in urban areas are some of the key growth drivers. Increasing available income allow the costumer to spend more on furniture, home accessories and furnishings among which decorative laminates play a key role. Besides those parameters the wide range of colours, designs, textures and styles led to increase consumer interest and is expect to provide ample growth opportunities for decorative laminates market [5].

Regarding the global HPL consumption, according to the Figure 2.1.2 the Asia/Pacific region was the largest market for the decorative market in 2013, with nearly 50 % of the global total and continues to lead in 2018.

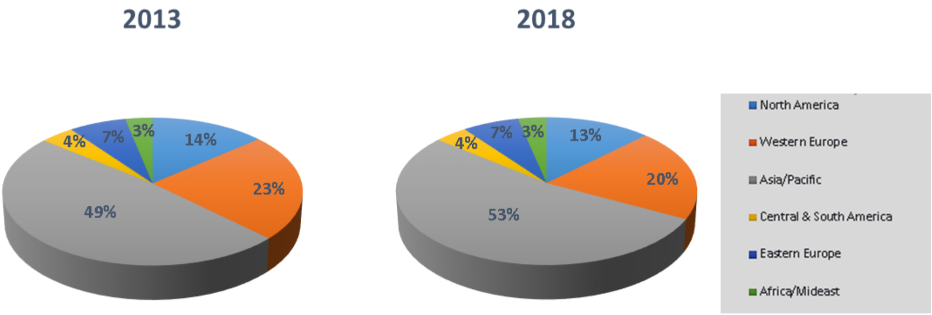

Figure 2.1.2 – World decorative laminates demand (Adapted from Wood-based Panels International).

Although the high demand on Asia/Pacific region, well-established decorative laminate industries are found in Western Europe and the US, where engineering wood and paper industries are highly developed. Despite an ongoing shift in the production of decorative laminated products to China, India and other developing areas, the demand for laminates in Western Europe is still significant, being Germany, France and Sweden the regional leaders in the production of ready-to-assemble furniture [4].

The major companies operating in the decorative laminates market include Sonae Indústria de Revestimentos (SIR), Formica, Trespa, Arpa, Fundermax, Abet Laminati, PolyRey, Egger and Coveright.

2.1.1. Manufacturing Process Overview

Behind the apparent simplicity of high-pressure laminates lies a well and complex established process. A schematic example of the overall high-pressure laminates process can be seen in Figure 2.1.3. In the next sections, the raw-materials used, paper impregnation process and its storage, the build-up and subsequent pressing of HPLs, and characterization of HPLs will be explained in detail.

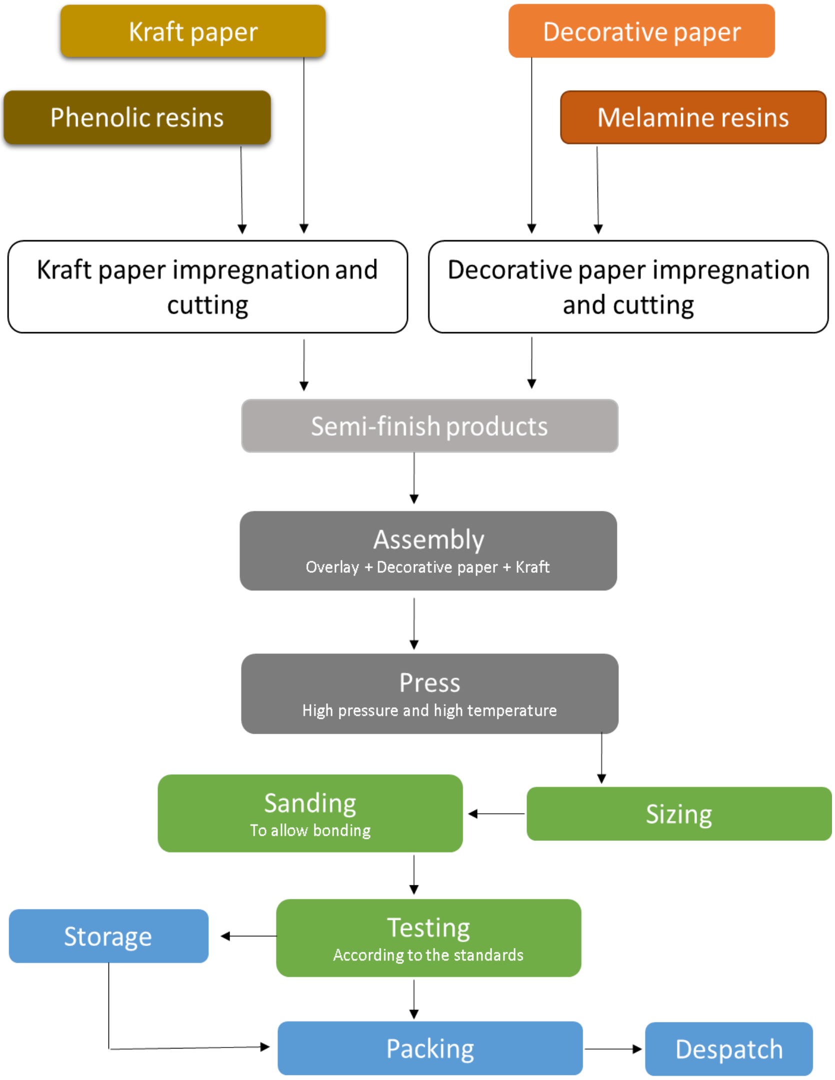

Figure 2.1.3 - The manufacturing process for HPL.

2.1.2. Raw Materials for High-Pressure Laminates

The main raw-materials for HPL production are cellulose-based materials and thermosetting resins, being the cellulose-based composed of 60-70 % of the overall HPL, with the remaining being the thermosetting resins.

In relation to the HPL cost, its value is indexed to the raw-materials price and energy demanded, changing according to the key drivers cost (Figure 2.1.4), such as: fuel oil, natural gas, melamine powder, phenol and paper [6].

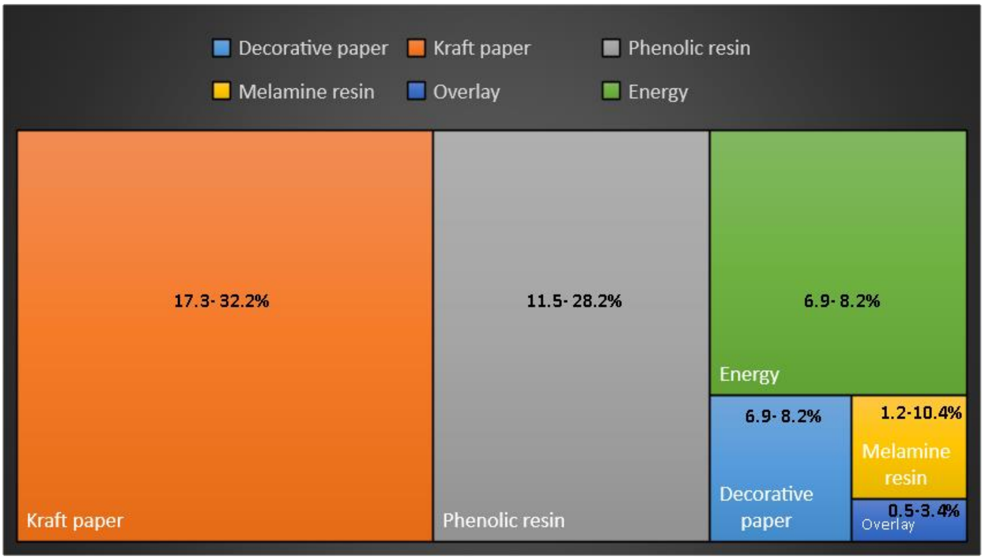

Figure 2.1.4 – Percentage of product cost in HPL.

Paper

Mainly three types of paper are used in the manufacture of HPL: *kraft* paper, decorative paper, and overlay (Figure 2.1.5).

The *kraft* paper is the “heart” of HPL. This is impregnated with phenolic resin and provides mechanical, moisture and chemical resistance to the HPL, being the mechanical resistance highly depended on fibre orientation. The grammage of *kraft* paper ranges between 80 and 260 g/m^2 [7].

The decorative paper is made of cellulose fibers, with the pulp being based predominantly on hardwoods such as eucalyptus, sometimes in combination with minor amounts of softwood pulps. Pigments (such as titanium dioxide) and fillers are added in amounts generally up to 45 wt% (based on the total dry weight prior to resin impregnation) to obtain the required opacity [8]. Furthermore, it should comply with general requirements related to capillary absorption, porosity, air permeability, durability in dry or humid conditions, surface pH and specific requirements related to appearance characteristics as light resistance, smoothness, colour and pattern. Normally, this kind of paper shows a grammage between 40 and 200 g/m^2 [9]. The use of higher grammages is required when white papers are used, in order to provide the adequate opacity that will hide the brown colour of the *kraft* paper. Another way to improve the opacity while maintaining lower basis weight is to use a paper called a barrier [10].

The overlay paper, mainly composed by alpha-cellulose, contributes mostly to increase the resistance to scratching and abrasion, which allows the use of HPL in flooring applications. For that purpose, mineral particles such as silica, alumina, corundum or tungsten carbide are added to the thermosetting resin used on the impregnation of such papers. This kind of paper has an initial grammage between 24 and 32 g/m^2 [11].

Overlay Decorative Kraft

Figure 2.1.5 – Paper types used in the manufacture of HPL.

Phenol-formaldehyde resins

Phenol-formaldehyde resins (PF) are the polycondensation products of the reaction between phenol (C_6H_5OH) and formaldehyde (CH_2O). Phenolic resins have been industrially produced since 1911, and are considered the first synthetic polymer ever manufactured. After more than a hundred years of industrialization, their average global production reaches 6 millions of tons each year and phenolic resins are now ubiquitous materials. They are used in a broad range of applications such as electric laminates, carbon foams, adhesives, moulding compounds, acid-resistant coatings and fibre-reinforced composites among others.

With characteristically high cross-linking and aromatic density structures, phenolic resins are well-known for their chemical and mechanical stability, strength and used in thermal and acoustic insulation[12,13].

Urea-formaldehyde resins

Driven by cost constraints, urea formaldehyde (UF) resin is, in some cases, used as impregnation resin instead of the more expensive melamine-formaldehyde [14], mainly for the core impregnation of paper [15]. UF resins are based on the reaction of two monomers: urea (CH_4N_2O) and formaldehyde (CH_2O). In addition to their more affordable prices, they are valuable due to fast curing when compared with other resins. However they lack in water resistance of the hardened resin [16].

Melamine-formaldehyde resins

Melamine-formaldehyde resins are made by the reaction of melamine ($C_3H_6N_6$) and formaldehyde (CH_2O). These resins are widely used as adhesives for wood, as resins for decorative laminates, varnish, mouldings, and for improving the properties of paper and cellulosic textiles.

In comparison to urea/formaldehyde resins, a melamine-based resin has higher resistance against heat and moisture [17].

2.1.3. Paper Impregnation

In the impregnation process, *kraft* paper from an unwinding device is transferred to an impregnation bath filled with phenolic resin. With squeezer rolls the resin content of the paper is adjusted before the paper enters in the drying sections. With an appropriate temperature/line speed profile the impregnated paper finally reaches the desired parameters, regarding remaining volatile content, flow, and condensation degree of the resin. After a cooling section, the paper is cut to sheets for multi daylight presses.

For the décor paper the principle is quite similar: the printed paper with different decors is impregnated with melamine resin. In some cases, urea resins are used in a first bath and the paper is coated with a melamine resin in an additional coating stage [7]. While the oven temperatures on solid colour paper normally range from 105 to 135 °C, for overlay the temperatures are normally 150 °C and for printed papers it ranges from 125 to 150 °C [18]. An example of a horizontal impregnation system for decorative laminates is presented in Figure 2.1.6 [19].

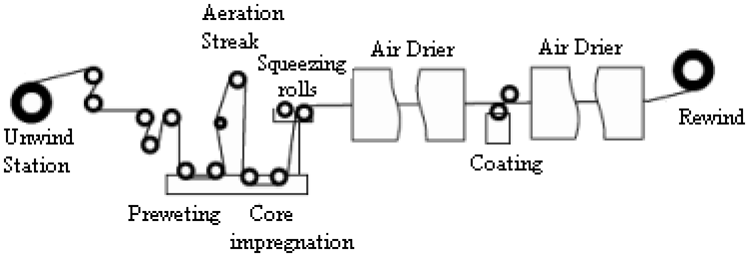

Figure 2.1.6 – Schematic representation of the impregnation process (Adapted from Figueiredo AB, Evtuguin DV, Monteiro J, Cardoso EF, Mena PC and Cruz P. Structure - Surface Property Relationships of Kraft Papers : Implication on Impregnation with Phenol - Formaldehyde Resin. *Ind Eng Chem Res* 2011; 50: 2883-2890.).

The properties of the impregnated paper are ruled by the manufacturing conditions. Important parameters that need to be carefully adjusted during the manufacture are the composition of the resin solution, the dryer conditions and the type of paper [15].

The raw paper has a huge importance in the industrial quality of an obtained laminate. Parameters such as density, wet strength and ash content influence the production process. The porosity affects resin penetration and consequently the production speed and the ash content typically improves the drainage in the paper machine [15,19,20].

For impregnation, a catalyst is normally added to the resin to increase the speed at which impregnated papers can be processed. To improve the penetration of resin in the paper, wetting agents are used. Sometimes, other additives are also added to improve the gloss or to decrease the dust formation. The resultant polymer solution is normally clear and shows a solid content between 40-65 % [7,10,15].

After paper impregnation, some basic parameters are measured in order to ensure that the paper fits the demands of the laminates manufacture, namely: resin content, volatile content, flow and curing time.

Characterization of impregnated paper

Resin Content (RC) - The determination of the resin content is accomplished by differential weighing after the impregnation. The resin content can influence the flow of the resin and consequently the aesthetics of the HPL. The melamine-impregnated papers usually contain 50–60 % by weight of resin [21].

Volatile content (VC) - The determination of the residual moisture content (volatile content) is also accomplished by differential weighing, but in this case after a 5-minute drying at 160 °C.

The amount of volatiles in the impregnated paper is used to characterize dried semi-finished paper sheets. If the moisture content is too high, the stacked or rolled sheets are often found to stick together (block formation) before being sent to the hot press for curing. On the other hand, a low content may indicate that drying was excessive and the resin has reacted too much during drying. Due to this fact, the paper will not show sufficient adhesion when the impregnated papers are cured.

Usually, when the semi-dried paper contains a residual moisture in a range between 5 % and 7 % of volatile content, the storability and the resin flow during curing are found to be satisfactory [22].

Flow time - Flow is determined from weight differences after pressing a 3 inch diameter piece of partially cured, submitted to pressing and heating (temperature = 150 ± 5 ºC) during 5 minutes. After the pressing process, the disk laminate is cooled and weighed (initial weight). After removing the resin which has flown out of the disk, the laminate is weighed again (final weight). The difference between the initial and final weight, related to the weight of the original disk laminate, gives the flow of the impregnated paper [23]. This parameter is important since it provides an indication of the degree of pre-condensation of the resin [24]. A too low flow causes an inhomogeneous film leading to optical defects like low gloss, stains, flow marks or bad cleanability [15].

Cure time - The measuring principle consists in curing a specimen (95 mm × 60 mm) in a silicone oil bath set at 140 °C. In order to measure the curing degree, the impregnated paper is automatically rotated clockwise at certain intervals. The torque associated with the rotation is directly dependant on the curing degree of the impregnated paper, and is registered in a computer. At the same time a curing graph is plotted on the screen. This method is normally called the Werzalit method, and the curing time is defined as the time length in which the hardening of the sample is 95 % of the maximum hardness [25].

Other methods are reported in the literature, such as differential scanning calorimetry (DSC). However, this methodology still shows unreliable results since the pre-dried impregnated samples are not flat (ideal feature), which hampers good contact of the sample with the bottom of the equipment. This behaviour leads to large deviations of thermograms between repeated samples [26].

Although this method allows the estimation of the degree of “chemical curing,” it is not able to predict the bond strength development between layers during the industrial hot-pressing of HPL [25]. Automated Bonding Evaluation System (ABES) described by Philip Humphrey [27] can be alternatively used to study the degree of cure of the resin in impregnated papers. This methodology can be applied to the study of the curing step of the different impregnated paper and the development of bonds between them: overlay paper on decorative paper, decorative paper on kraft paper, and kraft paper on kraft paper [25].

Penetration and Saturation Time of Decor Paper - The inverted bottle method is commonly used in industry to evaluate how ease is the penetration of a resin on paper. The liquid resin is placed in a bottle with a neck having a diameter of 25 mm. A disk of decor paper is placed under the closure ring. After inverting the bottle, the external surface of the paper disk is monitored visually. The penetration time corresponds to the instant when liquid passage becomes visible at the surface. The saturation time corresponds to the disk surface becoming uniformly wet [28].

The penetration depends on void structure of the paper and viscosity of the resin while the saturation depends on the concentration of the voids and capillary forces of the resin [29].

2.1.4. Storage

During storage the sheets of impregnated paper are placed on horizontal shelves. Accordingly, the melamine décor paper should be stored at less than 50 % relative humidity (preferably 38 %) and less than 21 °C. Higher temperature or humidity can cause the sheets to stick together and increases the volatile content. On the other hand, the *kraft* paper should be stored above 35 % relative humidity and less than 21 °C. In dry climates, the bottom edges and top sheets will dry out, decreasing the effective flow of phenolic resin to the point it will not laminate [10].

In order to ensure paper quality during the storage, several algorithms were developed by Dessipri et al. (2003). The knowledge of the ageing status and the general quality of the laminating paper can protect manufacturers from the use of non-qualifying paper while, on the other hand, preventing the waste of well-preserved paper [30].

2.1.5. Build-up

During the build-up, the papers are properly collated for the pressing [10].

Conventionally, HPLs consist of an assembly of 5 to 50 layers of *kraft* paper (core) saturated with phenol-formaldehyde (PF) resin, topped by a single printed or coloured decorative paper layer saturated with melamine-formaldehyde (MF) resin and, in some cases, by a finishing protective translucent overlay also impregnated with MF resin [31], as shown in Figure 2.1.7.

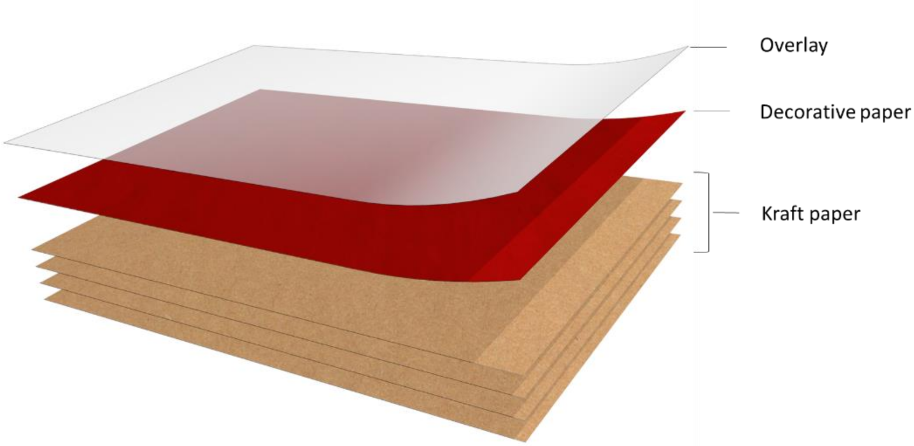

Figure 2.1.7 - Typical assembly for a high-pressure laminates build-up.

2.1.6. Pressing Process

For the decorative laminates production, the multi opening press (Figure 2.1.8) is the most commonly press method used [7]. The pressure in the hydraulic presses used is normally 8–12 MPa, and the pressing temperature is 140–180 °C.

To compensate the tension in the composite material and, in particular, to form a glossy surface, HPL is cooled under pressure to a temperature of 80 °C before it is released from the mould. The pressing cycle times can be 30 min or more, depending on the thickness and number of laminates produced. The use of different plates allow that a wide range of surface forms are made [10,32].

2.1.7. HPL Grades

The type of final application could change the main properties and specifications desired in a high-pressure laminate. The industry offers various grades of standardized HPL with specific characteristics for use in a wide variety of applications: HPL-standard, HPL-postforming, HPL-fire retardant and HPL-compact.

The post formable laminates are used especially for the production of kitchen tops. The laminates are curved around the edges of a wooden substrate in a post forming line. For this purpose, the laminate is exposed to heat for a short period of time provided by hot air or infrared radiation and then bent around the edges.

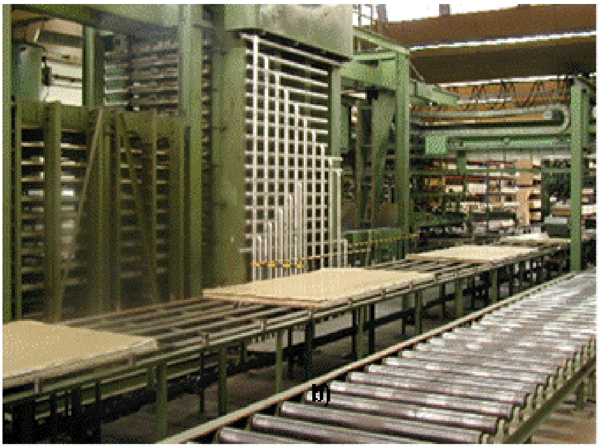

Figure 2.1.8 - Multi opening press process (Courtesy of Sonae Indústria de Revestimentos (SIR)).

The compact boards are self-supporting laminates, which means they are not glued on a wooden substrate. They consist of many layers of core paper, normally covered with an impregnated décor paper on both sides.

In the fire retardant laminate, normally is used a paper that contains alumina trihydrate or is add to the impregnation resin flame retardants additives, mainly the combination of phosphorous and nitrogen compounds [7].

2.1.8. Standard Requirements

For each different typology of laminate there are specific features, related to the intended purpose, which are evaluated using the test methods described in EN 438-2 and ISO 4586. However, for a standard HPL the minimum requirements needed are defined in EN 438-3. These are listed in Table 2.1.1[1,33].

Table 2.1.1 - HPL specifications according to EN438-3 [33].

Property	Requirements
Thickness	$0.5 \leq t \leq 1.0$ mm; ± 0.1 mm $1.0 < t < 2.0$ mm; ± 0.15 mm
Abrasion behaviour	Wear value of 350 revolutions
Scratch resistance	Grade 3
Resistance to staining	Grade 5 for group 1-2 Grade 4 for group 3
Resistance to impact	≥ 25 N
Resistance to dry heat	Grade 3 for bright finishes Grade 4 for other finishes
Resistance to boiling water	Grade 3 for bright finishes Grade 4 for other finishes
Light fastness (xenon arc)	Grade 4 to 5

2.2. MELAMINE-FORMALDEHYDE RESINS

The most common resins used in the impregnation of decorative paper are melamine-formaldehyde resins (MF resins). Melamine was first synthetized in 1834 by a German chemist called Justus von Liebig, after heating ammonium thiocyanate. The material had no documented uses until Henkel’s 1935 patent. In modern commercial production, melamine is produced from urea. This process requires six urea molecules to form one molecule of melamine.

Regarding the formaldehyde, Butlerov described in 1859, during its isolation, the possibility of forming polymers from this molecule. However what truly established the industrial utilisation of formaldehyde was when Baekeland patented the phenolic resins [34] .

Melamine-formaldehyde resins have a wide range of applications, such as furniture, construction, automobile, lamination, textile, and paper, among many others. However, as depicted in Figure 2.2.1, the laminates industry is the major consumer [35].

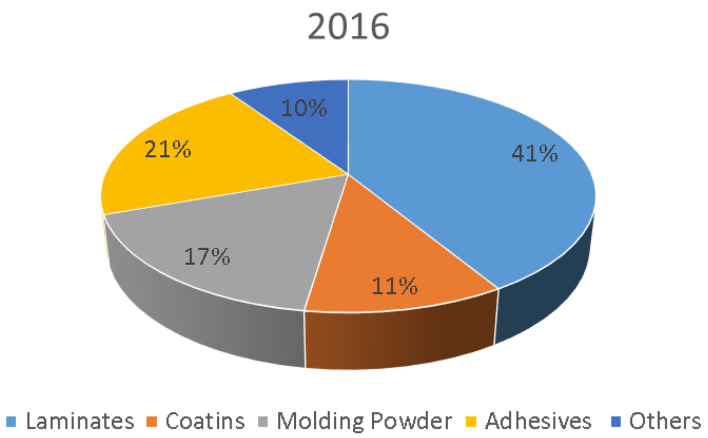

Figure 2.2.1 – Global melamine-formaldehyde market share, by application, 2016.

Melamine-formaldehyde market stood at $410 million in 2015 and is expected to reach $655 million by 2022, registering a CAGR of 6.9 % during 2016-2022 [36]. The global melamine-formaldehyde market is highly fragmented with major players such as BASF SE and Borealis Group dominating the market. In 2012, the top five companies of melamine-formaldehyde market include BASF SE, Mitsui Chemicals, Borealis Group, Momentive Speciality and INEOS Group. Together, these companies represent approximately 20 % of the overall market share [37].

2.2.1. Resin Synthesis

The generation of melamine-formaldehyde resins usually follows a two-step mechanism (Figure 2.2.2). The first step (methylolation step) leads to the formation of methylolated melamine species by the reaction of formaldehyde with melamine. The second step (bridging) forms ether or methylene bridges by condensation and either water or free formaldehyde is generated (depending on the pH) [38].

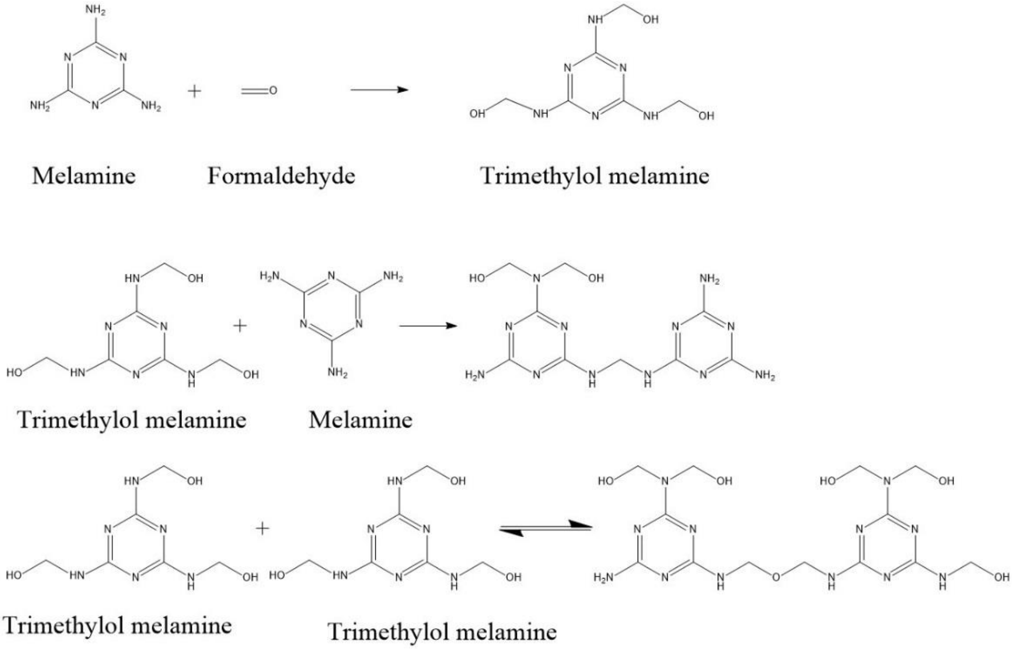

Figure 2.2.2 – Melamine-formaldehyde chemical reactions

During the MF synthesis, the most important parameters are [38]:

- Molar ratio of the different monomers:
  - – Molar ratio formaldehyde/melamine (F/M);
  - – Molar ratio formaldehyde/amine groups (F/NH_2);
  - – Solid content.

- Raw materials purity.

- Synthesis process:
  - – pH;
  - – Temperature;
  - – Sequence and addition of different raw materials;
  - – Length of the different stages of synthesis.

Depending on the type of final application, the referred parameters can be adjusted. Accordingly,

Figure 2.2.3 shows a typical diagram from the evolution of pH and temperature in a melamine-formaldehyde resin synthesis [39]. During the manufacture process, it is also important to control the turbidity point (the point during resin preparation at which addition of a drop of MF reaction mixture to a test tube of cold water gives slight turbidity) and the water tolerance, which mark the end of the reaction. The water tolerance is a direct measure of the extent of condensation of the resin and indicates the percentage of water or mass of liquid on the reaction mixture that the MF resin can tolerate before precipitating out [39]. After the synthesis, the main properties of a typical melamine-formaldehyde resins are described in the Table 2.2.1 [40,41].

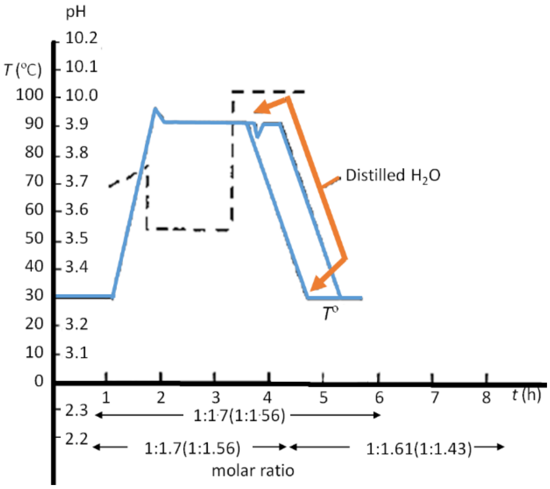

Figure 2.2.3 - Typical temperature and pH diagrams for the industrial manufacture of melamine-formaldehyde resins (Pizzi A and Mittal KL. *Handbook of adhesive technology*. New York: M. Dekker, 2003.).

Table 2.2.1 – Main properties of melamine-formaldehyde resins

Attribute	**Melamine - formaldehyde resin**
Appearance	Colourless
Solid Content (%)	50 ± 10
pH	9.5 ± 0.5
Density (g/cm^3)	1.250 ± 0.010
Kinematic Viscosity (s)	16 ± 2
Hardening Temperature	Starting at 100 °C

2.2.2. Characterization

2.2.2.1. Basic Characterization

The basic characterisation of the resin is carried out industrially using inexpensive methods. The most common are:

Solid content (%) - Solid contents of the resins are determined heating 3 g of each sample in an aluminum pan, which is then placed in an oven at 120 °C, for three hours, until reaching a constant mass.

Density (g/cm^3) - It is usually determined based on the weight/volume ratio, and measured using a hydrometer.

Kinematic viscosity (s) - Kinematic viscosity is determined as the resin flow time in [s] using a flow cup viscometer. The cup should be select according to the expected viscosity and place in the ring of the stand which has been levelled. The orifice of the cup has to be close with a finger and fill to overflowing with the conditioned sample, removing the excess.

A container should be placed directly under the orifice to catch the sample as it flows from the cup. The time measurement starts immediately after the finger removing. If desired, the time in seconds may be converted to centipoise unit using a conversion table.

pH-value - The pH is monitored automatically in a pH meter.

Water tolerance - The water tolerance of the resins is evaluated by transferring 5 mL of resin (at 25 °C) to a test tube, and determining the needed amount of distilled water to be added for it to become cloudy. The water tolerance is given according to the following expression:

$$\text{Water Tolerance (\%)} = \frac{V}{V'} \times 100 \qquad \textbf{(2.2-1)}$$

where *V* is the distilled water added (mL), and *V'* is total sample volume (mL).

Free formaldehyde – The determination of free formaldehyde in amino resins is accomplished according to the European Standard EN 1243. Accordingly, this test is based on the reaction of the free formaldehyde with sodium sulphite in the presence of a measured excess of acid, in the following stoichiometry:

$$\mathrm{CH_2O} + \mathrm{Na_2SO_3} + \mathrm{H_2O} \rightarrow \mathrm{CH_2(OH)SO_3Na} + \mathrm{NaOH} \qquad \textbf{(2.2-2)}$$

The acid-sulphite mixture provides an essentially neutral buffered system, which prevents hydrolysis of condensed formaldehyde. A reaction temperature close to 0 °C helps to ensure the absence of side reactions. In the end, the alkaline titration of the unreacted excess acid is performed.

The free formaldehyde content shall be calculated by the following formula:

$$\textbf{Free formaldeyhde}\ \% = \frac{(\boldsymbol{V_2} - \boldsymbol{V_1}) \times \boldsymbol{M} \times \mathbf{3.002}}{\boldsymbol{m}} \qquad \textbf{(2.2-3)}$$

where: V_1 is the volume (mL) of 0.1 M sodium hydroxide solution used for the adhesive test; V_2 is the volume (mL) of 0.1 M sodium hydroxide solution used for the blank test; M is the molarity of sodium hydroxide solution; m is the mass (g) of the adhesive test portion.

2.2.2.2. Spectroscopic Techniques

Several spectroscopic techniques are useful for the characterization of MF resin. These are described next:

Fourier Transform Near-Infrared spectroscopy (FT-NIR, 12000 – 4000 cm^{-1}) is a non-destructive, reliable, fast, versatile technique, that requires no sample preparation [42]. In melamine-formaldehyde resins this technique has been used to control the polycondensation progress of both melamine and formaldehyde, and to estimate the end point of the reaction samples [43].

Fourier Transform InfraRed spectroscopy or **Mid-InfraRed (FT-IR/MIR)** detects functional groups by measuring fundamental molecular vibrations in the range of 4000 – 400 cm^{-1} [44]. Fourier transform infrared spectroscopy has been already used in the investigation of the chemical reactions that occur during condensation. However, the provided information concerning the relative proportions of methylol, methylene and methylene ether groups by FTIR has proven to be insufficient, due to the high number of slightly different structures present in MF resins which result in very broad and overlapping absorption bands [45].

Raman spectroscopy involves the study of the interaction of radiation with molecular vibrations. However, while MIR and NIR spectroscopy are based on the absorption of radiation, Raman spectroscopy is a scattering technique [46]. A Raman spectroscopy method can be used in melamine-formaldehyde resin for the determination of free melamine content, not only in a soluble resin but also in a cured resin [47]. In addition, it can be also used for the quantitative and qualitative characterization of melamine-formaldehyde resin. This technology promises to be particularly useful to determine the amount of residual groups [48].

Nuclear Magnetic Resonance (NMR) spectroscopy is an useful technique to identify and analyse organic compounds [49]. ^{13}C NMR has been used to investigate melamine resins [50]. For instance, Subraya and Jones [51] described the structure of highly methylolated melamine resins using ^{13}C NMR. In turn, Wang [34] used the technology to develop a method to analyse the formation of melamine-formaldehyde resin *in situ*.

Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry allows fast and efficient analysis of complex synthetic polymers, which always exhibit varying degrees of polydispersity, including distributions of molar mass and chemical composition [52]. This technique can be used in melamine-formaldehyde resins for the identification of its individual species [53].

2.2.2.3. Chromatographic Techniques

Several chromatography techniques that exploit different separation mechanisms are commonly used to fractionate polymers [54]. These are described below:

Size exclusion chromatography (SEC) - Size exclusion chromatography (SEC) is currently the most commonly used chromatographic technique for polymer separations. In SEC an entropically controlled separation occurs according to hydrodynamic volume or size of molecules [54].

Among the different SEC techniques, Gel Permeation Chromatography (GPC) separation occurs via the use of porous beads packed in a column [55].

For the analysis of melamine-formaldehyde resins, dimethylformamide, dimethylsulfoxide, or salt solutions are generally used as solvents with a differential refractometer as a detector [39].

High performance liquid chromatography (HPLC) – is a technique that allows separation of a mixture of different molecular weight compounds by chromatographic principles. In general, the separation of the components occurs by differential migration of sample components when a liquid mobile phase containing them crosses a solid stationary phase [56]. This technique can be used to study the melamine-formaldehyde structure [57] and to reveal the nature of precipitated species in these resins [58].

2.2.2.4. Cure Evaluation Techniques

The curing behavior of a melamine-formaldehyde resin and its degree of crosslinking govern the customized product properties. If the resin is not sufficiently cured, particleboards glued with melamine-formaldehyde will lack mechanical strength and surface finishes based on MF-impregnated papers will lack hardness, durability, brilliance, and resistance towards hydrolysis and chemical agents [59].

In order to measure such parameters several techniques could be carried out.

Differential scanning calorimetry (DSC) measures the change of the difference in the heat flow rate between a sample and the reference sample, while they are subjected to a controlled temperature program [60]. The employment of such technique has been useful to better understanding of the thermal curing process of melamine-formaldehyde resins, namely the existence of two steps of reaction [45].

Thermogravimetric analysis (TGA) determines the change in weight as a function of a temperature program under a controlled atmosphere. The weight loss of the sample is recorded as a function of the temperature, which is related to the respective volatiles content [61]. The thermal decomposition of melamine-formaldehyde resins can be studied by this technique [62].

2.3. NEW FUNCTIONALITIES IN MELAMINE RESINS

The development of new and improved polymers and their applications in novel areas have led to the development of innumerable new products. Polymers show different characteristics due to their unique structural complexity. A change in the nature of pendant groups, arrangement of the monomeric units or change in the reaction conditions, etc., can tremendously change their properties [63].

2.3.1. Bioadhesives

Nowadays, the synthetic adhesive industry is encouraged to address environmental and health safety issues related to dismissing hazardous ingredients, VOCs emissions, and also in terms of the difficulties in recycling or remediating adhesives derived from petrochemical feedstock [64].

Within the melamine-formaldehyde resins context, the reported issues are mostly related to the reduction of synthetic monomer in the feed and to the introduction of sustainable compounds, such as casein, soluble potato starch, sucrose and glycerol.

The use of soluble potato, starch and sucrose has proven not to be a suitable approach since there is no covalent bonding to the melamine-formaldehyde oligomers and, besides that, the substitution of melamine by these polyols lead to severe losses in technological performance of the modified resulting resins. On the other hand, the use of casein and glycerol in such resins show interesting results. Regarding the use of glycerol, the addition immediately at the start of the synthesis demonstrated to be the best approach, resulting in modified resins with similar characteristics to those used in the impregnation of décor paper for the production of high-pressure laminates.

Concerning casein, its use decreases the free formaldehyde content in resins, and increases the gel time of them. Moreover, when used in the production of composites, the chemical resistance towards various mineral acids is found to increase with the increase of casein in the matrix [22,65].

2.3.2. Flexibility

One of the constraints of the use melamine resins in décor paper impregnation is related with the brittleness of paper after drying, which forbids application over curved surfaces or surfaces with sharp angles. In addition, the paper's brittleness impairs production in the form of continuous rolls, which would facilitate transport and storage [28]. In order to confer flexibility, plasticizers are often added to melamine formulations, with sorbitol, aliphatic polyols and caprolactam being the most common ones. However, these plasticizers often lead to laminates that are inappropriate in terms of colour, clarity, and chemical and water resistance [66].

2.3.3. Resin Storage

Unmodified melamine resins have very short shelf lives, e.g., no more than about 1-3 days, after which time the resin begins to separate from solution, going from clear to turbid. This gives the high-pressure decorative laminates a heterogeneous and cloudy appearance. In order to overcome this limitation, various modifiers can be added to MF resins [66]. Among these one may cite sucrose, diethylene glycol, caprolactam, which are recognized to ensure a prolonged storage life of melamine-formaldehyde resins. However, caprolactam itself absorbs water, leading to the residue after curing to absorb moisture and thus seriously affect the shelf life of the product. Sucrose and diethylene glycol also show a hygroscopic behaviour that can be counterproductive for its use in melamine resins [67]. This topic will be further explored in the Chapter 4.

2.4. NEW FUNCTIONALITIES IN HIGH-PRESSURE LAMINATES

The worldwide interest in high-pressure laminates has taken the industry to focus on the development of new products, with improved characteristics, such as mar resistance, abrasion resistance, resistance against strong chemicals, weathering resistance, dirt repellent features, self-healing, antibacterial and antifungal properties.

2.4.1. Mar and Abrasion Resistance

Mar is the term used to describe relatively fine surface scratches generally characterized by shallow damage, distributed over a relatively large area that typically spoils the appearance of a surface coating of a surface coating. The propensity for HPL surfaces to exhibit poor mar resistance is greater for laminates that have high gloss surfaces, especially when the décor sheet of the laminate is a solid colour, and even more especially when the solid colour is dark. Decorative laminates of this type show the "wear and tear" of everyday use more than laminates of a solid pastel colour or laminate having a matte finish, independently of the decorative pattern that is employed [68].

The abrasion resistance concerns the resistance to the erosion caused by scraping, rubbing and other types of mechanical wear. This feature allows the material to retain its integrity and hold its form, and it is particularly important in horizontal applications where wear is accentuated, in particular in products for flooring applications.

In order to impart these properties to HPL, some strategies that report the incorporation of additives in the decorative paper impregnation resin may be used. For mar resistance, the incorporation of polyethylene wax in impregnation resins with a particle size of about 1-25 microns and a melting point of 105-110 ºC is reported [69].

Another proposed solution consisted in the use of a combination of a thermosetting resin, hydrolysed polyvinyl alcohol, fumed amorphous silica and abrasive material [68]. However, the incorporation of abrasive materials in the paper often results in several damages to the delicate, highly polished or intricately etched surfaces of the press plates [70]. The damage in the press plates requires their replacement or reconditioning, which implies a rather high cost.

As a result, room for new studies exist, in order to simultaneously confer such property but protect the plates finishing. One of them is related to the use of a mixture of melamine-formaldehyde resin, alumina particles, a silane coupling agent and a thickening agent, that suspends the alumina and protects the plates [71].

In the case of abrasion, this property is nowadays achieved through the addition of aluminium trioxide (corundum) particles to the impregnation resins [72]. Another approach involves the addition of organosilica particles produced by the sol-gel method to the impregnation resin [73].

2.4.2. Resistance to Strong Chemicals

Taking into account the exceptional mechanical strength properties of HPL it is important to improve its resistance to strong chemical agents, making them a solution for use in different types of laboratories.

To achieve that feature, it is suggested that a chemical resistance decorative can be produced having the three layers: bottom one impregnated with phenolic resin; a top one impregnated and coated with bisphenol A epoxy-based vinyl ester resin; and an intermediate layer impregnated with aminotriazine-aldehyde resin which acts as a barrier to phenolic resin to contact with the terminated bisphenol A epoxy-based vinyl ester resin [74]. Alternatively, the use of urethane acrylate polymerized under UV radiation as impregnation resin is also a possibility [75].

In particular, for the improvement of acid resistance, it has been proposed the combination of melamine with another amino aldehyde compound of reduced basicity. This approach could not only reduce the basicity of the produced film reduce but also improve the acid resistance of it [76].

2.4.3. Weather Resistance

The exposure to climate conditions affects various aspects of the coatings properties such as physical and mechanical properties. Being the sunlight and humidity the most important weathering factors [77]. In HPL the weather resistance is essential in laminates used in facades of buildings, outdoor furniture and balconies. Known processes for improving the UV resistance of decorative laminates consists in the applications of top layers of polyacrylates or butyl rubber. However, these top layers show low scratch resistance. Another approach is related to the use of UV stabilizers (HALS-hindered amine light stabilizers alone) or in combination with UV absorbs as additives in impregnation resins [78].

2.4.4. Dirt Repellence

HPL are constantly subjected to touch and therefore commonly stained with undesirable fingerprints. These motivate the increasing demand of anti-fingerprint coatings by the consumer. The anti-fingerprint property provides material surfaces with self-cleaning or easy-to-clean features [79]. To provide such property typical commercial fluorinated and siloxane-based surfactants can be tested as additives in impregnation resins.

Also the use of polydimethysiloxane oxidized to the corresponding aldehyde as well as nonafluorohexyl polyhedral oligomeric silsesquioxane have been tested as impregnation additive, being the achieved results in all cases considered promising [80,81]. This topic will be further explored in the Chapter 5.

2.4.5. Antibacterial Action

HPL are a breeding ground for bacteria, fungi, and other microorganisms [82] due to (cross-)contaminations from different sources, such as infected people, animals, food and/or water [31].

The incorporation of antibacterial agents in HPL should take into account not only the efficiency and stability of the incorporated agents but also their toxicity. Compounds like quaternary ammonium salts, triclosan and silver nanoparticles are described in the literature for this purpose but they exhibit long-term consequences on human health. On the other hand, poly(hexamethylenebiguanide) is a powerful, safe antiseptic which, due to this feature, can be used as an additive in the resin impregnation formulation. The antimicrobial activity against *L. innocua* and *E. coli* has been evaluated, showing HPL with this compound a bacteriostatic and bactericidal behaviour, besides the fact that the latter was maintained at least for 2 months after the HPL production [31].

2.4.6. Self-healing Properties

One major problem in polymeric layers is the tendency to undergo damage when exposed to critical conditions or long-term use. The surfaces may develop microcracks with negative visual impact, which are impossible to remove in thermosetting materials [83]. A possible solution for this problem relies in the development of HPL with self-healing properties.

Self-healing materials have the ability to regenerate microcracks independently of their location, restoring the structure and performance of the material, and to some degree minimize the negative visual impact of the damaged surface [84].

For this purpose, Antunes et al. [85] proposed an autonomic extrinsic self-healing system that requires the use of an additional regeneration agent. In this purpose, microcapsules of urea-formaldehyde having a mean diameter of 10 ± 7 µm with a core of linseed oil (self-healing agent) and cobalt solution (drying agent) were synthesized by *in situ* polymerization. These microcapsules were incorporated in the HPL decorative paper by impregnation. The feasibility of microcapsule incorporation in the laminate surface was confirmed by SEM. A microcapsule loading of 3 % in the laminate gives the best self-healing efficiency results.

2.5. REFERENCES

1. DIN EN 438-2. European Standard EN438-2 Decorative High-pressure Laminates (HPL) - High-pressure decorative laminates (HPL) -Sheets based on thermosetting resins (usually called Laminates).
2. (ICDLI) ICotDLI. *Information Data Sheet - Characteristics and Possibilities of Use for Decorative High-pressure Laminates*. Information Data Sheet. October 2006. Frankfurt am Main:

Internacional Committee of the Decorative Laminates Industry (ICDLI).

3. S.p.A. AI. *Technical Information Part 1: Thin HPL*. Technical Information. May 2013. Italy: Arpa Industrial S.p.A.
4. The significant global rise of decorative laminates. *Wood based panels international*. World Market Intelligence Ltd., 2015.
5. Research PM. *Decorative Laminates Market: Global Industry Analysis and Forecast to 2020*. Report. Report no. PMRREP3502, 2016. New York: Persistente Market Research.
6. Adamson M. Formica Laminates & Panels, https://fletcherbuilding.com/assets/incoming/141009formicainvestor presentation.pdf (2011, accessed December 2016).
7. Lepedat K, Wagner R and Lang J. Laminates. In: Pilato L (ed) *Phenolic Resins: A Century of Progress*. 1st ed. Bound Brook: Springer Berlin Heidelberg, 2010, pp.243-264.
8. Acton QA. *Aldehydes—Advances in Research and Application: 2013 Edition*. Atlanta, Georgia: ScholarlyEditions, 2013, p.934.
9. Istek A, Aydemir D and Aksu S. The effect of décor paper and resun type on the physical, mechanical, and surface quality properties of particleboards coated with impregnated décor paper. *BioResources* 2010; 5: 1074-1086.
10. Hoenigman T. An introduction to high-pressure laminates. In: *Plastic Laminates Symposium* Atlanta, 19th-22nd August 1996, Technical Association of the Pulp and Paper Industry.
11. Ungar IS, O'Dell RD and Lex JA. *Abrasion resistant laminate*. Patent Patent 5037694 A, U.S. , 1991.
12. Foyer G, Chanfi BH, Boutevin B, Caillol S and David G. New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors. *Eur Polym J* 2016; 74: 296-309.
13. Pizzi A. Phenolic Resin Adhesives. In: Pizzi A and Mittal KL (eds) *Handbook of Adhesive Technology*. Marcell Dekker, Inc., 2003.
14. Kandelbauer A, Petek P, Medved S, Pizzi A and Teischinger A. On the performance of a melamine–urea–formaldehyde resin for decorative paper coatings. *Eur J Wood Wood Prod* 2010; 68: 63-75.

15. Kandelbauer A and Teischinger A. Dynamic mechanical properties of decorative papers impregnated with melamine formaldehyde resin. *Eur J Wood Wood Prod* 2009; 68: 179-187.
16. Dunky M. Urea–formaldehyde (UF) adhesive resins for wood. *Int J Adhes Adhes* 1998; 18: 95-107.
17. Fink JK. *Reactive Polymers Fundamentals and Applications: A Concise Guide to Industrial Polymers*. Oxford: Elsevier Science, 2013, p.576.
18. Hoenigman T. Plastic Laminates Symposium. In: 1996, Technical Association of the Pulp and Paper Industry.
19. Figueiredo AB, Evtuguin DV, Monteiro J, Cardoso EF, Mena PC and Cruz P. Structure - Surface Property Relationships of Kraft Papers : Implication on Impregnation with Phenol - Formaldehyde Resin. *Ind Eng Chem Res* 2011; 50: 2883-2890.
20. Lourenço A, Gamelas J and Ferreira P. Increase of the filler content in papermaking by using a silica-coated PCC filler. *Nordic Pulp & Paper Research* 2014; 29: 240-245.
21. Nemli G and Usta M. Influences of some manufacturing factors on the important quality properties of melamine-impregnated papers. *Building and Environment* 2004; 39: 567-570.
22. Kohlmayr M, Zuckerstätter G and Kandelbauer A. Modification of melamine-formaldehyde resins by substances from renewable resources. *J Appl Polym Sci* 2012; 124: 4416-4423.
23. Van der Zwan R and Strunk S. *Compressible decorative paper impregnating agent which can be printed by the inkjet method*. Patent 8460767 B2, USA, 2013.
24. Kandelbauer A, Petek P, Medved S, Pizzi A and Teischinger A. On the performance of a melamine–urea–formaldehyde resin for decorative paper coatings. *Eur J Wood Wood Prod* 2009; 68: 63-75.
25. Martins JM, Almeida M, Coelho C, Ferra JM and Carvalho LH. A New Methodology to Evaluate the Cure of Resin-Impregnated Paper for HPL. *The Journal of Adhesion* 2015; 91: 792-800.
26. Kohlmayr M, Stultschnik J, Teischinger A and Kandelbauer A. Drying and curing behaviour of melamine formaldehyde resin impregnated papers. *J Appl Polym Sci* 2014; 131: 1-9.

27. Humprey PE. Outline Standard for Adhesive Dynamics Evaluation Employing the ABES (Automated Bonding Evaluation System). In: *International Conference on Wood Adhesive* Lake Tahoe, 28-30 September 2009.
28. Antunes A, Henriques A, Lima F, Ferra J, Martins J, Carvalho L and Magalhães FD. Postformable and Self-Healing Finish Foil Based on Polyurethane-Impregnated Paper. *Industrial & Engineering Chemistry Research* 2016; 55: 12376-12386.
29. Raymond R. *Liquid penetration into paper*. PhD Thesis, Australian National University, Canberra, 2004.
30. Dessipri E, Minopoulou E, Chryssikos G, Gionis V, Paipetis A and Panayiotou C. Use of FT-NIR spectroscopy for on-line monitoring of formaldehyde-based resin synthesis. *Eur Polym J* 2003; 39: 1533-1540.
31. Magina S, Santos M, Ferra J, Cruz P, Portugal I and Evtuguin D. High-pressure Laminates with Antimicrobial Properties. *Materials* 2016; 9: 100.
32. Wittmann O and Wolf F. Wood-Based Materials. In: Ullmann's (ed) *Encyclopedia of Industrial Chemistry*. 7th ed.: Wiley-VCH Verlag GmbH & Co. KGaA, 2000, pp.1-39.
33. DIN EN 438-3. European Standard EN438-3 Decorative High-pressure Laminates (HPL) - High-pressure decorative laminates (HPL) -Sheets based on thermosetting resins (usually called Laminates).
34. Wang Y. *Real Time NMR analysis of melamine-formaldehyde resin reactions*. University of Waikato, Hamilton, New Zealand, 2012.
35. Wire B. Global Melamine Formaldehyde Market Witnessing Rising Adoption in Automotive Manufacturing Facilities: Technavio, http://www.businesswire.com/news/home/20170612006160/en/Global-Melamine-Formaldehyde-Market-Witnessing-Rising-Adoption (2017, accessed January 2017).
36. Research AM. Melamine Formaldehyde Market to Reach $655 Million By 2022, Globally - Allied Market Research, http://markets.businessinsider.com/news/stocks/Melamine-

Formaldehyde-Market-to-Reach-655-Million-By-2022-Globally-Allied-Market-Research-1001874727 (2017, accessed April 2017).

37. Linker R. *Melamine Formaldehyde Market for Tableware, Laminates, Adhesives, Paints & Coatings, Sanitary Ware, Electricals & Household Appliances and Other Applications - Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2013 - 2019*. Market Reserach. 6 May 2014. Transparency Market Research.
38. Binder WH and Dunky M. Melamine–Formaldehyde Resins. In: Mark H and Kroschwitz J (eds) *Encyclopedia of Polymer Science and Technology*. Michigan University: John Wiley & Sons, Inc., 2002, pp.369-384.
39. Pizzi A and Mittal KL. *Handbook of adhesive technology*. New York: M. Dekker, 2003.
40. Grunwald D. Molecular structure of melamine-formaldehyde impregnation resins. In: *European Laminates Conference and Workshops* Vienna, 21-22 March 2002.
41. Kües U. *Wood Production, Wood Technology, and Biotechnological Impacts*. 1st ed.: Universitätsverlag Göttingen, 2007.
42. Henriques A, Cruz P, Martins J, Ferra JM, Magalhães FD and Carvalho LH. Determination of formaldehyde/urea molar ratio in amino resins by near-infrared spectroscopy. *J Appl Polym Sci* 2012; 124: 2441-2448.
43. Pawliczek M, Reischer T, Kowalski J, Märzinger W, Kantner W and Brandstetter M. Long-term in-line monitoring of melamine formaldehyde resins using NIR spectroscopy. *Lenzinger Beriente* 2015; 92.
44. Socrates G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*. 3rd ed. West Sussex: Wiley, 2004.
45. Merline D, Vukusic S and Abdala A. Melamine formaldehyde: curing studies and reaction mechanism. *Polym J* 2012; 45: 413-419.
46. Burns DA and Ciurczak EW. *Handbook of Near-Infrared Analysis, Second Edition (Practical Spectroscopy)*. New York: CRC Press.
47. Scheepers ML, Meier R, Markwort L, Gelan JM, Vanderzande DJ and Kip BJ. Determination of free melamine content in melamine-

formaldehyde resins by Raman spectroscopy. *Vib Spectrosc* 1995; 9: 139-146.

48. Scheepers ML, Gelan JM, Carleer RA, Adriaensens PJ, Vanderzande DJ, Kip BJ and Brandts PM. Investigation of melamine-formaldehyde cure by Fourier transform Raman spectroscopy. *Vib Spectrosc* 1993; 6: 55-69.
49. Balci M. *Basic 1H- and 13C-NMR Spectroscopy*. Amsterdam: Elsevier Science, 2005.
50. Tomita B and Ono H. Melamine–formaldehyde resins: Constitutional characterization by fourier transform 13C-NMR spectroscopy. *Journal of Polymer Science: Polymer Chemistry Edition* 1979; 17: 3205-3215.
51. Subrayan RP and Jones FN. 13C-NMR studies of commercial and partially self-condensed hexakis(methoxymethyl)melamine (HMMM) resins. *J Appl Polym Sci* 1996; 62: 1237-1251.
52. Mautjana NA and Pasch H. Matrix-Assisted Laser Desorption Ionization Mass Spectrometry of Synthetic Polymers. *Macromolecular Symposia* 2012; 313-314: 157-161.
53. Leidl M, Huber WF, Schwarzinger C and Endesfelder A. Characterization of a Linear Melamine Formaldehyde Resin. *Int J Polym Anal Charact* 2007; 12: 301-314.
54. Messaud FA, Sanderson RD, Runyon JR, Otte T, Pasch H and Williams SKR. An overview on field-flow fractionation techniques and their applications in the separation and characterization of polymers. *Prog Polym Sci* 2009; 34: 351-368.
55. Wu CS. *Handbook Of Size Exclusion Chromatography And Related Techniques: Revised And Expanded*. New York: CRC Press, 2003.
56. Paiva N. *Development of resins with very low formaldehyde emission*. Ph.D. Thesis, University of Porto, Porto, 2015.
57. Lavrič S, Kočar D, Mihelič I and Braybrook C. Accurate mass determination of melamine–formaldehyde synthetic polymers after separation on preparative HPLC. *Prog Org Coat* 2015; 81: 27-34.
58. Jahromi S. Storage stability of melamine-formaldehyde resin solutions, 1. The mechanism of instability. *Macromol Chem Phys* 1999; 200: 2230-2239.

59. Kandelbauer A, Wuzella G, Mahendran A, Taudes I and Widsten P. Model-free kinetic analysis of melamine–formaldehyde resin cure. *Chem Eng J* 2009; 152: 556-565.
60. Höhne G, Hemminger WF and Flammersheim HJ. *Differential Scanning Calorimetry*. New York: Springer Berlin Heidelberg, 2013.
61. Sperling LH. *Introduction to Physical Polymer Science*. New Jersey: Wiley, 2015.
62. Ullah S, Bustam MA, Nadeem M, Naz MY, Tan WL and Shariff AM. Synthesis and Thermal Degradation Studies of Melamine Formaldehyde Resins. *Sci World J* 2014; 2014: 6.
63. Parameswaran PS. *Modification of phenol formaldehyde resin for improved mechanical properties*. Cochin University of Science and Technology, 2009.
64. Patel AK, Mathias J-D and Michaud P. Polysaccharides as Adhesives. *Reviews of Adhesion and Adhesives* 2013; 1: 312-345.
65. Raval D, Patel A and Narola B. A Study on Composites from Casein Modified Melamine-Formaldehyde Resin. *Polym Plast Technol Eng* 2006; 45: 293-299.
66. Gadup B, Shoemake M and Searcy E. *Melamine-formaldehyde resins modified with dicyandiamide and sorbitol for impregnation of substrates for post-formable decorative laminates*. Patent 6001925 A, USA, 1999.
67. Chegzhen J, Zhifang L, Baoyin Z and Xiaojian K. *Modification method of melamine formaldehyde resin*. Patent 103319673 B, China, 2013.
68. Park J, White P and Richardson C. *Damage resistant decorative laminate*. Patent 4880689 A, USA, 1989.
69. O'Dell RD, Ungar IS and Scher HI. *Scuff-resistant laminates*. Patent 4499137 A, USA, 1985.
70. Fuerst PE. *Abrasive-resistant decorative laminates and method for making same*. Patent 3445327 A, USA, 1969.
71. Albrinck DJ and Mascavage JJ. *Wear resistant decorative laminates comprising mineral particles and methods for producing same*. Patent 5362557 A, USA, 1994.

72. Gaa P, Lay T, Ma M and Oliver J. *Method of impregnating decorative paper with melamine resin*. Patent 0819794 A3, European, 1999.
73. Magina S, Evtuguin D, Portugal I, Ferra JM and Cruz P. Organic-inorganic sol-gel coating of paper surfaces for high-pressure laminates. In: *12th International Chemical and Biological Engineering Conference* (ed Porto), Porto, 10-12 September 2014.
74. Brooker LG and Jarrell DL. *Chemical resistant decorative laminates*. Patent 4543290 A, USA, 1985.
75. Dion AN. *Urethane acrylate surfaced laminate*. Patent 0474470 B1, European, 1998.
76. Blank WJ, He ZA, Hessel ET and Abramshe RA. Melamine formaldehyde networks with improved chemical resistance *Proc ACS PMSE* 1997; 77: 1-5.
77. Mohseni M, Ramezanzadeh B and Yari H. Effects of Environmental Conditions on Degradation of Automative Coatings. In: Chiaberge M (ed) *New Trends and Developments in Automative Industry*. London: In Tech, 2011.
78. Ratzsch M, Jocham D, Muller U and Haubold W. *Uv-resistant, thermocurable aminoplast composite, the production thereof and the use of the same*. Patent 20050148698 A1, USA, 2005.
79. Wu L, Ngian S, Chen Z and Xuan D. Quantitative test method for evaluation of anti-fingerprint property of coated surfaces. *Appl Surf Sci* 2011; 257: 2965-2969.
80. Magina S, Ferra J, Cruz P, Nogueira HIS, Portugal I and Evtuguin DV. Fluorinated polyhedral oligomeric silsesquioxane nanoparticles to boost the dirt repellence of high-pressure laminates. *Chem Eng J* 2016; 301: 362-370.
81. Badila M, Kohlmayr M, Zikulnig-Rusch E, Dolezel-Horwath E and Kandelbauer A. Improving the cleanability of melamine-formaldehyde-based decorative laminates. *J Appl Polym Sci* 2014; 131: 1-9.
82. Trogolo JA and Barry JE. *Antibiotic high-pressure laminates*. Patent 6248342 B1, USA, 2001.

83. Ghosh K. Self-Healing Materials: Fundamentals, Design Strategies, and Applications. In: Ghosh SK (ed) *Self-Healing Materials*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, 2009, pp.1-28.
84. Ghosh K. *Self-Healing Materials: Fundamentals, Design Strategies, and Applications*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, 2009.
85. Antunes A, Ferra JM, Martins J, Magalhães FD and Carvalho L. Self-healing laminates for surfacing wood-based panels. In: *Workshop COST ACTION FP1006: Process and service life modelling* Ghent, 17-19th April 2013.

CHAPTER 3

CHAPTER 3 – NEAR INFRARED SPECTROSCOPY IN THE WOOD-BASED PRODUCTS INDUSTRY[1]

3.1. ABSTRACT

"Near infrared" is the designation of the electromagnetic spectrum region immediately after the visible region. According to ASTM (American Society of Testing and Materials), its wavelength is between 780 and 2500 nm.

Although some experiments have been carried out in the 20's, it wasn't until the 60's that near infrared spectroscopy started being used to its full potential. Since then, this technique has been widely used in fields as pharmaceutical, food processing, agriculture, petrochemical, forestry, cosmetic, environmental, medical and polymers.

The main advantages of near infrared (NIR) spectroscopy are: it is non-destructive, may be performed online of offline, samples can be in solid or liquid state, sampling preparation is minimal, analysis is fast and equipment operation simple. On the other hand, NIR spectroscopy also has its drawbacks. Due to the complexity of the signal, it is necessary to process the data in order to obtain values of interest. Chemometric methods (e.g., data-based modeling techniques) must be used to allow establishing relations between several measurements and the characteristics of the analysed product.

In the context of forestry and forest products, NIR applications have been mostly focused on analysis of chemical composition of wood, and characterization of paper and wood properties. Recently, work has been done in the context of wood based panels industry, mainly for characterization of physical and mechanical properties of the panels, and for online monitoring of fibre properties, such as moisture content and

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[1] Carvalho LH, Magalhães FD, Ferra J, Martins J and Henriques A. Near-infrared spectroscopy in the wood-based products industry. In: Cozzolino D (ed) *Infrared spectroscopy: theory, developments and applications*. New York: Nova Publishers, 2014.

fibre length distribution. In addition, NIR methodologies have been developed to identify and check the conformity of laminating paper impregnated with formaldehyde-based resins.

Formaldehyde-based resins are widely used in the production of wood-based panels. In this industry, NIR spectroscopy has been used for monitoring the industrial process, analyzing of raw materials and to check the conformity of raw materials. Moreover, NIR has been used on-line for continuously evaluation of raw materials content during synthesis, to provide a methodology for monitoring resin production and to ensure reproducibility of the final product.

In the wood preservation industry, preliminary studies with decayed wood indicated that NIR may be useful in detecting and quantifying biodeterioration of wood.

3.2. NIR SPECTROSCOPY FUNDAMENTALS

“Near infrared” is the designation of the electromagnetic spectrum region immediately after the visible region. According to ASTM (American Society of Testing and Materials), NIR region corresponds to the wavelength interval between 780 and 2500 nm [1].

Although some experiments had been carried out in the 20’s, only in the 60’s near infrared spectroscopy started being explored in its full potential [2].

Near infrared spectroscopy is based on electromagnetic radiation absorption. When radiation hits an elementary particle (molecule, atom, or ion) energy absorption occurs if the radiation energy matches exactly the energy difference between the ground state and a state of heightened energy of the particle.

The molecules are subjected to three types of quantized transition when excited by ultraviolet, visible and infrared radiation: electronic transition, vibrational transition and vibrational rotation. The total energy E associated to one molecule is given by:

$$\mathbf{E} = \mathbf{E}_{\mathbf{electronic}} + \mathbf{E}_{\mathbf{vibrational}} + \mathbf{E}_{\mathbf{rotation}} \qquad \textbf{(3.1-1)}$$

where $E_{electronic}$ is the energy associated to electrons in the various orbitals exteriors of the molecule, $E_{vibrational}$ is the energy of the molecule as a whole due interatomic vibrations and $E_{rotacional}$ quantifies the energy associated with the molecule rotation about its center of gravity.

The vibrations in a molecule can be described using the harmonic oscillator model, where only the transitions between consecutive energy levels in a molecule that cause a change in dipole moment are possible. However, this model cannot explain the behavior of actual molecules, which resemble the quantum mechanical model of an anharmonic oscillator. In an anharmonic oscillator energy levels are not equally spaced and transitions occur between noncontiguous vibrational states. These vibrational states yield absorption bands known as overtones, which are much less likely than the fundamental transitions [3].

The intensity of an absorption band is related to the magnitude of dipole change during displacement of the atom into a vibration and the anharmonicity of the bond.

Thus, homonuclear molecules are not detectable in NIR while heteronuclear are easily detected. Thereby, NIR spectroscopy is very sensitive to C-H, S-H, O-H and N-H bonds.

NIR absorption bands are typically broad, overlapping, with poor baseline resolution and of much lower amplitude than those found in Mid Infrared (MIR). The low absorption coefficient, however, permits high penetration depth and, thus, an adjustment of sample thickness. This aspect is actually an analytical advantage, since it allows direct analysis of strongly absorbing and even highly scattering samples, such as turbid liquids or solids in either transmittance or reflectance mode without further pretreatments [2].

3.2.1. Instrumentation

NIR equipment can include a variety of devices that can be categorized in several ways according to the characteristics of the sample and the need of analysis, which makes this technique quite flexible [3]. A NIR spectrometer is generally composed of a light source, a monochromator, a sample holder or a sample presentation interface, and a detector, allowing for transmittance or reflectance measurements [2].

The light source is usually a tungsten halogen lamp, n multi-channel detectors several detection elements are arranged in rows (diode arrays) or planes (charged coupled devices - CCD’s) in order to record many wavelengths at once, increase the speed at which spectral information can be acquired [3].

The most frequently employed detectors for the NIR spectral region are based on silicon, PbS (lead sulfide) and InGaAs (Indium Gallium Arsenide) photoconductive materials, that are able to impart a very high signal-to-noise ratio for NIR measurements.

Depending on how the NIR response data are collected, measuring techniques can be normally classified as transmittance, reflectance and trans-reflectance.

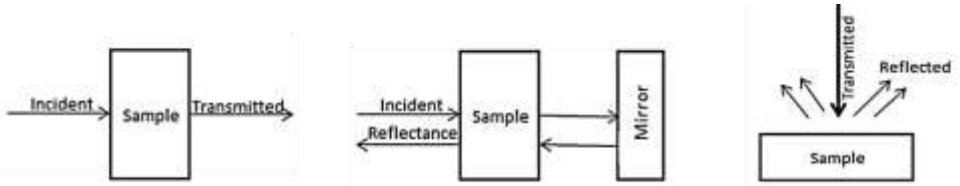

Figure 3.1.1 - Modes of measurement employed in NIR spectroscopy. Adapted from Pasquini C. Near Infrared Spectroscopy: fundamentals, practical aspects and analytical applications. J Brazil Chem Soc 2003; 14: 198-219.

In transmittance measurements, the emitted radiation crosses a sampling window and the transmitted fraction is collected and sent to the light detector. In reflectance measurements, the emitted radiation is partially reflected at the interface probe/sample and sent to the light detector [4]. In trans-reflectance the light crosses the sample, is reflected off a mirror material and travels back through the sample before reaching the detector [5].

The selection of the measurement mode depends on the optical properties of the samples. Usually reflectance measurements are used for solids, transmittance measurements for liquids, and trans- reflectance measurements for emulsions and turbid liquids [4].

In order to find the most useful instrument, the user must balance the benefits of the instrument’s characteristics with the cost.

Figure 3.1.2 - FT-NIR spectrometer.

3.3. CHEMOMETRICS

In order to collect the maximum information from the spectra, chemometrics is often used in NIR spectroscopy. Chemometrics is the use of mathematical and statistical techniques for extracting relevant information from analytical data [6].

Due the complexity of NIR signal, it is necessary to treat the data in order to obtain values of interest. A large amount of samples is necessary for the calibration step, in order to minimize the impact of data variability, and development of a reference method is required [7].

3.3.1. Pre-Processing Techniques

To minimize problems in the spectra caused, between other, by detector saturation, which hamper reproducibility and heighten nonlinearity characteristics that would cause less robust estimates, spectral pretreatments should be used [8].

The most widely used pre-processing techniques in NIR spectroscopy can be divided into two categories: scatter correction methods and spectral derivatives.

The scatter correction methods are built to reduce the variability between samples due to data scattering. This pre-processing method includes: multiplicative scatter correction, standard normal variate, normalization, inverse multiplicative scatter correction and extended multiplicative scatter correction.

The spectral derivatives methods have the capability to remove both additive and multiplicative effects in the spectra. Into this group, Norris-Williams (NW) derivatives and Savitzky-Golay (SG) polynomial derivatives are the most common [8].

The most common techniques used on near infrared spectra are the first and second derivative of the original spectra, the multiplicative scatter correction and the standard normal variate [6].

First and second derivatives are used to remove background and increase spectral resolution. The algorithm used most often for differentiation is the Savitzky-Golay , where the data within a moving window are fitted by a polynomial of a given degree to generate a differential of a chosen degree [9].

Standard normal variate transformations remove the slope variation from spectra caused by scatter and variation of particle size. The transformation is applied to each spectrum individually by subtracting the spectrum mean and scaling with the spectrum standard deviation [9].

The multiplicative scatter correction is carried out based on the assumption, that all samples have the same scatter coefficient at all NIR wavelengths. Usually the average spectrum of a representative data set, is used to estimate the scatter of the spectra [10].

3.3.2. Multivariate Analyses

In problems containing high number of variables, a univariate study can only provide very limited information. Multivariate analysis is therefore a more appropriate approach.

There are several algorithms to study multivariate analysis, such as: principal components analysis, multiple linear regression, analysis of clusters, the partial least squares regression and principal component regression [8].

These methods establish mathematical criteria that allow similarity between two samples, or a sample and a class, to be expressed quantitatively.

The method of choice will depend on the purpose of the analysis, the characteristics of the samples and the complexity of the system concerned.

The principal component analysis (PCA) is a chemometric tool used in the data reduction that rearranges the obtained information by the sampling data. This tool consists in the transformation of the data matrix spectra into orthogonal components, whose linear combinations should represent the original data.

This approach is typically used for the identification of different groups and sample selection for the construction of calibration models [11].

The partial least squares regression (PLS) is a technique of multivariate data analyses, used to relate one or more response variables (matrix Y) with several independent variables (matrix X), which correlates them in order to obtain a linear relationship. This is a model that determines quantitative correlations, allowing construction of a multivariate calibration [12].

Cluster analysis is a data grouping method. It comprises a number of different algorithms and methods for grouping different objects types into categories or classes.

Multiple linear regression (MLR) is a technique for solving a number of simultaneous equations. Using MLR there is no consistent solution available when more variables than samples are present as an infinite number of solutions exist [13]. It should therefore be used only when the size of the independent variables matrix is larger than the one of the response variables.

Principal component regression (PCR) uses the principal components provided by PCA to perform regression on the sample property to be predicted.

NIR literature indicates that calibration models are mostly based on MLR, PCR and PLS techniques, regardless on the particular field of application [4].

3.4. INDUSTRIAL APPLICATIONS

NIR spectroscopy is a technique with many advantages: it is nondestructive, may be performed online or offline, samples can be in solid or liquid state, sampling preparation is minimal, analysis is fast and equipment operation simple.

Due these facts, NIR has been widely applied in fields as varied as pharmaceutical and cosmetics, agriculture and food processing, petrochemical, forestry, environmental, medical, textiles and polymers [6].

It has also been used on constituent analysis in agriculture and food industry, related to fruit, wine, meat, oil and corn, both after harvest and during growth [9].

In petrochemical industry NIR spectroscopy is an alternative to classic methods, in the determination of hydrocarbons, fuels, petroleum fractions, polymers and other petroleum derivatives [14]. A review of the use of NIR in refinery and petroleum process is given by Workman [15].

NIR is used for the identification of raw materials in pharmaceutical industry, for quantitative analyses and on-line process control. A large number of references is cited by Blanco's review testifying the potential of NIR spectroscopy for qualitative and quantitative analysis of pharmaceutical preparations [16].

In forestry products industry, near infrared spectroscopy is mainly used for the analysis of chemical composition of wood, characterization of paper and wood properties [17].

A major contribution of NIR spectroscopy to environmental analysis is on recycling of plastic packaging. By using chemometric sorting techniques and appropriate hardware, the plastics are separated in real time and collected in different containers according to their major constituent polymer.

NIR spectroscopy has been used in medical area as indicator of specific diseases and on monitoring of the oxygen level in tissues during surgical processes [3].

Many different applications exist in textiles, such as the analysis of fibres and their properties, and for on-line monitoring of different textile coating [18].

The NIR applications in the polymer filed are mainly related to the identification of polymer sample and for the testing the final product quality.

3.5. MONITORING INDUSTRIAL PROCESSES

The monitoring of a process contributes to: guarantee and improve product quality and constancy, increase the efficiency of the process, ensure safe operation, safe time for analysis and sample transport, and reduce emissions by avoiding sample withdrawal and transport.

Process analytical methods may be classified as either off-line, at-line, on-line or in-line techniques with respect to sampling, sample transport, and analysis itself [19].

Due the benefits of NIR spectroscopy, the number of works that report actual in situ and on-line monitoring is growing.

In in-line applications of NIR one of the major problems regards the fouling of NIR probes during long operations periods. In addition, the fluctuation of operating conditions can disturb the collection of spectral data and the performance of calibration models and created the necessity to provide an extensive training in order to create a reliably calibration. Another problem with NIR measurements is the frequent change in equipment components, such as probes, lamps, and detectors.

3.6. FOREST PRODUCTS APPLICATIONS

The forest-based sector in Europe provides society with a wide variety of products and services, ranging from paper, packaging, tissue paper, furniture, carpentry and construction materials made from solid wood and wood-based panels to textile fibres, biofuels, bio-energy and specialist chemicals. Today it contributes some 8 % of the EU's total manufacturing added value and sustainably manages forests covering 35 % of the EU's landmass. It also provides income for about 16 million forest owners and supports 3-4 million industrial jobs in the areas of wood processing, transport, machinery, construction, instrumentation, ICT, chemicals and energy [20]. The use of non-destructive systems for process monitoring and control will permit to meet highest process efficiency, improving material flow resource efficiency, process stability, machine productivity, etc. In the context of forestry and forest products, NIR applications have been mostly focused on analysis of chemical composition of wood, and characterization of paper and wood properties. Recently, work has been done in the context of wood-based panels industry, mainly for the characterization of physical and mechanical properties of the panels, and for online monitoring of fibre properties, such as moisture content, fibre length distribution. In addition, NIR methodologies have been developed to identify and check the conformity of laminating paper impregnated with formaldehyde-based resins [17].

3.6.1. Wood Quality

Wood is a natural material extremely nonhomogeneous and its structural and chemical variability is reflected in its physical and mechanical properties. Trees are divided into two broad classes, usually referred to as hardwoods and softwoods. The structure of typical softwood is relatively simple. The axial or vertical system is composed mostly of axial tracheids, and the radial or horizontal system is the rays, which are composed mostly of ray parenchyma cells. The structure of a typical hardwood is much more complicated than that of softwood. The axial system is composed of fibrous elements of various kinds, vessel elements in various sizes and arrangements, and axial parenchyma in various patterns and abundance. NIR spectroscopy could be used to rapidly assess wood quality of standing trees. The genetic improvement has been focused in the improvement of wood properties as stem straightness, removal of reaction wood (formed in response to a non-vertical orientation of the stem caused by prevailing winds, snow, slope, or asymmetric crown shape), increasing of disease resistance and increasing volume. Many properties related to its structure, like density, stiffness, microfibril angle, tracheid diameter and length, and chemical composition of wood can be measured using x-ray diffraction, x-ray densitometry and image analysis. These data can be used to calibrate NIR instrument which permits to predict these properties or to complement this type of analysis [17,21].

Wood is a composite material consisting of three major polymers, cellulose, hemicellulose, and lignin, which serve as skeletal, matrix, and encrusting substances respectively [22].

The use of NIR analysis for the prediction of the chemical composition of solid wood is a relatively new area. Yeh et al. [23] reported a near-infrared spectroscopy method to predict the variation in chemical composition of solid wood. While Svensson et al. [24] monitored with NIR the chemical differences of cellulose derivatives. Alves et al. [25] used analytical pyrolysis data to develop a NIR method for determining the natural variation of lignin composition in maritime pine wood.

The density of wood is a measure of its gross porosity. Gross porosity has an important influence on mechanical and other physical properties of wood and it’s the most useful index of the suitable of wood for many end-product uses [22]. Hoffmeyer and Pedersen [26] and Santos et al. [27] showed that NIR could be used to predict wood density.

Wood stiffness (longitudinal modulus of elasticity, E_L) is an important wood property for solid timber applications [28]. Schimelck et al.[28] use the near-infrared spectroscopy for predicting the radial variation of the longitudinal modulus of elasticity, while Thumm and Meder [29] reported stiffness prediction of radiata pine wood.

Microfibril angle (MFA) is a property of the cell wall of wood fibres, which are made up of millions of strands of cellulose called microfibrils [30]. The microfibril angle has important influence in the mechanical properties of wood in axial direction. Schimleck et al. [31], Kelley et al. [32], and Huang et al. [33] used softwoods to build their NIR calibrations for MFA based on measurements made on polyvalent XRD apparatus. Hein et al.[30] developed a partial least square (PLS) regression models for microfibril angle (measured on tangential sections by X-Ray diffraction) based on NIR spectra measured on tangential and radial surfaces.

A rapid measurement of tracheid length is desirable by tree improvement programs who wish to assess tracheid variation from increment cores [34]. The calibrations for several tracheid morphological characteristics of radiate pine increments core samples – coarseness, perimeter, radial and tangential diameter, and wall thickness were examined by Schimleck and Evans [28].

Haartveit and Flaete [35] used NIR combined with multivariate statistical analyses for classification of wood species. Gindl et al. [36] have shown that NIR spectra taken from solid European larch wood samples subjected to axial bending and compression tests revealed an excellent ability to model the variability of mechanical properties using NIR spectroscopy.

3.6.2. Pulp and Paper

Paper is an essential part of our culture and daily lives, as it is used to store and share information, for packaging goods, personal identification, among other end uses [37]. In recent years, there has been a growing interest in the development of NIR applications to the pulp and paper industry [38].

Pulp yield is an important parameter for the industry. It is defined the proportion of oven-dry wood (consisting mainly of alpha-cellulose but also some hemicellulose and residual lignin) that remains after extraction of the most of the lignin using NaOH, Na_2S, and standardized heat and pressure regimes [39].

The recent development of NIR reflectance analysis for predicting pulp yield [39-42] provides a rapid and cost effective alternate technique to traditional assessment of *kraft* pulp yield.

The residual lignin in pulp can be approximately expresses as kappa number, which is regarded as an important indication of delignification. According to Zhang et al. [43] and Yang and Song [44] the kappa number of pulp can be predicted by NIR.

A NIR spectrum of pulp has been used to predict paper properties and estimate service life [17].

3.6.3. Wood-based Panels

Wood-based panels (WBP), a general term for a variety of different board products with an impressive range of engineering properties [45], are used in a wide range of applications, from non-structural to structural applications, outdoor and indoor. Most uses involve, construction and furniture, but decoration and packaging applications are also relevant. Conventional wood-based composites are manufactured products made primarily from wood with only a few percent resin and other additives. A useful way to classify conventional wood-based composites based on specific gravity, density, raw material, and processing methods [46]. Common wood-based panels products are made with veneers, particles or fibres and fall into three basic types: plywood, particleboards, and fibreboards (manufactured by the wet process, such as hardboard or dry process such as MDF). Other less common WBPs are solid wood panel, laminated veneer lumber (LVL), oriented strand board (OSB) and cement-bonded particleboard. These products can be presented as unfaced, overlaid, veneered or coated. An overlaid wood-based panel is surfaced with one or more overlay sheets or films, for example melamine impregnated paper, high-pressure laminates, plastics, resin film or metal.

In wood-based industry, NIR reflectometry has already been used for in-line moisture content measurement [47]. An example of this technology is provided by Grecon [48]. Perten Instruments provides NIR equipment to estimate the moisture content of wood pellets. They also use NIR technology to predict the formaldehyde content in wood-based panels defined by the perforator method (EN 120) and formaldehyde emission defined by the small scale chamber test (ASTM D6007) [49].

NIR reflectometry is considered an important tool for gathering this type of process data. However, some problems must be addresses such as fluctuations of the light source “flutter” effects (i.e. rising or falling surface, measurement out of focus), and optical density fluctuations on the fast moving conveyor. Other applications of NIR were studied in the literature but some of them were never been implemented in industry [47].

Figure 3.1.3 - In-line Moisture Measurement with Infrared Technology [45].

Due to the fact that raw materials in particleboards industry are always changing, controlling the quality of products is required in order to maintain the same quality standard [50]. Cowan and Landers [51] developed a method using NIR for quantitative analysis of resin-wood composites. The method makes feasible measure resins of different types, wax, moisture and other additives of resin-wood composites. Andre et al. [52] used near infrared for real-time quantitative measurement of the emission of formaldehyde from wood products.

Rials and others [53] used NIR to predict the mechanical strength of MDF samples with a wide range of physical properties. Meder et al. [54] show the potential for using NIR spectroscopy for on-line assessment of wood veneer stiffness prior to layup of plywood or LVL panels.

Horwath et al. [55] installed a NIR system on a hardboard plant and were able to provide feedback to control bending strength, internal bond (IB), and water absorption.

BoardModel^{TM} is an NIR spectroscopy-based optimizing system developed by Casco Products in Sweden [56] developed to generate predictions of wood-based panel properties in real time, especially density, density profile, internal bond, thickness swelling, absorption value, permeability value, perforator value and emission chamber value. Metso Panelboard has also used NIR spectroscopy to develop the system PanelProTM for monitoring important parameters in MDF production. Figure 3.1.4. shows an on-line probe which monitors the swelling, the formaldehyde content, moisture and internal bond in wood-based panels and a probe installed in a laboratory which monitors the same parameters.

Partial least squares regression (PLS-R) calibration based on near infared spectroscopy data were developed by Hein et al [57] in order to predict mechanical and physical properties of agro-based particleboards. Kniest [58] used NIR spectroscopy to characterizes urea resined wood particles while Niemz et al [59] have shown that the resin content and the mixing ratio of softwood and hardwood can be measured in the mat of a particleboard line.

Dessipri et al [60] provided a non-destructive methodology for the fast and reliable determination and prediction of the quality of the impregnated papers and their remaining useful lifetime and an on-line method for the optimization of the pressing conditions of impregnated paper based on its initial quality.

Figure 3.1.4 - a) On-line monitoring graphs of wood-based panel properties; b) Probe installed in a laboratory and c) On-line probe (Courtesy of Tafisa, Sonae Indústria (Valladolid plant)).

NIR spectral imaging has also been used in this field. Images which comprise reflection spectra for each pixel are called hyperspectral images. This image is obtained by scanning a moving surface with a line spectrograph and a NIR camera [47]. It is possible to detect compounds such as resins or water by their absorption at typical wavelengths. Principal technique analysis (PCA) can be also applied to segment a hyperspectral image as demonstrated in Figure 3.1.5.

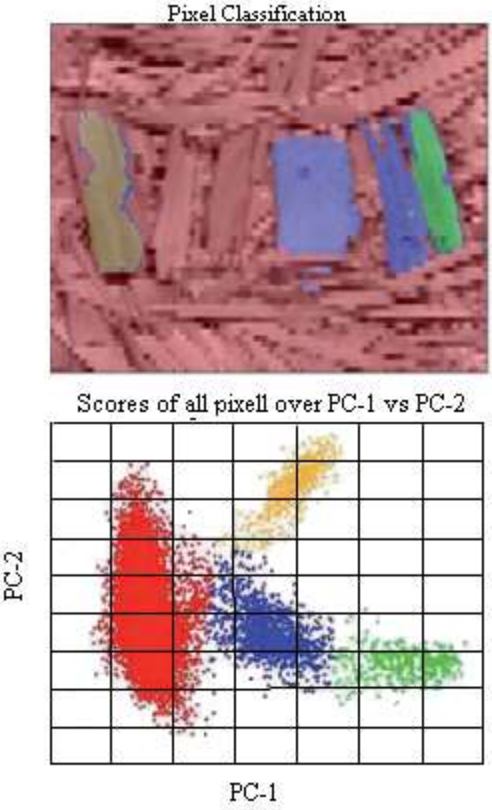

Figure 3.1.5 - Application of PCA in spectral imaging to detect different resin types [47].

3.6.4. Biodeterioration and Wood Modification

Wood degradation is caused principally by fungi, insects, bacteria, and marine borers, it considered undesirable, and preventive measures are necessary. NIR spectroscopy may provide a useful monitoring technique for wood degradation [21].

Lignin loss of sterilised spruce wood shavings (0.4–2.0 mm particle size) that had been degraded by various species of white rot fungi could be monitored by FT-NIR during the first 2 weeks [61]

Degradation experiments on surfaces of spruce (*Picea abies L. Karst*) and beech (*Fagus sylvatica L.*) were carried out with white rot basidiomycetes or the ascomycete Hypoxylon fragiforme. Experiments with brown rot or soft rot caused by *Chaetomium globosum* were also performed. FT-NIR spectra collected from the degraded wood were subjected to principal component analysis. The lignin content and mass loss of the specimens were estimated based on univariate or multivariate data analysis (partial least squares regression) [62].

Fackler et al [63] monitored de physicochemical changes in beech wood subjected to brown rot and white rot fungal degradation and to evaluate them with FT-NIR combined with multivariate method of spectral analysis.

Wood products can be protected from the attack of wood-degradation organisms by applying chemical preservatives. These treatments greatly increase the life of wood structures, thus reducing replacement costs and allowing more efficient use of forest resources [46]. However, these chemicals can cause environmental hazards during the use and disposal of treated wood. NIR was used for the identification of various inorganic preservatives in timber, such as those containing arsenic, copper, and boron [21].

Wood modification is another way to increase wood durability or improve other properties as dimensional stability. Thermal modification is one of the environmentally friendly wood preservation technologies since does not present any environmental hazard, at the end of product life cycle. Heat treatment changes the chemical composition of wood causing mass loss. Another draw-back is the degradation of mechanical properties. NIR spectroscopy was used as an inexpensive and non-destructive method to determine the properties of heat-treated wood [64-67]. Sandak et al [68] proposed the combination of NIR spectroscopy and selected chemometric techniques as tools for characterization and identification treatment intensities of thermally modified samples.

3.7. CURRENT USE OF NIR IN FORMALDEHYDE-BASED RESINS

3.7.1. Urea-Formaldehyde Resins

Urea-formaldehyde (UF) resins are the most widely used adhesives in the manufacture of wood-based panels, such as particleboard and medium density fibreboard (MDF); this is mostly due their high reactivity, low cost, and excellent adhesion to wood. To characterize a liquid UF resin, several analytical tools have been used, namely ^{13}C-NMR and FTIR for investigations of the resin structure, GPC/SEC for the determination of average molecular weights and molecular weight distribution. More recently, the capabilities of FT-NIR spectroscopy have been exploited [69]. In UF resins synthesis, NIR spectroscopy has been used for the analysis of intermediates and to check the conformity of raw materials [70]. Moreover, NIR has been used on-line for continuously evaluating the urea and formaldehyde content during synthesis, in order to provide a methodology for monitoring the resin production and to ensure the reproducibility of the final product [70]. These works demonstrated that FT-NIR spectroscopy can be used for on-line monitoring of the consumption of $–NH_2$ groups during the early stages of the synthesis and the decrease of both primary and secondary amides during polycondensation [70].

NIR was also used to provide a method for assessing the influence of pH and temperature on the structure of the final product. It is the purpose of this study to explore the capabilities of NIR spectroscopy for the on-line monitoring of the aminoplastic resin synthesis. UF compounds and adhesives have been synthesized and measured at systematically varying temperature and pH conditions. The various reaction products have been studied also by gel permeation chromatography (GPC), ^{1}H- and ^{13}C-Nuclear Magnetic Resonance (NMR) spectroscopy and FT-Raman spectroscopy to provide reference structural information and assist the interpretation of the NIR spectra [71].

Kasprzyk et al. [72] used NIR spectroscopy for qualitative and quantitative analysis of aminoplastic resins and also described the band assignments for the major amino resins bands [72], they also identified the regions between 7502 and 6098 cm^{-1} and 5000-4246 cm^{-1} (Table 3.1.1) as being the most important for UF resins.

Table 3.1.1 - Band assignments for the major of UF and mUF bands**. (**Adapted from Kasprzyk H, Józwiak M and Proszyk S. Application of NIR spectroscopy for analysis of amino adhesive resins applied on wood based materials. Folia Forestalia Polonica 2001: 67-74.)

Wavenumber in FT-NIR spectra (cm^{-1})	**Bands**
7042	1st overtone $2\upsilon\mathrm{NH}_{asymmetrical}$
6920	Combination $\upsilon\mathrm{NH}_{asymmetrical} + 2\upsilon\mathrm{NH}_{symmetrical}$
6720	1st overtone $2\upsilon\mathrm{NH}_{symmetrical}$
5973	1st overtone $2\upsilon\mathrm{CH}_{2,asymmetrical}$
5834	1st overtone $2\upsilon\mathrm{CH}_{2,asymmetrical}$
5055	$\upsilon\mathrm{NH}_{asymmetrical} + \delta\mathrm{NH}$ amide II
5050	$\upsilon\mathrm{NH}_{symmetrical} + \upsilon\mathrm{CO}$ amide I
4916	$\upsilon\mathrm{NH}_{asymmetrical} + \upsilon\mathrm{CN}$ amide III
4878	$\upsilon\mathrm{NH}_{symmetrical} + \upsilon\mathrm{CN}$ amide III
4642	$\upsilon\mathrm{NH}_{asymmetrical} + \delta\mathrm{NH}_{rocking}$
4549	$\upsilon\mathrm{NH}_{symmetrical} + \delta\mathrm{NH}_{rocking}$
4436	$\upsilon\mathrm{CH}_{2,asymmetrical} + \delta\mathrm{CH}$ and $\upsilon\mathrm{CH}_{2,symmetrical} + \delta\mathrm{CH}$

Henriques et al. [73] implemented chemometric techniques for off-line monitoring of formaldehyde/urea molar ratio on finished resins using near infrared spectroscopy, concluding that different molar ratios affect bands near 4530,4440 and 6650 cm^{-1}. For implementation of calibration methods for the determination of these parameter spectral regions between 7502-6098 and 5000-4246 cm^{-1} were identified as being the most relevant.

The same authors also developed a chemometric technique that can be used for in-line or off-line determination of the UF resins viscosity during synthesis [74]. For the determination of UF viscosity the spectral region that yield the lowest region is 5000-4246 cm^{-1}. This region is associated with vibrations bands from starch and amino groups, vibrations from methylol hydroxyl groups (5000-4878 cm^{-1}) and CH vibration bands (4600-4400 cm^{-1}). This is in agreement with the known formation of methylene ether (- CH_2-O-CH_2-) and methylene (-CH_2-) linkages during the condensation stage. Using NIR spectroscopy simplifies the measurement procedure, avoiding the need to remove the sample from the reactor, and reducing operator intervention.

The determination of formaldehyde/urea molar ratio was also studied by Costa el al.[75], using PCA. PCA allowed separate the resins according to the molar ratio and to distinguish them between two groups of resins. They suggested that a method for the determination of the F/U molar ration in UF resins can be obtained using only 15-20 samples.

3.7.2. Melamine-Formaldehyde Resins

Melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF) resins are among the most used adhesives in the manufacture of wood-based panels for indoor and covered exterior applications, for impregnation of paper to be used in low and high-pressure paper laminates and overlays, and for bonding of these products on wood-based panels. Their high water resistance is the main distinguishing characteristic in relation to urea-formaldehyde resins [76].

The high cost of melamine, however, limits the use of MF resins. Melamine-urea-formaldehyde (MUF) resins are therefore a more interesting alternative, with a wide range of formulations originating resins with different properties, performance and durability. 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 % [77] [71].

In melamine resins, NIR has been used for the determination of melamine content and for determination of resin properties performance [72,78]. The determination of melamine content in MUF resins was described by Kasprzyk et al. [72] and Henriques et al. [79].

According to the latter work for analysis of melamine content in amino resins, spectral regions 4400-4800 cm^{-1} and 5200-5600 cm^{-1} were identified by iPLS (interval partial least squares regression) in which data are subdivided into nonoverlapping sections that each undergo a separate PLS processing to determinate the most useful variable range [13] as providing the best results, in agreement with the spectral regions described in literature as being associated with this property.

The spectrum of MUF resins has close behavior to the spectra of UF resins according Figure 3.1.6. Basic differences are occurring in the range 5200-4650 cm^{-1}, that is connected with presence of s-triazine ring of melamine [72].

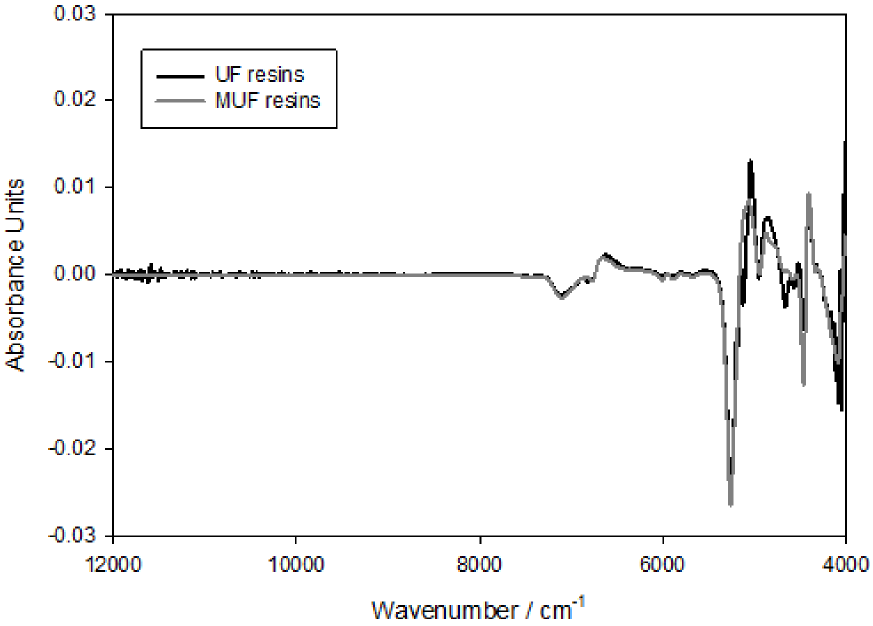

Figure 3.1.6 - Representation of UF and MUF resins spectra with first derivative.

Near infrared spectroscopy also provides a potential means for in-line or at-line determination of resin quality. Meder et al. [78] had correlated a number of conventional and non-conventional resin properties to establish rapid measures of key parameters which can be inserted into control charts to measure resin performance.

3.7.3. Phenolic Resins

Phenolic resins are the polycondensation products of the reaction of phenol with formaldehyde and were the first synthetic polymer to be developed commercially. Phenolic resins are used as binders for exterior-grade plywood and particleboard, which need the superior water resistance provided by these resins [80].

In phenolic resins, the resin content, the resin solid content and the volatile content are key factors to ensure the quality material impregnated with a pre-catalyzed phenolic resin [81]. So, many studies have been done for the determination of resin content, volatile content in phenolic resins [33,82]. Chimar Hellas developed the system gnosis (General Non-destructive on-line spectroscopic investigation) to determine in real time the volatile content in impregnated paper production (Figure 3.1.7). Taylor and Via [83] tested the ability of NIR coupled with multivariate statistical methods to predict the resin content in OSB. They observed that the 614 nm was significantly different between resin loadings. They conclude that NIR may provide the basis for an on-line, real-time quality control tool providing feedback information.

Magalhães et al. [84] used near infrared spectroscopy to predict curing degree of phenol-formaldehyde resin in *kraft* impregnated paper.

Figure 3.1.7. – Real time monitoring of paper’ volatile content. Courtesy of Chimar Hellas S.A.

3.8. SUMMARY AND FUTURE PERSPECTIVES

The current application and future potential of near infrared (NIR) spectroscopy in forest products is enormous. NIR spectroscopy has revolutionized the analysis by providing a rapid examination of material properties. It requires a minimal sample preparation and it is nondestructive. Several applications were described in this chapter, throughout the entire production chain, from wood raw material to final products. Although some NIR technologies are still available in research labs, others have already been applied in industry.

In recent years, forest products industry, particularly in case of paper and wood-based panels, has increased the capacity of production lines and the speed of production, but at the same time producers have to deal with increasingly variable raw materials and product requirements. The most important goals are the reduction of costs, high flexibility and constant product quality. To achieve these goals, the producers, need more information about the fluctuations within the process. They need equipment that supports the management of the complex process, provides monitoring of significant parameters, supports production changes and recipe management and facilitates process analysis. Non–destructive testing method, as NIR spectroscopy, which are capable for in-line monitoring of raw materials and product properties, are helpful tools for plant operators and quality controllers.

Further research is needed to develop NIR technology that can properly function under harsh industrial settings and to explore potential applications of NIR reflectometry in industry. Due to its nature, NIR processing techniques have still a long path to follow. More work has to be done both on noise reduction strategies and the calibration step, in order to increase the method robustness and also to reduce the tune-up time. This will permit us to cope with the unstable nature of industrial environments and to deal with the fluctuations on raw materials quality and with products continuous evolution.

3.9. REFERENCES

1. Workman J and Burns D. Commercial NIR instrumentation. In: Ciurczak B and Burns D (eds) Handbook of Near-Infrared Analysis. 3rd edition ed. Boca Raton: CRC Press, 2008, pp.834.
2. Reich G. Near-infrared spectroscopy and imaging: Basic principles and pharmaceutical applications. Adv Drug Deliver Rev 2005; 57: 1109-1143.
3. Blanco M. NIR spectroscopy: a rapid-response analytical tool. TrAC, Trends Anal Chem 2002; 21: 240-250.
4. Santos A, Silva F, Lenzi M and Pinto JC. Monitoring and Control of Polymerization Reactors Using NIR Spectroscopy. Polym Plast Technol Eng 2005; 44: 1-61.
5. Blanco M and Romero MA. Near infrared transflectance spectroscopy: Determination of dexketoprofen in a hydrogel. J Pharm Biomed Anal 2002; 30: 467-472.
6. Pasquini C. Near Infrared Spectroscopy: fundamentals, practical aspects and analytical applications. J Brazil Chem Soc 2003; 14: 198-219.
7. McClure WF. Near-infrared spectroscopy. The giant is running strong. Anal Chem 1994; 66: 43A-53A.
8. Rinnan Å, Berg Fvd and Engelsen SB. Review of the most common pre-processing techniques for near-infrared spectra. TrAC, Trends Anal Chem 2009; 28: 1201-1222.
9. Cen H and He Y. Theory and application of near infrared reflectance spectroscopy in determination of food quality. Treend Food Sci Tech 2007; 18: 72-83.
10. Candolfi A, De Maesschalck R, Jouan-Rimbaud D, Hailey PA and Massart DL. The influence of data pre-processing in the pattern recognition of excipients near-infrared spectra. J Pharm Biomed Anal 1999; 21: 115-132.
11. Naes T, Isakson T, Fearn T and Davies T. A user-friendly guide to multivariate calibration and classification. 1st ed. Chichester: IM Publications LLP, 2002, p.354.

12. Conzen J. Multivariate Calibration - A pratical guide for developing methods in the quantitative analytical chemistry. 2nd ed. Ettlingen: Bruker Optik GmbH, 2006, p.116.
13. Xiaobo Z, Jiewen Z, Povey MJW, Holmes M and Hanpin M. Variables selection methods in near-infrared spectroscopy. Anal Chim Acta 2010; 667: 14-32.
14. Macho S. Near-infrared spectroscopy and multivariate calibration for the quantitative determination of certain properties in the petrochemical industry. TrAC, Trends Anal Chem 2002; 21: 799-806.
15. Workman J. Review: A brief review of near infrared in petroleum product analysis. J Near Infrared Spectrosc 1996; 4: 69-74.
16. Blanco M, Coello J, Iturriaga H, Maspoch S and de la Pezuela C. Near-infrared spectroscopy in the pharmaceutical industry . Critical Review. Analyst 1998; 123: 135R-150R.
17. So CL, Via B, Groom LH, Schimleck LR, Shupe T, Kelley S and Rials T. Near Infrared Spectroscopy in the Forestry Industry. Forest Prod J 2004; 54: 6-16.
18. Cleve E, Bach E and Schollmeyer E. Using chemometric methods and NIR spectrophotometry in the textile industry. Anal Chim Acta 2000; 420: 163-167.
19. Hergeth W-D. On-line Monitoring of Polymerization and Cure. Sensors Update 1999; 5: 191-242.
20. Forest Platform, http://www.forestplatform.org/ (2013).
21. So C, Groom L, Rials T, Snell R, Kelley S and Meglen R. Rapid assessment of the fundamental property variation of wood. Eleventh Biennial Southern Silvicultural Research Conference. Knoxville, Tennessee2002.
22. Tsuchikawa S. A Review of Recent Near Infrared Research for Wood and Paper. Appl Spectrosc Rev 2007; 42: 43-71.
23. Yeh T-F, Yamada T, Capanema E, Chang H-M, Chiang V and Kadla JF. Rapid Screening of Wood Chemical Component Variations Using Transmittance Near-Infrared Spectroscopy. J Agric Food Chem 2005; 53: 3328-3332.
24. Svensson O, Josefson M and Langkilde FW. Classification of Chemically Modified Celluloses Using a Near-Infrared Spectrometer

and Soft Independent Modeling of Class Analogies. Appl Spectrosc 1997; 51: 1826-1835.

25. Alves A, Schwanninger M, Pereira H and Rodrigues J. Calibration of NIR to assess lignin composition (H/G ratio) in maritime pine wood using analytical pyrolysis as the reference method. Holzforschung 2006; 60: 29-31.
26. Hoffmeyer P and Pedersen JG. Evaluation of density and strength of Norway spruce wood by near infrared reflectance spectroscopy. Holz als Roh- und Werkstoff 1995; 53: 165-170.
27. Santos A, Alves A, Simões R, Pereira H, Rodrigues J and Schwanninger M. Estimation of wood basic density of Acacia melanoxylon (R. Br.) by near infrared spectroscopy. J Near Infrared Spectrosc 2012; 20: 267-274.
28. Schimleck L, Evans R and Ilic J. Application of near infrared spectroscopy to a diverse range of species demonstrating wide density and stiffness variation. IAWA Journal 2001; 22: 415-429.
29. Thumm A and Meder R. Stiffness prediction of radiata pine clearwood test pieces using near infrared spectroscopy. J Near Infrared Spectrosc 2001; 9: 117-122.
30. Hein PRG, Clair B, Brancheriau L and Chaix G. Predicting microfibril angle in Eucalyptus wood from different wood faces and surface qualities using near infrared spectra. J Near Infrared Spectrosc 2010; 18: 455-464.
31. Schimleck LR, Sussenbach E, Leaf G, Jones PD and Huang CL. Microfibril Angle Prediction of Wood Samples Based on Tangential Face Nir Spectra. IAWA Journal 2007; 28: 1-12.
32. Kelley SS, Rials TG, Groom LR and So CL. Use of near infrared spectroscopy to predict the mechanical properties of six softwoods. Holzforschung 2004; 58: 252-260.
33. Huang A, Fu F, Fei B and Jianz Z. Rapid estimation of microfibril angle of increment cores of Chinese fir by near infrared spectroscopy. Chi For Sci Technol 2008; 7: 52-56.
34. Via BK, Stine M, Shupe TF, So C-L and Groom L. Genetic improvement of fibre length and coarseness based on paper product

performance and material variability - a review. IAWA Journal 2004; 25: 401-414.

35. Haartveit E. Near infrared spectroscopy (NIRS) as a tool for effective classification of wood. In: International Convention of Wood Science and Technology Conception, Chile, 10-12 November 2008.
36. Gindl W, Teischinger A, Schwanninger M and Hinterstoisser B. The relationship between near infrared spectra of radial wood surfaces and wood mechanical properties. J Near Infrared Spectrosc 2001; 9: 255-261.
37. Aguilar L, Carvalho LH, Martins J and Costa C. Transport Phenomena in Paper and Wood-Based Panels Production. In: El-Amin M (ed) Mass Transfer in Multiphase Systems and its Applications. London: InTech, 2011, pp.313-342.
38. Sefara N, Conradie D and Turnee P. Progress in the use of near-infrared absorption spectroscopy as a tool for the rapid determination of pulp yield in plantation eucalypts. In: TAPPSA Conference “African Paper week ‘2000 and beyond’” South Africa, 17 – 20 October 2000.
39. Stackpole DJ, Vaillancourt RE, Downes GM, Harwood CE and Potts BM. Genetic control of kraft pulp yield in Eucalyptus globulus. Can J Forst Res 2010; 40: 917-927.
40. Michell AJ. Pulpwood quality estimation by near-infrared spectroscopic measurements on eucalypt woods. Appita J 1995; 48: 425-428.
41. Schimleck LR, Michell AJ, Raymond CA and Muneri A. Estimation of basic density of Eucalyptus globulus using near-infrared spectroscopy. Can J Forst Res 1999; 29: 194-201.
42. Terdwongworakul A, Punsuwan V, Thanapase W and Tsuchikawa S. Rapid assessment of wood chemical properties and pulp yield of Eucalyptus camaldulensis in Thailand tree plantations by near infrared spectroscopy for improving wood selection for high quality pulp. J Wood Sci 2005; 51: 167-171.
43. Zhang H, Song S, Lang Q, Zhang J and Pu J. Rapid predictive models for minimally destructive kappa number and pulp yield of acacia spp,

with near infrared reflectance (NIR) spectroscopy. BioResources 2011; 7: 616-623.

44. Yang CJ, He C and Song ZH. The online measurement for pulp kappa number based on near infrared spectroscopy and support vector machine. Spectrosc Spect Anal 2008; 28: 1795-1798.
45. Thoemen H. Preface. In: Thoemen H, Irle H and Sernek M (eds) Wood-based panels: an introduction to specialists. London, England: Brunel University Press, 2010, pp.xiii-ix.
46. Risbrudt C, Ritter A and Wegner T. Wood handbook: wood as an engineering material. Centennial ed. Madison, Wisconsin: Forest Products Laboratory, 1987, p.509.
47. Aderhold J and Plinke B. Innovative methods for quality control in the wood-based panel industry. In: Thoemen H, Irle M and Sernek M (eds) Wood based panels: An introduction for specialists. London, England: Brunel University Press, 2010, pp.225 - 249.
48. Inline G. Inline Moisture Measurement with Infrared Technology, www.grecon.com. (accessed 2014).
49. Engström B, Lestander T, Lidén P and Sundström H. Multivariate process control and real time sensors in pratical use. In: 2nd Biennal International Conference on Processing Technologies for the Biobased Products Industries Georgia, USA, November 6-7 2012.
50. Campos A, Hein P, Mendes R, Mendes L and Chaix G. Near infrared spectroscopy to evaluate composition of agro-based products particleboards. BioResources 2009; 4: 1058-1069.
51. Cowan J and Landers A. Method using NIR spectroscopy to monitor components of engineered wood products. Patent 7279684 B2, USA, 2007.
52. Andre N, Young TM and Rials TG. Spectroscopic Prediction of Formaldehyde Emission and Thickness Swell of Wood Panels. Patent 20090230306 A1, USA, 2009.
53. Rials TG, Kelley SS, So CL and Groom LH. Characterization of Wood Composites by Near Infrared Spectroscopy. Madison: Forest Products Research Soc, 2003, p.113-116.

54. Meder R, Thumm A and Bier H. Veneer stiffness predicted by NIR spectroscopy calibrated using mini-LVL test panels. Holz als Roh- und Werkstoff 2002; 60: 159-164.
55. Dolezel-Horwath E, Hutter T, Kessler R and Wimmer R. Feedback and feedforward control of wet-processed hardboard production using spectroscopy and chemometric modelling. Anal Chim Acta 2005; 544: 47-59.
56. Engstrom B and Hedqvist M. Prediction of the properties of board by using a spectroscopic method combined with multivariate calibration. Patent 5965888 A, USA, 1999.
57. Hein P, Campos A, Mendes R, Mendes L and Chaix G. Estimation of physical and mechanical properties of agro-based particleboards by near infrared spectroscopy. Eur J Wood Wood Prod 2011; 69: 431-442.
58. Kniest C. Characteristic of urea resined wood paticles by NIR spectroscopy. Holz als Roh- und Werkstoff 1992; 50: 73-78.
59. Niemz P, Dutschmann F and Stölken B. Using NIR-spektroskopy for evaluating resin content in chip mixtures. Holz als Roh- und Werkstoff 1994; 52: 6-8.
60. Dessipri E, Chryssikos G, Gionis V, Nakos P and Paipetis A. Method for assessing remaining useful life and overall quality of laminating paper. Patent 20040113078 A1, USA, 2004.
61. Fackler K, Gradinger C, Hinterstoisser B, Messner K and Schwanninger M. Lignin degradation by white rot fungi on spruce wood shavings during short-time solid-state fermentations monitored by near infrared spectroscopy. Enzyme Microb Technol 2006; 39: 1476-1483.
62. Fackler K, Schwanninger M, Gradinger C, Srebotnik E, Hinterstoisser B and Messner K. Fungal decay of spruce and beech wood assessed by near-infrared spectroscopy in combination with uni- and multivariate data analysis. Holzforschung 2007; 61.
63. Fackler K, Schwanninger M, Gradinger C, Hinterstoisser B and Messner K. Qualitative and quantitative changes of beech wood degraded by wood-rotting basidiomycetes monitored by Fourier

transform infrared spectroscopic methods and multivariate data analysis. FEMS Microbiol Lett 2007; 271: 162-169.

64. Schwanninger M, Hinterstoisser B, Gierlinger N, Wimmer R and Hanger J. Application of Fourier Transform Near Infrared Spectroscopy (FT-NIR) to thermally modified wood. Holz als Roh- und Werkstoff 2004; 62: 483-485.
65. Esteves B and Pereira H. Quality assessment of heat-treated wood by NIR spectroscopy. Holz als Roh- und Werkstoff 2008; 66: 323.
66. Bächle H, Zimmer B, Windeisen E and Wegener G. Evaluation of thermally modified beech and spruce wood and their properties by FT-NIR spectroscopy. Wood Sci Technol 2010; 44: 421-433.
67. Todorovic N, Schwanninger M, Popovic Z and Millic G. Comparison of NIR and colour change in prediction of heat-treated beech wood properties. In: Sixth European Conference on Wood Modification Ljubljana, Slovenia, 2012.
68. Sandak A, Sandak J, Alegretti O, Ferrari S and Pauliny I. Evaluation of Thermally Treated Soft and Hardwood with FT-NIR. In: Sixth European Conference on Wood Modification Ljubljana, Slovenia, 2012.
69. Carvalho LH, Costa MRP and Costa C. A very simple empirical kinetic model of the acid-catalyzed cure of urea–formaldehyde resins. J Appl Polym Sci 2006; 102: 5977-5987.
70. Dessipri E, Minopoulou E, Chryssikos GD, Gionis V, Paipetis A and Panayiotou C. Use of FT-NIR spectroscopy for on-line monitoring of formaldehyde-based resin synthesis. Eur Polym J 2003; 39: 1533-1540.
71. Minopoulou E, Dessipri E, Chryssikos GD, Gionis V, Paipetis A and Panayiotou C. Use of NIR for structural characterization of urea-formaldehyde resins. Int J Adhes Adhes 2003; 23: 473-484.
72. Kasprzyk H, Józwiak M and Proszyk S. Application of NIR spectroscopy for analysis of amino adhesive resins applied on wood based materials. Folia Forestalia Polonica 2001: 67-74.
73. Henriques A, Cruz P, Martins J, Ferra JM, Magalhães FD and Carvalho LH. Determination of formaldehyde/urea molar ratio in

amino resins by near-infrared spectroscopy. J Appl Polym Sci 2012; 124: 2441-2448.

74. Henriques A, Ferra J, Cruz P, Martins J, Magalhães FD and Carvalho L. Viscosity determination of amino resins during synthesis using near-infrared spectroscopy. International Wood Products Journal 2012; 3: 64-66.
75. Costa N, Amaral S, Alvim R, Nogueira M, Schwanninger M and Rodrigues J. Assessment of resin formulations and determination of the formaldehyde to urea molar ratio by near- and mid-infrared spectroscopy and multivariate data analysis. J Appl Polym Sci 2013; 128: 498-508.
76. Pizzi A and Mittal KL. Handbook of adhesive technology. 2nd ed. New York: Marcel Dekker, 2003, p.1000.
77. Paiva N, Henriques A, Cruz P, Ferra JM, Carvalho LH and Magalhães FD. Production of melamine fortified urea-formaldehyde resins with low formaldehyde emission. J Appl Polym Sci 2012; 124: 2311-2317.
78. Meder R, Ebdon N, Stahl W, Wooley S and Grayston G. Rapid QC of MUF resin or MDF manufacture via NIR. In: IUFRO Conference Division 5 Forest Products Lisbon, Portugal, 2012.
79. Henriques A, Cruz P, Ferra JM, Martins J, Magalhães FD and Carvalho LH. Determination of melamine content in amino resins by near-infrared spectroscopy. Wood Sci Technol 2013; 47: 939-948.
80. Pizzi A. Phenolic Resin Adhesives. In: Pizzi A and Mittal KL (eds) Handbook of Adhesive Technology. New York: Marcell Dekker, Inc., 2003, pp.1000.
81. Jiang B and Huang Y. Near Infrared Spectroscopy for On-line Monitoring of Alkali- Free Cloth /Phenolic Resin Prepreg During Manufacture. Int J Mol Sci 2007; 8: 1625-1636.
82. Dong Y and Qu SY. Analysis of rapid method for the quality index of phenolic resins and benefit. Russ J Nondestr Test 2012; 48: 69-73.
83. Taylor A and Via BK. Potential of visible and near infrared spectroscopy to quantify phenol formaldehyde resin content in oriented strandboard. Eur J Wood Wood Prod 2009; 67: 3-5.

84. Magalhães WL, Kelley SS and Lucia LA. Calibration of the mechanical properties of saturating kraft paper sheets using near ir spectroscopy and physical testing. O papel 2009; 70: 62-71.

CHAPTER 4

CHAPTER 4 – IMPROVEMENT OF STORAGE STABILITY AND PHYSICOCHEMICAL PROPERTIES BY ADDITION OF BENZOGUANAMINE IN MELAMINE-FORMALDEHYDE RESIN SYNTHESIS[1]

4.1. ABSTRACT

The improvement of melamine-formaldehyde resin storage stability was achieved using benzoguanamine as partial replacement of melamine during synthesis (up to 15 % substitution of melamine). The results showed that when benzoguanamine is added in the later stages of reaction, the resulting resins have improved storage stability (4 days or more, compared to 1 day in unmodifed melamine-formaldehyde resin). High-pressure laminates produced with décor paper impregnated with the new developed resins showed surface properties equivalent to those obtained using commercial melamine-formaldehyde resins.

4.2. INTRODUCTION

High-pressure decorative laminates (HPL), manufactured with paper impregnated with thermosetting resins, are a value-added product that has been increasingly used for home and commercial uses. They are an effective solution for horizontal or vertical surfaces that require high physical, mechanical and chemical resistances, with a diversified range of uses, such as scholar furniture, laboratory countertops, exterior flooring, hospital furniture and whiteboards. The market share of laminates has been growing over the years. Global demand for decorative laminates is

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[1] Henriques A, Paiva N, Bastos M, Martins J, Carvalho L and Magalhães FD. Improvement of storage stability and physicochemical properties by addition of benzoguanamine in melamine-formaldehyde resin synthesis. *J Appl Polym Sci* 2017; 134: 1-11.

expected to rise 5.6 % per year to 10.7 billion m^2 in 2018, valued at US$40.8bn [1].

Two types of paper are used in the manufacture of HPL: *kraft* and décor. The *kraft* paper, used in the bottom layers, is impregnated with phenolic resin and provides mechanical resistance and moisture resistance to HPL. Décor paper is used on the top layer, providing the colour and pattern of the surface. It is most commonly impregnated with a melamine-formaldehyde resin (MF resin). These are used because of their unique surface properties in terms of hardness, chemical stability and transparency, which allow a glossy visual appearance of the surface decors and good performance in use, at reasonable prices [2]. Sometimes an overlay paper is placed over the décor, to provide an additional protective layer. It has lower grammage than the previous two, and becomes transparent after impregnation and pressing, allowing for the decor paper to be perfectly visible. The range of pressures used in the production of high-pressure laminates varies from 5.5 to 10.3 MPa, with the layers consolidated at temperatures of 120 – 150 °C [3].

The basic chemical reactions involved in formation and condensation of MF resins are presented in Figure 4.1.1. In the first step (methylolation), that depends on the reaction conditions (mainly the melamine to formaldehyde molar ratio) up to six molecules of formaldehyde may react with melamine to form water-soluble methylolated melamine compounds, also known as methylols. These methylols may further condense under liberation of water to form MF prepolymers, which consist of either methylene- or methylene ether-bridged melamine rings [4]. Typically, MF resin prepolymers intended for paper impregnation have low-molecular weight and consist of a statistical mixture of oligomers with about three to five melamine units, in order to keep the viscosity low and allow good penetration in paper [5].

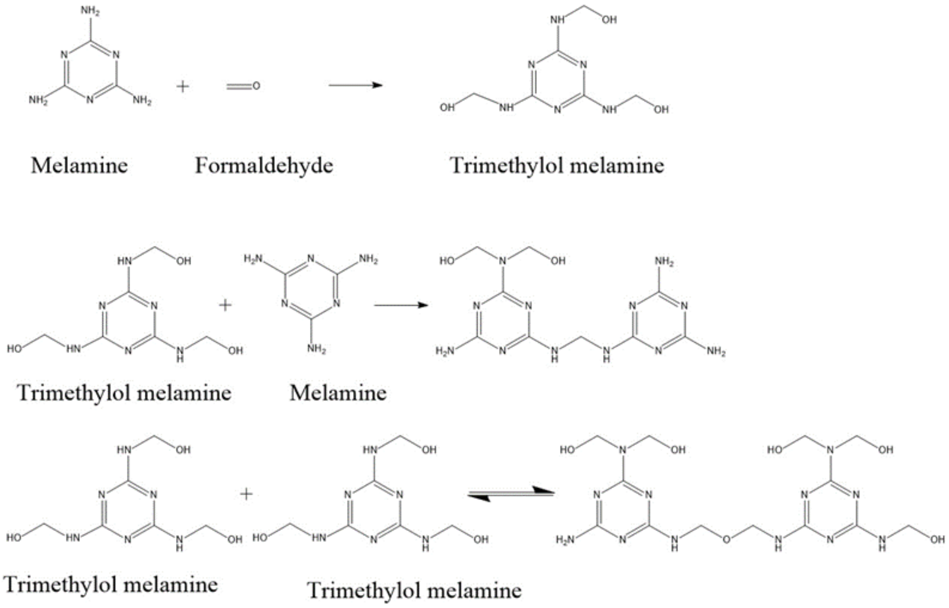

Figure 4.1.1 – Melamine-formaldehyde resins chemical reaction

Unfortunately, unmodified melamine resins have very short shelf lives, e.g., no more than about 1-3 days, after which the resin begins to separate from solution, going from clear to turbid. This gives the high-pressure decorative laminates a heterogeneous and cloudy appearance. In order to overcome this limitation, various modifiers can be added to MF resins [6], in the form of co-monomers, at a concentration of 7 to 10 % in the final resin weight. Most commonly used are caprolactam, *p*-toluenesulfanamide and sugar [7-9]. Use of cycloaliphatic guanamines has also been described [10].

Benzoguanamine (BG) is a phenyl substituted triazine related to melamine (Figure 4.1.2). Like melamine, benzoguanamine may be methoxymethylated and/or butoxymethylated to various extents. The average functionality is lower than melamine because there are only two NH_2 groups per molecule [11].

Benzoguanamine has been used to modify the melamine-formaldehyde resins [12-14]. Improvements in melamine-formaldehyde resins properties when blended with benzoguanamine resins, namely in terms of heat resistance and anticorrosion performance have been reported [15].

Due to the lower functionality of BG, the films obtained from its reaction with formaldehyde tend to be more flexible and glossy than for melamine-formaldehyde resins [16-18]. The reaction between benzoguanamine and formaldehyde is described in Figure 4.1.2 [19].

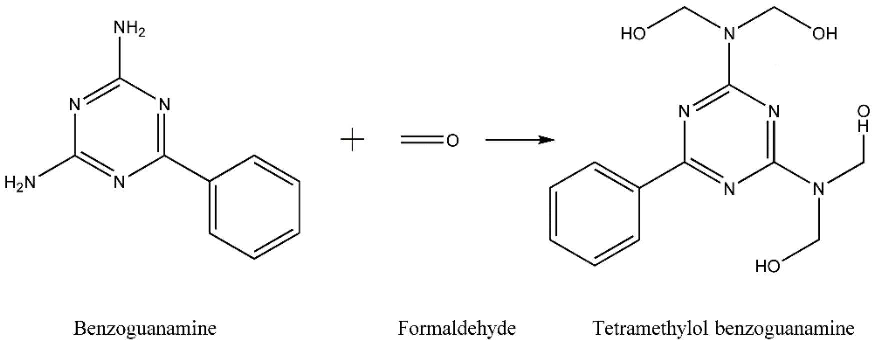

Figure 4.1.2 – Reaction between benzoguanamine and formaldehyde.

It is interesting to note that BG is known as a stabilizer for aqueous formaldehyde solutions. It prevents or retards the precipitation of polymeric paraformaldehyde at low storage temperatures and/or high formaldehyde concentrations [20].

The purpose of the current work is to provide a systematic study on the storage stability of melamine-formaldehyde resins modified with benzoguanamine co-monomer, and on the properties of high-pressure laminates impregnated with these resins.

4.3. EXPERIMENTAL

4.3.1. Materials

Formaldehyde (37 wt% solution), melamine, sodium hydroxide 10 %, as well as impregnation additives (acid catalyst, release agent and surfactant) and the décor paper for impregnation (a red décor paper of 100 g/m^2) were supplied by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal). Benzoguanamine was used as received by Sigma Aldrich.

A commercial melamine-formaldehyde was also supplied by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal).

4.3.2. Resin Characterization

Kinematic viscosity- Kinematic viscosity was determined as resin flow time in [s] using a flow cup viscometer according to DIN EN ISO 2431.

Solids content - Solid contents of the resin samples were determined by heating 3 g of each sample in an aluminum pan and placed in an oven at 120 °C for three hours until constant mass.

pH measurements - The pH electrode was calibrated at the operating temperature, i.e room temperature, using the pH= 7.0 and 9.0 as buffer solutions. The pH was monitored automatically.

Storage stability - The storage stability was defined as the time, in days, from resin preparation until the solution became turbid to the naked eye.

Resin water tolerance - The water tolerance of the resins was evaluated by transferring 5 mL at 25 °C of resin to a test tube and determining the amount of distilled water to add to the resin until it becomes cloudy. The water tolerance is given according to the equation:

$$\textbf{Water Tolerance}\ (\%) = \frac{\mathbf{V}}{\mathbf{V'}} \times \mathbf{100} \qquad \textbf{(4.1-1)}$$

Where:
V – The distilled water add (mL)
V’ – Sample volume (mL)

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 were PSS GRAM with a pore size 30 Å and a particle size of 100 µm, conditioned at 60 °C using an external oven. The flow rate is 1 $mL \cdot min^{-1}$ and dimethylformamide (DMF) was used as the mobile phase. Samples for analysis are prepared by dissolving a small amount of resin (100 mg) in DMSO (dimethylsulfoxide), followed by vigorous stirring during 1 minute. Subsequently, the sample was left to rest (10 minutes), filtered through a 0.45 µm nylon filter and then the sample was injected.

^{13}C-NMR analysis - About 40 mg of liquid sample was directly mixed with 0.75 mL DMSO-d_6 and the mixture was placed in an NMR tube. The high concentration of the samples allowed very good signal/noise ratios. The spectra were obtained on a Bruker Avance III 400 NMR spectrometer using a repetition delay of 10 s.

The quantitative analysis was performed through a decoupling process of proton–carbon interactions without introducing NOE effect (nuclear Overhauser effect) on the peak intensities. A 5 s pulse interval was sufficient to allow the relaxation of all carbons and to obtain reliable spectra, as seen from the measurement of the spin-lattice relaxation time T1. The quantitative spectra were obtained at 400 MHz with 3200 scans and took about 10 hours to accumulate.

Chemical shifts in DMSO-d_6 solution were calculated by defining a ^{13}C chemical shift of DMSO-d_6 at 39.5 ppm.

FTIR analysis - Fourier transform infrared spectroscopy: FTIR studies were performed in a Bruker Vertex 70 spectrophotometer. The samples were scanned using a Platinum-ATR single reflection diamond ATR module. Spectra were recorded in the wavenumber of 4000-500 cm^{-1} by signal averaging of 64 scans at a resolution of 4 cm^{-1}.

Resins films were prepared by an evaporation technique. Approximately 50 g resin was poured into a PTFE-coated mold, then dried in an oven at 60 °C until constant mass.

Determination of free formaldehyde - Determination of free formaldehyde in resin was done according to the European standard EN 1243. This test takes into account the reaction of the free formaldehyde with sodium sulphite, in the presence of a measured excess of acid, in accordance with the reaction:

$$\mathbf{CH_2O + Na_2SO_3 + H_2O \rightarrow CH_2(OH)SO_3Na + NaOH} \qquad \textbf{(4.1-2)}$$

and alkaline titration of the unreacted excess acid.

The acid-sulphite mixture provides an essentially neutral buffered system, which prevents hydrolysis of condensed formaldehyde. A reaction temperature close to 0 °C helps to ensure the absence of side reactions.

The free formaldehyde content shall be calculated by the following formula:

$$\textbf{Free formaldehyde}\ \% = \frac{\mathbf{(V_2 - V_1) \times M \times 3.002}}{\mathbf{m}} \qquad \textbf{(4.1-3)}$$

Where:

V_1 is the volume (mL) of 0.1 M sodium hydroxide solution used for the adhesive test;

V_2 is the volume (mL) of 0.1 M sodium hydroxide solution used for the blank test;

M is the molarity of sodium hydroxide solution;

M is the mass (g) of the adhesive test portion.

4.3.3. High-Pressure Laminates

Paper impregnation - Paper sheets of 21 × 30 cm^2 were impregnated with all synthesized resins using small amounts of additives (acid catalyst, release agent, and surfactant). All papers were impregnated in a two-step process. In the first bath, there is the complete impregnation of the core paper and the paper sheets were oven-dried at 140 °C until a resin content between 40-42 % is achieved. After that, the sheets are subjected to a second bath, designate coating, to ensure good impregnation, resubmitted to the oven at 140 °C. All papers had a resin content of 54-56 % and moisture content after drying of 6-7 %.

Impregnated paper characterization

Volatile Content - The determination of the residual moisture content (volatile content) occurred by differential weighing after a 5-minute drying at 160 °C.

Flow - Flow is determined from weight differences after pressing a 3-inch diameter piece of partially cured, submitted to pressing and temperature during 5 minutes. After the pressing process, the disk laminate is cooled and weighed (initial weight). After removing the resin, which has flown out of the disk (the amount of resin located at the side of the blank), the laminate is weighed again (final weight). The difference between the initial and final weight, related to the weight of the original disk laminate, gives the flow of the impregnate.

Cure time - The measuring principle consists in curing a specimen (95 mm x 60 mm) in a silicone oil bath set at 140 °C. In order to measure the curing degree, the impregnated paper is automatically rotated clockwise in certain intervals. The torque associated with the rotation is directly dependant on the impregnated paper curing degree. This torque need is acquired by a computer and a curing graph is plotted on the screen.

Resin Content - The determination of the resin content occurred by differential weighing after impregnation.

High-pressure laminates production

High-pressure laminates consist of layers made up of two distinct phases: a core layer consisting of an assembly of four *kraft* paper sheets impregnated with phenolic resin and one sheet of décor paper impregnated with the synthetized resins.

The set of impregnated sheets of paper is then pressed between plates at 140 – 150 °C under a pressure of 80 - 100 bar.

High-pressure laminates characterization

The tests performed on high-pressure laminates were done accordingly to EN 438-2 standard [21], and are described in Supporting Information.

4.4. RESULTS AND DISCUSSION

Different resins were synthesized and characterized. The chemical structure of selected resins was then studied using ^{13}C-NMR and FTIR. The paper impregnation performance and the properties of the resulting high-pressure laminates are finally presented, in order to evaluate the viability of using the new BG-modified resins for this type of application.

4.4.1. Resin Synthesis

The resin samples were produced in a 2 L round bottom flask equipped with a mechanical stirrer and a thermometer (immersed in the solution). A heating mantle was used to heat the flask.

Pure melamine-formaldehyde resin was prepared by the condensation of melamine and formaldehyde with a final formaldehyde/amine ratio (F/NH_2) of 1.90. Before reaction, the pH value of the formaldehyde solution was maintained at 8.5-9.0 using NaOH 10 % solution. The modified resin was synthesized by the same process, replacing part of the melamine with benzoguanamine. To find out the appropriate moment to add the modifying agent, BG was added at four different stages of the synthesis: stage A - right after the addition of formaldehyde in the initial phase; stage B - after complete solubilisation of melamine; stage C – in the final phase of the condensation step, when a water tolerance of 500 – 600 % is attained; stage D - after the condensation process is finished, at a water tolerance of 100 – 300 %. Figure 4.1.3 depicts the temperature program followed for MF resin synthesis and the different stages of BG addition.

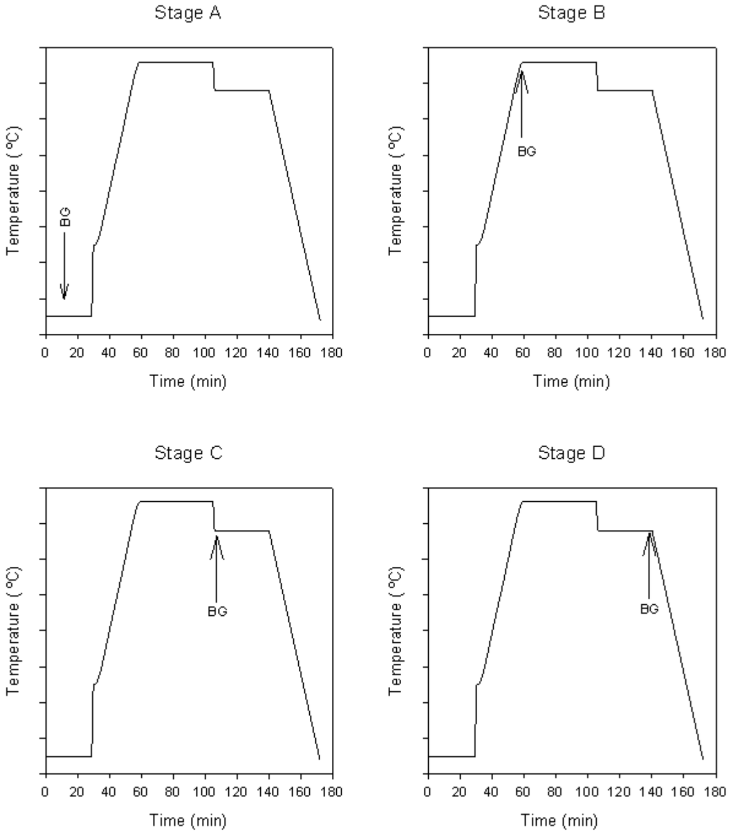

Figure 4.1.3 - Schematic representation of the benzoguanamine addition stages, relative to the evolution of temperature during melamine-formaldehyde resin synthesis.

4.4.2. Resin Synthesis and Characterization

A conventional, non-additivated, melamine-formaldehyde resin (MF_{ref}) was used as reference. In the modified resins, melamine was partially replaced with benzoguanamine. This was added at four different reaction stages, as described in the experimental section. A commercially available MF resin (MF_{comm}), which contains special purpose additives for improving storage stability, was also characterized.

Different substitutions levels of melamine (ML) by benzoguanamine (BG) were tested: i) substitution of 7.5 % ML by 7.5 % BG, ii) substitution of 7.5 % ML by 16.8 % BG and iii) substitution of 15 % ML by 33.5 % BG. In the first case, ML was replaced with an equal mass of BG. In the second, the stequiometric equivalence between ML and BG was taken into account: up to six molecules of formaldehyde may react with melamine while up to four molecules of formaldehyde may react with benzoguanamine. Finally, in the third case, the previous mass of BG was doubled, to ensure an excess concentration in relation to the stequiometric amount. In all cases, BG was introduced at four different reaction stages.

Table 4.1.1 summarizes the results. Substitution of melamine by the same mass percentage of benzoguanamine resulted on transparent resins, hence a priori suitable for paper impregnation. However, BG addition in stages A, B and C resulted in resins with poor stability (1 day or lower), and for that reason these were not selected for impregnation.

When replacing 7.5 wt% ML by 16.8 wt% BG, resins with low stability were again obtained when BG addition was performed in stages A and B. In addition, the viscosity was higher than desired. Addition in stages C and D yielded higher stability times. In the case of addition in stage D, the stability time was equivalent to the commercial resin.

Replacing 15 wt% ML by 33.5 wt% BG, led to resins with very high viscosity when BG addition was performed in stages A or B, and moderately high viscosity for addition in stages C or D. In the last two cases the presence of a large amount of undissolved benzoguanamine was visible in the form of a solid deposit, and the stability was not improved in relation to the 16.8 % BG addition. That formulation was therefore abandoned.

Table 4.1.1 - Resins properties after synthesis when there is substitution of different % of melamine content by different amounts of benzoguanamine.

ML-BG substitution (% relative to total resin solids)	Resin	Kinematic viscosity at 25 °C (s)	pH	Water tolerance (%)	Solid Content (%)	Density	Stability
None	**MF$_{\mathrm{ref}}$**	15’90	9.60	220	55.00	1.250	1 day
	MF$_{\mathrm{comm}}$	16’00- 18’00	9.00-10.00	180 - 260	55.00 57.00	1.245 - 1.265	> 10 days
Substitution of 7.5 % ML by 7.5 % BG	**Stage A**	23’15	9.70	Impossible to determine$^{(1)}$	57.20	1.254	0 days
	Stage B	16’18	9.41	220	57.80	1.260	0 days
	Stage C	16’95	9.49	220	57.10	1.254	1 day
	Stage D	16’43	9.66	180	57.40	1.240	5 days
Substitution of 7.5 % ML by 16.8 % BG	**Stage A**	33’73	9.87	Impossible to determine$^{(1)}$	58.20	1.260	0
	Stage B	65’15	10.00	Impossible to determine$^{(1)}$	59.00	1.290	0
	Stage C	18’12	9.80	220	58.30	1.260	4 days
	Stage D	55’23	9.22	90	58.30	1.285	> 10 days
Substitution of 15 % ML by 33.5 % BG	**Stage A**	> 300	9.89	Impossible to determine$^{(1)}$	60.20	1.260	0 days
	Stage B	> 300	9.83	Impossible to determine$^{(1)}$	61.00	1.260	0 days
	Stage C	35’04	9.40	150	62.50	1.270	4 days
	Stage D	144’45	9.27	120	68.70	1.290	4 days

(1) One day after synthesis the resin exhibited a cloudy appearance, preventing water tolerance measurement

The introduction of BG in different stages results in resins with different storage stabilities. In particular, introduction of BG in stage C or D leads to much higher stabilities than the reference resin. This is a key aspect, since a resin shelf life of more than 1 day is paramount for industrial uses. Taking into account that MF resins tend to exhibit higher storage stability as the formaldehyde content increases [22], it was important to check if the obtained results were due to the amount of free formaldehyde in the modified resins. The determination of free formaldehyde according to the standard EN 1243 was carried out, using the resins stage A and D, when 7.5 wt% melamine content was substituted by 16.8 wt% of benzoguanamine. These resins show the same amount of free formaldehyde, namely 0.24 % and 0.22 %, showing that this was not the determining factor.

Taking into account the storage stability results, it can be suggested that when BG is introduced at the end of the reaction, it reacts with free formaldehyde and with available hydroxyl groups in the polymer, leading to steric effects that prevent the growth of polymer during storage and consequently minimize resin destabilization.

4.4.3. ^{13}C-NMR Analysis

Figure 4.1.4 shows the main differences between the NMR spectra of a melamine-formaldehyde resin (Figure 4.1.4a)) and a melamine-formaldehyde resin that contains benzoguanamine, in this case a resin where BG was added at the end of the reaction, namely stage D (Figure 4.1.5b)). As shown in Figure 4.1.4a), the MF spectrum can be divided into three parts. The 160-170 ppm region corresponds to the aromatic carbons of the triazine ring. The region between 60-80 ppm corresponds to the carbon present in the methoxy group and region between 40-60 ppm to carbon atoms present in methylene units.

In the methylene carbon region, a large signal of monomethylolated amino groups at 64.2 ppm and a smaller at 68.2 ppm were observed. It is possible that the methylolmelamine mixture already contains linear methylene-ether linkages, as signals from this type of linkage overlap with signals from substituted methylol groups at 68 ppm.

The spectrum shows no evidence of the presence of free formaldehyde or polyoxymethylene oligomers (carbon signals at 80-90 ppm) maybe due the fact that the amount of free formaldehyde is too low [23].

Methylene linkages in which the two aminogroups are monosubstituted are observed at 48.8 - 47.2 ppm. Regarding the ring carbons of triazine, these can be classified into three sets of peaks: those related to primary (167.4-166.0 ppm), secondary (166.5 – 166.0 ppm) and tertiary (165.8-165.0) amino groups, respectively [24,25].

Concerning the spectrum related with the introduction of BG in the melamine-formaldehyde resin, besides the peaks described previously, new ones are observed, being associated with the phenyl carbons atoms of BG (128 -138 ppm) and with the ring carbons of the BG triazine (172.0 – 167 .6 ppm) [26].

Figure 4.1.5 shows the spectra of the melamine-formaldehyde resin and the resin where BG was added at stage D and stage A (in the end and in the beginning of the reaction). It can be observed that the introduction of BG at the end of the reaction reduces the number of methylol groups formed and at the same time increases the number of methylene linkages. This may indicate that the introduction at the end promotes the reaction between the hydroxyl groups present in the melamine polymer and the added BG, thus leading to formation of methylene groups.

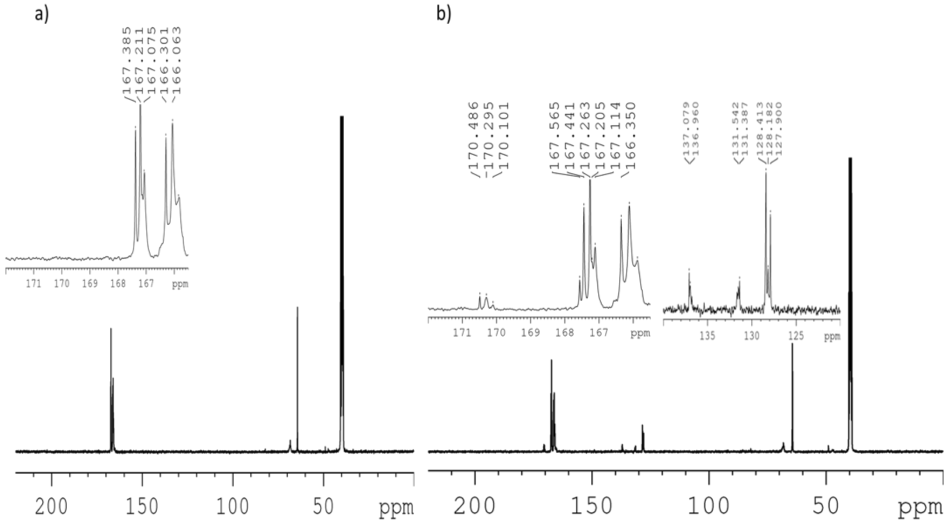

Figure 4.1.4 - ^{13}C- NMR spectra of a) melamine-formaldehyde resin and b) melamine benzoguanamine formaldehyde resin.

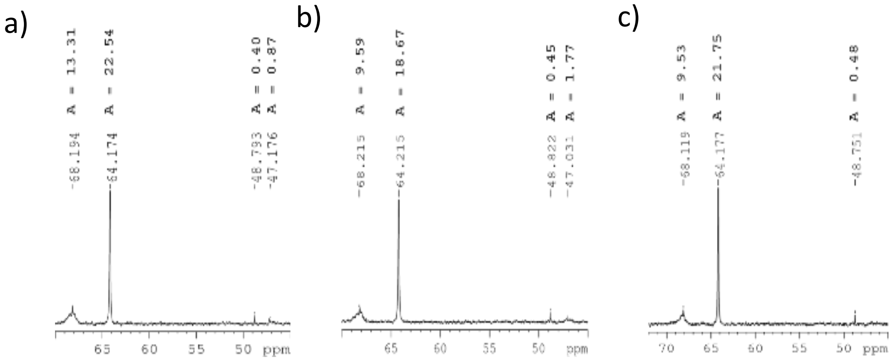

Figure 4.1.5 - Peak areas from ^{13}C-NMR spectra (between 70-45 ppm) of a) melamine-formaldehyde resin b) addition of BG at the end of the resin and c) addition of BG at the beginning of the reaction.

This is corroborated by the peak found at 167.2 ppm (Figure 4.1.6 a)), being associated with m-triazine at Nsec with methylene groups in benzoguanamine formaldehyde resins, which is not visible in the stage A resin.

This could indicate that the phenyl ring present in BG may create a steric hindrance effect, therefore decreasing reactivity of the methylol groups and therefore increase the stability of the resin, as previously suggested.

On the other hand, introduction of BG in early stages of the synthesis (Figure 4.1.6 b))leads to a larger amount of methylol groups, part of them being related to the formation of m-triazine at Ntert with methylol groups (166.2 ppm).

This might indicate that introduction at the beginning of the reaction results in the formation of larger amounts of BG with hydroxyl groups, which may hinder polymer growth and result in an unstable resin. It has been reported before that, for melamine-formaldehyde resins, a certain degree of condensation is needed to reduce the nucleation process and consequently increase the stability of the resin [27].

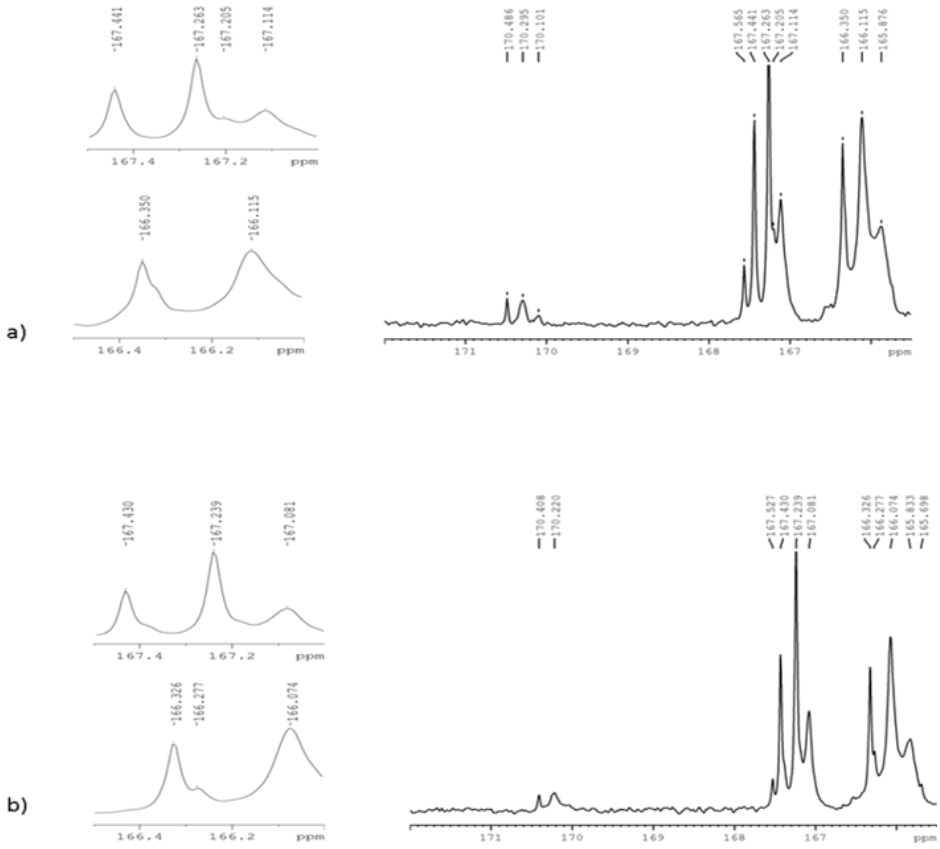

Figure 4.1.6 - Comparison between the ^{13}C-NMR spectra obtained in the region between 172-165.5 ppm for a) addition of BG at the end of the reaction and b) addition of BG in the beginning of the reaction.

4.4.4. GPC Characterization

The usefulness of GPC for comparison of formaldehyde-based resins has been demonstrated before [28-30]. Figure 4.1.7 shows the chromatograms obtained for the resins produced in both approaches, together with the reference melamine-formaldehyde resin. All resins show the same features, with a more intense peak at retention volume above 21 mL, corresponding to methylolmelamines and oligomeric species, and a broad peak that tails until retention volumes below 19 mL, which corresponds to higher molecular weight polymer.

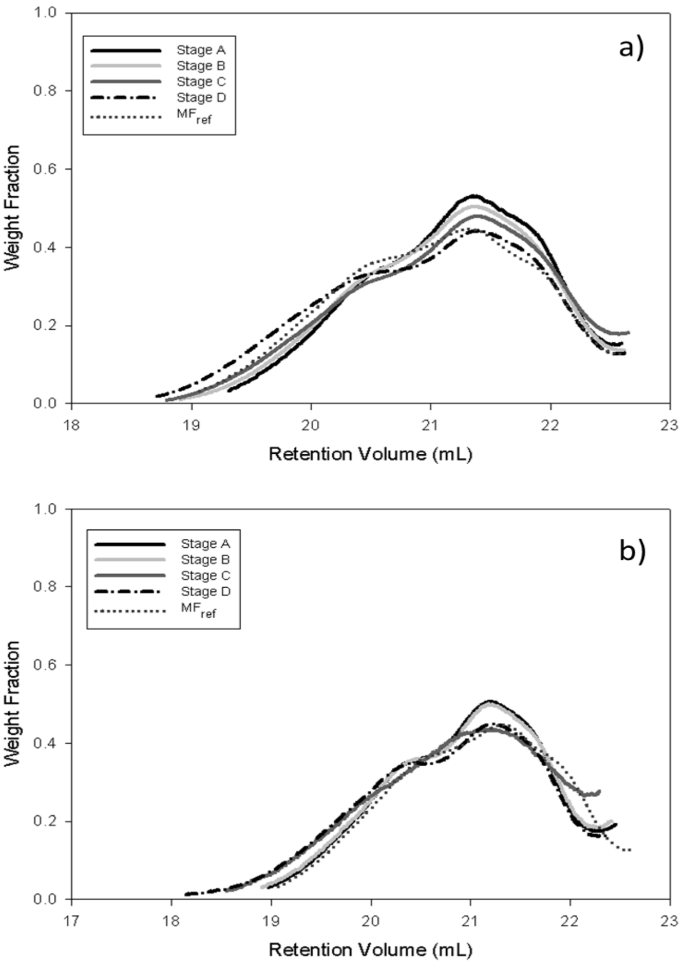

Figure 4.1.7 - Overlaid chromatograms of all resins samples when there is substitution of a) 7.5 % ML by 7.5 % BG and b) 7.5 % ML by 16.8 % BG.

Addition of BG in the early stages (A and B) results in a resin with higher content of low molecular weight compounds, in relation to addition in stage C and D and to the reference resin.

This is in accordance with the results achieved in the NMR analysis indicating that addition of BG at early stages blocks polymer growth. This may be expected, considering that BG has two amine groups, while melamine has three, and, after hydroxymethylation by formaldehyde, the phenyl ring present in BG may create a steric hindrance effect, therefore decreasing reactivity of the methylol groups.

Addition of BG in the later stages leads to polymer with higher molecular weight and stability.

4.4.5. FTIR Characterization

Figure 4.1.8 shows the spectra of the reference melamine-formaldehyde resin and of resins containing benzoguanamine. Merline et al.[5] and Kim and Kim [31] have reported similar FTIR spectra for melamine-formaldehyde resins [5,31].

Several characteristic bands can be identified in the spectra of the reference MF resin. The band at 3324 cm^{-1} corresponds to stretching vibration of secondary amines; 2956 cm^{-1} to C-H stretching vibration in OCH_2; 1540 cm^{-1} to C=N ring vibration; 1487, 1471, 1455 and 1336 cm^{-1} to CH_2 bending vibrations; 1159 cm^{-1} to stretching C-O-C of $–CH_2-O-CH_2-$ and $–CH_2-O-CH_3$; 992 cm^{-1} to C-H out of plane deformations; 809 cm^{-1} to bending vibrations of triazine ring in melamine.

The modified resins show spectra very similar to the melamine-formaldehyde resin, with the same major absorption bands. Monosubstituted benzenes, like benzenoguanamine, show a band between 690-710 cm^{-1}. In all the modified resins a new absorption band appears at 705 cm^{-1} (Figure 4.1.8), proving the presence of benzoguanamine [5,32-34].

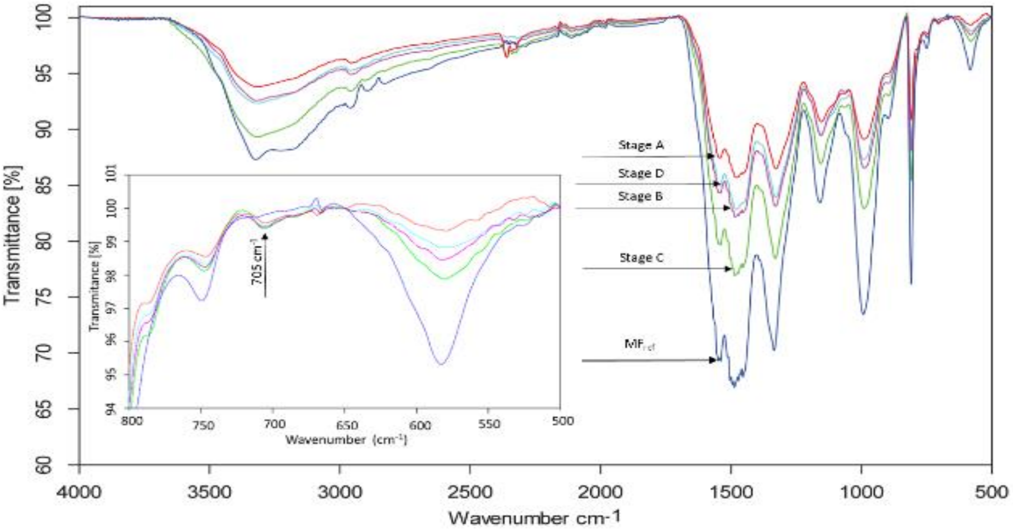

Figure 4.1.8 - Spectra of melamine-formaldehyde resin and resins containing benzoguanamine.

4.4.6. Paper Impregnation

The selected modified resins (substitution of 7.5 % ML by 7.5 % BG and substitution of 7.5 % ML by 16.8 % BG) showed good paper impregnation properties, equivalent to the melamine-formaldehyde resins, which resulted in a homogeneously impregnated décor paper.

After impregnation, the resin content, volatile content, flow and curing time were measured (Table 4.1.2) .

The resin content could influence the flow of the resin and consequently the aesthetic aspect of the HPL. In all the impregnated papers the ideal resin content (between 54 and 56 %) was obtained.

Table 4.1.2 - Paper impregnation properties.

Type of substitution	Resin	Resin Content (%)	Volatile Content (%)	Flow (%)	Cure time (min)
	MF_{ref}	55	7	4.20	2.20
	MF_{comm}	54-56	6-7	1.00 – 4.00	1.50-4.50
Substitution of 7.5 % ML by 7.5 % BG	**Stage A**	54	7	3.80	2.50
	Stage B	54	7	1.90	2.50
	Stage C	55	6	3.20	2.20
	Stage D	54	6	3.10	2.30
Substitution of 7.5 % ML by 16.8 % BG	**Stage A**	54	7	3.50	3.50
	Stage B	54	7	9.33	3.50
	Stage C	55	7	4.20	2.30
	Stage D	54	7	3.70	2.50

The amount of volatiles in the impregnated paper is used to characterize dried semi-finished paper sheets. The volatiles correspond mainly to moisture content, which must be between 6.0 – 7.0 %. If the moisture content is too high, the stacked or rolled sheets are often found to stick together (block formation) before being sent to the hot press for curing. On the other hand, a low content may indicate that drying was excessive and the resin has reacted too much during drying, and will not show sufficient adhesion when the impregnated papers are cured. In both cases, the final product will not fulfil the customer's requirements [2]. In all impregnations the optimum volatile content was achieved.

Resin flow is another important property of impregnated paper. The flow is a very important descriptor of impregnated paper. Resin flow governs film formation and the final surface properties. Too low flow causes an inhomogeneous film leading to optical defects like low gloss, stains, flow marks or bad cleanability [35]. If the flow is too low, most of the colour flows away and the colour becomes diffused [36].

Table 4.1.2 shows that only addition of benzoguanamine in stage B for the substitution of 7.5 wt% ML by 16.8 wt% BG leads to a resin out of specification. From all the analysed resins, this is the one with the higher final viscosity. This property affects resin penetration into the paper and consequently the flow. The flow of the other resins is within the desired range [37].

The cure time allows choosing which manufacturing speed in laminate pressing can be used to derive suitable press programs [35]. All papers impregnated with the modified resins showed cure times in the desired range, showing that the addition of benzoguanamine does not affect this property.

4.4.7. High-Pressure Laminates Characterization

The physical and mechanical properties of the high-pressure laminates produced using the impregnated papers, determined according to EN 438-2 standard, are listed in Table 4.1.3. Due to the very low stability displayed by the resins with BG addition in stages A and B, they were not used for production of high-pressure laminates.

HPL produced with the commercial resin, MF_{comm}, showed improved performance when compared to the reference resin, MF_{ref}, as expected from an additivated product. This occurs in terms of gloss and resistances to cigarette burn, water vapour and dry heat.

For the substitution of 7.5 % ML by 7.5 % BG, the resins containing benzoguanamine behave as the commercial resin in the case of resistance to water vapour, gloss, and resistance to staining. Abrasion resistance is intermediate between the reference and commercial resins when addition of BG occurs in stage C, and becomes equivalent to the commercial resin when addition is in stage D. Only the resistance to cigarette burn remains always low, being identical to the reference resin.

Table 4.1.3 - Physical and mechanical properties characteristics of high-pressure laminates.

Type of substitution	Resin	Boiling Water	Water vapour	Impact (N)	Dry heat	Scratch	Abrasion (cycles)	Staining	Cigarette burn	Specular Gloss (Gloss Units)
	MF_{ref}	5	3	15	3	2	587	5	1	60
	MF_{comm}	5	4	15	4	2	773	5	5	102
Substitution of 7.5 % ML by 7.5 % BG	Stage C	4	4	20	3	2	649	5	1	76
	Stage D	4	4	15	3	2	776	5	1	91
Substitution of 7.5 % ML by 16.8 % BG	Stage C	4	4	15	3	2	619	5	4	98
	Stage D	4	4	10	3	2	777	5	4	101

For the substitution of 7.5 % ML by 16.8 % BG, introduction of benzoguanamine at any stage improves water vapour and abrasion resistance of the laminates and increases their gloss level. Dry heat resistance and impact resistance are not affected. However, once again, the presence of benzoguanamine results in lower boiling water resistance. When compared with commercial melamine resins, the addition of benzoguanamine in stage D results in high-pressure laminates with results of resistance to water vapour, scratching, staining, gloss and abrasion similar to the commercial resin.

From the analysis of both substitutions, it can be concluded that addition of benzoguanamine in melamine-formaldehyde resins increases water vapour and abrasion resistances in the high-pressure laminate.

Addition of BG in Stage D for the two substitution levels results in high-pressure laminates with very similar properties to those produced with commercial melamine-formaldehyde resins. It must be recalled that the resins produced in this work are not additivated, contrary to the commercial resin.

4.5. CONCLUSIONS

Benzoguanamine was used as a partial substitute for melamine, being added at four different stages of the synthesis of a melamine-formaldehyde resin. Three approaches were tested: a) substitution of 7.5 wt% melamine by 7.5 wt% of benzoguanamine; b) substitution of 7.5 wt% melamine by 16.8 wt% of benzoguanamine; c) substitution of 15 wt% melamine by 33.5 wt% of benzoguanamine. In all approaches, the addition of benzoguanamine in the initial reaction phase and after solubilisation of melamine originated resins with low stability and high viscosity, consequently unsuitable for impregnation of décor papers.

On the other hand, the addition of benzoguanamine during the condensation stage, at a water tolerance of 400-500 %, and after condensation, at a water tolerance of 100-300 %, increased considerably the product storage stability. These resins showed stabilities equivalent to commercial melamine resins. The use of 6.5 % benzoguanamine, relative to the final resin weight, is an alternative to the use of several co-monomers currently used in commercial melamine-formaldehyde resins.

When used in décor paper impregnation, the modified resins behaved as regular melamine formaldehyde resins, resulting in homogeneously impregnated papers. Key properties, such as curing time and flow, are identical to the ones achieved with standard resins.

The high-pressure laminates produced with these resins show high performance properties. The introduction of benzoguanamine results in high-pressure laminates with properties similar to commercial melamine formaldehyde resins, in terms of gloss level and resistance to abrasion, water vapour, impact, dry heat and staining.

4.6. ACKNOWLEDGEMENTS

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4.7. REFERENCES

1. The significant global rise of decorative laminates. *Wood based panels international*. 2015.
2. Kohlmayr M, Zuckerstätter G and Kandelbauer A. Modification of melamine-formaldehyde resins by substances from renewable resources. *J Appl Polym Sci* 2012; 124: 4416-4423.
3. Figueiredo AB, Evtuguin DV, Monteiro J, Cardoso EF, Mena PC and Cruz P. Structure - Surface Property Relationships of Kraft Papers : Implication on Impregnation with Phenol - Formaldehyde Resin. *Ind Eng Chem Res* 2011; 50: 2883-2890.
4. Kohlmayr M, Stultschnik J, Teischinger A and Kandelbauer A. Drying and curing behaviour of melamine formaldehyde resin impregnated papers. *J Appl Polym Sci* 2014; 131: 1-9.
5. Merline DJ, Vukusic S and Abdala AA. Melamine formaldehyde: curing studies and reaction mechanism. *Polym J* 2012; 45: 413-419.
6. Gadup B, Shoemake M and Searcy E. *Melamine-formaldehyde resins modified with dicyandiamide and sorbitol for impregnation of substrates for post-formable decorative laminates*. Patent 6001925 A, USA, 1999.

7. Diethelm H and Gattlen R. *Process for the manufacture of new plasticised melamine formaldehyde condensates*. Patent 3753934 A, USA, 1973.
8. Hiroaki A, Teruo M, Hiroshi S, Zenzaburo S and Tadamoto T. *Production of melamine-acetoguanamine-toluenesulfonamide copolycondensate resins*. Patent 3515697 A, USA, 1970.
9. Pizzi A. *Advanced Wood Adhesives Technology*. 1st ed. New York: Marcell Dekker, 1994, p.292.
10. Bonzagni FA. *Resins prepared from amino compounds,aldehydes,polyhydroxyl compounds and monohydric alcohols*. Patent 3479247 A, USA, 1969.
11. Wicks ZW, Jones FN, Pappas SP and Wicks DA. *Organic Coatings: Science and Technology*. 3rd ed. New Jersey: John Wiley & Sons, 2007, p.656.
12. Sims CG. *Process for the manufacture of benzoguanamine - melamine - formaldehyde filled molding compositions*. Patent 3454529 A, USA, 1969.
13. Ross AJ. *Resinous blend of a benzoguanamine-formaldehyde resin and a melamine-formaldehyde resin*. Patent 3506738 A, USA, 1970.
14. Standish N and Yanik R. *Process for preparing a stain-resistant molding composition comprising dry blending melamine per se and melamine-formaldehyde molding powder*. Patent 3538026 A, USA, 1970.
15. Gündüz G. *Chemistry, Materials, and Properties of Surface Coatings: Traditional and Evolving Technologies*. 1st ed. Lancaster, Pennsylvania: DEStech Publications, Inc, 2015, p.751.
16. Board N. *Modern Technology of Synthetic Resins & Their Applications*. 1st ed. Delhi: Asia Pacific Business Press Inc., 2002, p.660.
17. Müller B and Poth U. *Bauernhäuser aus Oberbayern und angrenzenden Gebieten Tirols*. Hannover: Vincentz Network GmbH & Co KG, 2006, p.290.
18. Spencer F. *Benzoguanamine resin surface coating materials and processes for preparing the same*. Patent 2579980 A, USA, 1951.

19. Feng-qi L, Dong-hiu Z, Yiming L and Xin-yi T. The study of curing mechanism of benzoguanamine-formaldehyde resins at high temperature by IR. *Acta Polym Sin* 1988; 1: 171-176.
20. Crews G, Ripperger W, Kersebohm D, Güthner T and Mertschenk B. Melamine and Guanamines. In: Ullman's (ed) *Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
21. DIN ISO 438-2. European Standard EN 438-2 Decorative High-pressure Laminates (HPL)
22. No B, Harmon D and Miller T. *Storage stable amino-formaldehyde resins and applications thereof*. Patent 8741430 B2, USA, 2014.
23. Tomita B and Hatono S. Urea-formaldehyde resins. III. Constitutional characterization by 13C fourier transform NMR spectroscopy. *Journal of Polymer Science: Polymer Chemistry Edition* 1978; 16: 2509-2525.
24. Mercer A and Pizzi A. A 13C-NMR analysis method for MF and MUF resins strength and formaldehyde emission from wood particleboard. I. MUF resins. *J Appl Polym Sci* 1996; 61: 1687-1695.
25. Tohmura S-i, Inoue A and Sahari SH. Influence of the melamine content in melamine-urea-formaldehyde resins on formaldehyde emission and cured resin structure. *J Wood Sci* 2001; 47: 451-457.
26. Slonim I, Alekseyeva S, Arshava B, Matvelashvili G, Romanov N, Potseluyeva N and Bashta N. An NMR study of the synthesis of benzoguanamine-formaldehyde resins. *Polymer Science USSR* 1985; 27: 2843-2851.
27. Jahromi S. Storage stability of melamine-formaldehyde resin solutions, 1. The mechanism of instability. *Macromol Chem Phys* 1999; 200: 2230-2239.
28. Ferra JM, Mendes A, Costa MRN, Magalhães FD and Carvalho LH. Characterization of Urea-Formaldehyde Resins by GPC/SEC and HPLC Techniques: Effect of Ageing. *J Adhes Sci Technol* 2010; 24: 1535-1551.
29. Grunwald D. Molecular structure of melamine-formaldehyde impregnation resins. In: *European Laminates Conference and Workshop* Vienna, Austria, April 2002.

30. Paiva N, Pereira J, Ferra JM, Cruz P, Carvalho LH and Magalhães FD. Study of influence of synthesis conditions on properties of melamine–urea formaldehyde resins. *International Wood Products Journal* 2012; 3: 51-57.
31. Kim S and Kim H-J. Study of miscibility of melamine-formaldehyde resin and poly(vinyl acetate) blends for use as adhesives in engineered flooring. *J Adhes Sci Technol* 2006; 20: 209-219.
32. Zhang J, Wang X, Zhang S, Gao Q and Li J. Effects of Melamine Addition Stage on the Performance and Curing Behavior of Melamine-Urea-Formaldehyde (MUF) Resin. *BioResources* 2013; 8: 5500-5514.
33. Kandelbauer A, Despres A, Pizzi A and Taudes I. Testing by fourier transform infrared species variation during melamine–urea–formaldehyde resin preparation. *J Appl Polym Sci* 2007; 106: 2192-2197.
34. Mistry B. *A Handbook of Spectroscopic Data Chemistry: (UV, IR, PMR, 13CNMR and Mass Spectroscopy)*. Gujarat: Oxford Book Company, 2009.
35. Kandelbauer A and Teischinger A. Dynamic mechanical properties of decorative papers impregnated with melamine formaldehyde resin. *Eur J Wood Wood Prod* 2009; 68: 179-187.
36. Ungar IS, Scher HI and Williams DA. *High-pressure decorative laminate having registered colour and embossing*. Patent 4092199 A, USA, 1978.
37. Kandelbauer A, Petek P, Medved S, Pizzi A and Teischinger A. On the performance of a melamine–urea–formaldehyde resin for decorative paper coatings. *Eur J Wood Wood Prod* 2009; 68: 63-75.

4.8. SUPPORTING INFORMATION

4.8.1. Resistance to Dry Heat

A specimen of impregnated paper is subjected to dry heat by contact with a metal block initially at 160 °C during 20 min. The metal block (cast cylindrical aluminium) had an external diameter of (100 ± 1.5) mm and an overall height of (70 ± 1.5) mm. At the end of this period, the metal block is removed and the specimen allowed to cool down for a period of 45 min.

Afterward, the surface is classified according to the following scale:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles;

Rating 3: Moderate change of gloss and/or colour;

Rating 2: Marked change of gloss and/or colour;

Rating 1: Surface damage and/or blistering.

4.8.2. Resistance to Staining

In the staining resistance method, the specimens are left in contact with different staining agents for specific times. At the end of the contact period, the specimens are washed with water and examined for residual surface marks. The staining agents are sodium hydroxide (25 % solution); hydrogen peroxide (30 % solution); shoe polish and acetone. For the first three, the contact time is 10 minutes and the contact time for acetone is 16 hours. Afterwards the surface is classified according to the following scale:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles;

Rating 3: Moderate change of gloss and/or colour;

Rating 2: Marked change of gloss and/or colour;

Rating 1: Surface damage and/or blistering.

4.8.3. Resistance to Cigarette Burn

A burning cigarette (after being consumed at least 10 mm in length) is placed in full-length contact with the horizontal surface of the specimen in a draught-free area so that the glued seam of the cigarette is not in contact with the specimen. The cigarette continues burning until an additional 20 mm length is consumed. If the cigarette goes out before this occurs the test is repeated.

Afterwards the surface is classified according to a scale where:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles, and or/ slight brown stain;

Rating 3: Moderate change of gloss and/or moderate brown stain;

Rating 2: Severe brown mark, but not destruction of the surface;

Rating 1: Blistering and/or cracks.

4.8.4. Resistance to Scratching

The resistance to scratching is expressed as a numerical rating (Table 4.1.4) which defines the maximum applied load that does not produce a continuous surface scratch. A square test specimen (100 ± 1 mm) is subject to scratch with a diamond scratching point using a Taber Shear/Scratch Tester Model 551.

Table 4.1.4 - Rating scale for scratch resistance.

Rating scale	Discontinuous scratches, or faint superficial marks, or no visible marks	$\geq$ 90 % continuous double circle of scratch marks clearly visible
5	6 N	> 6 N
4	4 N	6 N
3	2 N	4 N
2	1 N	2 N
1	-	1 N

4.8.5. Resistance to Abrasion

The specimen rotates in contact with a pair of loaded cylindrical wheels covered with abrasive paper. As the wheels are turned by the rotating specimen, they abrade an annular track on the specimen´s surface. The number of revolutions of the specimen required causing a defined degree of abrasion is used as measures of resistance to abrasion. This test is applicable only to flooring grade laminates.

The specimen is observed after each 100 revolutions and the abrasive papers should be renewed after every 200 revolutions until the initial wear point (IP) is reached.

The initial wear point (IP) is that point at which the first clearly recognizable wear-through on the print, pattern or plain colour appears and the sub-layer becomes exposed in three quadrants. The initial wear point is reached when there are areas of at least 0.60 mm^2 wear-through in two quadrants and an area of 0.60 mm^2 wear-through becomes visible in a third quadrant. The sub-layer for printed patterns is the background on which the pattern is printed; for plain colours, it is the first sub-layer of a different colour.

The number of revolutions is recorded as the IP-value. The resistance to abrasion of the laminate under test shall be average of the initial wear-point (IP) values obtained on the three specimens, rounded to the nearest 100 revolutions.

4.8.6. Resistance to Immersion in Boiling Water

Specimens shall be taken from the same laminate with 50 ± 1 mm square. The specimens are placed in the vessel of boiling distilled water. After 120 ± 5 min, the specimens are removed from the boiling water and allow to cool for 15 ± 5 min in the vessel of distilled water maintained at (23 ± 2) °C. The specimens are dried with a clean dry cloth and then weighed again.

The percentage by mass of boiling water absorbed by the laminate under test and the percentage increase in thickness shall be the average of the values obtained on the three specimens.

The result of the examination for change in appearance shall be the lowest rating of the three specimens assessed in accordance with the following rating scale:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles, and or/ slight brown stain;

Rating 3: Moderate change of gloss and/or moderate brown stain;

Rating 2: Severe brown mark, but not destruction of the surface;

Rating 1: Blistering and/or cracks.

4.8.7. Resistance to Water Vapour

A specimen with 100x100 mm^2, cut from the laminate under test, is held in place over the neck of a flask containing boiling water, so that the decorative surface of the specimen is exposed to the water vapour. After 1 h, the specimen is removed and allowed to recover for 24 h in normal ambient conditions before the examination.

The result of the examination for change in appearance shall be expressed in accordance with the following rating scale:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles, and or/ slight brown stain;

Rating 3: Moderate change of gloss and/or moderate brown stain;

Rating 2: Severe brown mark, but not destruction of the surface;

Rating 1: Blistering and/or cracks.

4.8.8. Resistance to Impact by Small-diameter Ball

In this test, a specimen from the laminate is bonded to particleboard panel and its surface is subjected to the impact of a 5 mm diameter steel ball mounted at one end of a spring-loaded bolt. The resistance to impact is measured as the spring force for which no visible damage occurs.

The impact resistance of the laminate under test is the maximum value of the spring force, in Newton, for which no damage occurs in a series of five strikes.

4.8.9. Gloss

The gloss meter is placed on the surface of the high-pressure laminate and the surface gloss was determined from specular reflectance measurements at an incident angle of 20°. The gloss meter used was the REFO D from the manufacturer The Paul N. Gardner Company, Inc.

CHAPTER 5

CHAPTER 5 – IMPROVING HYDROPHOBIC AND OLEOPHOBIC PERFORMANCE OF HIGH-PRESSURE LAMINATES [1]

5.1. ABSTRACT

High-pressure laminates are decorative materials that are widely used in furnishing and building industries. One of their major handicaps, especially in the case of high gloss laminates, is the ease of staining by fingerprints. This problem can *a priori* be minimized by increasing the hydrophobicity and oleophobicity of the surface.

In order to improve hydrophobicity, the chemical composition of the resin used for impregnation of the decorative paper used as the laminate's top layer was modified. A melamine-benzoguanamine-formaldehyde resin was used as starting point, and caprinoguanamine was added as a comonomer at different stages of the synthesis. Addition at the end of the synthesis process showed to be the most promising approach for increasing, achieving a water contact angle of 91.2°, while the contact angle for a commercial laminate, impregnated with a standard melamine-formaldehyde resin is 58°.

Regarding oleophobicity, several commercial additives were tested with the previously formulated resin. A fluorocarbon additive lead to the best result, leading to contact angles of 114° for water and 76° for an artificial fingerprint liquid. In addition, it was shown that fingerprints were easier to clean from the modified laminate's surface. Other relevant surface properties (resistance to boiling water, water vapour, impact, dry heat, scratch and staining) remained equivalent to those obtained using a commercial melamine-formaldehyde impregnation resin.

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[1] Henriques A, Almeida M, Paiva N, Ferra JM, Martins J, Carvalho LH and Magalhães FD. Improving hydrophobic and oleophobic performance of high-pressure laminates, Submitted to European Journal of Wood and Wood Products.

5.2. INTRODUCTION

Decorative high-pressure laminates (HPL), are defined by European Standard EN 438-1 as high-density panels (≥ 1.35 g/cm^3), finished and ready for use, which have exceptional mechanical, physical strength and chemical resistance [1]. They are used by the furniture and building industries for the production of furniture, countertops, flooring and wall paneling surfaces used in different sectors, namely in residential and working environments and in public places [2].

Two types of paper are used in the manufacture of HPL: *kraft* and décor. The *kraft* paper, used in the bottom layers, is impregnated with phenolic resin and provides mechanical and moisture resistance to HPL. Décor paper is used on the top layer, providing the colour and pattern of the surface. It is most commonly impregnated with a melamine-formaldehyde resin (MF resin), because of its unique surface properties in terms of hardness, chemical stability and transparency, which allow a glossy visual appearance of the surface decors and good performance in use, at reasonable prices [3]. The synthesis of MF resin consists in two stages: methylolation and condensation. In the methylolation, melamine reacts with formaldehyde producing methylolmelamines.

In the second stage, condensation, methylolmelamines react with each other or with free formaldehyde, leading to formation of a large number of different oligomers containing methylene and methylene ether bridges [4].

High-pressure laminates are routinely subjected to hand contact, and are thus prone to undesirable staining with fingerprints, due to skin oil and sweat, which are especially visible on high-gloss surfaces. Anti-fingerprint performance is obtainable in materials that possess both hydrophobic and oleophobic properties, improving aesthetic appearance and facilitating maintenance [4, 5].

In the case of HPL surfaces, increased hydrophobicity and improved cleanability is usually achieved by increasing surface roughness, either using a textured finishing surface when pressing, or by using textured foils that are laminated onto the surface [5]. Wenzel and Cassie models describe how roughness can promote surface hydrophobicity [6].

However, when a high-gloss finishing is desired, this approach cannot be applied. One has, therefore, to incorporate hydrophobic additives in the impregnation resin formulation, like some silanes, siloxanes, and fluorinated compounds [5].

Badila *et al.* (2014) [5] studied the increase of hydrophobicity and stain cleanability on melamine laminate surfaces using different compounds in the impregnation bath, namely: hydroxyl-terminated polyether modified polydimethylsiloxane (PDMS-OH), hydroxyl-terminated fluorinated polyether, fluoroalkylfunctional oligosiloxane, polymeric surfactant, and emulsion of polydimethylsiloxane. Besides that, they also studied the effect of oxidation of the hydroxyl-functional surfactants, reporting an increase in the contact angle for water and n-hexadecane. Decrease of surface energy on HPL by incorporation of nonafluorohexyl polyhedral oligomeric silsesquioxane (FH-POSS) nanoparticles (up to 1 w/w%) into the melamine-formaldehyde resin matrix has been reported by Magina and co-workers [7].

Caprinoguanamine is a guanamine that shows a functionality up to 4 and an alkyl substituent chain with 9 carbons (Figure 5.1.1). Its use as comonomer in melamine-formaldehyde impregnation resins has been reported before, with the purpose of improving flexibility of the final product [8]. In the context of the present work, it is intended to take advantage of the alkyl chain in caprinoguanamine to improve the hydrophobic character of an HPL.

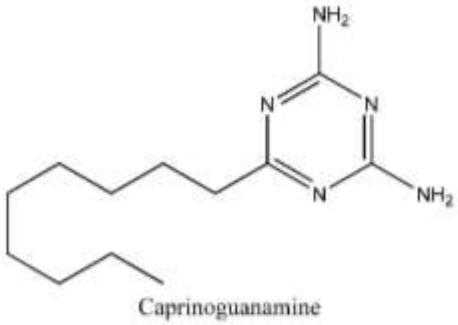

Figure 5.1.1 - Chemical structure of caprinoguanamine

In a previous work, we have shown how partial replacement of melamine (up to 15 wt%) by another guanamine, benzoguanamine, in a melamine-formaldehyde (MF) resin formulation changes the polymer chemical structure, leading to a product with improved storage stability without need for using additives traditionally used in industry [9].

Preliminary work has shown that addition of even a small amount of caprinoguanamine in the synthesis of a melamine-formaldehyde resin leads to an unstable product that becomes cloudy one day after synthesis. On the other hand, we have observed incorporation of caprinoguanamine in the aforementioned melamine-benzoguanamine-formaldehyde (MBF) resin formulation did not hinder its stability. Therefore, the present work uses that MBF resin as the starting point for studying the effect of copolymerization with caprinoguanamine.

5.3. EXPERIMENTAL

5.3.1. Materials

Formaldehyde (37 wt% solution), melamine, sodium hydroxide 10 wt%, as well as impregnation additives (acid catalyst, release agent and surfactant) and the décor paper for impregnation (a red décor paper of 100 g/m^2) were supplied by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal). A commercial melamine-formaldehyde resin was also supplied by Euroresinas – Indústrias Químicas.

Benzoguanamine (BG) was purchased from Sigma Aldrich and caprinoguanamine (CG) from AlzChem AG. Both were used as supplied.

Several commercial additives were tested to improve anti-fingerprint properties of the surfaces. Micro Powders Inc. (TarryTown, USA) supplied the additives described next. Micronized polytetrafluoroethylene (PTFE) powder additives Fluo X-1406 (Fluo X) and Fluo HT, with and 2.0-4.0 µm, respectively. An aqueous dispersion of finely micronized PTFE, Microspersion HT (MHT), with 50 % solid content, a mean particle size between 2.0-4.0 µm a pH 9.0- 10.5 and a viscosity of 5000-7000 cP, with a peach colour appearance. An aqueous dispersion of sub-micron PTFE particles with a mean particle size < 1.0 µm, Microspersion

1406 (M1406), with a viscosity of 3000-5000 cP, with 50 % solid content, pH 7.0- 8.0 and with an off-white appearance. A fluorinated oil-repellent additive (OR) was also tested, having a pH of 4.81, kinematic viscosity of 122 cSt (using a flow cup viscometer, according to DIN EN ISO 2431) and a solids content of 25.87 %. This additive had a tenuous opaque yellow colour.

5.3.2. Resin Synthesis

The resin samples were produced in a 2 L round bottom flask equipped with a mechanical stirrer and an immersed thermometer. A heating mantle was used to heat the flask.

Melamine-benzoguanamine-formaldehyde (MBF) resin was prepared as previously described ([9]) by condensation of melamine benzoguanamine and formaldehyde with a final formaldehyde/amine ratio (F/NH_2) of 1.90. Melamine and formaldehyde aqueous solution (at 37 % concentration) was first charged into the round bottom flask, and the pH value were adjusted to 8.5-9.0 using NaOH 10 % solution. The mixture was then heated to 90-100 ºC, upon which it became a clear solution. After that, the reaction proceeded until a water tolerance of 100-300 % was obtained. At this point benzoguanamine was added and the mixture was cooled until room temperature.

The MBF resins modified with caprinoguanamine (CG) were synthesized following the same procedure as before, but adding CG as a co-monomer at four different stages of the synthesis: stage A - right after addition of formaldehyde in the initial phase; stage B - after complete solubilisation of melamine; stage C – in the final phase of the condensation step; stage D - after the condensation process is finished, at a water tolerance of 100-300 %. The amount of CG added was 0.75 or 1.5 wt%, related to the amount of melamine.

5.3.3. Resin Characterization

Kinematic viscosity - Kinematic viscosity was determined using a flow cup viscometer, according to DIN EN ISO 2431.

Solids content - Solids content of the resin samples were determined by heating 3 g of each sample in an aluminium pan and placed in an oven at 120 °C for three hours until constant mass.

pH measurements - The pH electrode was calibrated at the operating temperature, i.e room temperature, using the pH= 7.0 and 9.0 as buffer solutions. The pH was monitored automatically.

Stability - The storage stability was defined as the time, in days, from resin preparation until the solution became turbid to the naked eye.

5.3.4. Impregnated Paper

Paper Impregnation - Paper sheets of 21 × 30 cm^2 were impregnated with all synthesized resins impregnation additives (acid catalyst, release agent and surfactant). All papers were impregnated in a two-step processes. In the first bath, there is the complete impregnation of the core paper and the paper sheets were oven-dried at 140 °C until a resin content between 40-42 % is attained. After that, the sheets are subjected to a second bath, designate coating, to ensure good impregnation, resubmitted to the oven at 140 °C until a resin content between 54-56 % and moisture content after drying of 6-7 % are attained.

All the commercials additives are used in the second bath in a range of concentrations according to supplier’s recommendations.

5.3.5. High-pressure Laminates Production

High-pressure laminates consist of layers made up of two distinct phases: a core layer consisting of an assembly of four kraft paper sheets impregnated with phenolic resin and one sheet of décor paper impregnated with the synthetized resins.

The set of impregnated sheets of paper are then pressed between plates at 140 – 150 °C under a pressure of 80 - 100 bar.

5.3.6. Characterization of High-Pressure Laminates

Contact angle measurements - Contact angles were measured using the sessile drop method on high-pressure laminate surfaces. The measurements were recorded 60 s after contact, in order to allow equilibrium to be reached. Water and a special liquid formulation for simulating fingerprint oil were used as probe liquids. The artificial fingerprint liquid (AFL) was prepared as described by Wu *et al.* [10], by mixing artificial sweat (described below) with hydroxyl-terminated polydimethylsiloxane and 1-methxy-2-propanol in a ratio of 3:3:4. The artificial sweat is a mixture composed of lactic acid 3 mL/L, acetic acid 5 mL/L, sodium chloride 10 g/L, sodium hydrogen phosphate 10 g/L and deionized water. The solution was stirred for at least 4 h at room temperature before being used.

SEM analysis - SEM/EDS analysis was performed in a Phenom XL Scanning Electron Microscope (SEM) microscope operating at 15 kV and equipped with an Energy Dispersive X-ray spectroscopy accessory (EDS Detector).

All the samples were applied on carbon tape and sputtered with Au/Pa.

Colour - Colour measurements were done using a Colour Eye XTH spectrometer according to the CIE L* a* b* system.

Fingerprint removal test - To test the ease of fingerprint removal, a fingerprint mark was applied on the HPL surface using the artificial fingerprint liquid mentioned above [10]. The mark was then cleaned using a cotton tissue, wiping 5 times. A Colour Eye XTH spectrometer was then used to compare the surface of the pristine HPL and the HPL subjected to the fingerprint mark and cleaning procedure.

Surface characterization

Resistance to dry heat - A specimen of impregnated paper is subjected to dry heat by contact with a metal block initially a 160 °C during 20 min. The metal block (cast cylindrical aluminium) had an external diameter of (100 ± 1.5) mm and an overall height of (70 ± 1.5) mm. At the end of this period, the metal block is removed and the specimen allowed to cool down for a period of 45 min.

Afterward, the surface is classified according to the following scale:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles;

Rating 3: Moderate change of gloss and/or colour;

Rating 2: Marked change of gloss and/or colour;

Rating 1: Surface damage and/or blistering.

Resistance to staining - In the staining resistance method, the specimens are left in contact with different staining agents for specific times. At the end of the contact period, the specimens are washed with water and examined for residual surface marks. The staining agents are sodium hydroxide (25 % solution); hydrogen peroxide (30 % solution); shoe polish and acetone. For the first three, the contact time is 10 minutes and the contact time for acetone is 16 hours. Afterwards the surface is classified according to the following scale:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles;

Rating 3: Moderate change of gloss and/or colour;

Rating 2: Marked change of gloss and/or colour;

Rating 1: Surface damage and/or blistering.

Resistance to scratches - The resistance to scratches is expressed as a numerical rating (Table 5.1.1) which defines the maximum applied load that does not produce a continuous surface scratch. A square test specimen (100 ± 1 mm) is subject to scratch with a diamond scratching point using a Taber Shear/Scratch Tester Model 551.

Table 5.1.1 - Rating scale for scratch resistance.

Rating scale	Discontinuous scratches, or faint superficial marks, or no visible marks	≥ 90 % continuous double circle of scratch marks clearly visible
5	6 N	> 6 N
4	4 N	6 N
3	2 N	4 N
2	1 N	2 N
1	-	1 N

Resistance to abrasion - For this test a Taber abraser was used (model 5135), being the specimen observed after each 100 revolutions and the abrasive papers should be renewed after every 200 revolutions until initial wear is observed. The initial wear point (IP) is the number of revolutions at which the first clearly recognizable wear-through on the plain colour appears and the sub-layer becomes exposed in three quadrants. This point is reached when there are areas of at least 0.60 mm^2 wear-through in two quadrants and an area of 0.60 mm^2 wear-through becomes visible in a third quadrant. The sub-layer; for plain colours it is the first sub-layer of a different colour.

The resistance to abrasion of the laminate under test shall be average of the IP values obtained on the three specimens, rounded to the nearest 100 revolutions.

Resistance to immersion in boiling water - In this test, a square specimen with 50 ± 1 mm lateral size is cut from the laminate. The specimens are placed in the vessel of boiling distilled water. After 120 ± 5 min, the specimens are removed from the boiling water and allow to cool for 15 ± 5 min in the vessel of distilled water maintained at 23 ± 2 °C. The specimens are dried with a clean dry cloth and then weighed again.

The average weight percentage of water absorbed by the laminate under test and the percentage increase in thickness are measured for three specimens.

The change in appearance is evaluated as shall be the lowest rating obtained for the three specimens in accordance with the following rating scale:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles, and or/ slight brown stain;

Rating 3: Moderate change of gloss and/or moderate brown stain;

Rating 2: Severe brown mark, but not destruction of the surface;

Rating 1: Blistering and/or cracks.

Resistance to water vapour - A specimen with 100 x 100 mm^2, cut from the laminate under test, is held in place over the neck of a flask containing boiling water, so that the decorative surface of the specimen is exposed to the water vapour. After 1 h, the specimen is removed and allowed to recover for 24 h in normal ambient conditions before the examination.

The result of the examination for change in appearance shall be expressed in accordance with the following rating scale:

Rating 5: No visible change;

Rating 4: Slight change of gloss and/or colour, visible only at some viewing angles, and or/ slight brown stain;

Rating 3: Moderate change of gloss and/or moderate brown stain;

Rating 2: Severe brown mark, but not destruction of the surface;

Rating 1: Blistering and/or cracks.

Resistance to impact by small-diameter ball - In this test, a specimen from the laminate is bonded to particleboard panel and its surface is subjected to the impact of a 5 mm diameter steel ball mounted at one end of a spring-loaded bolt. The resistance to impact is measured as the spring force for which no visible damage occurs.

The impact resistance of the laminate under test is the maximum value of the spring force, in Newton, for which no damage occurs in a series of five strikes.

Gloss - The gloss meter is placed on the surface of the high-pressure laminate and the surface gloss was determined from specular reflectance measurements at an incident angle of 20°.

5.4. RESULTS AND DISCUSSION

5.4.1. Resin Synthesis and Characterization

The best synthesis stage for addition of CG comonomer was investigated. Eight resins were synthesized, where 0.75 or 1.5 wt% of caprinoguanamine (relative to the amount of melamine) were added in the melamine-benzoguanamine-formaldehyde resin synthesis. These modified resins will be designated henceforward as caprinoguanamine-melamine-benzoguanamine-formaldehyde resins (CMBF).

These resins were compared to a melamine-benzoguanamine-formaldehyde resin containing no caprinoguanamine (MBF), and to a commercially available melamine-formaldehyde resin containing additives to insure storage stability (MF_{comm}).

The generic properties of all resins are shown in the Table 5.1.2.

Table 5.1.2 - Generic properties of studied resins.

Resin	**Additive**	**Amount of CG comonom**	**Kinematic viscosity at 25 °C (s)**	**pH**	**Water Tolerance**	**Solid Content (%)**	**Aspect**	**Stability**
Technical Specification	None	-	16.00-18.00	9.00-10.00	180-260	55.00-57.00	Translucent	> 10 days
MF$_{comm}$	None	-	16.70	9.39	190	56.20	Translucent	> 10 days
MBF	None	-	55.23	9.22	90	58.30	Translucent	> 10 days
CMBF	Stage A	0.75	14.86	9.85	0	57.55	Translucent	> 10 days
		1.5	15.56	9.52		56.93		
	Stage B	0.75	17.40	10.08		59.33	Translucent	> 10 days
		1.5	15.59	9.30		56.10		
	Stage C	0.75	17.04	9.97		54.72	Translucent	> 10 days
		1.5	17.90	9.40		56.13		
	Stage D	0.75	17.40	9.59		56.93	Translucent	> 10 days
		1.5	18.93	9.20		58.20		

Addition of CG does not affect the resin's stability or its visual appearance, two key properties for use in paper impregnation. Other parameters such kinematic viscosity, pH and solids content are also not significantly changed when compared with a commercial melamine-formaldehyde resin.

The only property that is worsened by introduction of CG is water tolerance, as a consequence of the presence of the alkyl substituent in the monomer [11]. These resins cannot withstand addition of water, which may be a problem for applications like textile treatment [12]. However, this is not necessarily critical for paper impregnation.

5.4.2. Paper Impregnation and High-Pressure Laminate Production

In order to compare the contact angles on high-pressure laminates, several impregnations were carried out using the MBF resin, the CMBF resins and the commercial resin.

The impregnated papers have a resin content of 54-56 % and a final moisture content of 6-7 %. After pressing, all the resulting laminates showed homogeneous and glossy appearance, identical to the laminate obtained from the commercial resin.

5.4.3. Contact Angle Measurements

Contact angle measurements using water and the artificial fingerprint liquid as probe liquids were performed on all the high-pressure laminates produced. The results are shown in Figure 5.1.2.

Resin MBF, when compared with the commercial resin, shows an improved hydrophobic character of the surface, due to the hydrophobic nature of benzoguanamine [11], however the 90° threshold for the water contact angle is not attained. On the other hand, incorporation of CG at any reaction stage, and in quantities of 0.75 and 1.5 % increases significantly the water contact angles. This hydrophobic behaviour was expected, taking into account the alkyl group present in the monomer.

Wu and co-workers [10] suggested that for a surface to possess anti-fingerprint behaviour the contact angle of the artificial fingerprint liquid should reach 87°. This implies adding an oleophobic character to the already hydrophobic surface (i.e. an amphiphobic surface) [13]. The results in Figure 5.1.2 show that presence of benzoguanamine increases the contact angle of the AFL by about 8°, but the value is still quite low (about 40°). Addition of caprinoguanamine in stage A at the highest concentration induces a slight further increase. Even though caprinoguanamine causes a significant increase in the water contact angle, its effect on the AFL contact angle is marginal. The formulation with the highest impact on water contact angle, with addition of 1.5 % of CG at stage D (that will be called CMBF1.5_D), was selected for the next phase of the work.

In order to further improve fingerprint resistance, several commercial additives were tested in the impregnation process, in combination with CMBF1.5_D. The results are compared to the commercial MF resin with the same additives.

All the additives were added in the second impregnation bath, in a range of concentrations chosen according to the supplier’s recommendations. For Fluo X, Fluo HT, MHT and M1406, the amounts used in the second bath were 0.5 and 1.0 wt%, respectively, while for OR the amount was 7.5 wt% and 10 wt%, related to the total mass of resin formulation.

Figure 5.1.3 provides images of the obtained formulations. It is notorious that the use of Fluo X, Fluo HT and M1406 results in a heterogeneous suspension with agglomerated particles while MHT and OR yield homogeneous solutions

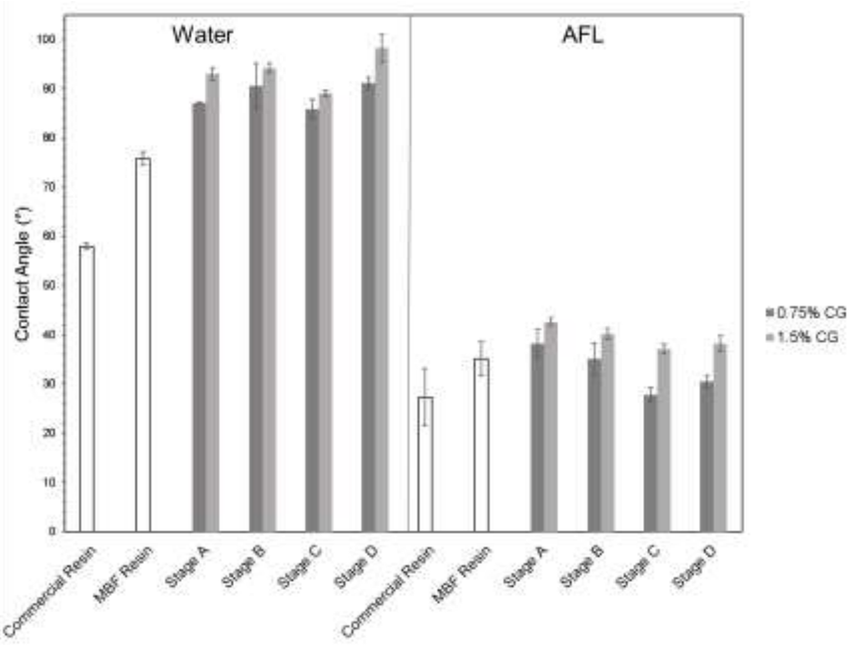

Figure 5.1.2 - Contact angle measurements using water (left) and an artificial fingerprint liquid (right) for CMBF resin with 0.75 %caprinoguanamine and 1.5 % caprinoguanamine

Despite this behaviour, when all resins were used for impregnation, the resulting high-pressure laminates had homogeneous appearance, without spots or stains.

Figure 5.1.4 and Figure 5.1.5 show the contact angle results obtained with MF_{comm} and CMBF1.5_D, respectively. The best combined hydrophobic and oleophobic behaviour is observed for when additive OR is used in resin CMBF1.5_D. The poor homogenization obtained with additives Fluo X, Fluo HT and M1406 could have caused the results for these additives (Figure 5.1.3).

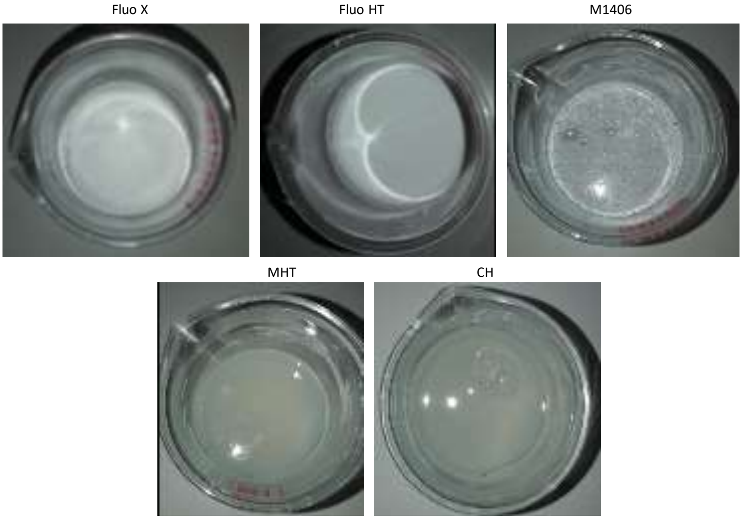

Figure 5.1.3 - Formulations made for the impregnation of décor paper using a commercial melamine-formaldehyde resin

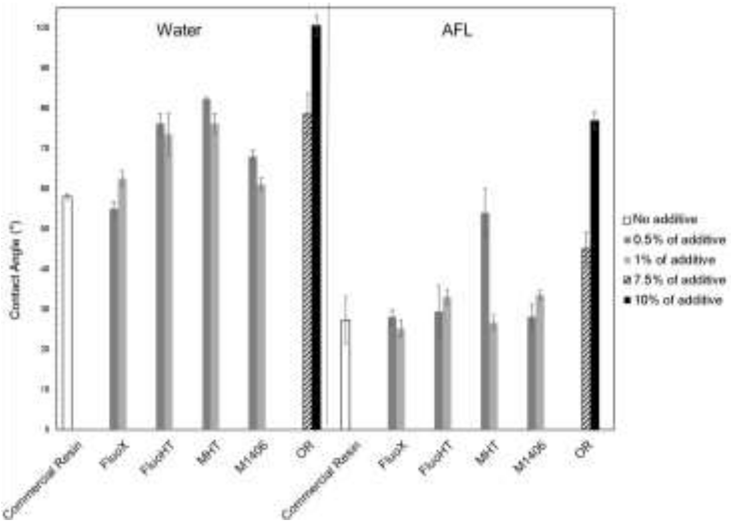

Figure 5.1.4 - Contact angle measurements using water (left) and an artificial fingerprint liquid (right) as probe liquids in high-pressure laminates produced with a melamine-formaldehyde commercial resin combined with several additives

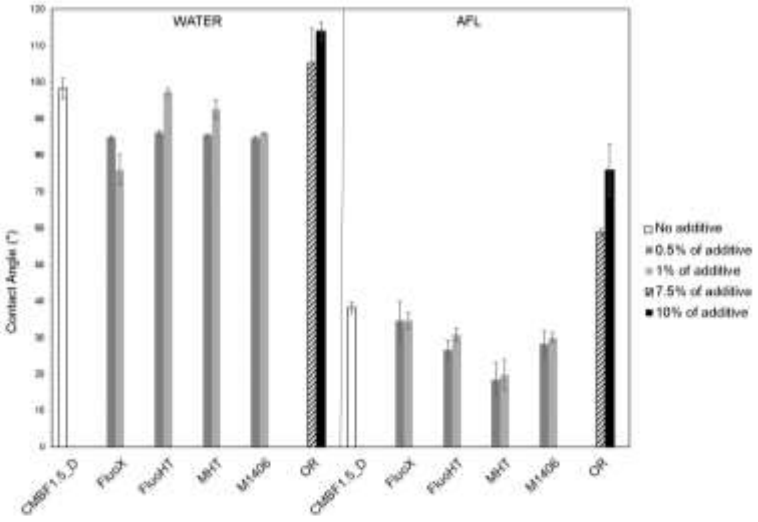

Figure 5.1.5 - Contact angle measurements using water and an artificial fingerprint liquid as probe liquids in high-pressure laminates produced with CMBF1.5_ D resin combined with several additives

A SEM-EDS spectral mapping was done to see how fluorine atoms were distributed in the surface of the high-pressure laminate. In Figure 5.1.6 it is shown the obtained results, where the bright spots correspond to fluorine atoms distribution in the surface. It is evident that in the case of the addition of OR, the distribution of fluorine is much more homogeneous than for all other additives. Poor distribution and the presence significant areas depleted of fluorine is observed for the latter.

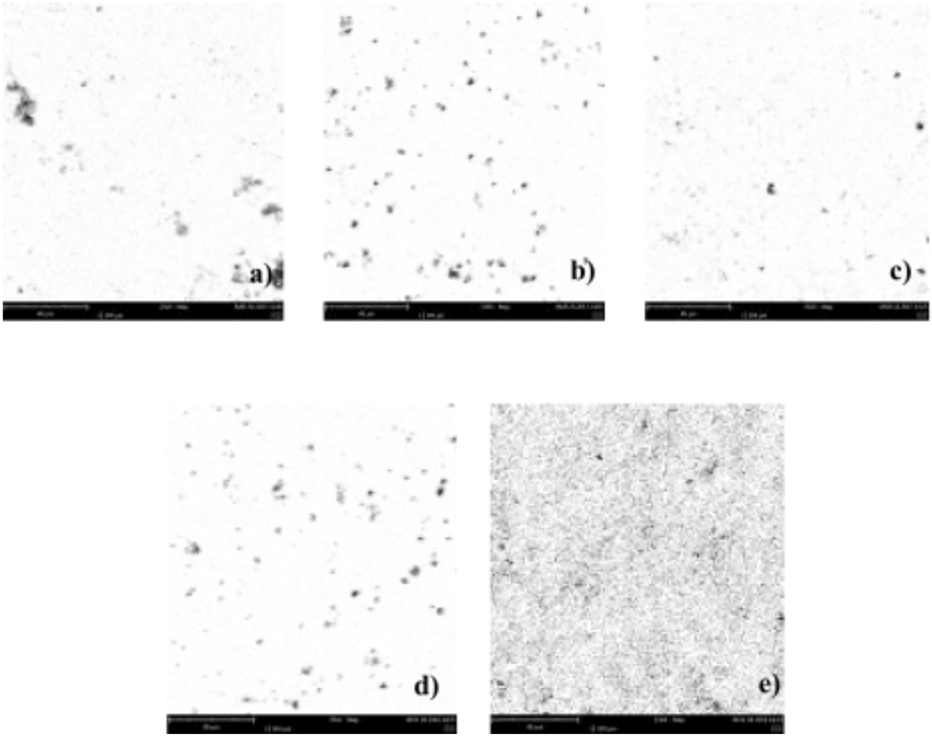

Figure 5.1.6 – SEM-EDS images for the fluorine distribution in HPLs containing different additives in the resin formulation: a) additive Fluo X; b) additive Fluo HT; c) additive M1406; d) additive MHT and e) additive OR (1000x magnification)

Since the commercial additive OR led to promising results, higher concentrations were tested, namely 12.5 and 15 %, related to the total mass of resin formulation. However, it was observed that the laminates acquired an undesirable light yellow tint. Table 5.1.3 shows the results of colour measurements for HPL with different contents of OR and with the commercial resin. For additive contents higher than 10 % the yellow colour is intensified (the a* parameter increases). This is related to the colour of the additive itself (light yellow). The use of higher concentrations of OR was therefore excluded.

Table 5.1.3 - Colour measurements in HPL.

Resin	Additive	L*	a*	b*
MF_{comm}	None	45.46	38.96	16.58
CMBF1.5_D	None	45.14	38.75	16.66
CMBF1.5_D	10 % OR	45.33	38.70	16.68
CMBF1.5_D	12.5 % OR	44.59	42.34	18.78
CMBF1.5_D	15 % OR	44.65	42.55	18.98

5.4.4. Fingerprint Removal Test

CMBF resin containing 10 % OR displays a significant oleophobic character, thanks to the presence of fluorinated compounds decreasing surface energy [13]. However, the attained contact angle values were below 87°, implying that fingerprint marks will still adhere to the surface of the HPL, although less visibly [9]. Nonetheless, the ease of cleaning of the surface may be different. This was compared using the CMBF1.5_D with 10 % of OR additive and the commercial HPL. The samples where subject to 5 consecutive rubs using a dry cotton tissue, after being stained with the artificial fingerprint liquid. The lightness of the surfaces was measured using a colorimeter.

As seen in Table 5.1.4, after 5 rubs the commercial HPL still shows a visible stain (the L* measured is considerably lower than for the pristine HPL). The HPL produced with CMBF1.5_D and OR, on the other hand, shows no visible stain after 5 rubs, and the L* value is very close to the original, non-stained surface. The commercial HPL only attains this value after 10 rubs.

Table 5.1.4 - Lightness values of HPL in fingerprint removal tests.

Resin	Additive		L*
MF$_{comm}$	None	Without mark	45.46
		After cleaning the fingerprint mark – 5 rubs	41.58
		After cleaning the fingerprint mark – 10 rubs	44.10
CMBF1.5_D	10 % OR	Without mark	45.33
		After cleaning the fingerprint mark – 5 rubs	44.05

5.4.4.1. High-pressure laminates characterization

Other relevant surface properties were measured for the high-pressure laminates produced with 10 wt% OR in the second bath, namely in terms of resistance to dry heat, staining, abrasion, immersion in boiling water, water vapour, and impact.

The physical and mechanical properties of the high-pressure laminates, determined according to standard EN 438-2, are listed in Table 5.1.5, where resins CMBF1.5_D, MFcomm additivated with 10 % of OR and MFcomm and CMBF1.5_D without any additive are compared.

The high-pressure laminates produced with the commercial resin and the newly synthesized resin showed as main differences the gloss and the resistance to abrasion, whereas the other characteristics did not change. Although this little differences, the high-pressure laminates obtained with the caprinoguanamine-melamine-benzoguanamine-formaldehyde resin still fulfil the standards for the gloss and abrasion resistance (70 gloss units to be named high gloss and in the case of abrasion the value should be higher than 400 revolutions) [1].

The introduction of the additive only affects the gloss surface properties of the high-pressure laminates. Despite this change, the high-pressure laminates retain high gloss, since the measured value is higher than 70 gloss units. The other properties are similar to the commercial reference.

Table 5.1.5 - Physical and mechanical properties characteristics of high-pressure laminates.

Resin	**Additive**	**Boiling Water**	**Water vapour**	**Impact (N)**	**Dry heat**	**Scratch**	**Abrasion (revolutions)**	**Staining**	**Specular Gloss (Gloss Units)**
MF$_{comm}$	None	5	4	15	4	2	773	5	102
MF$_{comm}$	10 % OR	5	4	15	4	2	700	5	93
CMBF1.5_D	None	5	4	15	4	2	706	5	87
CMBF1.5_D	10 % OR	5	4	15	4	2	796	5	86

5.5. CONCLUSIONS

Introduction of 0.75 and 1.5 % of caprinoguanamine in a melamine-benzoguanamine-formaldehyde resin, at four distinct phases, resulted in resins with similar properties to a commercial melamine-formaldehyde resin, regarding viscosity, pH, and storage stability. In addition, when used as impregnation resin, it resulted in high-gloss high-pressure laminates with improved hydrophobicity. Addition of 1.5 % of caprinoguanamine after the end of the condensation stage led to the highest value of water contact angle, 98.2°, an increase of around 40 % in relation to the commercial melamine-formaldehyde resin used as reference, and of around 23 % in relation to the melamine-benzoguanamine-formaldehyde base formulation.

In order to improve also the oleophobic character of the laminates, the newly synthesized resin was combined with different fluorinated additives. The best result was obtained with a 10 % of a commercial fluorinated aqueous dispersion. The resulting high-pressure laminate showed a contact angle of 114° for water and of 76° for a formulated artificial fingerprint liquid, which represents an increase of 49 % and 64 %, respectively, in relation to a laminate produced with the reference commercial resin. It was shown that this laminate is easier to clean than one made with the reference commercial melamine-formaldehyde resin. Furthermore, other relevant surface properties are equivalent to those of a standard high-pressure laminate.

5.6. ACKNOWLEDGEMENTS

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5.7. REFERENCES

1. DIN ISO 438-2. European Standard EN438-2 Decorative High-pressure Laminates (HPL) - High-pressure decorative laminates (HPL) -Sheets based on thermosetting resins (usually called Laminates).
2. Magina S, Santos M, Ferra J, Cruz P, Portugal I and Evtuguin D. High-pressure Laminates with Antimicrobial Properties. *Materials* 2016; 9.
3. Kohlmayr M, Zuckerstätter G and Kandelbauer A. Modification of melamine-formaldehyde resins by substances from renewable resources. *J Appl Polym Sci* 2012; 124: 4416-4423.
4. Merline DJ, Vukusic S and Abdala AA. Melamine formaldehyde: curing studies and reaction mechanism. *Polym J* 2013; 45: 413-419.
5. Badila M, Kohlmayr M, Zikulnig-Rusch EM, Dolezel-Horwath E and Kandelbauer A. Improving the cleanability of melamine-

formaldehyde-based decorative laminates. *J Appl Polym Sci* 2014; 131: 1-9.

6. Yang C, Tartaglino U and Persson BNJ. Influence of Surface Roughness on Superhydrophobicity. *Phys Rev Lett* 2006; 97: 1-4.
7. Magina S, Ferra J, Cruz P, Nogueira HIS, Portugal I and Evtuguin DV. Fluorinated polyhedral oligomeric silsesquioxane nanoparticles to boost the dirt repellence of high-pressure laminates. *Chem Eng J* 2016; 301: 362-370.
8. Adam WD, Ott JD, Scholl F, Schön MD and Wolf A. *Melamine formaldehyde impregnating resins for foils and edges*. Patent 0710682 A3, European, 2000.
9. Henriques A, Paiva N, Bastos M, Martins J, Carvalho L and Magalhães FD. Improvement of storage stability and physicochemical properties by addition of benzoguanamine in melamine-formaldehyde resin synthesis. *J Appl Polym Sci* 2017; 134: 1-11.
10. Wu L, Ngian S, Chen Z and Xuan D. Quantitative test method for evaluation of anti-fingerprint property of coated surfaces. *Appl Surf Sci* 2011; 257: 2965-2969.
11. du Fresne von Hohenesche C, Schmidt DF and Schädler V. Nanoporous Melamine−Formaldehyde Gels by Microemulsion Templating. *Chem Mater* 2008; 20: 6124-6129.
12. Watt W and West H. *Processes of preparing water-soluble melamine-formaldehyde resins and products thereof*. Patent 2529856 A, USA, 1950.
13. Siriviriyanun A and Imae T. Solvo-affinity property of glass surfaces modified by self-assembled monolayers of organic and/or inorganic chemicals. *J Taiwan Inst Chem E* 2014; 45: 3090-3098.

CHAPTER 6

CHAPTER 6 – DETERMINATION OF RESIN AND MOISTURE CONTENT IN MELAMINE-FORMALDEHYDE PAPER USING NEAR INFRARED SPECTROSCOPY[1]

6.1. ABSTRACT

This paper describes the use of NIR spectroscopy as a tool for the determination of moisture and resin content on papers impregnated with melamine-formaldehyde resins for high-pressure laminate production. The papers had different colours and grammages.

The NIR analysis range comprised wavelengths between 12000 cm^{-1} and 4000 cm^{-1}. Several multivariate calibration procedures and pre-processing techniques were tested for selection of the best spectral interval, including iPLS, fiPLS and siPLS. The performance of calibration models was evaluated computing the root mean squared error of cross-validations (RMSECV) and the coefficient of determination (R^2).

An external validation procedure was done using different decorative papers (red, pearl, yellow, violet and pale green). The performance of the best models was compared using the statistical criterion RMSEP (root mean square error of prediction). It was shown that the developed models can be applied in the determination of resin content independently of the grammage and colour of the papers. However, regarding the volatile content, the models seemed to be affected by external factors, such as the presence of dyes and pigments, and were only applicable to papers having spectra similar to those used in the calibration model.

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[1] Henriques A, Gonçalves M, Paiva N, Ferra JM, Martins J, Magalhães FD and Carvalho LH. Determination of resin and moisture content in melamine-formaldehyde paper using near infrared spectroscopy. *J Near Infrared Spectrosc* 2017; 25: 311-323.\

6.2. INTRODUCTION

High-pressure laminates (HPL), manufactured with paper and thermosetting resins, are a value-added product that have been increasingly used for home and commercial surfaces. Three types of paper are used in the manufacture of HPL: *kraft*, decorative and overlay. The *kraft* paper is impregnated with phenolic resin and used in the lower layers of the HPL. It provides mechanical and moisture resistance to the laminate. The decorative and overlay papers are impregnated with melamine-formaldehyde resin, which, unlike phenolic resin, is colourless. The decorative paper is responsible for the aesthetic aspect of the HPL (coulor and pattern), while the overlay, if used, provides improved abrasion resistance. Typically, an HPL is obtained by pressing a set of 4 *kraft* sheets topped with one decorative and one (optional) overlay paper, at 80-100 bar and 140-150 °C. The hot-pressing procedure promotes chemical curing of the impregnation resins leading to strong adhesion of the sheets and formation of a hard and mechanically resistant surface.

When the decorative paper is impregnated with resin it is essential to measure the volatile and resin contents, which ensure the quality of the final HPL. Resin content directly influences the visual appearance of the HPL since an appropriate amount of resin in the paper is necessary to form a homogeneous surface during hot-pressing. On the other hand, the volatile content indicates whether the paper has been dried properly. If the volatile content is too high the sheets can stick together when being piled before being sent to the hot press for curing. If this parameter is too low, the paper may have been dried excessively after impregnation and the resin may have reacted prematurely and inter-sheet bonding during the curing process may be compromised [1,2]. These parameters are currently measured by operators by sample weighing. This is time consuming and subject to operator and equipment error.

Near infrared (NIR) spectroscopy is an interesting approach for characterizing resin-impregnated paper, due to its non-destructive nature, straightforward data collection procedure, short processing time, and accuracy. This technology has been successfully applied in different fields such as pharmaceutical [3,4], forestry [5-7], cosmetics [8], industrial chemistry [9,10] and others.

So far, few studies have been done on the use of NIR for characterizing impregnated paper. Dessipri et al. [11] used the NIR technology to compare NIR spectra of a paper recently impregnated with resin and spectra of artificially aged impregnated paper. Very different spectra were obtained from aged and recently impregnated papers. These changes were attributed to the difference in resin content (RC) and moisture content (VC) of the samples. A methodology for measuring the volatile content on laminating paper products was reported by Nakos and co-workers, but lacked information on method reproducibility [12].

NIR spectroscopy must be combined with chemometrics in order to extract maximum information. Some of the techniques include PCA (Principal Component Analysis), DA (Discriminant Analysis) and PLS (Partial Least Squares) [3]. In the PLS approach the regressions are computed with least squares algorithms. The goal is to establish a linear relation between two matrices, the spectral data X and the reference values Y. This technique models both X and Y in order to find out the variables in X matrix that will best describe the Y matrix [3]. However, the full spectrum of the PLS model can be easily disturbed by irrelevant components, which influence the quality and precision of the calibration model. Thus, selecting an appropriate spectral region is important. In recent years, both theoretical and experimental evidence have been published to prove that spectral region selection can significantly improve the performance of the full-spectrum techniques, such as: interval PLS (iPLS), forward iPLS (fiPLS) and synergy iPLS (siPLS) [13,14].

Pre-processing of the data must be performed prior to PLS modelling, in order to minimize undesirable scatter effects that influence the recorded sample spectra [15].

The aim of this work was to determine the feasibility of using FT-NIR spectroscopy combined with different PLS methods and pre-processing techniques for the determination of resin and moisture contents in decorative papers impregnated with melamine-formaldehyde resin. The study includes papers of different colours and grammages.

6.3. EXPERIMENTAL

6.3.1. Materials

A commercial melamine-formaldehyde resin, impregnation additives (acid catalyst, release agent and surfactant) and impregnated decorative papers with different colours and grammage (red, 100 g/m^2; yellow, 100 g/m^2; violet, 82 g/m^2; pearl, 91 g/m^2; pale green, 91 g/m^2) were all supplied by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal).

6.3.2. Impregnated Paper

Paper impregnation - Red paper sheets of 21 × 30 cm^2 were impregnated with the commercial resin using additives (acid catalyst, release agent and surfactant). All papers were impregnated in a two-step processes consisting of two baths. The paper was fully impregnated in the first bath and then oven-dried at 140 °C. In the second bath, the sheets were impregnated only on the front side and resubmitted to an oven at 140 °C. The latter procedure, designated coating, ensured good resin impregnation in the front side of the paper. In both cases the drying time was optimized in order to obtain the desired resin and volatile contents.

Industrially impregnated papers have a narrow range of variability in terms of resin and volatile content (normally 54-56 % for resin content and 6-7 % for volatile content), due to the tight control of process variables. In order to increase the range of calibration of these two parameters, some decorative paper samples were manually impregnated and included in the model.

6.3.3. Calibration and Validation Samples

A total of 105 samples of impregnated decorative red paper (impregnated industrially and manually) were used for the resin content calibration. The resin contents ranged from 43.6 % to 58.5 %. Regarding volatile content, 87 samples of impregnated decorative red paper were used for the calibration of volatile content (once again impregnated manually and industrially) within a range from 3.1 % to 10.2 % related to the amount of volatile content.

Sets of impregnated decorative papers with different colours were used for validation analysis, namely: red with 100 g/m^2 (30 samples), yellow with 100 g/m^2 (33 samples), violet with 82 g/m^2 (29 samples), pearl coulor of with g/m^2 (24 samples) and pale green colour with 91 g/m^2 (29 samples). All impregnated papers for the validation set had a resin content within the range of 54-56 % and a volatile content of 6-7 %. These ranges are within the industrial range.

In the case of resin content, the determination was accomplished by differential weighing after the impregnation. For the volatile content the determination of the residual moisture content (volatile content) was also accomplished by differential weighing, but in this case after a 5-minute drying at 160 °C.

6.3.4. NIR Equipment and Software

The samples were scanned using a spectrometer Matrix-F Bruker with a probe QR400-7-VIS/BX Premium 400 μm Reflection from Ocean Optics (https://oceanoptics.com/product-category/nirquest-series/). The spectrum for each paper was recorded in the wavenumber range of 12000 - 4000 cm^{-1} by signal averaging of 64 scans at a resolution of 16 cm^{-1}. For each paper sample three NIR spectra were collected randomly and averaged. The reflection probe was placed directly on the paper samples for spectra collection.

The chemometric analysis was processed using iToolbox for Matlab (www.models.life.ku.dk/itoolbox) [16].

Principal component analyses (PCA) was performed using OPUS QUANT 2 (Bruker).

6.3.5. Data Analysis

Selection of wavelength regions by different PLS models

Partial least-squares (PLS) - Partial least-squares (PLS) is a multivariate data analytical technique designed to handle intercorrelated regressors. It is based on Herman Wold's general PLS principle, in which complicated, multivariate systems analysis problems are solved by a sequence of simple least-squares regressions [17]. Prior to PLS, a mean center of each spectrum was performed before any further pre-processing calculation.

Interval partial least-squares (iPLS) - The principle of this algorithm is to split the spectra into smaller equidistant regions and, afterwards, develop PLS regression models for each of the sub-intervals. Thereafter, an average error is calculated for each sub-interval and for the full-spectrum. The region with the lowest error is chosen [18].

Forward interval partial least-squares (FiPLS) - In the forward iPLS (FiPLS) algorithm the data set is split into a given number of intervals similar to iPLS, but the PLS models are built using successively improving intervals with respect to the root mean squared error of cross validation measure [18] .

Synergy interval partial least squares (SiPLS) -Synergy interval partial least squares algorithm is the expansion of the interval partial least squares algorithm. First of all, it equally divides the whole spectra into several sub-intervals, then performs a partial least squares regression through permutation and combination with different numbers and different sub-intervals [14].

Data processing

Typically, in NIR spectra the analytical information is contained in fine spectral variations that are usually dominated by features such as light scattering, background noise and baseline drift. These unwanted variations can have adverse effects on the development of a calibration [19]. Data processing techniques described below were tested as a strategy to minimize these issues.

First derivative - This technique is used to separate overlapping peaks and to correct for baseline shifts. A drawback of derivative spectra is the enhancement of noise. This drawback is avoided by smoothing the spectra with a Savistzky-Golay derivative algorithm. In this algorithm, a window is selected where the data is fitted by a first order polynomial. The central point in the window is replaced by the value of the polynomial. In this study a window of 5 points was used [20].

Standard Normal Variate (SNV) - Standard Normal Variate (SNV) is a mathematical transformation method of the spectra used to remove slope variation and to correct for scatter effects. Each spectrum is corrected individually by first centering the spectral values. Then, the centered spectrum is scaled by the standard deviation calculated from the individual spectral values [21].

Calibration models, evaluation and validation

The performance of calibration models was evaluated computing the root mean squared error of cross-validations (RMSECV) and the coefficient of determination (R^2). In RMSECV, a leave-one-sample-out cross-validation is performed: the spectrum of one sample of the training set is deleted from this set and a PLS model is built with the remaining spectra of the training set. The left-out sample is predicted with this model and the procedure is repeated with leaving out each of the samples of the training set. The RMSECV is determined according to [18]:

$$RMSECV = \sqrt{\frac{1}{I_c-1}\sum_{i=1}^{I_c}(\hat{y}_i - y_i)^2} \qquad \textbf{(6.1-1)}$$

Where $\hat{y}_i$ is the predicted value of the ith observation, y_i the measured value of ith observation and I_c is the number of samples in the training set.

The number of PLS factors required to model the data is another major parameter, which represents the optimal number of factors (or latent variables) to retain for generating a predictive model. If this value is too small, the sample information in the spectra is not fully utilized. If the value is too big, extra noise may be included in the model. Therefore, it is necessary to select an appropriate number of PLS factors [22]. In this study, the optimum number of factors was identified as the one that gave the minimum RMSECV, up to a maximum of 10.

The general goal was to obtain low values of RMSECV and high values of R^2.

Validation

The external validation set was constituted by different decorative papers (red, pearl, yellow, violet and pale green), which were not employed for the construction of the chemometric model, allowing for a true assessment. In this sense, the performance of models developed with different strategies was compared using a statistical criterion, the RMSEP (root mean square error of prediction). This is determined, according to [18]:

$$RMSEP = \sqrt{\frac{1}{I_c}\sum_{i=1}^{I_c}\left(\hat{y}_i - y_{i,ref}\right)^2} \qquad \textbf{(6.1-2)}$$

Where $\hat{y}_i$ and $y_{i,ref}$ are the prediction and reference value for sample i and I_c is the number of samples in the training.

Several algorithms were studied for different spectra interval divisions and interval combinations. For each PLS based methodology, the pretreatment of spectra was applied, including: no preprocessing, first derivative and first derivative + SNV. Figure 6.1.1. shows a schematic diagram of all the methodologies studied to develop the calibration model of the resin and moisture content of red decorative papers.

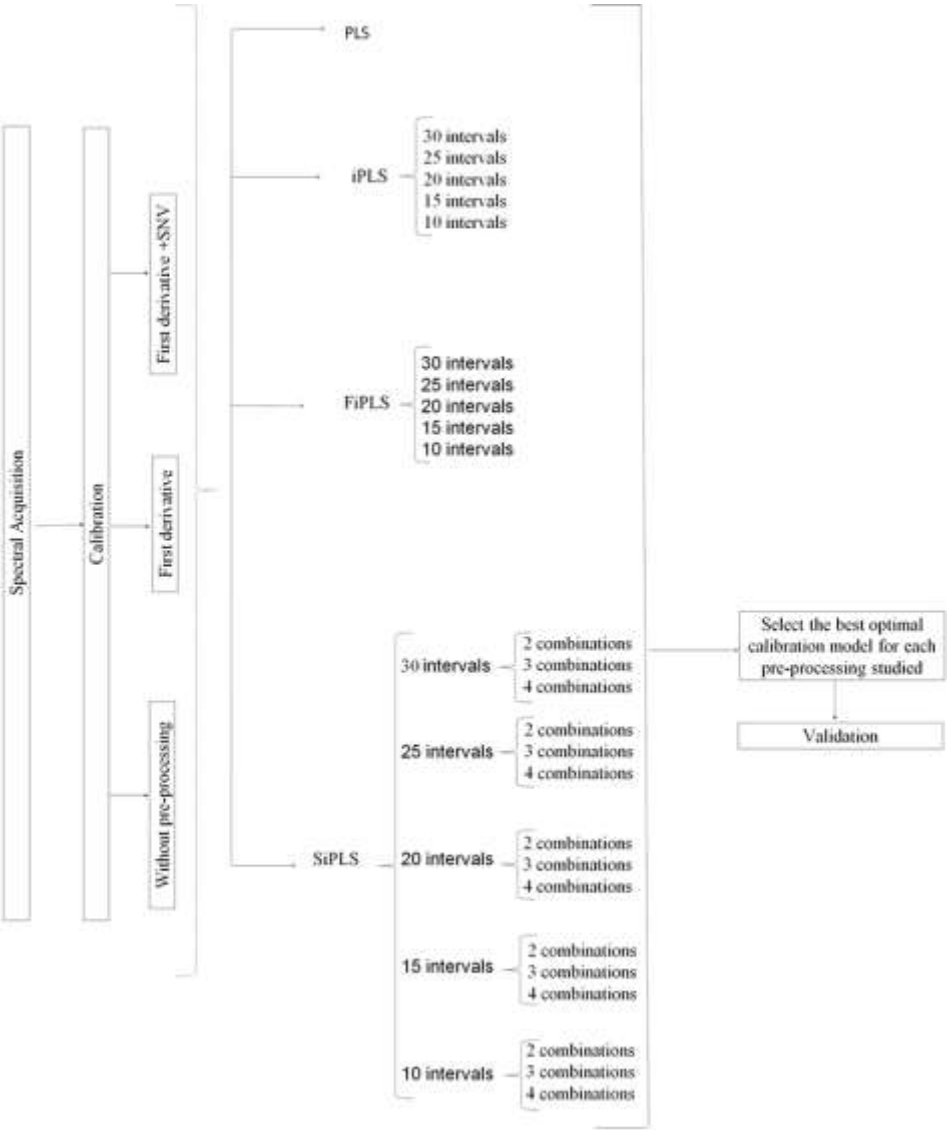


Figure 6.1.1 - Schematic diagram showing all the methodologies used during the calibration.

6.4. RESULTS AND DISCUSSION

Figure 6.1.2 a) shows a spectrum obtained for red decorative paper impregnated with melamine-formaldehyde resin. Pronounced bands are located in the regions between 7500-6000 cm^{-1} and 5200-4000 cm^{-1}. The peaks at 6803 cm^{-1} and 4787 cm^{-1} can be assigned to O-H stretching and C-H deformation of cellulose and hemicellulose or methylene vibrations. The peak at 5020 cm^{-1} to the O-H deformation vibration of water [23]. Between 6900-6450 cm^{-1} melamine shows three strong characteristics peaks. Of these, the peak at 6805 cm^{-1} is the N-H combination band from primary amides [24]. In the region 5000-4000 cm^{-1} the peaks can be assigned to: N-H bending, at 5080-4980 cm^{-1}, combinations vibrations of C-H at 4436 cm^{-1}, and combinations vibrations of N-H at 4642 and 4549 cm^{-1} [25].

Figure 6.1.2 b) and Figure 6.1.2 c) show the spectrum after the application of first derivative and first derivative combined with SNV pre-processing's, respectively. With the use of first derivative the overlapping peaks are separated. While the SNV eliminates linear and quadratic trends over the whole spectrum [26].

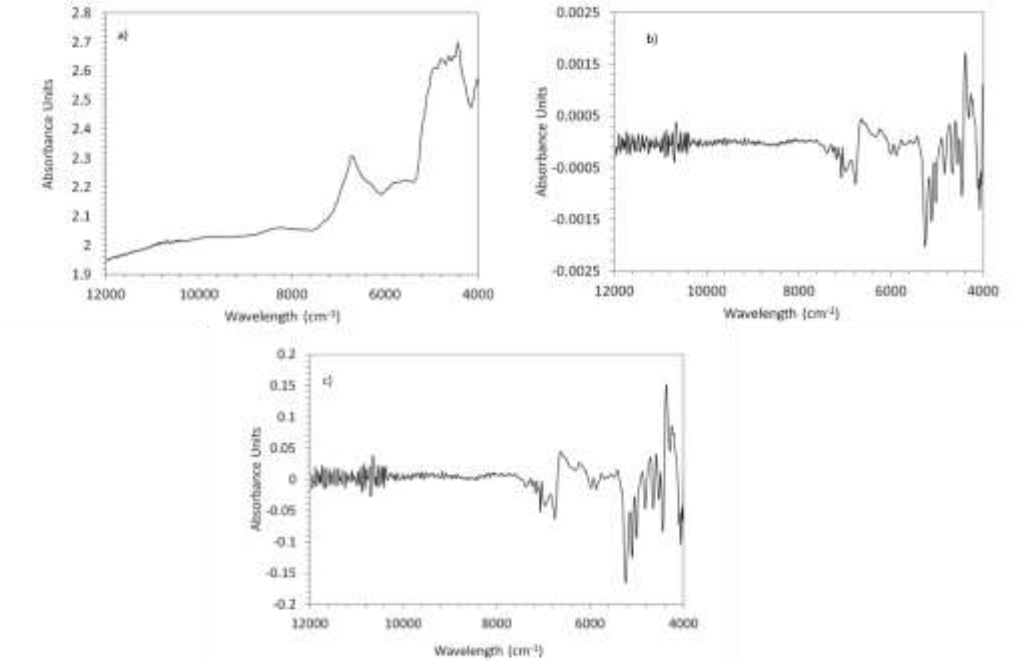


Figure 6.1.2 - Spectrum obtained for the décor paper a) without pre-processing; b) with first derivative and c) with first derivative + SNV pre-processings.

6.5. SELECTION OF SPECTRAL INTERVAL AND DATA PRE-PROCESSING METHOD FOR RESIN CONTENT DETERMINATION

Table 6.1.1, Table 6.1.2 and Table 6.1.3 summarize the results achieved for all the methodologies applied during the calibration of the resin content in decorative paper. For the two different pre-processing approaches studied and also without any pre-processing, the best results obtained (in terms of highest R^2 and lowest RMSECV) are highlighted in grey colour in the tables.

When no data pre-processing was used, the best results were achieved by using SiPLS with 30 intervals and 4 band combinations as calibration model with a R^2 and a RMSECV of 87.13 and 0.00518, respectively.

The use of first derivative did not improve the calibration model for the SiPLS methodology with 30 intervals and 4 band combinations and no pre-processing, yielding a R^2 of 86.25 and a RMSECV of 0.00535. Using the first derivative with SNV, the best calibration model was improved using SiPLS methodology with 20 intervals and 4 combinations, with a R^2 of 87.59 and a RMSECV of 0.00509.

Regarding the best calibrations models, the use of different pre-processings resulted in selection of different spectral interval. Without pre-processing, the selected regions pertain to 5886-6148 cm^{-1}, 6696-6958 cm^{-1}, 8045-8309 cm^{-1} and 8848-9103 cm^{-1}. The regions obtained with the use of first derivative are 5346-5608 cm^{-1}, 5885-6148 cm^{-1}, 6696-6958 cm^{-1} and 6966-7228 cm^{-1}. Finally, using the first derivative with SNV the calibration model corresponds to regions 4798-5192 cm^{-1}, 5600-5994 cm^{-1} and 8007-8400 cm^{-1}.

When no pre-processing is used, the spectral interval obtained are related mostly to vibrations of C-H of lignin and cellulose or to the methylene linkage (8848-9103 cm^{-1}), to the basic vibrations of NH and water presence (6696-6958 cm^{-1}), and to the first overtone of $2\nu NH_{sym}$ (5886-6148 cm^{-1}).

With the use of first derivative pre-processing the wavenumbers obtained are similar, corresponding to vibrations related to the water presence (5345-5608 cm^{-1}, 6696-6958 cm^{-1} and 6966-7228 cm^{-1}). The two latter regions are also related to basic vibrations of N-H and the first overtone $2\nu NH_{sym}$. Region 5885-6148 cm^{-1} can be associated to the first overtone 2ν $CH_{2,ass}$.

Regarding the use of the first derivative with SNV, the selected regions are related to the s-triazine ring of the melamine (4798-5192 cm^{-1}), and the other two bands are related with the first and second overtone of C-H [27,28].

Table 6.1.1 - Selection of the best spectral interval by PLS, iPLS, FiPLS and SiPLS for the prediction of the resin content, without the use of any pre-processing.

	Method	Intervals	Combinations	Region	RMSECV(%)	R^2	PLS factors
Without pre-processing	PLS				0.007	0.76	1
	iPLS	30		5	0.006	0.85	4
		25		4	0.006	0.84	5
		20		3	0.006	0.84	5
		15		3	0.006	0.84	4
		10		2	0.006	0.84	4
	FiPLS	30		5, 9, 16, 19, 20, 23	0.005	0.86	4
		25		4, 9, 14, 16, 19	0.006	0.85	6
		20		3, 11	0.006	0.85	5
		15		3, 8, 12	0.006	0.84	5
		10		2	0.006	0.84	4
	SiPLS	30	2	6, 11	0.005	0.86	9
			3	8, 11,16	0.005	0.86	7
			4	8, 11, 16, 19	0.005	0.87	7
		25	2	7, 9	0.005	0.86	6
			3	3, 4, 9	0.005	0.86	5
			4	6, 9, 16, 18	0.005	0.86	5
		20	2	3, 11	0.006	0.85	5
			3	5, 7, 11	0.005	0.86	5
			4	5, 7, 11, 12	0.005	0.86	5
		15	2	2, 8	0.006	0.85	5
			3	2, 9, 12	0.006	0.85	5
			4	4, 6, 10, 13	0.006	0.85	5
		10	2	2, 8	0.006	0.84	5
			3	2, 7, 8	0.006	0.84	5
			4	3, 4, 6, 8	0.006	0.85	5

Table 6.1.2 - Selection of the best spectral interval by PLS, iPLS, FiPLS and SiPLS for the prediction of the resin content, using the first derivative as pre-processing.

	Method	Intervals	Combinations	Region	RMSECV(%)	R^2	PLS factors
First Derivative	PLS				0.007	0.78	1
	iPLS	30		5	0.006	0.84	3
		25		4	0.006	0.84	3
		20		3	0.006	0.84	3
		15		2	0.006	0.84	3
		10		2	0.006	0.84	3
	FiPLS	30		5, 11, 13	0.006	0.85	4
		25		3, 4, 9	0.006	0.85	4
		20		2, 3, 7	0.006	0.85	3
		15		2, 6	0.006	0.85	3
		10		2, 5, 7	0.006	0.84	3
	SiPLS	30	2	8, 11	0.005	0.86	5
			3	5, 11, 13	0.006	0.85	4
			4	5, 8, 11, 12	0.005	0.86	10
		25	2	3, 9	0.006	0.85	6
			3	3, 4, 9	0.006	0.85	4
			4	3, 4, 9, 14	0.006	0.85	4
		20	2	2, 3	0.006	0.85	3
			3	2, 3, 7	0.006	0.85	3
			4	2, 3, 7, 13	0.006	0.85	3
		15	2	2, 6	0.006	0.85	3
			3	2, 6, 10	0.006	0.85	3
			4	2, 6, 8, 10	0.006	0.85	3
		10	2	2, 5	0.006	0.84	3
			3	2, 5, 7	0.006	0.84	3
			4	4, 5, 6, 7	0.006	0.84	3

Table 6.1.3 - Selection of the best spectral interval by PLS, iPLS, FiPLS and SiPLS for the prediction of the resin content, using the first derivative combined with SNV as pre-processing.

First Derivative + SNV	Method	Intervals	Combination	Region	RMSECV(%)	R^2	PLS factors
	PLS				0.007	0.75	1
	iPLS	30		5	0.006	0.83	2
		25		7	0.006	0.82	2
		20		4	0.006	0.81	5
		15		2	0.006	0.83	3
		10		3	0.006	0.82	2
	FiPLS	30		5, 11, 15, 16	0.005	0.86	7
		25		7, 9	0.006	0.85	3
		20		4, 7	0.006	0.84	4
		15		2, 6, 8, 13	0.006	0.85	3
		10		1, 2, 3, 4	0.006	0.84	4
	SiPLS	30	2	8, 11	0.006	0.85	3
			3	5, 11, 15	0.005	0.86	5
			4	6, 11, 15, 19	0.005	0.86	8
		25	2	7, 9	0.006	0.85	4
			3	2, 3, 4	0.006	0.85	3
			4	4, 6, 7, 14	0.005	0.86	6
		20	2	2, 3	0.006	0.85	3
			3	3, 5, 11	0.005	0.88	7
			4	3, 5, 10, 11	0.005	0.87	7
		15	2	2, 8	0.006	0.84	3
			3	2, 6, 13	0.006	0.85	3
			4	2, 4, 6 ,13	0.005	0.86	3
		10	2	1, 2	0.006	0.84	6
			3	1, 2, 4	0.006	0.84	6
			4	1, 2, 4, 5	0.006	0.84	5

6.6. SELECTION OF SPECTRAL INTERVAL AND DATA PRE-PROCESSING METHOD FOR VOLATILE CONTENT DETERMINATION

Regarding volatile content, for the three different pre-processings studied the best results obtained are once again highlighted in a grey colour, using the same criteria for the resin content method (higher R^2 and lower RMSECV) in tables Table 6.1.4,Table 6.1.5 and Table 6.1.6.

For all pre-processing approaches considered, the best calibration model was obtained using FiPLS with 30 intervals. It is interesting to notice that for this property the use of pre-processings does not enhance the results. When no data pre-processing was used, the best results were achieved with a R^2 and a RMSECV of 0.92 and 0.38, respectively. With the use of data pre-processing, first derivative led to R^2 of 0.88 and RMSECV of 0.45, while the use of first derivative with SNV led to R^2 of 0.88 and RMSECV of 0.44.

Concerning the spectral intervals, without pre-processing the best calibration model used the regions 5076-5338 cm^{-1}, 5616-5878 cm^{-1}, 5886-6148 cm^{-1}, 6966-7228 cm^{-1}, 10160-10414 cm^{-1} and 10422-10767 cm^{-1}. With the use of first derivative, the regions changed, corresponding to 5076-5338 cm^{-1}, 5346-5608 cm^{-1}, 6696-6958 cm^{-1}, 8045-8308 cm^{-1}, 8586-8840 cm^{-1}, 9635-9890 cm^{-1}. For the first derivative with SNV the selected regions were 4536-4798 cm^{-1}, 5076-5338 cm^{-1}, 7236-7498 cm^{-1} and 8046-8309 cm^{-1} [27,28].

Table 6.1.4 - Selection of the best spectral interval by PLS, iPLS, FiPLS and SiPLS for the prediction of the volatile content, without the use of any pre-processing.

	Method	Intervals	Combination	Region	RMSECV(%)	R^2	PLS factors
Without pre-processing	PLS				0.5	0.85	10
	iPLS	30		12	0.7	0.72	4
		25		5	0.5	0.85	4
		20		4	0.5	0.85	7
		15		3	0.5	0.85	5
		10		2	0.5	0.84	6
	FiPLS	30		5, 7, 8, 13, 24, 25	0.4	0.92	7
		25		2, 5, 6	0.4	0.89	5
		20		4, 5, 6, 17	0.7	0.90	6
		15		3, 4, 9, 10	0.4	0.91	7
		10		2, 3, 4, 5, 8	0.4	0.90	6
	SiPLS	30		5, 8	0.5	0.87	7
				3, 5, 7	0.4	0.90	6
				5, 7, 8, 25	0.4	0.91	6
		25		2, 5	0.4	0.88	5
				2, 5, 6	0.4	0.89	5
				5, 6, 7, 20	0.4	0.91	5
		20		4, 5	0.4	0.88	4
				4, 5, 17	0.4	0.89	4
				4, 5, 6, 16	0.4	0.91	6
		15		3, 4	0.5	0.88	7
				3, 4, 10	0.4	0.90	7
				2, 4, 6, 12	0.4	0.91	8
		10		2, 3	0.5	0.87	5
				3, 4, 8	0.4	0.89	4
				2, 4, 5, 8	0.4	0.89	6

Table 6.1.5 - Selection of the best spectral interval by PLS, iPLS, FiPLS and SiPLS for the prediction of the volatile content, using the first derivative as pre-processing.

	Method	Intervals	Combination	Region	RMSECV (%)	R^2	PLS factors
First derivative	PLS				0.7	0.74	10
	iPLS	30		5	0.7	0.68	4
		25		5	0.7	0.70	7
		20		4	0.6	0.76	8
		15		3	0.6	0.77	7
		10		2	0.6	0.76	5
	FiPLS	30		5, 6, 11, 16, 22	0.4	0.88	10
		25		5, 7, 8, 9, 13	0.5	0.87	10
		20		4, 6, 8	0.5	0.85	6
		15		2, 3, 5, 8	0.5	0.83	5
		10		2, 4, 5	0.6	0.82	5
	SiPLS	30	2	3, 11	0.6	0.78	4
			3	5, 6, 11	0.5	0.83	7
			4	5, 6, 11, 18	0.5	0.85	8
		25	2	5, 9	0.5	0.83	6
			3	5, 8, 9	0.5	0.54	6
			4	5, 8, 9, 12	0.5	0.86	6
		20	2	4, 6	0.6	0.81	6
			3	4, 6,8	0.5	0.85	6
			4	4, 10, 11, 14	0.5	0.85	8
		15	2	2, 3	0.6	0.81	5
			3	3, 5, 6	0.5	0.82	5
			4	3, 5, 6, 8	0.5	0.84	6
		10	2	2, 4	0.6	0.81	5
			3	4, 5, 6	0.6	0.82	4
			4	2, 3, 4, 5	0.6	0.82	5

Table 6.1.6 - Selection of the best spectral interval by PLS, iPLS, FiPLS and SiPLS for the prediction of the volatile content, using the first derivative combined with SNV as pre-processing.

	Method	Intervals	Combination	Region	RMSECV(%)	R^2	PLS factors
First derivative + SNV	PLS				0.6	0.76	10
	iPLS	30		5	0.6	0.78	7
		25		4	0.7	0.75	7
		20		3	0.7	0.73	3
		15		3	0.6	0.80	5
		10		2	0.5	0.84	8
	FiPLS	30		3, 5, 13, 16	0.4	0.88	9
		25		3, 4, 11, 14	0.5	0.87	8
		20		3, 9, 12, 14	0.5	0.88	7
		15		2, 3, 8	0.5	0.86	4
		10		2, 4, 5	0.5	0.86	4
	SiPLS	30	2	2, 5	0.5	0.85	10
			3	5, 16, 17	0.5	0.88	10
			4	3, 5, 13, 16	0.4	0.88	8
		25	2	04, 11	0.5	0.84	4
			3	3, 5, 9	0.5	0.87	5
			4	3, 5, 9, 11	0.5	0.87	5
		20	2	3, 9	0.5	0.86	7
			3	3, 9, 14	0.5	0.87	5
			4	3, 9, 12, 14	0.5	0.88	7
		15	2	2, 3	0.5	0.86	4
			3	2, 3, 8	0.5	0.86	4
			4	2, 3, 5, 7	0.5	0.86	4
		10	2	2, 4	0.5	0.85	4
			3	2, 4, 5	0.5	0.86	4
			4	1, 2, 4, 5	0.5	0.86	8

6.7. VALIDATION

In order to validate the developed models, the best calibrations were applied to decorative paper with different resin (54 -56 %) and volatile contents (6 -7 %) and, additionally, with different colours and grammages. The results are summarized in Table 6.1.7 and Table 6.1.8.

Table 6.1.7 - RMSEP values (%) of the developed models for the resin content.

Colour of validation sample	Pre-Processing		
	Without Pre-processing	First Derivative	First Derivative + SNV
Red	0.006	0.02	0.008
Pale Green	0.12	0.04	0.03
Pearl Colour	0.09	0.01	0.04
Yellow	0.03	0.04	0.007
Violet	0.56	0.04	0.02

Table 6.1.8 - RMSEP values (%) of the developed models for the volatile content.

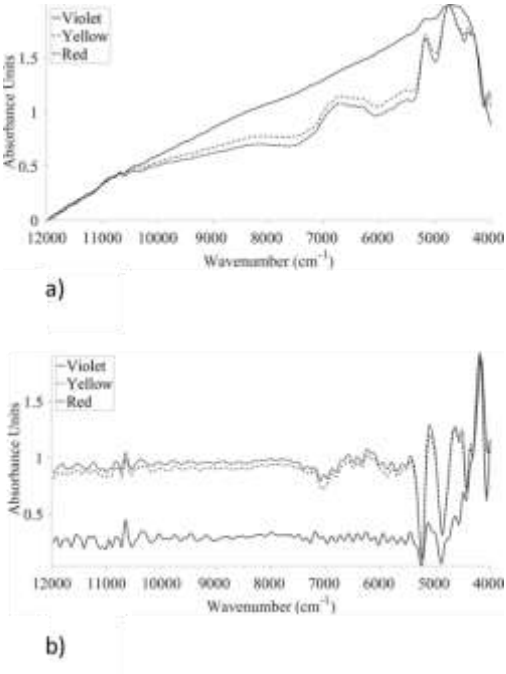
Colour of validation sample	Pre-Processing		
	Without Pre-processing	First Derivative	First Derivative + SNV
Red	4.55	2.74	0.77
Pale Green	1.36	5.13	0.84
Pearl Colour	3.70	4.52	0.10
Yellow	8.21	3.82	0.79
Violet	20.6	3.70	6.33

For the two studied parameters, the use of the first derivative with SNV pre-processing resulted in the lowest RMSEP values in the validation process, for almost all of the papers studied. This result may be due to the separation of the overlapping peaks and to the removal of slope variations provided by first derivative calculation and by the removal of differences between samples due to the use of SNV.

The results showed that the resin content model, developed for red paper, can be applied to papers with different colours and grammages, without affecting accuracy. However, the same conclusion cannot be drawn for the volatile content. The use of the first derivative combined with SNV results in the lowest RMSEP values in the validation process for the volatile content. However, the obtained values are less accurate than the ones obtained for the resin content, for the validation sets. In addition, it is clear that properties of papers with violet colour are not accurately predicted by the model. In order to understand this result, the spectral intervals obtained were analysed in both models, to ensure that those selections were not influenced by other parameters apart from the ones under study, such as the presence of particular pigments or dyes. For that, papers with different colours (red, yellow and violet) were compared with and without resin impregnation.

The spectrum of the violet paper spectrum was significantly different from the spectra of the yellow and red papers in all wavenumber ranges. Spectral shape and peak intensity differences were not completely attenuated by the use of pre-processings (Figure a). This explains why the PLS model was not able to predict violet paper properties as well as for other paper colours.

Figure 6.1.4 shows a PCA scores plot of NIR spectra with pre-processings from different papers with a total of 5 colours. 10 spectra were used for each colour. The first principal component (PC1) explained 68.56 % of the variances between samples. The violet coloured paper appeared in a cluster far to the right in relation to the other papers, confirming that the pre-processed spectra of this paper was different from the rest. Different colour pigments can have different chemical compositions, which may interfere with the NIR spectra. This results shows that violet pigments absorb in the NIR range, making the model inapplicable for this kind of paper.



a)

b)

Figure 6.1.3 - Spectra of red, yellow and violet non-impregnated papers a) without pre-processing and b) after first derivative and SNV.

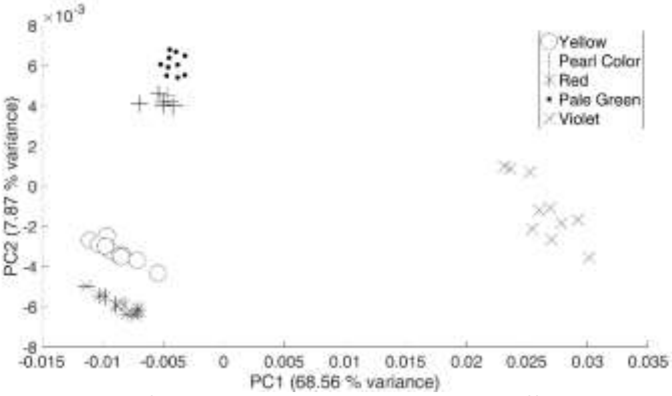


Figure 6.1.4 - Score plot of principal component analysis using different coloured papers

6.8. CONCLUSIONS

In order to develop calibration models for the determination of resin and volatile content in decorative papers impregnated with melamine-formaldehyde resins, several calibration techniques were used such as

PLS, iPLS, FiPLS and SiPLS. The most appropriate model was selected by testing different intervals and combinations of intervals and by evaluating the lowest RMSECV. In addition, this approach was employed with spectra without any pre-processing, and with spectra that were subjected to the use of the first derivate and also the first derivative combined with SNV.

Regarding the resin content model, the best result was achieved with the use of the first derivate combined with SNV as pre-processing and the SiPLS with 20 intervals and 3 combinations model. This model achieved an R^2 of 0.88 and an RMSECV of 0.005. Regarding the volatile content, the best model was obtained without the use of any pre-processing and choosing FiPLS with 30 intervals as methodology resulting in a R^2 of 0.92 and a RMSECV of 0.38.

The developed models were applied to an external validation set composed of decorative papers with different colours and grammages. Concerning the results achieved in the validation process, it was found that the use of the first derivative combined with SNV as pre-processing allows for accurate determination of resin content within the range of all the papers studied. This is a relevant result, since it does not imply having to adapt a model to each type of paper used. However, for the volatile content it was found that the developed models were only applicable to papers with a spectrum similar to those used in the calibration, since the quality of the results is highly affected by external factors associated with the colour of the papers.

6.9. ACKNOWLEDGEMENTS

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6.10. REFERENCES

1. Nemli G and Usta M. Influences of some manufacturing factors on the important quality properties of melamine-impregnated papers. *Build Environ* 2004; 39: 567-570.

2. Kohlmayr M, Zuckerstätter G and Kandelbauer A. Modification of melamine-formaldehyde resins by substances from renewable resources. *J Appl Polym Sci* 2012; 124: 4416-4423.

3. Roggo Y, Chalus P, Maurer L, Lema-Martinez C, Edmond A and Jent N. A review of near infrared spectroscopy and chemometrics in pharmaceutical technologies. *J Pharm Biomed Anal* 2007; 44: 683-700.

4. Reich G. Near-infrared spectroscopy and imaging: Basic principles and pharmaceutical applications. *Adv Drug Deliv Rev* 2005; 57: 1109-1143.

5. Meder R, Stahl W, Warburton P, Woolley S, Earnshaw S, Haselhofer K, van Langenberg K, Ebdon N and Mulder R. At-line validation of a process analytical technology approach for quality control of melamine-urea-formaldehyde resin in composite wood-panel production using near infrared spectroscopy. *Anal Bioanal Chem* 2017; 409: 763-771.

6. Meder R and Tsuchikawa S. Guest editorial: Coming full circle: back to basics in the application of near infrared spectroscopy to the forest and wood products sector. *J Near Infrared Spectrosc* 2016; 24: v-vii.

7. Carvalho LH, Magalhães FD, Ferra J, Martins J and Henriques A. Near-infrared spectroscopy in the wood-based products industry. In: Cozzolino D (ed) *Infrared spectroscopy: theory, developments and applications*. New York: Nova Publishers, 2014.

8. Grunewald H, Kurowski C, Timm D, Grummisch U and Meyhack U. Rapid non-destructive raw material identification in the cosmetic industry with near-infrared spectroscopy. *J Near Infrared Spectrosc*; 6: 215-222.

9. Henriques A, Ferra JM, Cruz P, Martins J, Magalhães FD and Carvalho LH. Viscosity determination of amino resins during synthesis using near-infrared spectroscopy. *Int Wood Prod J* 2012; 3: 64-66.

10. Henriques A, Cruz P, Ferra JM, Martins J, Magalhães FD and Carvalho LH. Determination of melamine content in amino resins by near-infrared spectroscopy. *Wood Sci Technol* 2013; 47: 939-948.

11. Dessipri E, Minopoulou E, Chryssikos GD, Gionis V, Paipetis A and Panayiotou C. Use of FT-NIR spectroscopy for on-line monitoring of formaldehyde-based resin synthesis. *Eur Polym J* 2003; 39: 1533-1540.

12. Nakos P and Minopoulou E. Novel Process Control for the Resin and Panel Industries Based on FT-NIR. *5th European Wood-Based Panel Symposium*. Hanover 2006, p. 1-6.

13. Xiaobo Z, Jiewen Z, Povey MJW, Holmes M and Hanpin M. Variables selection methods in near-infrared spectroscopy. *Anal Chim Acta* 2010; 667: 14-32.

14. Xu J, Huang F, Li Y, Chen Z and Wang Y. Rapid detection of total nitrogen content in soy sauce using NIR spectroscopy. *Czech J Food Sci* 2015; 33: 518-523.

15. Rinnan Å, Berg Fvd and Engelsen SB. Review of the most common pre-processing techniques for near-infrared spectra. *TrAC Trends in Analytical Chemistry* 2009; 28: 1201-1222.

16. Leardi R and Nørgaard L. Sequential application of backward interval partial least squares and genetic algorithms for the selection of relevant spectral regions. *J Chemom* 2004; 18: 486-497.

17. Bjørsvik H-R and Martens H. Data Analysis: Calibration of NIR Instruments by PLS Regression. In: Burns D and Ciurczak E (eds) *Handbook of Near-Infrared Analysis*. Boca Raton: CRC Press, 2007.

18. Zou X, Zhao J and Li Y. Selection of the efficient wavelength regions in FT-NIR spectroscopy for determination of SSC of ‘Fuji’ apple based on BiPLS and FiPLS models. *Vib Spectrosc* 2007; 44: 220-227.

19. Pizarro C, Esteban-Diez I, Nistal A and Gonzalez-Saiz J. Influence of data pre-processing on the quantitative determination of the ash content and lipids in roasted coffee by near infrared spectroscopy. *Anal Chim Acta*; 509: 217-227.

20. Luypaert J, Heuerding S, Heyden YV and Massart DL. The effect of preprocessing methods in reducing interfering variability from near-

infrared measurements of creams. *J Pharm Biomed Anal* 2004; 36: 495-503.

21. Chen Q, Zhao J, Zhang H and Wang X. Feasibility study on qualitative and quantitative analysis in tea by near infrared spectroscopy with multivariate calibration. *Anal Chim Acta* 2006; 572: 77-84.

22. Pan T, Huang W, Liu Z and Tao L. Near-Infrared Spectroscopy Analysis of Hemoglobin with Stability Based on Human Hemolysates Samples. *Am J Analyt Chem* 2012; 3: 19-23.

23. Yang Z, Zhang M, Pang X and Lv B. Classifications of Decorative Paper using Differential Reflection Spectrophotometry Coupled with Soft Independent Modeling of Class Analogy. *BioResources* 2014; 9: 2521-2528.

24. Yang Z, Han L, Wang C, Li J, Pierna JAF, Dardenne P and Baeten V. Detection of Melamine in Soybean Meal Using Near-Infrared Microscopy Imaging with Pure Component Spectra as the Evaluation Criteria. *Journal of Spectroscopy* 2016; 2016: 1-11.

25. Henriques A, Cruz P, Martins J, Ferra JM, Magalhães FD and Carvalho LH. Determination of formaldehyde/urea molar ratio in amino resins by near-infrared spectroscopy. *J Appl Polym Sci* 2012; 124: 2441-2448.

26. Terhoeven-Urselmans T. *Usefulness of Near Infrared Spectroscopy to Assess the Composition and Properties of Soil, Litter and Growing Media*. 1st ed. Kassel: Kassel University Press, 2007.

27. Schwanninger M, Rodrigues J and Fackler K. A review of band assignments in near infrared spectra of wood and wood components. *J Near Infrared Spectrosc* 2011; 19: 287-308.

28. Kasprzyk H, Jóźwiak M and Proszyk S. Application of NIR spectroscopy for analysis of amino adhesive resins applied in wood based materials. *Folia Forestalia Polonica* 2001; 32: 67-74

CHAPTER 7

CHAPTER 7 – GENERAL CONCLUSIONS AND FUTURE WORK

7.1. GENERAL CONCLUSIONS

One major objective of this thesis was to develop new impregnation resins and formulations for achieving high-pressure laminates with differentiated surface properties.

The first part of the work was focused on the introduction of benzoguanamine in melamine-formaldehyde resins for improving their storage stability. The substitution of 7.5 % of melamine resin by 16.8 % of benzoguanamine during and at the end of the condensation step, leads to a stable resin for at least 10 days. For these resins, a decrease in the amount of formed hydroxyl groups was noticed, at the same time of an increase in the amount of methylene linkages. When used for paper impregnation, these resins show similar properties to a commercial resin concerning gloss and resistance to abrasion, water vapour, impact, dry heat, and stains. From an industrial point of view, the introduction of benzoguanamine in the production of melamine formaldehyde resins can result in a reduction of additives used during the synthesis process. Consequently, it might simplify the process, allowing savings at logistics and operational levels. More than one additive is traditionally used during the synthesis process to achieve stability.

Subsequently to the previous work, another guanamine, namely caprinoguanamine, was added to the melamine-benzoguanamine-formaldehyde resin previously formulated. This addition resulted in an increase of 40 % in the hydrophobic character of the resulting HPL, when compared to the product produced with a commercial melamine-formaldehyde resin. Further addition of fluorinated compounds allowed obtaining a HPL with a contact angle of 114° for water, and 76° for a liquid fingerprint simulator, in comparison to 100° and 77°, respectively, for the standard laminate. Furthermore, other surface properties were not affected by addition of the fluorinated compound.

The third part of this work involved the application of near-infrared (NIR) spectroscopy on process quality control in high-pressure laminates production. In particular, the determination of volatile and moisture content in impregnated papers was studied. An exhaustive evaluation of numerous calibration methods and pre-processing techniques was performed. As a result, the developed models were applied to an external validation set composed of decorative papers with different colours and grammages. For all the papers studied, the developed method for resin content allows an accurate determination of this property. On the other hand, its application to the volatile content is only possible for papers with similar spectra to those used in the calibration, since the quality of the results is highly affected by external factors associated with the pigments and dyes existing in the papers. This work has shown that implementation of near-infrared spectroscopy in this industrial sector will certainly be beneficial, in what concerns waste reduction, reduction of customer complains due to non-compliant product and gains in productivity

In the whole, this thesis contributed to the improvement of the HPL industry, at resin synthesis, product functionalization and quality control levels. The latter through a promising and unexplored technique for the field.

7.2. FUTURE WORK

Industrial implementation of benzoguanamine in the synthesis of a melamine resins is a topic that should be looked into in the future. A detailed economic analysis should be performed, together with test productions at an industrial scale.

Moreover, despite the promising results achieved for high-pressure laminates (HPL) with hydrophobic and oleophobic properties, new additives should be studied, such as ethylene bis-stearamide. The latter is a long apolar carbon chain molecule, with two polar amides bonds, exhibiting interesting properties such as stability and lubricity. Literature reports show that the use of this compound with melamine formaldehyde resin can confer lubricity, which suggests that it might facilitate stain cleaning.

On the other hand, the promising use of near infrared (NIR) spectroscopy in the HPL sector can be further explored. The off-line studies show how this type of technology might be used to optimize the determination of the quality parameters in the paper impregnation process. In fact, the use of this methodology can be extended to the evaluation of other parameters of the impregnation process, such as resin cure, which has direct consequences on the surface properties of the laminate. Besides that, the on-line application of the NIR technology can contribute to important time/cost savings in an industrial scale.

As for the HPL sector in general, the introduction of nature-based products should be studied and optimized in order to allow new solutions to be found, such as black liquor, glycerol or starch. In particular, those that are cost-effective, stable, and that have the appropriate physico-chemical properties for its use in the impregnation process and, consequently, in the HPL industry. Moreover, the impregnation and pressing processes are important steps in the build-up of a HPL. Accordingly, new studies should be accomplished for impregnation in order to improve the steps required during this process. In turn, an extensive study of the temperature histories during the pressing stage could result in a better understanding of the cure process of the resins and their influence on the physico-mechanical properties of the laminate. In fact, the development of new resins may require different curing times and, consequently, the temperature and time during the pressing process should be adjusted.