Introducing new functionalities in resins for paper impregnation and cork binding

Ana Isabel Filipe Antunes

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by
Chemical Engineering Department - University of Porto
and
Chemical Department - University of Aveiro

Supervisors:
Fernão Domingos de Magalhães (UP)
Ana Barros-Timmons (UA)
Enterprise coordinator:
Nádia Tatiana Neto de Paiva

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ABSTRACT

Amino-formaldehyde resins are thermosetting polymers. These resins are characterized, after cure, by high crosslink density, high stiffness and high tensile strength. They are currently used on a wide range of products such as: abrasives, foams, impregnated paper laminates, textiles, molded compounds, and adhesives. However, this stiffness may be undesirable when a final product with some flexibility is desired, such as postformable finish foils or agglomerated cork panels.

The first aim of this thesis was obtaining an impregnation resin suitable for producing postformable finish foils, which is not possible with the traditionally used formaldehyde-based resins. This goal was met by developing an appropriate polyurethane (PU) resin. The second aim, which implied more extensive work, was the development of new formaldehyde-based resins capable of being used in production of flexible agglomerated cork panels. Agglomerated cork panels must have water resistance, E1 classification for formaldehyde content, and must not rupture when flexed on cylindrical mandrels with 9 mm diameter.

Moisture-curable polyurethanes were synthesized and used to impregnate décor paper. Raw materials were isophorone diisocyanate (IPDI) and polypropylene glycol (PPG) with different molecular weights (400, 1000, and 2000 g/mol). The influence of the NCO/OH molar ratio and polyol molecular weight on the physical properties of the resultant polymers and composite foils were investigated in detail, namely using dynamic mechanical analysis (DMA), tensile-strain testing, and contact angle measurements. The most promising polyurethane-impregnated foils were additionally tested according to European Standard EN 438-2. The surfaces showed self-healing behavior, in addition to

being highly flexible. This material is an innovative solution for finish foils, presenting distinctive properties and processing capabilities.

In the context of agglomerated cork panels, work started by studying the effect of resin nature and content of the panels properties. Commercial melamine-urea-formaldehyde (MUF) and PU resins were compared. Physical-mechanical properties, mandrel flexibility, and resistance to boiling water were evaluated. The resins' wettability on the cork surface was also evaluated. At the same resin content, panels bonded with MUF resin present considerable higher stiffness and tensile strength when compared to panels bonded with PU. On the other hand, PU resin lends resilience and water resistance to the panels, and is the only binder that can be used when panel flexibility is desired (at same 6 wt. % of resin content, MUF resin present mandrel diameter of 18 mm and PU resin 6 mm).

The work then faced the challenge of providing MUF resins with the resilience needed to provide flexibility when used in agglomerated cork panels. The first approach consisted in decreasing the high degree crosslinking of these resins by using chain-growth blockers. Caprolactam and o-p-toluenesulfonamide were added at three different steps in the synthesis process. Besides evaluation of standard properties, resins were characterized using characterized gel permeation chromatography (GPC) and Fourier-transform infrared spectroscopy (FTIR). The modified resins showed better storage stability and improved water tolerance, especially when caprolactam was employed. When used as binders in agglomerated cork panels, the blocked resins allowed for significantly better flexibility, evaluated in terms of mandrel bending test (mandrel diameter of 12 mm).

A second approach for MUF flexibility improvement consisted on introducing bulky substituents into MUF structure to obtain a less densely crosslinked, and hence more flexible structure after cure. Benzoguanamine was used to partially replace melamine in two different steps of the synthesis. Modified MUF resins were characterized using GPC, DMA, FTIR and carbon-13 nuclear magnetic resonance (^{13}C-NMR). The results suggest that benzoguanamine and its derivatives were integrated into the polymer structure. This strategy significantly improved the flexibility of agglomerated cork panels (mandrel diameter of 12 mm), while the remaining key properties of the panels were maintained. The formaldehyde content of the panels (determined according to EN120) allowed E1 classification.

The last approach followed consisted on incorporating linear segments (hydroxyl and amine terminated) in UF resin to improve the flexibility of agglomerated cork panels. Polyethylene glycols (PEGs) and polyetheramines (PEAs) with different molecular weight were tested.

The addition of PEGs with different molecular weights (106, 200 and 400 g/mol) were done to the urea-formaldehyde (UF) resins synthesis. The chemical and physical-mechanical properties of the resulting products were investigated in detail, namely using FTIR, ^{13}C-NMR, GPC, DMA analysis, adhesive bond strength, and tensile-strain testing. Using PEG with molecular weight 200 g/mol was produced a high flexible resin with good adhesion properties and agglomerated cork panels with mandrel diameter of 3 mm. However, high free formaldehyde content and poor water resistance was observed in agglomerated cork which is not desirable.

Additionally, PEAs with different molecular weights (230, 600, 900 and 2000 g/mol) were incorporated in formaldehyde-based resins. Resins were

characterized by thermal gravimetric analysis (TGA), FTIR, and ^{13}C-NMR, which analysis suggest the presence of imine linkages in new PEA-UF resin structure. Polyetheramine with molecular weight 900 g/mol yielded the most promising resin to agglomerated cork panel application, with remarkable flexibility (mandrel diameter of 9 mm) and very low formaldehyde content (E1 class, according to European Standard EN 12460-5).

The strategies followed to decrease the high crosslinking density of formaldehyde-based resins and improve flexibility of agglomerated cork panels bound with the modified resins were successful. However, the major objective outlined, was successfully achieved with just one of the developed solutions: a PEA-UF resin. The high price of PEA makes this new resin not competitive in relation to existing PU adhesives. Nonetheless, the more economical solutions developed, in particular the use of carprolactam and benzoguanamine, may find use in other applications with less demanding flexibility requirements.

SUMÁRIO

As resinas amino-formaldeído são polímeros termoendurecíveis e caracterizam-se, após cura, por elevada densidade de reticulação, elevada rigidez e elevada resistência à tração. Estas resinas são usadas numa ampla gama de produtos, tais como abrasivos, espumas, laminados de papel impregnado, têxteis, compostos moldados e adesivos. No entanto, a referida rigidez pode ser indesejável quando se pretende um produto final com alguma flexibilidade, tais como folhas de acabamento pós-moldáveis ou painéis de aglomerado de cortiça.

O primeiro objetivo desta tese foi a obtenção de uma resina de impregnação adequada para produzir folhas de acabamento pós-moldáveis, o que não é possível com as resinas à base de formaldeído usadas tradicionalmente. Este objetivo foi atingido com o desenvolvimento de uma resina de poliuretano (PU) apropriada. O segundo objetivo, que implicava um trabalho mais extenso, foi o desenvolvimento de novas resinas à base de formaldeído capazes de serem usadas na produção de painéis flexíveis de cortiça aglomerada. Os painéis de cortiça aglomerada devem ser resistentes à água em ebulição, o seu teor de formaldeído não deve ser superior à classificação E1 e não devem quebrar quando flexionados em mandris cilíndricos com 9 mm de diâmetro.

Poliuretanos curáveis à humidade ambiente foram sintetizados e utilizados na impregnação de papel decorativo. As matérias-primas foram diisocianato de isoforona (IPDI) e polipropileno glicol (PPG) com diferentes pesos moleculares (400, 1000 e 2000 g/mol). A influência da razão molar NCO/OH e do peso molecular do poliol nas propriedades físicas dos polímeros resultantes e das folhas compósitas foram estudadas em detalhe, nomeadamente usando análise mecânica dinâmica (DMA), testes de tensão-deformação e medições de ângulo de contato. Os papéis impregnados com as resinas de poliuretano mais promissoras foram adicionalmente testadas de acordo com a norma europeia EN 438-2. As superfícies apresentaram propriedades de auto-regeneração, além de serem altamente flexíveis. Este material é uma solução inovadora para folhas de acabamento, apresentando propriedades distintas.

No contexto dos painéis de cortiça aglomerada, o trabalho iniciou-se com o estudo do efeito da natureza e teor de resina nas propriedades físico-mecânicas dos painéis. Foram utilizadas resinas de melamina-ureia-formaldeído (MUF) e PU e avaliadas as propriedades físico-mecânicas, a flexibilidade no mandril e a resistência à água em ebulição dos painéis resultantes. A molhabilidade das resinas na superfície da cortiça também foi avaliada. Com o mesmo teor de resina, os painéis aglutinados com a resina MUF apresentam uma rigidez considerável e maior resistência à tração quando comparados aos painéis aglutinados com PU. Por outro lado, a resina de PU proporciona aos painéis distinta resiliência e resistência à água em ebulição, sendo o único adesivo que pode ser usado quando a flexibilidade do painel é desejada (com o mesmo teor de 6 % de resina, a resina MUF apenas consegue ser flexionado num mandril de 18 mm de diâmetro, a resina de PU consegue um mandril de 6 mm de diâmetro).

Assim, surge o desafio de desenvolver resinas MUF com a resiliência necessária para a produção de painéis flexíveis de aglomerado de cortiça. A primeira abordagem consistiu em diminuir o elevado grau de reticulação destas resinas usando bloqueadores de crescimento da cadeia polimérica. Caprolactama e o-p-toluenossulfonamida foram adicionados em três etapas diferentes do processo de síntese. Além das propriedades usuais, as resinas foram caracterizadas através de cromatografia de permeação em gel (GPC) e espectroscopia de infravermelho com transformada de Fourier (FTIR). As resinas modificadas apresentaram melhor estabilidade de armazenamento e melhor tolerância à água, especialmente na utilização da caprolactama. As resinas bloqueadas permitiram melhorar a flexibilidade dos painéis de aglomerado de cortiça produzidos com estas resinas (12 mm de diâmetro do mandril).

Uma segunda abordagem para melhorar a flexibilidade das resinas MUF consistiu na introdução de substituintes volumosos na estrutura da resina para obter uma estrutura menos densamente reticulada e, portanto, mais flexível após a cura. A benzoguanamina foi utilizada para substituir parcialmente a melamina em duas etapas diferentes da síntese. As resinas MUF modificadas foram caracterizadas utilizando GPC, DMA, FTIR e ressonância magnética nuclear de carbono 13 (^{13}C-RMN). Os resultados sugerem que a benzoguanamina e seus derivados foram integrados na estrutura do polímero. Esta estratégia melhorou a flexibilidade dos painéis de cortiça aglomerada (diâmetro do mandril de 12 mm), sendo que as restantes propriedades dos painéis foram mantidas. O teor de formaldeído dos painéis (determinado de acordo com a EN 120) permitiu a classificação E1.

A última abordagem consistiu na incorporação de segmentos lineares (terminados em grupos hidroxilo ou amino) para melhorar a flexibilidade dos painéis de cortiça aglomerados. Foram testados polietilenoglicóis (PEGs) e poliéteraminas (PEAs) com diferentes pesos moleculares.

A adição de PEGs com diferentes pesos moleculares (106, 200 e 400 g/mol) foi feita na síntese de resinas ureia-formaldeído (UF). As propriedades químicas e físico-mecânicas dos produtos resultantes foram investigadas em detalhes, nomeadamente utilizando análise de FTIR, ^{13}C-RMN, GPC, DMA, e testes de tensão-deformação. A utilização do PEG com peso molecular 200 g/mol originou uma resina altamente flexível com boas propriedades adesivas e painéis de cortiça aglomerada capazes de flexionar no mandril de diâmetro 3 mm.

Contudo, apresentaram elevado teor de formaldeído livre e pouca resistência à água em ebulição.

As PEAs com diferentes pesos moleculares (230, 600, 900 e 2000 g/mol) foram incorporadas nas resinas à base de formaldeído. As resinas foram caracterizadas por análise gravimétrica térmica (TGA), FTIR e ^{13}C-RMN, cuja análise sugere a presença de ligações imina na nova estrutura da resina PEA-UF. A poliéteramina com peso molecular 900 g/mol originou a resina mais promissora para aplicação em painéis de aglomerado de cortiça, com flexibilidade notável (9 mm de diâmetro do mandril) e muito baixo teor de formaldeído (classe E1, de acordo com a norma europeia EN 12460-5).

As estratégias seguidas para diminuir a elevada densidade de reticulação das resinas à base de formaldeído e melhorar a flexibilidade dos painéis de cortiça aglomerados ligados com as resinas modificadas foram bem sucedidas. No entanto, o objetivo principal foi alcançado com sucesso apenas com uma das soluções desenvolvidas: a resina PEA-UF. O elevado preço da PEA faz com que esta nova resina desenvolvida não seja competitiva em relação aos adesivos de PU existentes. No entanto, as soluções mais econômicas, em particular o uso de carprolactama e benzoguanamina, podem ser usadas noutras aplicações com menores exigências de flexibilidade.

RÉSUMÉ

Les résines amino-formaldéhyde sont des polymères thermodurcissables. Ces résines sont caractérisées, après le durcissement, par une densité de réticulation élevée, une rigidité élevée et une résistance à traction élevée. Actuellement, elles sont utilisées dans une large gamme de produits, tels que: abrasives, mousses, papier imprégnés pour stratifiés, textiles, produits moulés et adhésifs. Cependant, cette rigidité peut être indésirable, si un produit final avec une certaine flexibilité est désiré, tel que les décors films où les panneaux agglomérés de liège.

Le premier but de cette thèse a été d'obtenir une résine d'imprégnation convenable pour la production de papiers décors post-formables, ce que n'ai pas possible avec les résines traditionnelles à base de formaldéhyde. Ce but a été atteint avec le développement d'une résine de polyurethane (PU). Le deuxième but, ce qui a exigé un travail plus étendu, a été le développement de nouvelles résines capables d'être utilisées dans la production de panneaux agglomérés de liège. Les panneaux agglomérés de liège doivent avoir résistance à l'eau, le classement E1 pour le dégagement de formaldéhyde et ne pas casser lorsqu'ils sont pliés dans les mandrins cylindriques avec un diamètre de 9 mm.

Polyuréthanes durcis par l'humidité ont été synthétisés et utilisés pour l'imprégnation de papier décor. Isophorone diisocyanate (IPDI) et polypropylène glycol (PPG) avec différents poids moléculaires (400, 1000, et 2000 g/mol) ont été utilisé comme matières premières. L'influence du rapport molaire NCO/OH et du poids moléculaire sur les propriétés physiques des polymères résultants et des films composites a été investigué en détaille, en utilisant des méthodes comme l'analyse thermomécanique (TMA), essais de traction et des mesures d'angles de contacts. Les films de polyurethane imprégnés ont été essayés selon

la norme Européenne EN 438-2. Les surfaces ont montré un comportement auto-régénérant, en plus d’être très flexibles. Ce matériau est une solution innovante pour les décors films et ont présentés des propriétés distinctives aussi que des aptitudes de transformation.

Dans le contexte des panneaux de liège agglomérés, le travail a débuté par l’étude de l’effet de la nature et teneur de résine dans les propriétés des panneaux. Des résines melamine-urea-formaldéhyde (MUF) et PU ont été comparées. Des propriétés physico-mécaniques, flexibilité mandrin et résistance à l’eau bouillante ont été évaluées. La mouillabilité de la surface de liège a aussi été évalué. Pour la même teneur de résine, les panneaux collés avec MUF présentent une rigidité et résistance à la traction considérablement élevée par rapport avec les panneaux collés avec PU. Par contre, la résine PU donne résilience et résistance à l’eau, en étant le seul liant que peut être utilisé quand la flexibilité du panneau est désirée (pour la même teneur en résine, la résine MUF présente un mandrin avec un diamètre de 18 mm et la résine PU un mandrin de 6 mm).

Le travail a ensuite fait face au défi d’obtenir des résines MUF avec une résilience suffisante pour donner de la flexibilité lorsqu’elle est utilisée pour des panneaux agglomérés de liège. La première approche consistée à baisser le dégrée élevée de réticulation de ces résines en utilisant des bloqueurs de croissance de chaines. Caprolactame et o-p-toluènesulfonamide ont été ajoutés à trois étapes différentes du processus de synthèse. Au-delà de l’évaluation des propriétés standards, les résines ont été caractérisées par chromatographie par perméation de gel (GPC) et spectroscopie infrarouge à transformée de Fourier (FTIR). Les résines modifiées ont montré une stabilité de stockage et tolérance à l’eau améliorée. Lorsqu’elles sont utilisées comme liant dans les panneaux agglomérés de liège, les résines bloquées ont permis une flexibilité suffisamment mieux, évaluée par l´essai de flexion du mandrin (diamètre de 12 mm).

La deuxième approche pour améliorer la flexibilité a consisté à introduire des substituants volumineux dans la structure de la résine afin d’obtenir une densité de réticulation plus baisse et donc une structure plus flexible après le durcissement. Benzoguanamine a été utilisé pour remplacer la mélamine en deux stages de la synthèse. Les résines MUF modifiées ont été analysées par GPC, DMA, FTIR and carbon-13 nuclear magnetic resonance (^{13}C-NMR). Les résultats suggèrent que la Benzoguanamine et ses dérivées ont été intégré dans la structure du polymère. Cette stratégie a amélioré la flexibilité des panneaux agglomérés de liège (diamètre du mandrin de 12 mm), tandis que les autres propriétés clés des panneaux ont été maintenues. La teneur en formaldéhyde des panneaux (déterminé selon la norme EN 120) a permis la classification E1.

La dernière approche a consisté dans l’incorporation de segments linéaires (terminés par hydroxyl et amine) pour améliorer la flexibilité des panneaux agglomérés de liège. Polyethylene glycols (PEGs) et polyetheramines (PEAs) avec différent poids moléculaires ont été testés.

Des PEGs avec différent poids moléculaires 106, 200 et 400 g/mol) ont été ajoutés pendant la synthèse de la résine urée-formaldéhyde. Les propriétés chimiques et physico-mécaniques des produits obtenues ont été investiguées en détail par FTIR, ^{13}C-NMR, GPC, DMA, résistance du joint adhésif et essai de traction. Le PEG avec poids moléculaire de 200 g/mol a permis de produire une résine très flexible avec des bonne propriétés d’adhésion et panneaux agglomérés de liège avec mandrin de diamètre 3 mm. Cependant, la teneur de formaldéhyde des panneaux était élevée et la résistance à l’eau très baisse, ce que n’est pas désirable.

De plus, PEAs avec différent poids moléculaires (230, 600, 900 et 2000 g/mol) ont été incorporés en résines de base formaldéhyde. Les résines ont été caractérisées par Analyse thermogravimétrique (TGA), FTIR, et ^{13}C-NMR, ce que suggère la présence de liaisons imine dans la nouvelle structure de la résine PEA-UF. Polyetheramine avec un poids moléculaire 900 g/mol a donné la résine plus prometteuse pour l'applications en panneaux agglomérés de liège, avec une remarquable flexibilité (diamètre du mandrin de 9 mm) et une très baisse teneur en formaldéhyde (classe E1, selon la norme européenne EN 12460-5).

Les stratégies suivis pour baisser la densité élevée de réticulation des résines à base de formaldéhyde et améliorer la flexibilité des panneaux agglomérés de liège collé avec les résines modifiées ont été bien réussi. Néanmoins, le principal objectif considéré a été atteint avec une des solutions développées: la résine PEA-UF. En face du prix élevé de la résine PEA, cette nouvelle résine développée n'est pas compétitive, par rapport aux adhésifs de PU. Toutefois, la plus économique des solutions développées, en particulier l'utilisation de la caprolactame et benzoguanimine, peuvent trouver utilisation pour des autres applications avec des exigences moins strictes pour la flexibilité.

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CHAPTER 1

Introduction

1. Introduction

EuroResinas - Indústrias Químicas S.A., a company from Sonae Arauco group located in Sines, is mainly engaged in the production of formaldehyde, formaldehyde based synthetic resins and impregnated paper. Formaldehyde based resins are thermosetting adhesives used in both wood and cork industries as well as paper impregnation used in the production of laminates or finish foil. The success of these resins is due to their good physical-mechanical performance, together with low cost. The stiffness and brittleness of amino-formaldehyde resins, however, are a limiting factor when they are used as binders for products where flexibility is desired. Two examples are postformable impregnated paper and agglomerated cork panels stocked as rolls. The main objective of the present work is the development of flexible resins for these two applications.

Due to strategic interest of the sponsoring company, part of the thesis period was dedicated to development of polyurethane resins with self-healing properties for application on impregnated paper. On a second phase, the properties of agglomerated cork panels produced with polyurethanes and formaldehyde-based resins were studied. The last and more extensive work was the backbone modification of formaldehyde-based resins in order to make them appropriate for use in agglomerated cork panels. Agglomerated cork panels must have water resistance, E1 classification for formaldehyde content, and must not rupture when flexed on cylindrical mandrels with 9 mm diameter.

1.1. Polyurethane resins

1.1.1. Production

Polyurethanes are considered one of the most versatile class of polymers for numerous commercial applications such as coating, foams, adhesives, sealants, membranes and elastomers [1].

These polymers are characterized by their tailor-made synthesis, which allows the design of alternating soft and hard-segmented structures exhibiting microphase-separated morphologies [2]. The soft phase comes from the relatively long and flexible chains as polyol segments, which gives extensibility to the polymer. The hard phase corresponds to the monomeric or polymeric isocyanate segments that create rigid domains. Figure 1.1 shows typical polyurethane morphology [1], [3], [4]. Chemical crosslinks may be introduced in a controlled way through the soft segment, using tri or multifunctional polyols and amines or through water reaction to produce physical crosslinked material [1], [4].

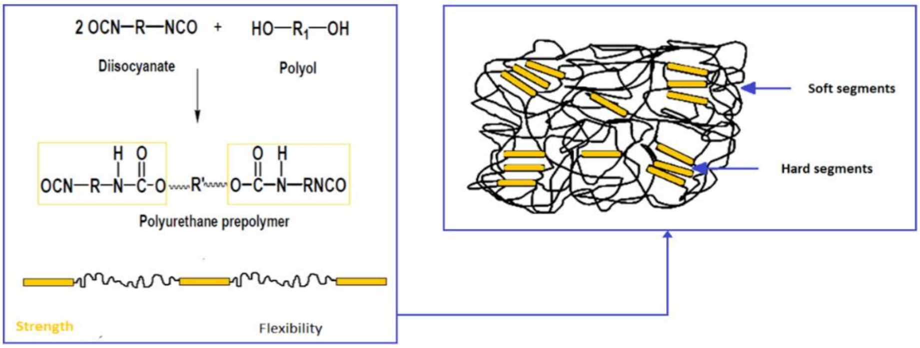
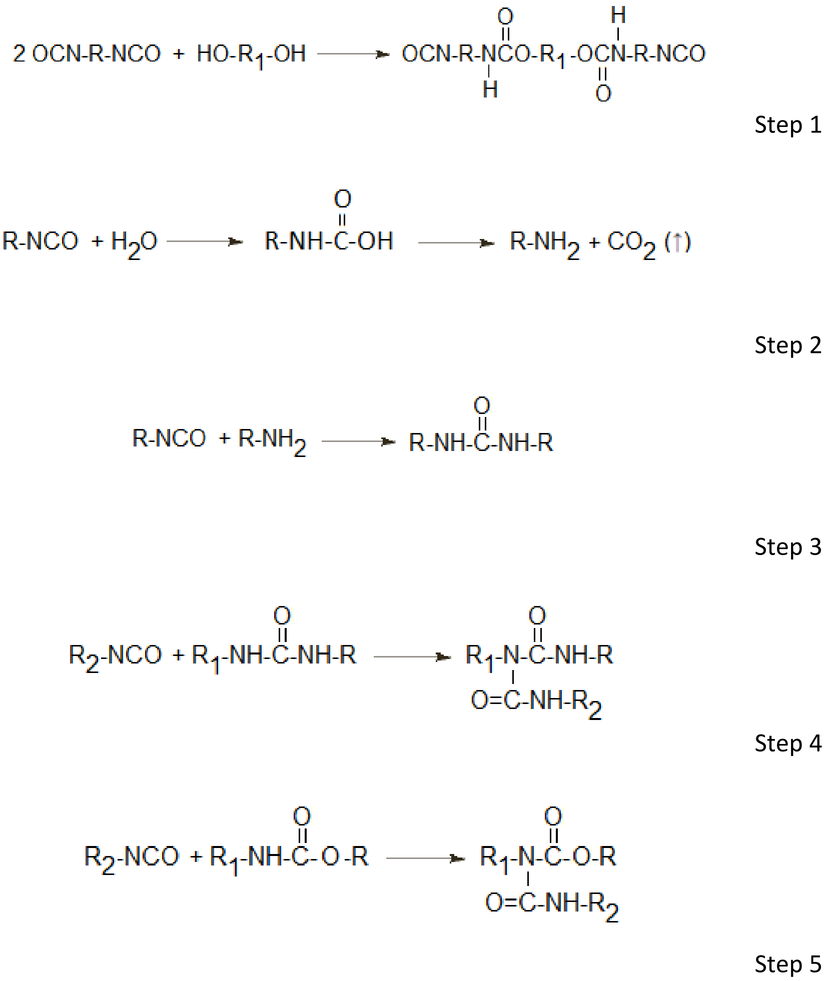


Figure 1.1. Schematic representation of a segmented polyurethane (adapted from [2]).

These polymers can be cured at UV radiation, by heat or can be moisture cured polymer [1]. Moisture-cure polyurethane are isocyanate-terminated polymers that are formulated to cure with atmospheric water.

Polyurethanes prepolymers are synthesized by reacting a polyol and an isocyanate (Figure 1.2 – Step 1).



$$2\,OCN\text{-}R\text{-}NCO + HO\text{-}R_1\text{-}OH \longrightarrow OCN\text{-}R\text{-}\underset{H}{N}\overset{O}{C}O\text{-}R_1\text{-}O\underset{O}{C}\overset{H}{N}\text{-}R\text{-}NCO$$

Step 1

$$R\text{-}NCO + H_2O \longrightarrow R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \longrightarrow R\text{-}NH_2 + CO_2\,(\uparrow)$$

Step 2

$$R\text{-}NCO + R\text{-}NH_2 \longrightarrow R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R$$

Step 3

$$R_2\text{-}NCO + R_1\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R \longrightarrow R_1\text{-}\underset{O=C\text{-}NH\text{-}R_2}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R$$

Step 4

$$R_2\text{-}NCO + R_1\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R \longrightarrow R_1\text{-}\underset{O=C\text{-}NH\text{-}R_2}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R$$

Step 5

Figure 1.2. Reaction scheme of polyurethanes: synthesis and moisture cure.

Water vapour from the atmosphere diffuses into the polymer and the nucleophilic attack of water on NCO end-groups results in an irreversible reaction that produces carbamic acid. This is unstable at room temperature and decomposes into carbon dioxide and a primary amine (Figure 1.2 – Step 2). The amine reacts with another NCO end-group of the prepolymer, forming an urea linkage (Figure 1.2 – Step 3) [5].

When the isocyanate content is in excess, chemical cross-linking through biuret (Figure 1.2 – Step 4) and allophanate (Figure 1.2 – Step 5) linkages also occurs [3], [5], [6].

Cured polyurethane are segmented copolymer polyurethane-ureas exhibiting microphase-separated morphologies. They display phase segregated morphologies due to the thermodynamic incompatibility between the domains formed by these blocks [7]. Depending on the chemical composition, chain length, molar ratio of the components, method of preparation and processing (prehistory), different degrees of interphase mixing may exist between the two types of domains [8], [9]. Polyurethane can have the chemical structure of a thermoplastic or thermoset and can have the physical structure of a rigid solid, a soft elastomer or a foam [1].

New generation of polyurethanes is waterborne polyurethane dispersion (PUD). Low viscosity prepolymers are emulsified in water, followed by chain extension with water-soluble glycols or diamines. These adhesives are preferred because the restriction on the use of solvents in order to prevent VOCs emissions. Polyurethanes are known for their good mechanical and chemical resistances, in combination with high flexibility but PUD present disadvantages such as poor surface properties, poor solvent and water resistance, and limited mechanical properties caused principally by low crosslinking density [10].

Critical parameters in designing segmented polyurethanes are: 1) the selection of the synthesis method, the solvent to be used and molar ratio of each compounds; 2) the characteristics of hard segments, such as chemical structure, hydrogen bond strength, symmetry, average chain length and length distribution; and 3) the chemical structure, solubility parameter and the molecular weight of the soft segments [11].

1.1.2. Application

The wide range of polyols and the wide variety of diisocyanates can be used to produce a broad spectrum of polyurethane to materials and specific applications. Figure 1.3 illustrates the polyurethane application universe.

Rigid polyurethane foams are inside the metal and plastic walls of most freezers or behind paper, metals and other surface materials in the case of thermal insulation panels in the construction sector. Flexible and low density foams are used in bedding, furniture, automotive interiors, carpet underlay and packaging [1].

Polyurethanes are also used as structural materials, coatings, adhesives, sealants and elastomers [1]**.** Adhesives can provide strong bonding, while sealants provide tighter seals. Polyurethane elastomers can be molded into almost any shape, are lighter than metal, offer superior stress recovery and can be resistant to many environmental factors [1]**.** The polyurethane resin has been applied in impregnation systems for wood and textile products to improve dry and wet tensile strength properties [1], [12].

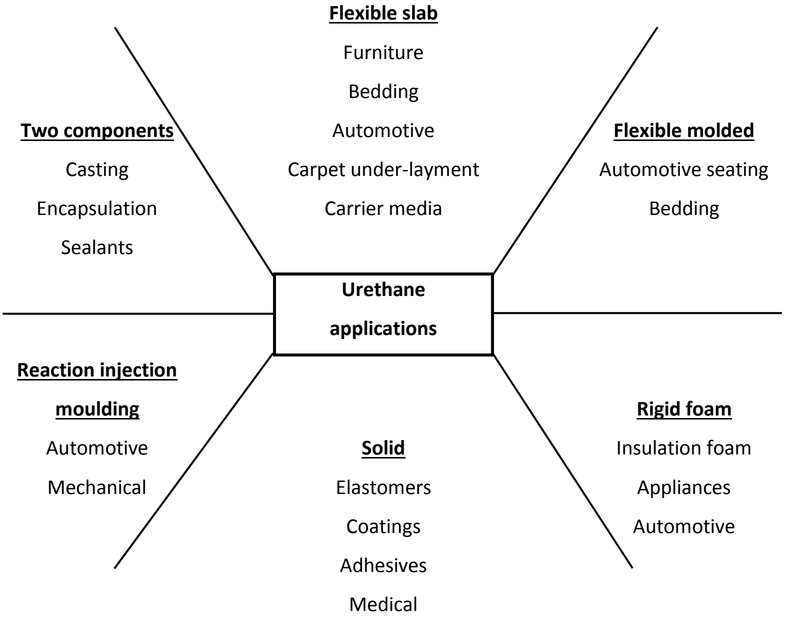


Figure 1.3. Polyurethane: production methods and application universe (adapted by [1]).

Thermoplastic polyurethane offers a wide range of physical property combinations and processing applications [1]. It is elastic, flexible and resistant to abrasion, impact and weather [1]. Thermoplastic polyurethane can be colored and used in construction and automotive compounds and footwear [1].

Polyurethane are also used to reaction injection molding to produce for example car bumpers, electrical housing panels and computer and telecommunication equipment [1]. Polyurethanes are commonly used in a number of medical applications, including catheter, hospital bedding, surgical drapes, wound dressings and a variety of injection-molded devices [1]. Their most common use is in short-term implants [1]. Polyurethane use in medical applications can be more cost-effective and provide for more longevity and toughness [1].

Polyurethane binders are used to adhere numerous types of particles and fibres to each other [1]**.** Their primary areas of use are in the manufacturing of wood panels, rubber or elastomeric flooring surfaces and sand casting for the foundry industry [1]**.**

Polyurethanes are among the most important class of specialty polymers because in addition to the above mentioned, these polymers can be formulated so as to be self-regenerative under exposure to moderate heat, without the need for other type of direct maintenance [13]. This approach allows obtaining more durable materials and to stay competitive in surface industries.

1.2. Urea / Melamine-Formaldehyde resins

1.2.1. Production

Amino resins are condensates formed when carbonyl compounds react with compounds containing amino, imino or amide groups, releasing water. Before the cure, these products consist principally of oligomers. Aniline resins, urethane resins, sulfonamide resin and urea and/or melamine resins are members of this big polymer family [14]. The popularity of last resins is associated with lower costs, processing advantages and balanced good performance in final products [14].

Urea-formaldehyde (UF), melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF) resins are applied in a large industrial products such as: abrasives, foam structures, foundry sand core binders, paper impregnation for laminates, textile industry, leather tanning, moulding compounds and adhesives industry [14], [15]. Wood-based panel industry is the major consumer of amino resins due to their competitive price, reactivity and performance [16], [17].

The synthesis of UF and MF resins is similar and are both carried out in two stages: methylolation and condensation. First refers to the addition of formaldehyde to urea to give the so-called methylolureas, generally under excess of formaldehyde (Figure 1.4) [18], [19].

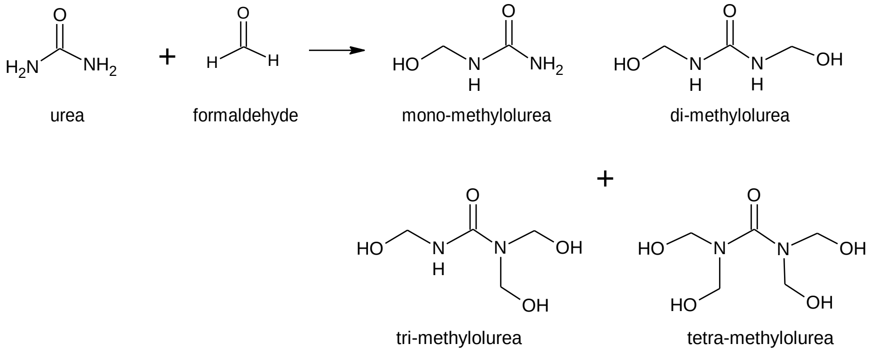


Figure 1.4. Reaction scheme of methylolureas formation.

At second stage occurs the condensation (Figure 1.5) of hydroxymethylolated urea and hydrogen of amine group forming methylene ether bridges (-CH_2-O-CH_2-) and/or methylene bridges (-CH_2-) resulting in UF polymer with simultaneous water release [18], [19]. Methylene bridges are more stable than ether bridges, due to the necessity of the presence of two formaldehyde molecules in the ether bond. Rearranged to methylene bridges can happen releasing one molecule of formaldehyde [18], [19].

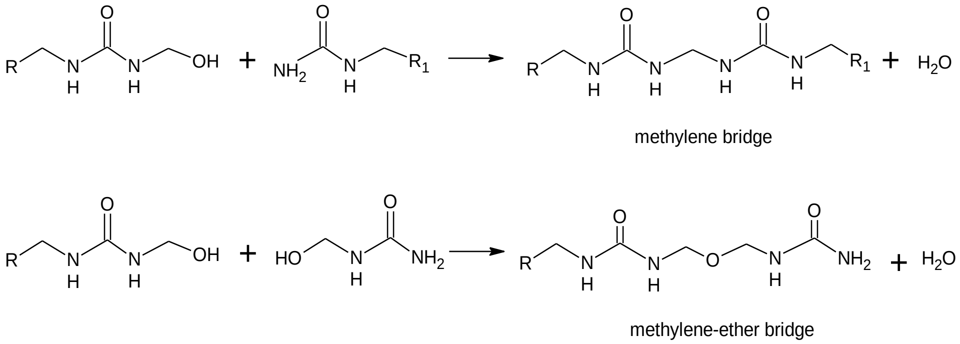


Figure 1.5. Reaction scheme of methylene and methyelene-ether bridges formation in UF resins.

Both methyolation and condensation reactions are catalyzed in alkaline or acid conditions [18], [19]. However, the velocity of UF polymer builds up is higher in acid condensation conditions [18], [19]. The rate at which reaction occurs is essentially dependent on the pH of the step. Typically, the methylolation reaction occurs under basic conditions of pH 8 to 9 and condensation reaction is not promoted. The condensation reaction is promoted by acidifying the reaction mixture to pH 5 - 6 [18].

In addition to pH, the characteristics of the reaction products are essentially dominated by the molar ratio of formaldehyde / NH_2 groups and reaction temperature [20]. These conditions determine the growth rate of the polymer: the speed of molecular weight increase will affect the mixture viscosity, water retention, rate of cure and adhesive properties of final product [20].

On the final application of UF adhesive, polymer is hardened by curing reaction at temperature and acid catalysed conditions [21]. One of the most common catalysts used in the cure of amino-formaldehyde resins is ammonium sulphate which is a latent catalyst [21]. This compound just act at temperature conditions consuming formaldehyde and forming sulphuric acid, water and hexamine [21]. The acid environment is essential to the gelation of the resin [21].

The final resin structure is a tridimensional network (Figure 1.6) completely (or partially crosslinked if it contains some -NH- and $-CH_2OH$ unreacted groups).

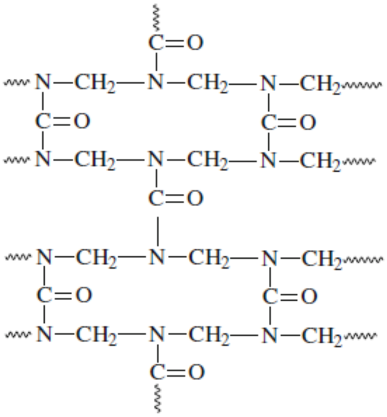


Figure 1.6. Tridimensional network of cured UF resin (adapted from [22]).

The synthesis of melamine-formaldehyde resins is similar to UF. First step is methylolation (Figure 1.7) in which formaldehyde is attacked by the amino groups of the melamine compound forming methylolmelamines. However, compared with UF resins, the methyolation, condensation (Figure 1.8) and the cure steps are provided under acidic, neutral or basic conditions forming methylene and ether bridges [20]. The curing of the MF resins resembles to UF resins, where pH and temperature conditions accelerate the formation of tridimensional network (Figure 1.9).

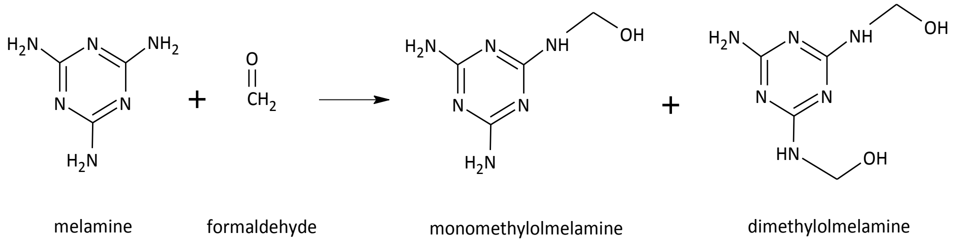


Figure 1.7. Reaction scheme of methylolmelamines formation.

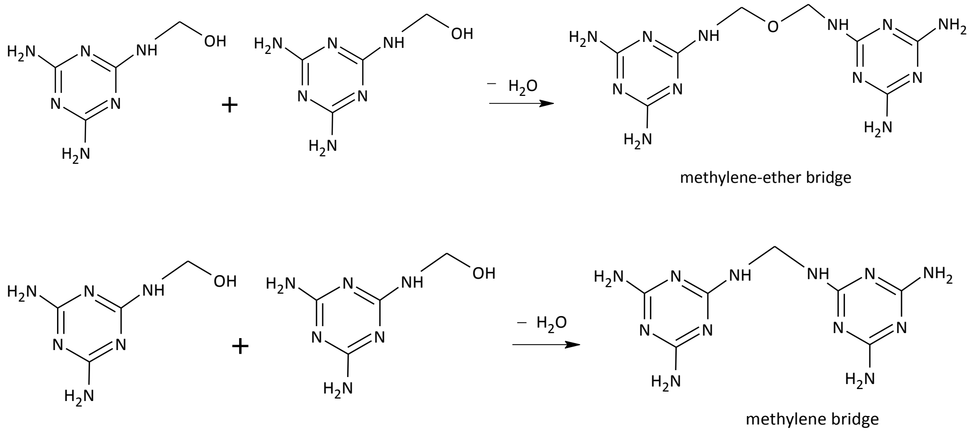


Figure 1.8. Reaction scheme of methylene-ether and methyelene bridges formation in MF resins.

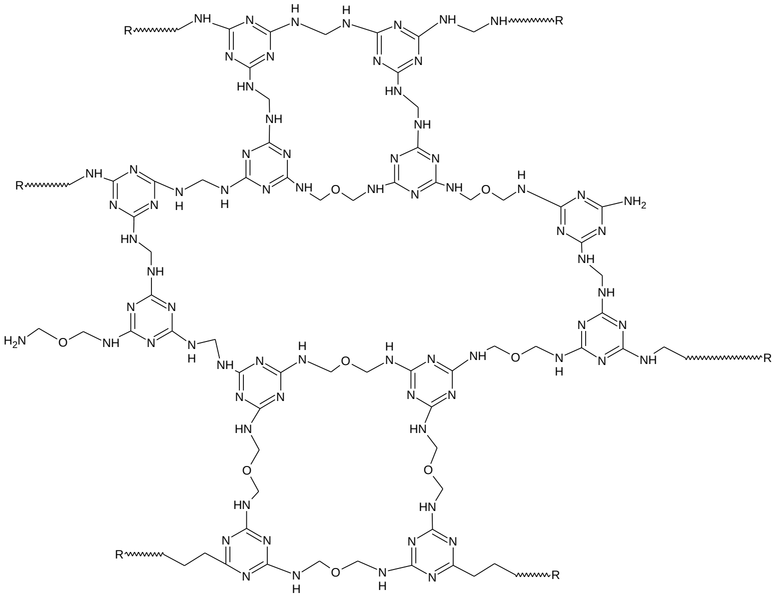


Figure 1.9. Tridimensional network of cured MF resin (3) (adapted from [20], [22]).

UF resins are less expensive because urea is cheaper than melamine. However, MF resins have high resistance to hydrolysis compared to UF because methylene linkages with melamine ring are less susceptible to hydrolysis [17]. For this reason, MF and MUF resins are fully used in production of wood-based panels for exterior applications [20].

The third kind of amino-formaldehyde adhesives are MUF resins. MUF resins are copolymers of UF and MF with the economic advantage of the UF and resistance to hydrolysis of MF resins [20]. Thus, the MUF adhesives have become increasingly application when the final product has sufficient added value to pay the cost of melamine used in the synthesis process.

Urea and/or melamine-formaldehyde resins are characterized, after cure, by colourless, good adhesion to lignocellulosic substrates showing high tensile strength, excellent solvents and heat resistance and their high crosslink density results in high stiffness and brittleness.

1.2.2. Applications

Amino-formaldehyde resins are typically applied as binder for wood subtracts.

A very important application for UF adhesives is in the manufacture of particleboard (PB), medium density fiberboard (MDF) and plywood. Beyond these applications, UF resins are also used for impregnation of décor paper, although the consumption is lower.

Melamine–formaldehyde and melamine–urea–formaldehyde resins are among the most used adhesives for exterior and semi-exterior applications. Their much higher resistance to water attack is their main distinguishing characteristic from urea–formaldehyde resins. MUF resins are used to manufacture of PB, MDF, plywood and cork-based panels. Melamine resin is widely used for surface coatings and for paper impregnation used in the production of decorative low and high-pressure laminates.

1.3. Conferring flexibility to formaldehyde-based resins

Amino-formaldehyde resins are very old thermosetting polymers. First UF resin was synthesized in 1824 and commercial application of UF resins as wood adhesive occur at 1920s.

Flexibility is one of the biggest challenges in development of new generation of amino-formaldehyde resins. The characteristic stiffness of amino-formaldehyde resins may be undesirable when a final product with some mobility is desired.

Flexibility is desired for different products and applications. One of the theses products is the postforming melamine foil. Paper sheets impregnated with a thermosetting amino resin form a finish foil frequently used for surface protection and decoration of wood based panels in the furniture industry. A melamine-formaldehyde resin is typically used, hence its common designation is “melamine finish foil” [23]. After impregnation, the paper is dried and afterwards pressed over the intended substrate, upon which the MF resin becomes fully cured [24]. The paper becomes extremely brittle after drying, which forbids application over curved surfaces or surfaces with sharp angles. Figure 1.10 shows the differences between impregnated paper with and without postforming ability. From this point, the flexible performance of MF resin is desired.

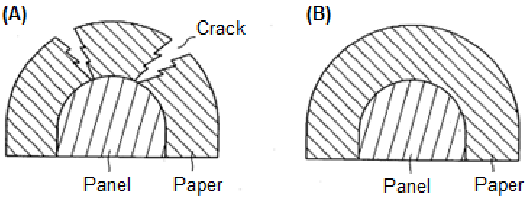


Figure 1.10. Finish foil paper (A) without and (B) with postforming ability (adapted from[25]).

Another similar objective is impregnating resins for fabric substrates as textile finishing [14], [15]. Amino resin improves wrinkle resistance and tear strength, and decrease tensile strength and the shrinkage. In leather tanning industry, the presence of a small quantity of melamine resin in the tanning material improves the strength of the leather [15]. In such applications, the increased flexibility permits these articles to be soft handle, readily hot-punched and postformed [26].

Formaldehyde based resins are also used for the manufacture of abrasive articles [14], [15]. Abrasive substrate can be paper or fabric with abrasive powder coated with a resin [15]. Phenolic and melamine-formaldehyde resins are used for this purpose. In the final of the productive process, articles take the form of sheets, discs and belts which can be adapted to mechanical or manually uses [27]–[29]. Depending on their area of application, flexibility of final product is required, however, melamine and phenolic resins are brittle polymers [27]–[29].

Melamine-formaldehyde foam has great potential in acoustic and thermal insulation applications. MF foam presents high stability and fire-retardant properties because melamine is rich in nitrogen and has a stable triazine ring structure [30]. The advantages of MF foam is their ability to be prepared from very cheap raw materials and the possibility of foaming directly at the point of application compared with other foams [31]. The biggest disadvantages comparing with other kind of foam (as polyurethane) is the break of their 3D crosslinked structure and the possible formaldehyde emission [30]–[32]. Because of the absence of flexible functional groups in MF molecules, foam suffers from high brittleness and thus applications are greatly restricted [31], [32]. Figure 1.11 shows the differences between a flexible and no flexible foam during compressive test. Researchers have done lot of studies to solve its rigidity problem trying to modify melamine foam by chemical and physical methods to improve their toughness [31], [32].

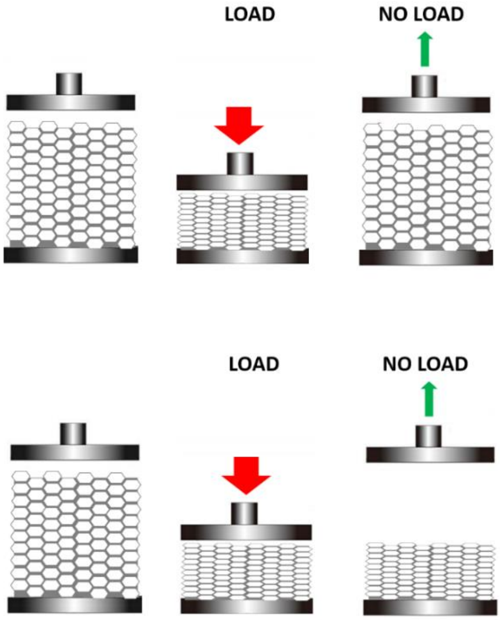


Figure 1.11. Schematic description of the foam cellular structure at compressive deformation: flexible foam returns to position before compressive load (up); flexible foam does not return to start test position (down).

Melamine acrylic clearcoat is the most common paint used in the automotive industry because of its good cost and performance balance [33]. Principal attractions of amino resins in this application are their colourless after cure and their water solubility before cure, which allows unlimited colour ability with dyes and pigments. However, questions about formaldehyde emissions and brittleness forbid the admission of amino resins as universal material in this engineering area. Flexibility is desired to decrease cracking (Figure 1.12) in clear coats of automotive industry during wet-dry weather changes. Some scientific works have been published for reduce formaldehyde emission but an increase in softness and flexibility polymeric paint layer is still limited [34]–[36].

Figure 1.12. Example of crack in automotive clear coat.

As presented before, the biggest market for formaldehyde adhesives is the wood based products. Wood-based panels are manufactured from virgin and/or recycle wood having different geometries, combined with an adhesive and bonded in a hot press. Final product exhibits specific mechanical and physical properties. However, during resin cure and wet–dry exposures in costumer utilization, panels are subject to internal stress. To improve the durability and dimensional stability of urea-formaldehyde bonded in wood products some reports show that resin linkages would be modified improving the flexibility of the polymer because it will decrease the internal stress and resin cracks [37]–[39]. Figure 1.13 presents the changes of wood-based panel under internal stress conditions.

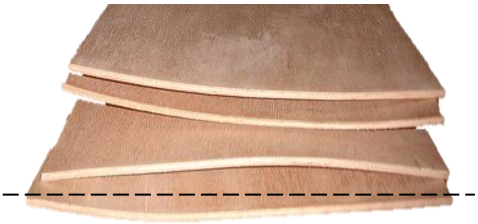


Figure 1.13. Schematic description of the changes in dimensional unstable wood based panel.

Agglomerated cork panels are cork-based products that can be used for surfacing, flooring and insulation purposes [40], [41]. They are composed from cork granules with variable dimensions, bound together by rubber, polyurethane adhesive or MUF resin [40], [41]. Agglomerated cork panels can be sold as flat panels or as rolled panels (so called “cork roll”). MUF resins cannot be used for the latter form, since its stiffness causes the material to crack when bended (Figure 1.14). This product is another motivation for research and development of new generation of melamine and/or urea formaldehyde resins with flexible properties.

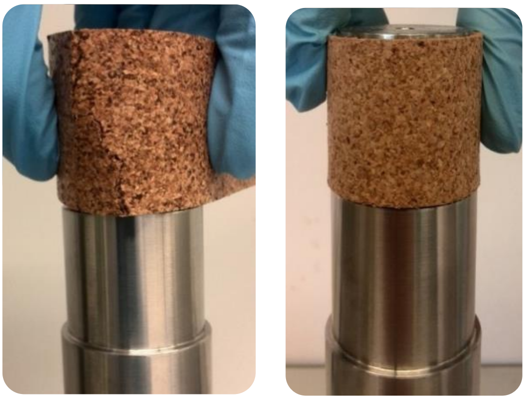


Figure 1.14. Differences between brittle and flexible cork panel: panel fracture on folding (left) and cork panel does not break when is rolled (right) in same curved diameter.

1.3.1. State of the art for flexible amino-formaldehyde resins

Once the amino resins are known and required by the high density of crosslinking, literature offers few solutions to confer flexibility at this family of resins. Some of the oldest references are related to patents of well-known industries: Formica® and BASF®.

DeLapp *et al.* (1978) [42] claim the patent US4093579 of melamine-formaldehyde resin for producing a panel with crack resistance to low humidity conditions. DeLapp *et al.* tested additives which generally have been added to melamine-formaldehyde resins to reduce the crosslinking (such as sucrose and dipentaerythritol sebacate) but do not prevent cracking to a satisfactory degree. The MF resin is prepared from formaldehyde 37 % solution in water and melamine powder, at molar ratio of formaldehyde-melamine of 1.6 to 2.5 and solids content from about 50 to about 65 %. During or after MF synthesis, an additive is added and blended with aqueous resinous solution. Additives can be: 2-20 wt.% of ethylene glycol with molecular weight from 62-2000 g/mol; 0.25-1.25 wt.% of polyamines as tetraethylene pentamine, ethylene diamine, diethylene triamine and triethylene tetramine; 5-25 wt.% of polyvinyl chloride dispersion; 3-10 wt.% of polyurethane dispersion; or 1-5 wt.% of butadieneacrylonitrile copolymer [42]. Excellent abrasion and low humidity crack resistance were observed in final product.

Also in 1978 from Formica® corporation, Huffman *et al.* [43] patented US4112169, where the same objective is described. Authors changed some additives and quantities from patent US4093579. Additives are: 5-25 wt.% of polyvinyl chloride dispersion; 3-10 wt.% of polyurethane dispersion; and 2-20 wt.% of bisphenol A-ethylene oxide adduct of 2800 g/mol molecular weight [43].

Brooker *et al.* (1983) [44] patented a modified MF resin, useful for impregnating surface sheets for postformable laminates in US4405690. Impregnated paper with a resinous composition of MF resin at molar ratio F/M from about 1.5 to about 3.0 and 1 to 45 wt.% (based on weight of melamine) of polyethylene glycol having a molecular weight from 200 to 1000 g/mol.

Different approach is reported by Mahnke *et al*. (1982 and 1985) [45], [46] in US4334971 and US4540717 BASF® patents. A process for the manufacture of a resilient foam based on a melamine-formaldehyde condensate and competitive with flexible polyurethane foams. The foam may be employed for heat/sound insulation and as a packaging material. Product containing a melamine-formaldehyde pre-condensate, an emulsifier, a blowing agent, a hardener and it is foamed by ultra-high-frequency irradiation. Long list of suitable products for each necessary compound is shown but responsible additive for the resilient property is not discussed.

At 1992, Weiser *et al.* [47] patented a melamine-formaldehyde foam at BASF® US5084488 in which from 1 to 15 mol % of the melamine have been replaced by N-mono-, N,N'-bis and N,N',N"-tris(5-hydroxy-3-oxapentyl) melamine during polymer synthesis increasing foam elasticity. In BASF internet site, melamine-formaldehyde foams are presented by product name BASOTECT®.

The improvement of flexibility of amino resins is shown at least in another three patents. Blackman *et al.* (1964) [48] patented an invention to provide a novel melamine and/or urea formaldehyde resin with improved flexibility provide by a plasticizer N,N,N,N'- tetrakis (Z-hydroxyethyl) ethylenediamine tetraacetate. The plasticizer used are compatible with formaldehyde based resin and it is stable at normal curing temperatures. According to the invention, selected plasticizer resin system may be transparent or pigmented to be incorporated in paper, textiles or other similar products. Usually melamine-formaldehyde resin is brittle but paper coated with the plasticized resin mixture from this invention has a high gloss surface and does not fracture on folding. The plasticizer will comprise from 10 to 20 % by weight of the final plasticized composition.

In 1965, Conbere *et al.* [49] report a flexible amino resin introducing plasticizers in the system (US3174943). The compositions of the invention comprise an urea-formaldehyde resin and an effective amount of an adduct of ethylene oxide and hexadecyl alcohol. The invention provides a cured flexible coating with high gloss surface for paper and fabric applications which does not fracture on folding.

Diethelm *et al.* (1973) [50] in US3753934 patent claim a process for the manufacture of new plasticized melamine-formaldehyde condensates with a lactam and sugar for paper impregnation products. The authors claim a product with improved stability. The plasticized melamine resin shows better flow properties, which is a especially advantageous during paper impregnation. Their strategy implies three possible synthesis process:

1) Simultaneous condensation of formaldehyde, melamine, lactam and sugar;
2) First condensation of formaldehyde, melamine and lactam; sugar is introduced in the second condensation;
3) First condensing of formaldehyde and melamine; the introduction of lactam and sugar occurs in second condensation.

Suggested amounts of lactams and sugars are 5 wt. %.

Others patents are found with a flow-promoting plasticizer for example from Wohnsiedler *et al*., 1951 [51] wich MF resin was plasticized with a compatible polyvinyl acetal and a flow promoting secondary plasticizer compatible with both resin and acetal consisting of ortho-cresyl glyceryl ether, benzamide and acrylamide. Wohnsiedler *et al.* claims MF resin for moulded products with increased toughness, flexibility, impact strength and improved craze and crack resistance in comparison with the unplasticized MF polymer.

As regards scientific publications, Osemeahon *et al.* (2007) [52] studied the mixture of methylolureas and natural rubber (poly (cis-isoprene)), in order to evaluate the emission of formaldehyde and the resulting physical and mechanical properties from this mixture. The strategy was to mix different natural rubber content (0-60 %) to a solution of methylolureas in the condensation step, to produce films with this mixture and evaluate the reaction between the methylolureas and rubber. FTIR studies, formaldehyde emission, viscosity, density, melting temperatures and elongation at break of the blend films were tested. Authors could not conclude by FTIR analysis if reaction occurs. Comparing the elongation at break obtained with polymer studied and a standard PUD, results are 405 % and 713 %, respectively. However, authors did not test the adhesive properties of these composites, nor if the breakage during elongation at break occurs in the elastic or plastic deformation regime.

In continuous efforts to develop a paint binder from amino resin, low formaldehyde emission methyol urea-triethanolamine (MUT) composite was synthesized through *in situ* esterification of formaldehyde with triethanolamine (TEA) and subsequent copolymerization of the synthesized polyester with methylol urea by Barmidas *et al.* (2010) [53]. The effects of addition of TEA (0-10 %) on the polymerization process and on some physical properties of the synthesized copolymer were evaluated. The copolymer was characterized by IR spectroscopy and macro phase separation techniques. IR spectra shows the presence of the polyester in the composite, but authors observed the formation of a two phase separated copolymer in the cured resin film. The elongation at break was 240 % for resin with 4 % TEA and 84 % in resin without TEA. Authors concluded that esterification of formaldehyde is possible using TEA which is reflected in the consumption of formaldehyde and its emissions. According with author this copolymer could be a potential candidate as a binder for the coating industry.

Osemeahon *et al.* also published three scientific works (2007, 2009 and 2013) about UF resin in continuous efforts to develop a paint binder from amino resins. Formaldehyde was replaced with another aldehyde (acetaldehyde, proparaldehyde and butaldehyde), soybean oil was introduced in UF resin to produce a copolymer with improved performance, and cassava starch was blended with UF resin [54]–[56].

In their first work [54], authors changed aldehydic groups to produce urea-acetaldehyde (UA), urea-proparaldehyde (UP) and urea-butaldehyde (UB) at different degree of substitution (mono to tetra). Physical properties of these resins were evaluated and their results show that UF were too hard brittle and has low water resistance while UP and UB resins were too soft and remained as semi solid in the cured state at room temperature. These results indicate that these resins cannot be used alone as paint binder. Therefore, a compromise is necessary between brittle and soft candidates. UA can be an interesting candidate but further research is suggested in order to modify these polymers with the aim of satisfying the requirements of the coating industry.

A green approach from Osemeahon *et al*. (2009) [55] was the copolymerization reaction of urea-formaldehyde resin and soybean oil. UF samples with different viscosities were obtained by removing from synthesis process. The study was done introducing the same amount of soybean oil in these UF samples. Among other tests, this study show how important is the effect of UF viscosity on physical properties of UF/soybean oil copolymer. Ductile performance is obtained when a specific viscosity range is 5.11 - 260.04 mPa·s and it shows an interesting flexible performance for emulsion paint formulations of urea-formaldehyde.

In the last study, Osemeahon *et al*. (2013) [56] presents a UF resin blended with various concentrations (10 to 70 %) of cassava starch in order to develop a paint binder for a emulsion paint formulation. Similarly to most of other works, some physical properties and formaldehyde emission of the blended resin were investigated. About elongation at break, it increased initially but gradually decreased with cassava starch content in the blend. The interaction between the two different polymers shows that 50 % starch was the optimal loading inclusion. This new system has the advantages of low brittleness and low formaldehyde emission characteristics. Therefore, the polymer blend can be recommended as binder for coating industry.

Another work was reported by Wang *et al*. (2012) [32] in order to improve the flexibility of MF foams for thermal insulation, sound insulation and flame retardancy. The study involved the use of surfactants in MF resin and to evaluate the foam performance. It is not clear if authors do it during synthesis or in a previously synthesized resin. The non-ionic surfactants tested were: dimethyl silicone oil (M-201), Tween-80, octyl phenol ethoxylates (OP-10), sodium dodecylbenzenesulfonate (SDBS) and a combination of OP-10 and SDBS. The simultaneously use of OP-10 and SDBS confer flexibility to the foam, uniform cells and it was found that the compression modules decreased from 0.2 MPa to 0.004 MPa when foams are 70 % compressed. Further work was suggested to improve the desired properties: increase the size of flexible chains; reduce the degree of crosslinking (as a process similar to what happens in the crosslinkable rubber) and replacing part of the melamine group by other groups with flexible chain. However, these strategies have not yet been tested.

In a different approach, Choi *et al*. (2002) [57] studied the incorporation of long diacid chains in phenol-formaldehyde (PF) resins in order to make them less brittle. The diacids used are: adipic acid, suberic acid, sebacic acid and lauric acid. The diacids were added to a resole type commercial resin, before curing. Authors confirmed the reaction of diacids with the PF resin during cure and showed an improvement in the strength of the all cured product. However, the increase in the elongation at break was only 16 % in the best conditions (suberic acid).

Tihić (2004) [27] published a master's thesis also on the flexibility of phenolic resins. As in previous work, the approach was based on adducts with flexible segments: diacids, dimethylethanolamine and polyethylene glycol. However, results show high dispersion and it was inconclusive.

An elastic co-polymerized urea-formaldehyde and melamine-formaldehyde foam was reported by Liu *et al.* (2016) [31]. The elastic property is justified by cell size and size distribution, higher open cell porosity and lower apparent density compared with pure UF foam reported in the literature. During the compression test, recoverable deformation can be observed without physical structure degradation, which was resulted from the elasticity and toughness properties.

To improve the durability and stability of urea-formaldehyde bonded wood products by decreasing the internal stress developed during resin cure and by improving the ability of the cured resin to withstand cyclic stresses, Ebewele *et al*. (1991) [37], present initial results from modifying a urea-formaldehyde resin by incorporating flexible di- and trifunctional amines: difunctional amines – hexamethylenediamine and triethyleneoxidediamine; trifunctional amines – bis-hexamethylenetriamine, triethylaminetriamine and poly(propyleneoxide)triamine. Resistance of UF-bonded joints to cyclic stress was substantially improved by modifying the resins through curing the resins with di- and trifunctional amine hydrochlorides and it was also shown that crazing was also reduced when resins was cured with either triethylaminetriamine or hexamethylenediamine allowing lower formaldehyde emissions.

Ebewele *et al.* (1991 and 1993) [38], [39], complemented his previous work by examining the effects of additional amines and subjecting bonded products to additional testing. The fracture behaviour of joints made with modified and unmodified adhesives showed different performances. Modified adhesives were used to produce particleboards with enhanced cyclic stress resistance and low formaldehyde emission. From three cited reports, authors concluded the more effective amines appear to be those of low to moderate molecular weight that possess inherent flexibility or trifunctionality or both characteristics. Depending on the backbone structure of amine, higher molecular weight amines may be less effective because they become incompatible with the aqueous UF system.

To improve the toughness and moisture resistance of the UF wood composites without significantly altering the processing or excessively increasing the cost of the product, Rachtanapun and Heiden (2002) [58]–[60] tested the addition of acrylic thermoplastic copolymers with different degrees of hydrophilicity. The work is divided into 3 chapters [58]–[60]. In the first chapter, [58] authors prepared and introduced thermoplastics into aqueous UF suspensions to determine their stability and viscosity, because the final formulation would be sprayed through conventional wood composite spray equipment. The most hydrophobic thermoplastics were introduced into the UF suspension as surfactant-stabilized latices and the most hydrophilic were introduced into the suspension as an aqueous solution. Acrylics with intermediate degrees of hydrophilicity were introduced into the aqueous UF suspension as self-dispersed suspensions in water. At 5 % w/v, all formulation of thermoplastic-modified UF had viscosity below the target of 200 cP. The morphology of neat resin specimens was investigated to determine the thermoplastic phase separated into UF. The self-dispersed and the surfactant stabilized thermoplastic showed phase-separated thermoplastic domains within a continuous UF phase. The cured UF modified with water-soluble thermoplastic showed no phase separation and their fracture did not show the brittle behaviour of the unmodified UF. In chapter II [59], the goal was to investigate the effect of the former thermoplastic modifiers on the mechanical properties of wood composites using a notched Izod impact test. The effect of the thermoplastic molecular weight, the thermoplastic loading and the methods of introducing it into the UF resin was studied. Increasing the thermoplastic content from 5 to 10 % w/v had no further improvement on the impact test results. Only the formulations with self-dispersed thermoplastics increased the notched Izod impact strength comparing with the UF control. In chapter III [60] acrylic monomers were combined with a radical initiator and were polymerized *in situ* in aqueous UF via heating at 65–70 °C for 1.5 h. The modified UF suspension (5 wt % thermoplastic in UF) remained within a processable viscosity range and was used to bond wood composites. Similar to the previous work, the effect of the thermoplastic-modified UF adhesive was evaluated on the notched Izod impact strength and equilibrium moisture uptake of the wood particleboards.

In order to improve the toughness of UF, Yuan et al. (2015) [61] studied the UF/PU blends prepared via *in situ* polymerization. The elongation at break and notched impact strength of the blends increased with increasing PU content, while the tensile strength was still maintained at a relative high level. The blends showed lower modulus, but higher *Tg* compared with neat UF due to the improved crosslinking degree of the blend. However, a microphase-separated morphology could be observed for the blends, which was believed to be critical for improving the toughness of the blend.

Some author also report the properties of the mixture of UF/MUF with PVAc and latex emulsion [62]–[66]. However the main goals of these works are to decrease formaldehyde emissions or to improve water resistance of UF resin, which is outside the scope of this work.

Although for a distinct application, Chai et al. [67] modified melamine-formaldehyde resin with hydroxyl terminated polydimethylsiloxane to reduce the cracking ratio of microcapsule's shell. The modified microcapsules were fabricated successfully and showed a better flexibility.

1.3.2. Summary of possible strategies

Papers and patents showed how to improve the flexibility of amino-formaldehyde resins in order to: decrease the crack and craze in melamine-formaldehyde resin to produce postforming melamine finish foil, achieve impregnation of leather and fabric without breaking and requiring a soft tact, produce resilient foams to compete with polyurethane market, decrease the internal stress of wood products, and change the stiffness of cork panels to permit their storage in rolls form without breaking.

According to the literature, during modification of amino-formaldehyde resins, additives can be introduced at beginning, during or at the end of synthesis process. The functional groups involved in the reaction or interaction between the polymer and additives are hydroxyl (-OH), amino (-NH) and carboxylic acid groups (-COOH). Three approaches (schematized in Figure 1.15) may be considered to flexibilize amino-formaldehyde resins.

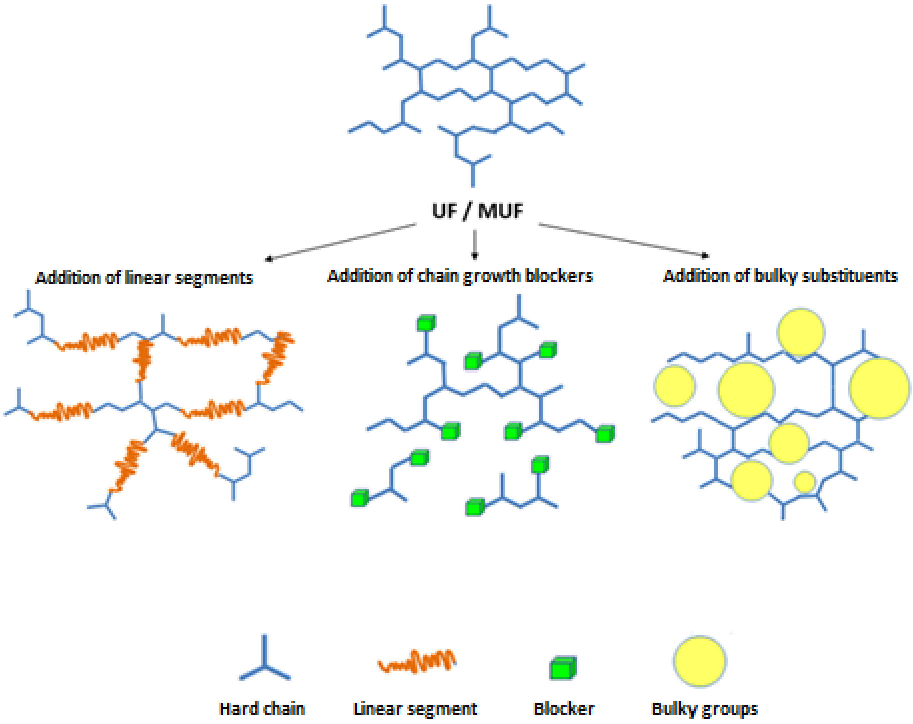


Figure 1.15. Schematic approaches to introduce flexibility in amino-formaldehyde resins.

First strategy to increase the flexible of amino-formaldehyde resin is through adding reactive long and linear additives to move away the crosslink sites. Similar to polyurethane chemistry, these additives result in flexible segments introduced into typical hard amino-formaldehyde segments. Improved flexible behaviour also should come from incorporating monofunctional modifiers into the amino-formaldehyde resin acting as a chain growth stopper to decreased crosslinking efficiency. On the other hand, adding bulky constituents such as plasticizers (chemical or physical compound or thermoplastic resin) in amino-formaldehyde resins can modified the tridimensional structure, decrease the crosslinking points and improve the flexibility of final product.

All strategies are based in the same principle: decrease the high crosslink density that characterize amino-formaldehyde resins. The most effective chemicals described in this review are presented in Table 1.1 with the respective price, an important factor for any modification of UF resin used in industrial applications.

Table 1.1. Chemicals to modify amino-formaldehyde resins and improve flexible ability

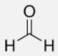
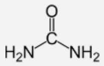
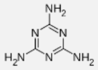
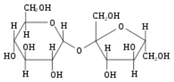
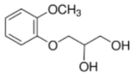
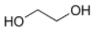
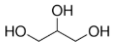
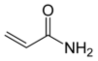
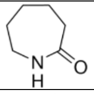
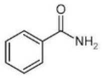
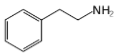
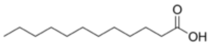
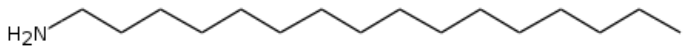
Strategy	Chemical name	Chemical struture	Price (€ /kg or l)
Base	Formaldehyde (37% in water)		160
	Urea		40
	Melamine		80
Plasticizer	Sacarose		2
	Ortho-cresyl glyceryl ether		*Not found*
	Ethylene glycol		100
	Glycerol		155
Blocker	Acrylamide		350
	Caprolactam		40
	Benzamide		420
	Phenethylamine		80
	Lauric acid		40
	Hexadecylamine		90

Table 1.1. Chemicals to modify amino-formaldehyde resins and improve flexible ability *(cont.)*

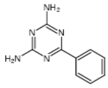
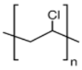
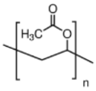
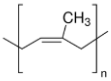
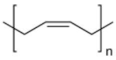
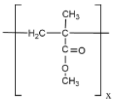
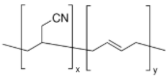
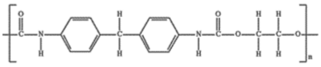
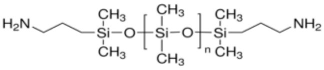
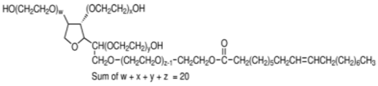
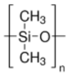
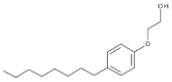
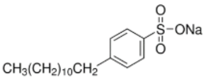
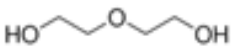
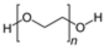
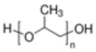
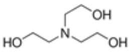
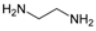
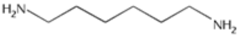
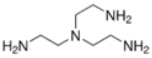
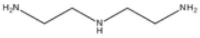
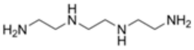
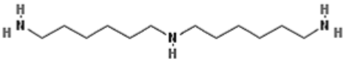
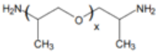
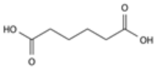
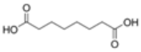
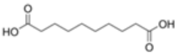
Strategy	Chemical name	Chemical struture	Price (€ /kg or l)
Bulky microdomains	Benzenoguanamine		65
	Poly(vinyl chloride) (according MW 400-4000 g/mol)		100 -300
	Poly(vinyl acetate) (according MW 100000-500000 g/mol)		300-400
	Polyisoprene (natural rubber)		800
	Poly(butadiene)		160
	Poly(methyl methacrylate)		350
	Poly(acrylonitrile-co-butadiene) (40% in water)		1300
	Polyurethane dispersion		*Not found*
	Poly(dimethylsiloxane), bis(3-aminopropyl) terminated		4700
Surfactant	Tween-80		80
	Dimethyl silicone oil		190
	Octylphenol Ethoxylates		400
	Sodium dodecylbenzenesulfonate		85

Table 1.1. Chemicals to modify amino-formaldehyde resins and improve flexible ability *(cont.)*

Strategy	Chemical name	Chemical struture	Price (€ /kg or l)
Linear chain	Diethylene glycol		200
	Polyethylene glycol (according MW 400-4000 g/mol)		40 - 200
	Poli(propylene glycol) (according MW 400-4000 g/mol)		60-250
	Triethanolamine		50
	Ethylenediamine		35
	1,4 - Diaminobutane		450
	Hexamethylenediamine		100
	Tris(2-aminoethyl)amine		1400
	Diethylenetriamine		55
	Triethylenetetramine		720
	Bis(hexamethylene)triamine		90
	Polyetheramine		300
	Adipic acid		28
	Suberic acid		220
	Sebacic acid		180

1.4. Impregnated paper and finish foil

1.4.1. Production

Paper impregnated with thermosetting resin is commonly used as decorative and protective layer for wood composites. Its application in furniture can be done by high pressure laminates (HPL), low pressure laminates (LPL) (also called as continuous pressed laminate (CPL), melamine foil or finish foil).

Impregnation is the first step in the production of these products. Figure 1.16 shows the process, wherein the dry papers are immersed in a bath with the corresponding resin which promotes the penetration of it into the cellulosic fibres [24]. Then, the paper is soaked with the resin and the excess is mechanically removed by the action of squeezing rollers [24]. After impregnation, the paper is directed to the dryers in order to evaporate much of the volatile compounds present in the resin [24]. Depending on the type of paper in question, the paper may further be subjected to a second bath, termed coating. Thereafter, the paper is cooled by passing through rollers with internal circulation of cold water and cut according to the desired size.

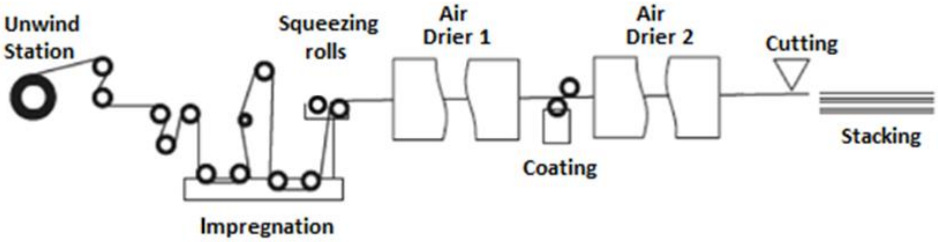


Figure 1.16. Schematic representation of the impregnation process of paper (adapted from [24]).

Final impregnated papers should to present specific parameters such as resin content (RC) and volatile content (VC) to ensure: a good storability of dry paper, the resin flow during the pressing step and the appearance and quality of the final laminate [68]. Melamine-impregnated papers usually contain 50 – 60 % resin what it generally means weighing between 60 – 130 g/m^2 [69]. The dried paper contains residual moisture in a range between 5 – 7 % [68].

After impregnation step, the dried paper is stocked for posterior application: the production of HPL or LPL. HPL consist of sheets of paper impregnated with resins, joined together by the application of heat and high pressure, which promote the flow and the total cure of the resins. The HPL are essentially composed of three distinct layers (Figure 1.17): a substrate consisting of a set of kraft paper sheets impregnated with phenol-formaldehyde resin; a sheet of decorative paper of the desired color or pattern, impregnated with melamine-formaldehyde resin; and a translucent overlay sheet also impregnated with melamine resin, which provides additional resistance to abrasion [70]. LPL just consist in melamine impregnated paper pressed and total cured in surface of wood-based panel to cover this substrate (Figure 1.17) or applied on wood based product using an external adhesive such as polyvinyl acetate (PVA) to glue the paper to the panel.

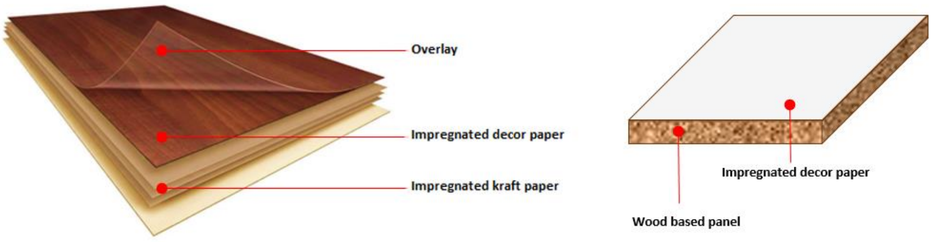


Figure 1.17. Schematic representation of HPL (left) and LPL (right).

The thickness of the final product and the pressure applied are the major differences between high and low pressure laminates. LPL present typical ranges from 0.2 to 2 mm, up to 3 mm is typical in HPL thickness [71]. LPL is joint to the substrate under pressures of 20 to 30 bar, while in HPL production, sheets are pressured from 70 to 100 bar. The pressed temperatures applied in HPL are around 140 – 160 °C but LPL needs higher temperature between 180 °C and 190 °C [68], [71], [70], [72].

Although both are resistant to heat and chemicals, HPL are slightly more durable. The price of finish foil is usually less expensive than HPL because kraft paper impregnated with phenolic resin is not applied. LPL using external adhesive is typical used when postformable foil is desired to cover continuous and curve edges (Figure 1.18).

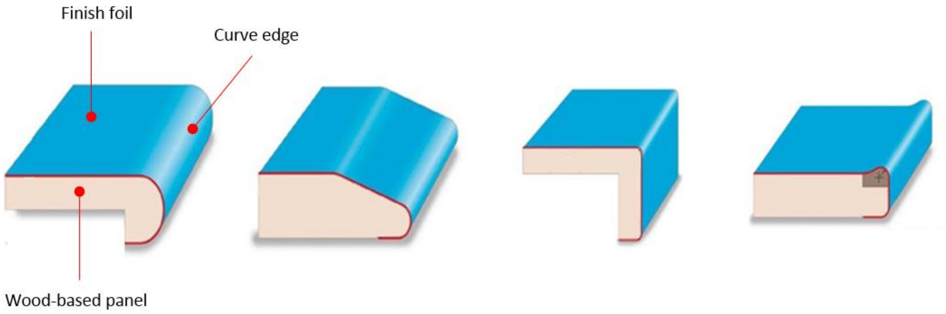


Figure 1.18. Schematic representation of different profiled edges in wood-based composites (adapted from [73]).

1.4.2. Application

Decorative laminates are widely used indoor and outdoor applications, as desk and table tops and facing for walls, doors and flooring [70]. Intensive applications as school furniture, laboratory and hospital worktops, decks and flooring for public buildings demand multifunctional surfaces with special properties as *mar* and abrasion resistance [74], [75], self-cleaning [76], antibacterial [77], or resistance to UV light [78]. However, laminates are susceptible of damages when exposed to critical conditions or long-term use. These materials may develop microcracks with negative visual impact, which are impossible to remove in traditional formaldehyde-based resins. A possible solution for this problem may be the development of laminates 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, minimizing negative visual impact of the damaged surface [79], [80]. This approach allows to obtain more durable materials, with reduced maintenance costs and with a broader range of application in aggressive environments.

Flexible CPL offers a unique range of formable decorative laminates suitable for profile wrapping and edge banding applications [71]. Surface properties are similar to vertical grade HPL and it is used significantly to complement HPL [71]. Flexible CPL allows postformable finishes because it can be curved around the edges [71]. Similar solutions when flexible surfacing material is desired are founded at low pressure laminates and finished foils which are supplied fully cured and require a glue system to bond them to a substrate [71]. In order to add postformability to a laminate, some solutions have been described in patents. Patents and scientific papers suggest to modify the melamine resin that is used to impregnate the decorative layer, with caprolactams [81], glucosides [82], carbamates [26], mannatin [83], epoxies [84] and polyethylenoglycol [44] as described before. Also several patents describe the modifications of the phenolic resins to improve the postforming characteristics [85]. Another patented product to make postforming laminates was polyurethane resin [86] instead amino-formaldehyde resin.

1.5. Cork-based panels

1.5.1. Cork: structure and composition

Cork is a natural cellular suberous material covering the species *Quercus suber L.*, commonly known as the cork oak and harvested from the tree periodically, usually every 9–12 years, depending on the country [87]. Cork oak forests spread in the western Mediterranean areas (Iberian Peninsula, south of France and Italy) of Southern Europe and North Africa [88].

Cork is a recyclable and renewable source of raw material characterized by an interesting combination of properties: low density (120 to 190 kg/m^3), low thermal conductivity, fire retardancy, impermeability to liquids and gases, elasticity and resilience, chemical stability and durability [87]–[89]. Chemically, it is mostly composed by suberin (45 %) which is a glyceridic polyester of linear long chain fatty acids and alcohols responsible for cork compressibility and elasticity); lignin (27 %), an aromatic crosslinked polymer which is responsible for the structural rigidity of the cells and their resistance to compression; saccharides (12 %) also linked to construction of the cork structure; and extractives (16 %), i.e. non-polar compounds (e.g. lipids and terpenes) and polar compounds, mostly of phenolic nature, which can be solubilized without impairing the materials properties [88], [90]–[92]. Cork also contains ashes, ceroids and tannins which contribute to impermeability and provide colour and protection/conservation [88], [90]–[92].

This green material presents an alveolar cellular structure similar to that of a honeycomb, formed by small regular hexagonal prismatic closed cells [88] as schematized in Figure 1.19.

The insulation characteristics of cork are due to these tiny cells filled with gas. The volume of the cell walls is about 10-15 % of the total volume, so there is an empty space of about 85-90 %, which gives this material its insulation properties and resilience [92].

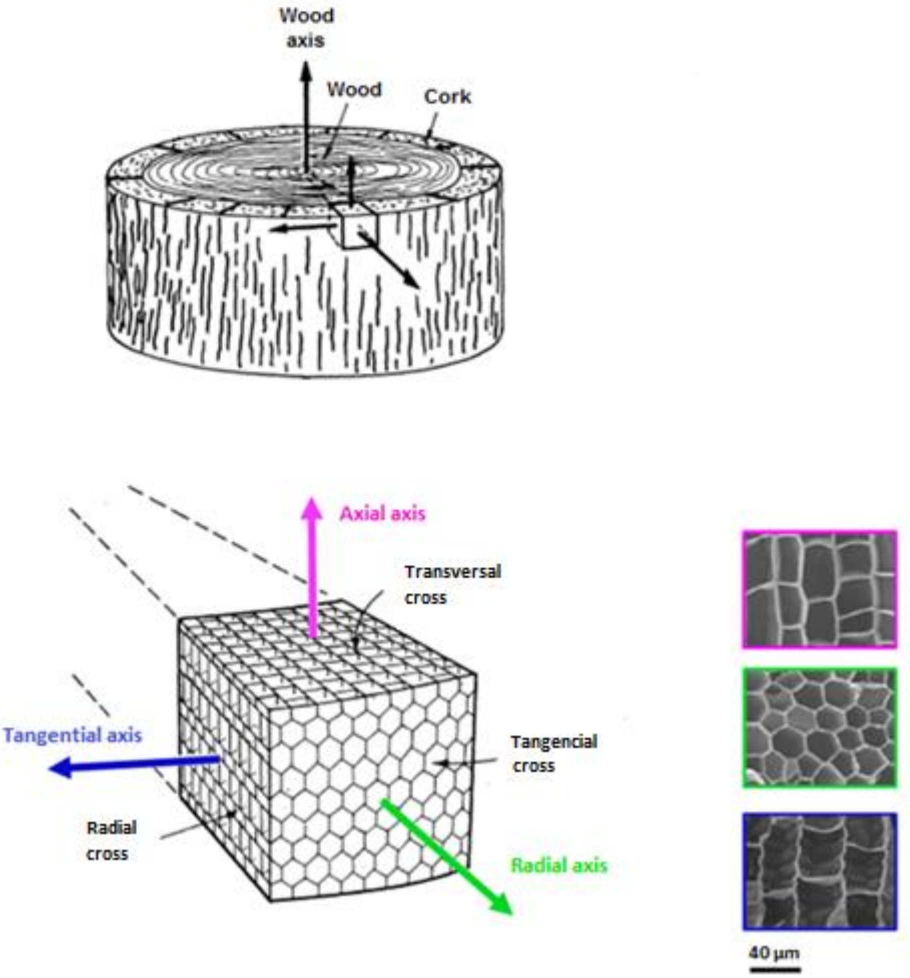


Figure 1.19. Schematic representation of cork cells (adapted from [93]–[95]).

The cork structure is anisotropic. The three main directions for cork are the radial (parallel to the spokes of the tree), the axial (vertical direction in the tree) and tangential (perpendicular to the other two, tangent to the circumference of the section of the tree) [88]. The sections perpendicular to these three directions are respectively designated as tangential, transverse and radial [88]. However, the anisotropy is no longer felt when we have a cork agglomerate, given the random orientation of the granules, which is the case of cork products for the construction industry.

1.5.2. Production and application of agglomerated cork panels

In many applications, agglomerated cork is used. This material is made from a mixture of natural cork and an organic adhesive. The process is carried out under a moderate pressure and heating adequate for the specific polymer curing and bonding [96].

Construction is the most common application for cork agglomerate. The residual cork from other productions is crushed to produce cork granules of different dimensions and density (typical range 1–10, 2–5, 1–2, 0.5–1 and 0.2–0.5 mm) [90]. Cork granules can assume three products direction: expanded cork agglomerates, rubber-cork composites and agglomerate cork mixed with a polymeric binder [88], [90]–[92].

The production of expanded cork agglomerates occurs under superheated steam and without external binding agent. The agglomeration is made by the autoclaving process. Granulates are introduced into the mold and this is slightly compressed. The cooking is effected under superheated steam at temperature ranging from 300 to 370 °C and cooking times from 17 to 30 minutes. The superheated steam passes through the mass of granules and produces the extraction of the cork resins to the surface of the granules. Inside the mold, the granules volume increase and the presence of natural adhesive results in the cork granules agglutination. The blocks produced are cut into plates of different thicknesses, followed by sanding surfaces when desired [88], [90]–[92].

Rubber-cork composites are copolymerized with rubber and other additives (vulcanizing and curing agents, anti-oxidants, dyes) to make the final product. The mixture is homogenized, compressed and heated in rotating cylindrical mixers. When the mixture form a homogeneous mass, this material is put into the mold, pressed and cured. The cure can be done by heat or high frequency radiation. In the last case, the cure time are 10-12 minutes [88], [90]–[92].

The flooring and surfacing agglomerates are produced from rectangular prismatic or cylindrical blocks. The final product is laminated into boards or rotary lamination originating a continuous cork sheet roll (Figure 1.20), respectively [90].

Figure 1.20. Example of agglomerated cork panels in roll form.

The binders include thermosetting polymers, such as urea–formaldehyde, melamine-urea-formaldehyde or phenolic adhesives or thermoplastic polymers such as polyurethanes [41]. The polymeric cure can be done under heat furnaces or continuous or discontinuous high-frequency systems. In the first case, the generally used temperatures are between 110-150 °C, with a duration of 4 to 22 hours. In the second case, the residence time is 3 and 4 minutes. At the end, the sanding is performed to correct its thickness and to obtain the desired roughness [88], [90]–[92].

The final application of cork composites are thermal and acoustic insulation (walls, ceilings, floors), expansion joints, ceiling tiles or underlays, floating floor panel and linoleum, external cladding, road pavement, industrial proposes for anti-vibration and insulation of machinery, automobile and fashion industry [88], [90]–[92].

1.5.3. Characterization of agglomerated cork panels

CT 16 “Cortiça” is the Portuguese Technical Commission for Standardization that was created to care this point. At international level, there is the Technical Commission ISO / TC 87 Cork [92].

At European level, there are three Technical Committees of the European Committee for Standardization directly linked to the implementation of specific agglomerated cork products: the thermal "expanded" (CEN / TC 88 “Thermal insulating materials and products”), the "parquet" (CEN / TC134 “Resilient, textile and laminate floor coverings”) and wall coverings in panels and rolls (CEN / TC 99 “Wall coverings”) [92].

Each product presents different requirements and specific test methods referring to the respective standards. For this reason, the following are tables on the standardization of cork products for construction, where formaldehyde-resins could be used. Table 1.2 and Table 1.3 also show the characteristics, requirements and methods to classify the final product.

Table 1.2. Agglomerated cork board for wall cladding: characteristics, requirements and methods (adapted from [92])

Characteristics	**Requirements**		**Methods**
Side length	Tolerance without nominal value: ± 0.5 %		NP EN 427
Total thickness	Minimum	Tolerance	NP EN 428
Type I:	10 mm	± 0.8 mm	
Type II and III:	2 mm	± 0.3 mm	
Tensile strength	≥ 300 kPa		ISO 7322
Dimensional stability	Maximum variation: ≤ 0.4 %		NP EN 434
Curling	≤ 6 mm		NP EN 434
Humidity	≤ 7 %		NP EN 12105
Density	To be declared by the manufacturer		NP EN 672
Joint strength	Should not take off		ISO 8724
Formaldehyde emission	≤ 95 mg/kg		NP EN 12149

Table 1.3. Cork particle rolls for wall cladding: characteristics, requirements and methods (adapted from [92])

Characteristics	Requirements	Methods
Dimensions Thickness: Length:	Tolerance without nominal value: ± 1 % ≥ Nominal value	NP EN 426
Total thickness	Tolerance without nominal value: ± 0.3 mm	ISO 7322
Tensile strength	≥ 200 kPa	ISO 7322
Humidity	≤ 7 %	NP EN 12105
Flexibility	Must not crack	EN 4708
Formaldehyde emission	≤ 95 mg/kg	NP EN 12149

All tests mentioned above are used to characterize wood based panels, produced with resins of different nature [97]. However, it must be noted that flexibility evaluation is only performed on polyurethane cork composites, and formaldehyde emission only on amino-formaldehyde composites.

Flexibility

The flexibility of agglomerate cork panels was evaluated following a cylindrical mandrel bending test, according to ASTM F147-87. The method consists in bending the specimen on cylindrical mandrels with different diameters ranging from F3 to F16, respectively, from 3 to 48 mm. The flexibility of the specimen corresponds to the minimum mandrel diameter about which the specimen could be flexed without exhibiting any signs of failure. A flexibility factor may also be calculated by dividing this minimum diameter by the nominal original thickness of panel.

Formaldehyde content

With the purpose of to reduce formaldehyde emissions from wood composite products, which will reduce exposures to formaldehyde and result in benefits from avoided adverse health effects, determination of formaldehyde emission can be performed by several methods and standards. Table 1.4 summarize the classification of wood-based panels according to the formaldehyde emission level and the most important test method which could be used in agglomerated cork panels.

Table 1.4. Classification of wood-based panels according to the formaldehyde emission level (adapted from [98])

Classification	Standard	Analysis method	Region	Limit Value
E2	EN 13986	EN 717-1	Europe	$> 0.124\ \mathrm{mg \cdot m^{-3}}$ air
		ISO 12460-3		$3.5 < \mathrm{mg \cdot m^{-2} \cdot h^{-1}} \leq 8$
		ISO 12460-5		$8 <$ mg/100 g oven dry board ≤ 30
E1		EN 717-1		$\leq 0.124\ \mathrm{mg \cdot m^{-3}}$ air
		ISO 12460-3		$\leq 3.5\ \mathrm{mg \cdot m^{-2} \cdot h^{-1}}$
		ISO 12460-5		≤ 8 mg/100 g .d.b.
E1 plus		EN 717-1		$< 0.08\ \mathrm{mg \cdot m^{-3}}$
F**	JIS A 5908 & 5905	JIS A 1460	Japan	$\leq 1.5\ \mathrm{mg \cdot l^{-1}}$
F***				$\leq 1.0\ \mathrm{mg \cdot l^{-1}}$
F****				$\leq 0.3\ \mathrm{mg \cdot l^{-1}}$
CARB I	CARB	ASTM E1333	USA	0.18 ppm
CARB II				0.09 ppm

Perforator method – EN ISO 12460-5 – This method measures the formaldehyde content of wood-based panels emitted under forceful conditions. The principle of the method is that formaldehyde is extracted from test samples by boiling in toluene and then transferred into distilled or demineralized water. The formaldehyde content of this aqueous solution is determined photometrically by the acetylacetone method. Due to this fast execution, this method is used daily as a factory control. The biggest disadvantage of this method is the toluene environmental impact.

Gas analysis method – ISO 12460-3 – It is used to determine formaldehyde released at accelerated conditions (temperature of 60 °C, period of 4 hours). The principle is that a test sample of known surface area is placed in a closed chamber in which temperature, relative humidity, airflow and pressure are controlled to defined values. In the chamber the formaldehyde released mixes with the air. This air is continually drawn from the chamber and passes through gas bottles, containing water, which absorbs the released formaldehyde. At the end of each test, the formaldehyde concentration is determined photometrically using the acetylacetone method.

Desiccator method – ASTM D 5582 – It is defined in the Japanese standard JIS A 1460 and it is one of the most economical methods. The principle of the test is that the quantity of formaldehyde emitted is obtained from the concentration of formaldehyde absorbed in distilled water or deionized water when the pieces of specified surface are placed in the desiccator. The principle for this determination is made using the acetylacetone method.

Chamber method – EN 717-1 – The quantification of formaldehyde emission from a product under typical indoor conditions in real-life and over defined time scales requires the use of a climate-controlled chamber. In this test, the samples are placed in a chamber that has its temperature, relative humidity, air velocity and exchange rate controlled. The formaldehyde concentration is determined by drawing air trough gas washing bottles containing water that absorbs the formaldehyde.

1.6. Thesis motivation and outline

The big challenge of this PhD Thesis is the development of flexible resins for finish foil and cork-based panels.

This PhD work started within the scope of the project entitled “2GLAM – Second generation laminates” under the framework of “QREN – I&D em Co-promoção”-Compete programme. This project involved three academic partners and an industrial promoter: The academic partners are Faculty of Engineering of University of Port (FEUP), Polytechnic Institute of Viseu (IPV) and University of Aveiro (UA) and the industrial promoter are EuroResinas – Indústrias Químicas S.A. (Sines, Portugal). The motivation of this work was to acquire know-how and develop a polyurethane resin for paper impregnation for high and low pressure laminates. According to the strategic interests of the industrial partner, this resin should be: one component, transparent and high gloss, flexible and it could show self-healing properties.

At the end of the 2GLAM project, the challenges have changed and this PhD was supported by another project: “2GAR – Second generation of amino-resin” under the framework of “COMPETE2020” programme. This project involved two academic partners (FEUP and IPV) and an industrial promoter EuroResinas – Indústrias Químicas S.A. (Sines, Portugal). The aim of 2GAR was the development of amino-resins which specific performance, including amino-formaldehyde resin to produce flexible agglomerated cork panels. This resin should be water-based and hydrolysis resistant, with formaldehyde content ≤ 8 mg/100 g oven dry panel (class E1). Agglomerated cork panels done with this resin must present a tensile strength ≥ 200 kPa (APCOR requirement) and not rupture when flexed on cylindrical mandrels ≤ 9 mm (F3). Resin price could be lower than 1500 €/ton.

From first challenge, polyurethane finish foil with self-healing ability was developed. From second challenge, the impact of resin nature and resin content in agglomerated cork panels were studied. From third challenge, some strategies were suggested and tested to improve the flexibility of the amino-formaldehyde resin: introduction of long flexible chains in amino-formaldehyde structure; decrease the high crosslinking degree of amino-formaldehyde resins using chain growth blockers; and plasticize the amino-formaldehyde resin adding bulky domains.

The present thesis is divided into seven chapters, including a global introduction in Chapter 1.

Chapter 2, “Postformable and self-healing finish foil based on polyurethane-impregnated paper”, describes the development of a self-healing and post-formable finish foil, based on impregnation with an optimized formulation of polyurethane resin.

Chapter 3, “Effect of resin nature and content on mechanical properties of cork-based panels” explores the impact of resin nature and content on the physico-mechanical properties of agglomerated cork panels.

Chapter 4, “Blocked melamine-urea-formaldehyde resins and their usage in agglomerated cork panels” describes a strategy to improve the flexibility of agglomerated cork panels bound with amino-formaldehyde resins based on the use of chain growth blockers added in the synthesis of the resins.

Chapter 5, “Partial replacement of melamine by benzoguanamine in MUF resins towards improved flexibility of agglomerated cork panels” describes an alternative strategy, based on introduction of bulky substituent groups in the highly crosslinked structure of melamine-urea-formaldehyde resin.

Chapter 6, “Introduction of linear segments in amino-formaldehyde resins” describes the third and last strategy, which incorporated linear segments (hydroxyl and amine terminated) to improve the flexibility of agglomerated cork panels.

The main conclusions of this work and suggestions for future work that can be done in the future can be found in Chapter 7.

Figure 1.21 shows a schematic illustration of the correlation between the chapters of this thesis.

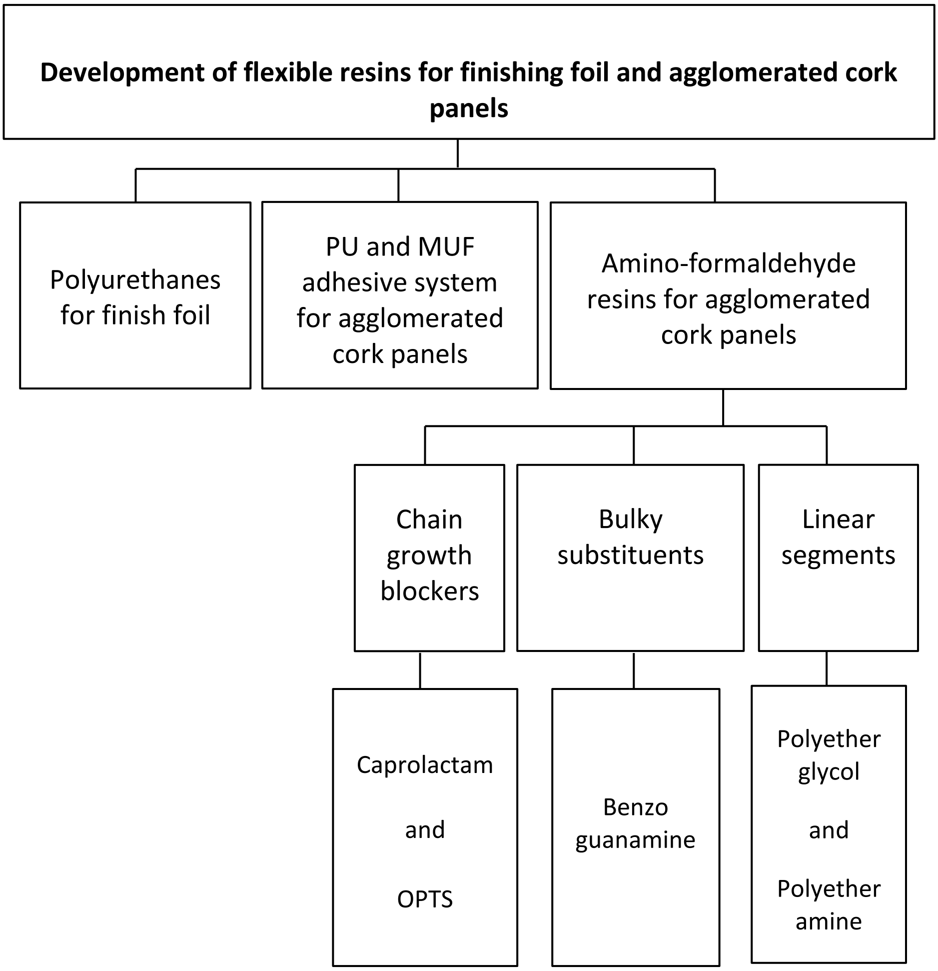


Figure 1.21. Schematic illustration of the correlation between the chapters in this thesis.

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CHAPTER 2

Postformable and self-healing finish foil based on polyurethane-impregnated paper

2. Postformable and self-healing finish foil based on polyurethane-impregnated paper [1]

Abstract

Polyurethane moisture-curable resins obtained from isophorone diisocyanate (IPDI) and polypropylene glycol (PPG) with different molecular weights (400, 1000, and 2000 g/mol) were used for impregnating décor paper. In addition to providing the same level of physicomechanical surface performance and visual appearance as the traditional melamine-formaldehyde impregnated paper, these finish foils are postformable and self-healing. The influence of the NCO/OH molar ratio and polyol molecular weight on the physical properties of the resultant polymers and composites foils were investigated in detail, namely using dynamic mechanical analysis, tensile-strain testing and contact angle measurements. The most promising polyurethane-impregnated papers were additionally tested according to European Standard EN 438-2.

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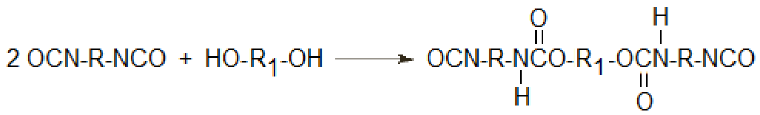
2.1. Introduction

Paper sheets impregnated with a thermosetting amino resin form a finish foil frequently used for surface protection and decoration of medium density fibreboards (MDF) and particleboards in the furniture industry. A melamine-formaldehyde (MF) resin is typically used, hence its common designation as “melamine finish foil” [1]. After impregnation, the paper is dried and afterward pressed over the intended substrate, upon which the MF resin becomes fully cured [2]. The paper becomes extremely brittle 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.

Polyurethanes are considered one of the most versatile class of polymers for numerous commercial applications, such as coatings, foams, adhesives, sealants, membranes, and elastomers [3]. These polymers can be cured by UV, electron beam radiation, heat, or reaction with moisture [3].

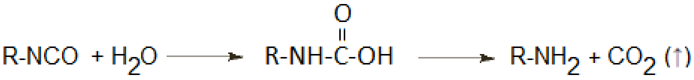
Moisture-curable polyurethanes are isocyanate-terminated prepolymers synthesized by reacting a polyol and an isocyanate (Eq. 2.1).



$$2\ \mathrm{OCN{-}R{-}NCO} + \mathrm{HO{-}R_1{-}OH} \longrightarrow \mathrm{OCN{-}R{-}\underset{\overset{|}{H}}{N}\overset{\overset{O}{\|}}{C}O{-}R_1{-}O\underset{\underset{O}{\|}}{C}\overset{\underset{|}{H}}{N}{-}R{-}NCO}$$

Eq. 2.1

Water vapor from the atmosphere diffuses into the polymer and the nucleophilic attack of water on NCO end-groups results in an irreversible reaction that produces carbamic acid. This is unstable at room temperature and decomposes into carbon dioxide and a primary amine (Eq. 2.2). The amine reacts with another NCO end-group of the prepolymer, forming an urea linkage (Eq. 2.3) [4].



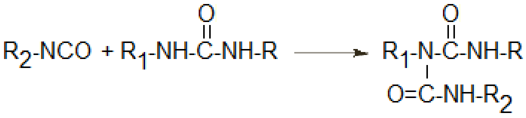
$$\text{R-NCO} + \text{H}_2\text{O} \longrightarrow \text{R-NH-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OH} \longrightarrow \text{R-NH}_2 + \text{CO}_2\ (\uparrow)$$

Eq. 2.2

$$\text{R-NCO} + \text{R-NH}_2 \longrightarrow \text{R-NH-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH-R}$$

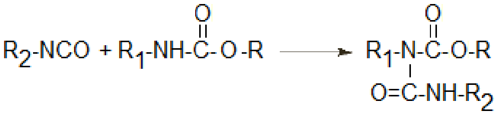
Eq. 2.3

When the isocyanate content is in excess, chemical cross-linking through biuret (Eq. 2.4) and allophanate (Eq. 2.5) linkages also occurs [4]–[6].



$$\text{R}_2\text{-NCO} + \text{R}_1\text{-NH-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH-R} \longrightarrow \text{R}_1\text{-}\underset{\text{O=C-NH-R}_2}{\underset{|}{\text{N}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH-R}$$

Eq. 2.4



$$\text{R}_2\text{-NCO} + \text{R}_1\text{-NH-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-R} \longrightarrow \text{R}_1\text{-}\underset{\text{O=C-NH-R}_2}{\underset{|}{\text{N}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-R}$$

Eq. 2.5

Cured polyurethanes are segmented copolymers exhibiting microphase-separated morphologies. One phase, referred to as soft phase, comes from the relatively long and flexible polyol segments. The hard phase, on the other hand, corresponds to the monomeric or polymeric isocyanate segments that create rigid domains of intermolecular physical cross-links through hydrogen bonding [3], [6].

Polyurethanes are known for their good mechanical and chemical resistances, in combination with high flexibility. In addition, these polymers can be formulated so as to be self-regenerative under exposure to moderate heat, without need for other type of direct maintenance [7]. The use of a polyurethane-based resin in the context of impregnated décor paper has been described before [8]. However, the polyurethane resin was used as a lacquer over a foil that had been previously impregnated with melamine-formaldehyde resin. The purpose was to minimize microcracks that normally occur in this material, and at the same time improve its weather resistance.

The purpose of the current work is to evaluate the possibility of using a polyurethane moisture-curable resin to impregnate décor paper, replacing the traditional melamine-formaldehyde resin. The resulting finish foil is intended to display novel properties, namely postformability and self-healing, which are absent in the traditional melamine finish foil. Aliphatic isocyanate IPDI was selected for the polyurethane synthesis. Aromatic isocyanate alternatives [9], [10] were rejected because of the characteristic yellowish [11] tint that would alter the final appearance of the impregnated paper. The use of IPDI in polyurethane synthesis has been widely reported in the literature [12]–[18]. The final foil should comply with the physicochemical requirements specified in European Standard EN 438-2. This norm is used in industry for decorative high-pressure laminates, being actually more demanding than the one commonly used for melamine finish foil, which is EN 14323. To the best of our knowledge, this is the first report of a finish foil based on décor paper impregnated with polyurethane moisture-curable resin and self-healing properties.

2.2. Materials and Methods

2.2.1. Materials

Polypropylene glycols (PPG) were obtained from Dow Chemical Company: Voranol2000L (PPG2000), number-average molar mass 2000 g/mol with a hydroxyl value of 56; Voranol1010L (PPG1000) number-average molar mass 1000 g/mol with a hydroxyl value of 110; VoranolP400 (PPG400) number-average molar mass 400 g/mol with a hydroxyl value of 260. The polyols were vacuum-dried at 80 °C overnight. Isophorone diisocyanate (IPDI) and dibutyltin laurate (DBTL) were purchased from Sigma-Aldrich, U.S.A. Table 2.1 shows some raw material properties.

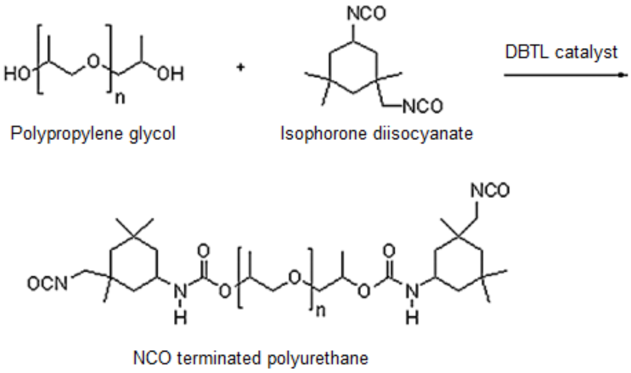
Melamine-formaldehyde (MF) resin was provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal). Its physical characteristics are 55 % solid content; pH range of 9.00-10.00 and kinematic viscosity range of 16 – 18 seconds (using Ford Cup no. 4 viscosity method).

Table 2.1. Properties of IPDI and PPG used for the synthesis of polyurethane moisture-curable resins

property	IPDI	PPG400	PPG1000	PPG2000
average functionality	2.0	2.0	2.0	2.0
OH number (mg KOH/g)	0.0	260	110	56
NCO content (wt %)	37.7			
molecular weight (g/mol)	222	400	1000	2000
viscosity 25 °C (cP)	15	70	145	320

2.2.2. Synthesis of polyurethane moisture-curable resin

The polyurethane resin (PU) was prepared by reaction of PPG polyol with IPDI and catalyst DBTL (0.5 %) in a three-necked 1000 ml glass flask, under dry nitrogen atmosphere. The chemical reaction scheme is depicted in Eq. 2.6 [19].



Eq. 2.6

The system was kept at 70 °C during 2 h and mechanically stirred at 200 rpm. Four different molar ratios of the NCO to OH group were chosen for the formulations, i.e., NCO/OH of 1.0, 1.5, 2.0, and 2.5. Table 2.2 shows compositions of the synthesized polyurethanes. After 2 h of reaction, a small portion (approximately 2 g) of polyurethane was taken out from the reactor for determination of % NCO content determined by titration with N,N'-dibutylamine (ASTM D 2572-91). The reaction was stopped when the measured NCO content corresponded to the intended NCO/OH ratio. Samples were named according to the molecular weight of polyol used in the synthesis and the NCO/OH ratio. For example "PPG2000_2.5" signifies: polyurethane moisture-curable resin synthesized with PPG polyol with molecular weight of 2000 g/mol and NCO/OH ratio of 2.5.

An excess of isocyanate was used in most formulations, as it was intended to obtain a reactive resin. Formulation PPG2000_1.0, with a NCO/OH ratio of 1.0, serves as a reference.

Table 2.2. Compositions of the synthesized polyurethane moisture-curable resins

System	NCO/OH molar ratio	IPDI (g)	PPG400 (g)	PPG1000 (g)	PPG2000 (g)	% NCO
PPG2000_2.5	2.5	215	_	_	785	4.8
PPG2000_2.0	2.0	180	_	_	820	3.4
PPG2000_1.5	1.5	140	_	_	860	1.7
PPG2000_1.0	1.0	100	_	_	900	0.0
PPG1000_2.5	2.5	355	_	645	_	8.0
PPG1000_2.0	2.0	310	_	690	_	5.9
PPG1000_1.5	1.5	250	_	750	_	3.2
PPG400_2.5	2.5	580	430	_	_	13.1
PPG400_2.0	2.0	520	480	_	_	9.6
PPG400_1.5	1.5	450	550	_	_	5.5

2.2.3. Production of polyurethane films

Free standing polyurethane films were prepared by the casting-evaporation process. Approximately 10 % solution of polyurethane resin in tetrahydrofuran was prepared and poured into a PTFE-coated mold. This was then kept at room temperature for 48 h, until all the solvent evaporated and a transparent film was formed. To ensure complete solvent evaporation, films were afterward dried in a vacuum oven at 60 °C until constant mass. The films obtained were about 1 mm thick and 100 mm in diameter.

2.2.4. Production and cure of impregnated paper

Décor paper (grammage 100 g/m^2) was impregnated with polyurethane by soaking. The impregnated sheets were submitted to hot pressing at 140 bar and a temperature of 100 °C during 1 h. Preliminary calorimetric data obtained with a simultaneous thermal analyzer (STA), not shown here, revealed that the cure of the polyurethane resins occurs around 90 °C, below the selected pressing temperature. The final grammage of impregnated paper with PU was 190 g/m^2.

The décor paper impregnated with melamine resin was submitted to the same conditions.

2.2.5. Resin characterization

Viscosity

Kinematic viscosity of the polyurethane resin was determined by Brookfield viscometer. The measurements were performed at 25 ± 1 °C and 3 rpm using spindle LV-4 (64). Dynamic viscosity of the MF resin was determined by Ford Cup no. 4 method.

Penetration and saturation time of décor paper

The inverted bottle method is commonly used in industry to evaluate the ease of penetration of a resin on paper. The liquid resin is placed in a bottle with a neck 25 mm in diameter. A disk of décor 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.

Pot life

To determine the pot life, about 50 ml of the polyurethane resin is poured in a polypropylene bottle at room temperature. The bottle is kept open at room temperature, and the viscosity is measured until attaining a maximum value of 600 000 cP by Brookfield viscometer. The time taken to attain this viscosity is recorded.

Flexibility of films

The flexibility of the polyurethane films and impregnated papers was measured according to ASTM F147-87. The method consists in bending the specimen on a mandrel. Mandrels have rings with diameters ranging from 3 mm to 48 mm, corresponding to designations F1 to F16. The flexibility of the specimen corresponds to the mandrel diameter on which fracture occurs. A flexibility designation of F1 would therefore corresponds to maximum flexibility in this test.

Color, gloss and tack of films

The color and gloss of the polyurethane films was evaluated by visual observation. To assess the tack, a clean finger touched with light pressure the film surface and its tack was evaluated. This qualitative evaluation was considered sufficient for the purpose of the discussion presented here.

Automated bonding evaluation system

The bond strength of polyurethane resin as a function of molecular weight of polyol and NCO/OH ratio was measured using automated bonding evaluation system **(**ABES) (see Figure 2.1) [20], [21]. Two beech veneer strips measuring 0.5 mm thick, 20 mm wide and 117 mm in length, with a square of decor paper (100 g·m^{-2}) measuring 20 mm wide and 20 mm in length stored at 25 °C and 65 % of relative humidity were glued together with an overlap of 5 mm. The veneers and papers were prepared using a die cutter supplied by Adhesive Evaluation Systems (Corvallis, Oregon). Adherent pairs were mounted in the system with an overlapping area of 100 mm^2, pressed together at 1.2 N/mm^2 and 100 °C. After that the system was cooled to room temperature. The amount of adhesive system used for each test was 10 mg. The bond strength was tested almost instantaneously in shear mode (the system is digitally controlled and pneumatically driven). The results provided are the average of three measurements.

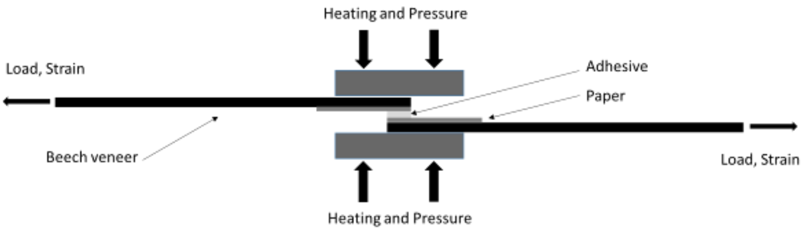


Figure 2.1. Schematic of the ABES test procedure. Adapted with permission from [Martins et al. Adhesive bond strength development evaluation using ABES in different lignocellulosic materials. Int. J. Adhes. Adhes. 2013, 47, 105–109]. Copyright [2013/Elsevier] [Elsevier/Elsevier].

Contact angle of polyurethane resin on paper

Contact angles were measured in a DataPhysics Contact Angle System OCA20, a video-based measuring device equipped with software for image analysis, using the sessile drop method. The droplet volume was 4 µl. Contact angles of resins on décor paper were measured during approximately 50 s, allowing the droplets to reach equilibrium.

Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM 35C-Noran Voyager equipment, at CEMUP – Centro de Materiais da Universidade do Porto.

Polyurethane and melamine impregnated papers were fractured under liquid nitrogen. Samples were coated with a gold/palladium alloy before analysis.

Dynamic mechanical analysis of polymer

Dynamic mechanical measurements (DMA) of polyurethane films were performed using a DMA 242 E Artemis (Netzsch) in tensile mode, under a temperature range from -80 to +150 °C. The heating rate was 2 $°C \cdot min^{-1}$, and a gaseous nitrogen stream was used to keep a controlled atmosphere inside of the sample container. The frequency used was 1 Hz with maximum dynamic force of 2 N and maximum strain amplitude of 10 μm. The specimens had a rectangular shape with dimensions 5 mm x 12 mm x 1 mm.

Glass transition temperatures were identified as corresponding to the peak on damping coefficient (tan δ) curve.

2.2.6. Impregnated paper characterization

Dynamic mechanical analysis

Dynamic mechanical properties of cured impregnated paper were evaluated as described before for polyurethane films. Different specimen dimensions were used: 5 mm x 0.1 mm x 13 mm.

Mechanical properties

The tensile strength, Young's modulus and elongation at break of the paper impregnated with polyurethane moisture-curable resin were measured in a universal testing machine Mecmesin MultiTest-1-d equipped with a Mecmesin BFG 1000 dynamometer, at a crosshead speed of 10 mm/min under room temperature. At least three replicas were made for each measurement and their results averaged to determine tensile strength, tensile modulus, and elongation at break of the materials. The dimension of the test specimen was 75 mm x 15 mm x 0.1 mm.

EN 438-2 standard tests

Resistance to dry heat

A specimen of impregnated paper was subjected to dry heat by contact with a metal block initially a 160 °C during 20 min. The metal block had an external diameter of (100 ± 15) mm and an overall height of (70 ± 15) mm. At the end of this period the metal block was removed and the specimen allowed to cool for a period of 45 min.

Afterward, the surface was classified according to the following scale:
5 - No visible change;
4 - Slight change of gloss and/or color, visible only at some viewing angles;
3 - Moderate change of gloss and/or color;
2 - Marked change of gloss and/or color;
1 - Surface damage and/or blistering.

Staining

In the staining resistance method the specimens were left in contact with different staining agents for specific times. At the end of the contact period, the specimens were washed with water and examined for residual surface marks. The staining agents were: sodium hydroxide (25 % solution), hydrogen peroxide (30 % solution), shoe polish, and acetone. For the first three, the contact time was 10 min, while for acetone it was 16 h. Afterward, the surface was classified according to the following scale:
5 - No visible change;
4 - Slight change of gloss and/or color, visible only at some viewing angles;
3 - Moderate change of gloss and/or color;
2 - Marked change of gloss and/or color;
1 - Surface damage and/or blistering.

Cigarette burn

A burning cigarette was 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 was not in contact with the specimen. The cigarette was allowed to burn until an additional 20 mm length is consumed. If the cigarette went out before this occurs the test was repeated.

Afterward the surface was classified according to a scale where
5 - No visible change;
4 - Slight change of gloss and/or color, visible only at some viewing angles, and or/ slight brown stain;
3 - Moderate change of gloss and/or moderate brown stain;
2 - Severe brown mark, but not destruction of the surface;

1 - Blistering and/or cracks.

Scratching

A square test specimen (100 ± 1) mm was subject to scratch with a diamond scratching point in the equipment Taber Shear/Scratch Tester Model 551. The resistance to scratching was expressed as a numerical rating (Table 2.3) that defines the maximum applied load that does not produce a continuous surface scratch.

Table 2.3. 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

Cracking

The specimen was heated to (80 ± 2) °C in a heating oven for (20 ± 1) h. At the end of this period, the specimen was allowed to cool for 3 h at (23 ± 2) °C. The specimens were then examined, in order to determine the presence of cracks on the surface, and the result expressed as a numerical rating:

5 - No visible change;
4 - Slight change of gloss and/or color, visible only at some viewing angles;
3 - Moderate change of gloss and/or color;

2 - Marked change of gloss and/or color;
1 - Surface damage and/or blistering.

2.2.7. Fourier transform infrared spectroscopy of uncured resin, cured films and impregnated paper

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}.

Resin films were prepared as described in section “Production of polyurethane films” and the impregnated paper according to section “Production and cure of impregnated paper”.

2.2.8. Self-healing analysis

Surface damage was produced with a X-Act blade and with steel wool on the polyurethane film surface and on the impregnated paper surface. The recovery process was promoted blowing hot air with a hairdryer (T ≈ 110 °C) during 2 min. Self-healing performance during this time was observed visually. For the surfaces damaged with the blade, the roughness profile was recorded at several times with a Mitutoyo SJ-400 surface roughness measuring system, and the arithmetic average of maximum heights on the surface profile (Rz) was computed. The recovery index was calculated according to Eq. 2.7:

$$Recovery\ index = \frac{R_z^t - R_z^0}{R_z^{paper} - R_z^0}$$

Eq. 2.7

R_z^{paper} is the surface roughness of pristine impregnated paper; R_z^0 is the surface roughness of impregnated paper at zero seconds of recovery; R_z^t is the surface roughness of damaged impregnated paper, after t seconds of recovery.

For the surfaces damaged with steel wool, a charge-coupled device (CCD) video camera was used to obtain a high-contrast image of the surface and confirm damage recovery.

2.3. Results and Discussion

2.3.1. Polyurethane moisture-curable resins

General properties of liquid resins and cured films

Thermoplastic polyurethanes are linear block copolymers formed by alternating hard and soft segments. They display phase-segregated morphologies due to the thermodynamic incompatibility between the domains formed by these blocks [22]. Depending on the chemical composition, chain length, molar ratio of the components, method of preparation and processing (prehistory), different degrees of interphase mixing may exist between the two types of domains. The resulting material can generically be viewed as a rubbery matrix of polyol segments enveloping hard domains of urethane and urea segments that form reinforcing physical crosslinks thanks to strong intermolecular hydrogen bonding [23].

Table 2.6 (Supporting Information in the end of this chapter) shows some physical characteristics of the synthesized polyurethanes in liquid and cured film form.

The viscosity of the liquid resin decreases as the molecular weight of the polyol is increased, for the same NCO/OH ratio. Less NCO groups are available per mass of material when using higher molecular weight polyol in the polyurethane formulation. As a consequence, the concentration of urethane linkages formed is lower, and intermolecular interactions are reduced, thereby causing a decrease in viscosity [24]. When the polyol molecular weight is the same, the increase in NCO/OH ratio results in a decrease of polyurethane resin viscosity, since the higher content of unreacted IPDI has a solvent effect in the resin [25].

The pot-life is an important property for this system, as it indicates the maximum time for which the system remains usable, in a fluid state, after opening the container to ambient humidity. In this study, the pot-life was defined as the time for the resin to reach a viscosity of 600 000 cP, as a consequence of progressive reaction of isocyanate with atmospheric humidity, forming urea linkages. The results in Table 2.6 show that the stability of the resin is significantly lower when lower molecular weight polyol is used and when the NCO/OH ratio decreases. This is due, in both cases, to the higher concentration of NCO groups available in the polyurethane resin leading to increased reactivity [25], [26].

All films obtained are transparent, colorless and glossy. These characteristics are essential for surface finish products. Film tack tends to increase with increasing molecular weight of the polyol. This occurs because higher molecular weight polyol confers higher mobility to the polymer chains and decreases the concentration of physical cross-linking sites, both factors contributing to increase tack of the produced films [27].

Film flexibility increases with the increase of polyol molecular weight and decreases with increase of NCO/OH molar ratio. Higher polyol molecular weight and lower concentration of urethane and urea linkages result in a high proportion of soft microdomains toward hard segments and thus higher flexibility of the final film. Nonetheless, all cases passed the F1 mandrel test.

Polyurethane resin adhesion to paper

ABES tests were carried out to determine the adhesion of the synthesized resins on paper. Figure 2.2 shows the results of maximum shear strength, for a press temperature of 100 °C, as a function of NCO/OH ratio.

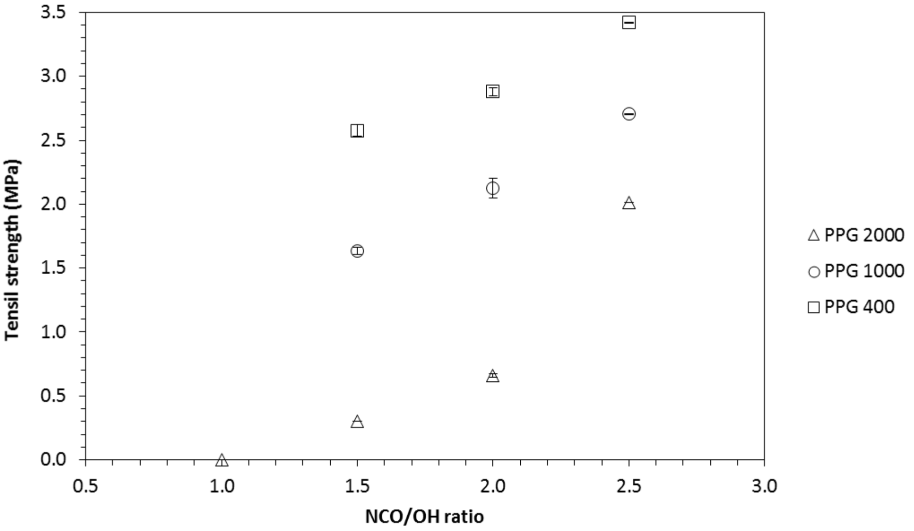


Figure 2.2. Shear strength results (ABES) obtained for polyurethane moisture-curable resins applied on paper.

As seen in Figure 2.2 and as expected, adhesive performance improves as NCO content increases. For NCO/OH molar ratio of 1.0 (tested with polyol molecular weight of 2000 g/mol), the shear strength is zero since there are no free isocyanate end groups to react with hydroxyls on paper surface. As NCO/OH molar ratio increases to 1.5, 2.0 and 2.5, shear strength increases to 0.30, 0.66, and 2.01 MPa, respectively, as a consequence of higher covalent interaction between paper and adhesive. On the other hand, for a constant NCO/OH molar ratio, the shear strength increases with decreasing polyol molecular weight. This trend is related to the higher concentration of reactive NCO groups in the resin as the molecular weight of polyol decreases, thus forming a denser physically-cross-linked structure.

Dynamic mechanical analysis of polyurethane films

The loss factor (tan δ) as a function of temperature for the films produced from the polyurethane moisture-curable resins are shown in Figure 2.3 and Figure 2.4.

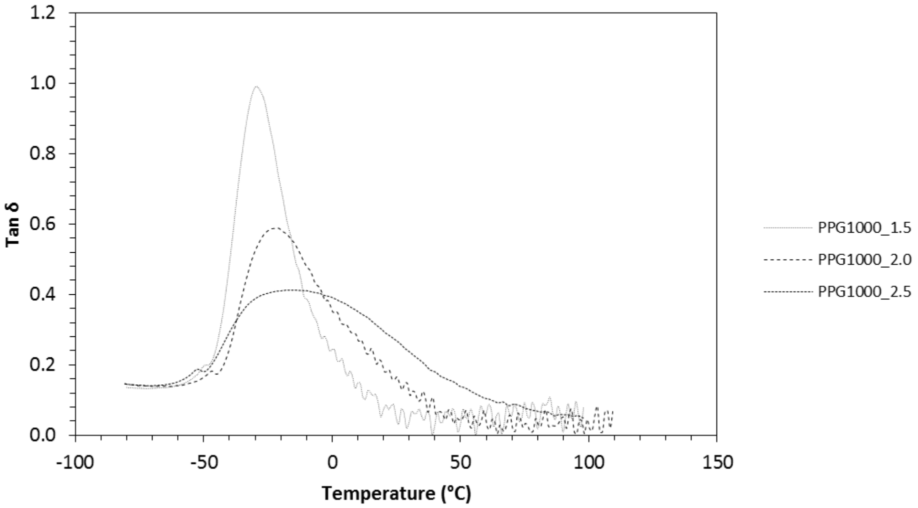


Figure 2.3. Loss factor, tan δ, as a function of temperature for polyurethane films obtained with PPG 1000 and different NCO/OH molar ratios.

Figure 2.3 shows tan δ for PPG 1000 and different values of NCO/OH molar ratio. Only one peak is distinctly visible in all cases, its maximum being located between -50 and 0 °C. This is assigned to the glass transition in soft segment domains, Tg_{SS}. As NCO/OH increases, Tg_{SS} also increases and the tan δ peak broadens. Higher NCO/OH ratio implies higher concentration of hard urethane and urea domains and more physical cross-linking within the film. This ends up restricting molecular mobility within amorphous regions and shifting Tg_{SS} from -29.5 to -17.3 °C. These observations are consistent with the DMA results obtained by Huh and Cooper for polyester and polyether-based polyurethanes [23]. In addition, these authors observed, like in our results, a very small peak in tan δ close to -49 °C. This was assigned to secondary relaxations associated with water attached by hydrogen bonds to –NH or –C=O groups. Films made with ratios of 1.5 and 2.0 soften significantly with heating, causing excessive instability in the measurements, as seen in Figure 2.3. The more densely physically cross-linked film obtained with NCO/OH of 2.5, on the other hand, yields a more stable behavior.

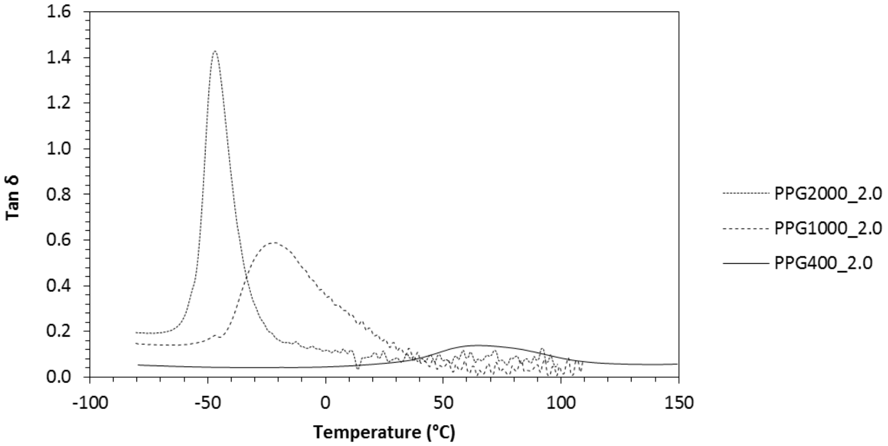


Figure 2.4. Loss factor, tan δ, as a function of temperature for polyurethane films synthesized with different PPG molecular weights and NCO/OH molar ratio of 2.0.

DMA runs with different PPG molecular weights, for a constant NCO/OH molar ratio of 2.0 are shown in Figure 2.4. As the soft segment length increases, there is an increased tendency for the soft segments to form larger and better defined domains. This results in a higher separation between hard and soft domains and effectively improves mobility of soft segments [17]. Tg_{SS} therefore decreases when polyol molecular weight is increased from 1000 to 2000, from -21 to -30 °C. In PPG400, a much higher glass transition is observed, at about 66 °C. In this case, the low mobility of the short soft segments, combined with the higher concentration of interacting polar groups, actually hinders their glass transition. The observed peak in tan δ corresponds to a transition within hard segment domains, associated to dissociation of intermolecular hydrogen bonds involving urethane and urea groups [23], [24]. A similar tan δ transition was observed for PPG400_2.5 (not shown here). The fact that this polyol yields a glass transition above room temperature is determinant for its self-healing properties, as will be discussed later.

Films made with PPG1000 and PPG2000 soften significantly at temperatures above 50 °C, causing excessive instability in the measurements and forcing the equipment to halt the run at 110 °C, as shown in Figure 2.4.

2.3.2. Impregnated paper

Paper impregnation

The molar ratio NCO/OH 2.5 resulted in the best adhesive properties; therefore, only the resins prepared with this ratio have been studied further.

The penetration of a wetting fluid in paper is favored by low viscosity and low contact angle, *i.e.,* good wetting performance [28]. The evolution of contact angles between the polyurethane moisture-curable resins and the décor paper along time is shown in Figure 2.5. The results evidence a difference in the affinity of décor paper toward the different resins. PPG2000_2.5 and PPG1000_2.5 have low contact angles (close to 40° and 30°, respectively, at equilibrium), while PPG400_2.5 has a contact angle of about 50°. When the ether-based polyol segment in the PU increases, the chain hydrophilicity also increases[29], facilitating wetting of the paper.

From the studied resins, PPG2000_2.5 shows similar affinity to the décor paper as the melamine formaldehyde resin.

A standard inverted-bottle saturation test was used to evaluate the rate of penetration of the resins in décor paper. PPG2000_2.5 has the lowest viscosity and higher hydrophilicity and shows the fastest penetration and saturation of the décor paper, as expected (Table 2.4). Nonetheless, all resins are able to impregnate the paper uniformly. SEM images of papers impregnated with melamine resin and polyurethane moisture-curable resin show, in both cases, homogeneously distributed polymer within the paper fibers (Figure 6).

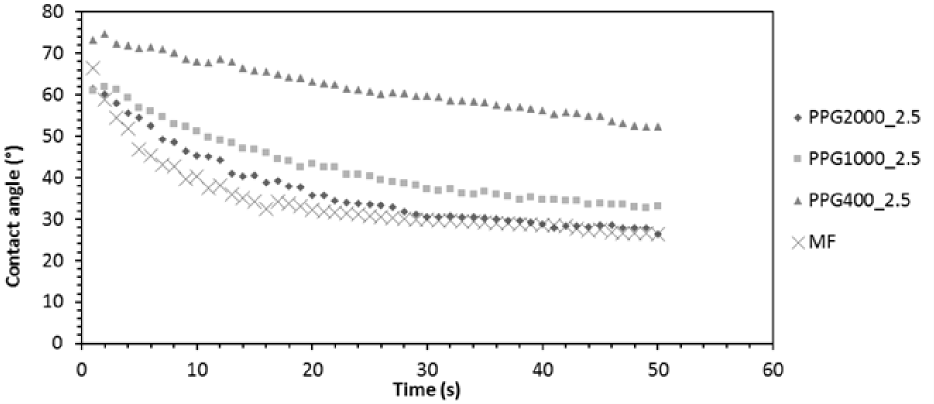


Figure 2.5. Contact angles recover over time for three polyurethane moisture-curable resins and melamine formaldehyde resin on décor paper.

Table 2.4. Penetration and saturation time for different polyurethane moisture-curable resins

polyurethane resin	penetration (s)	saturation (min)
PPG2000_2.5	12	4.2
PPG1000_2.5	90	6.4
PPG400_2.5	221	33.0

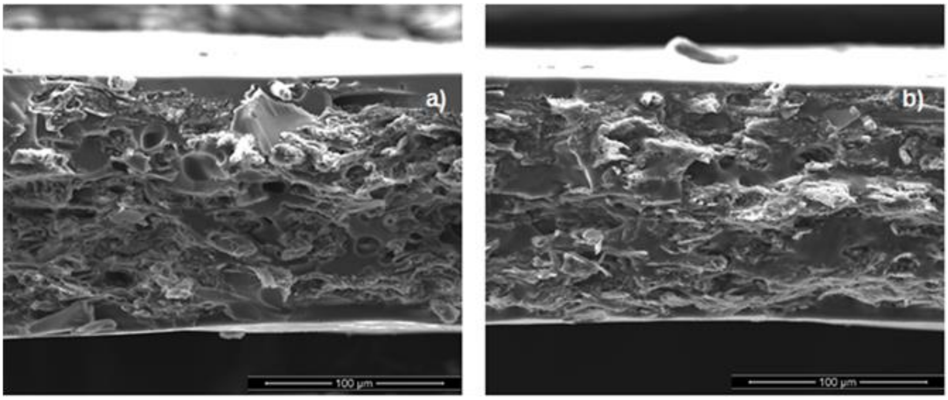


Figure 2.6. SEM micrographs of décor paper impregnated with (a) melamine resin and (b) polyurethane moisture-curable resin. Magnification is 1000× for both images.

Dynamic mechanical analysis of impregnated paper

The dynamic mechanical behavior of décor paper, alone and impregnated with polyurethane resins, is shown in Figure 2.7 and Figure 2.8. The paper shows three low intensity tan δ peaks, which can be associated with the transitions identified by Gregorova *et al.* for kraft paper [30]: motion of segments with intra/intermolecular hydrogen bonding in cellulose, at -50 °C (tan δ_1), motion of a lignin-cellulosic complex, at 25 °C (tan δ_2), and motion of segments in amorphous regions, above 100 °C (tan δ_3).

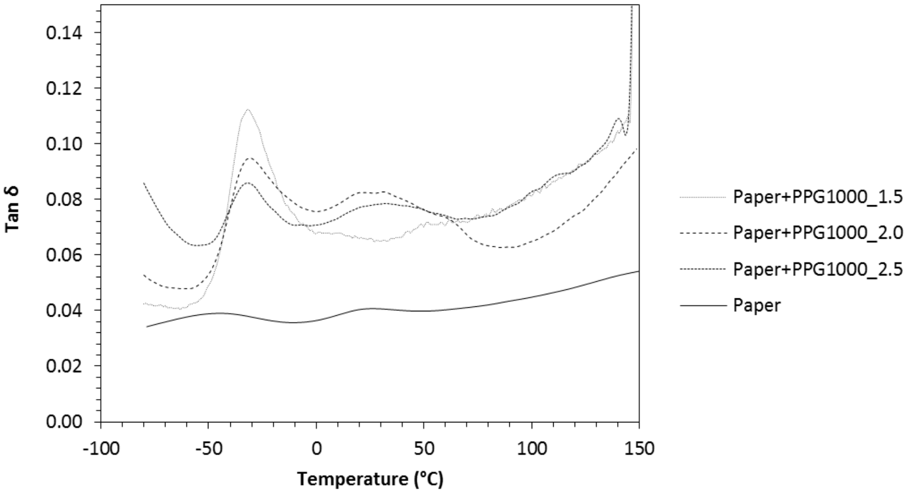


Figure 2.7 . Loss factor, tan δ, as a function of temperature for décor paper alone and décor paper impregnated with polyurethane synthesized from PPG1000 and different NCO/OH molar ratios.

In Figure 2.7, the PPG1000-based resin impregnated paper shows a transition peak around -30 °C, which corresponds to the soft segment glass transition previously observed in the polyurethane film. Interestingly, unlike with the films, in impregnated paper this transition does not shift with increasing NCO/OH molar ratio. Upon contact with paper, free isocyanate present in the polyurethane resin may react with hydroxyl groups in cellulose fibres, and not with water alone. Hydrogen bonding will also take place between polar groups from the hard segments and cellulose, and not only between polymer molecules. This leads to a different ordering of the hard segments, when compared with the free-standing films, and to a lower hindrance of soft segment mobility. A second transition is observed between 0 and 50 °C, being assigned to tan δ_2. Above 100 °C, the observed increase in loss factor is a consequence of the tan δ_3 transition in paper, combined with the onset of polymer softening.

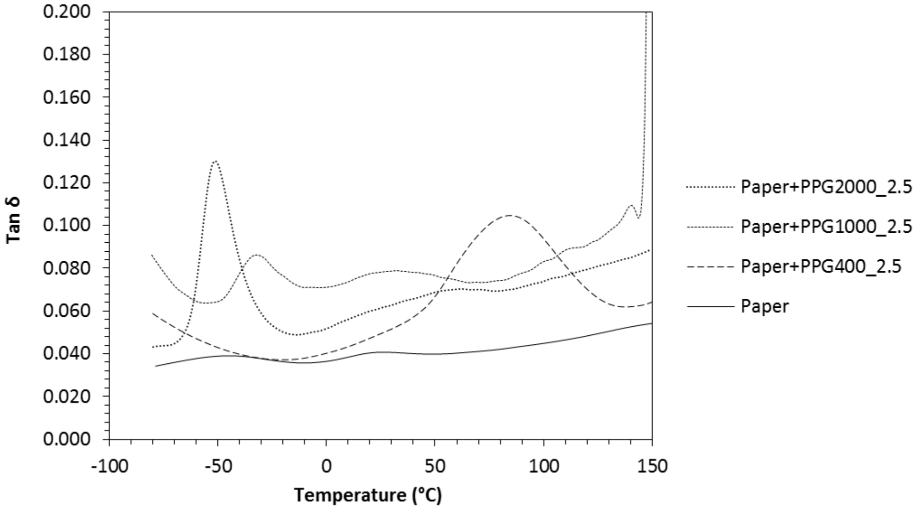


Figure 2.8. Loss factor, tan δ, as a function of temperature for décor paper alone and décor paper impregnated with polyurethane synthesized from PPG with different molecular weights and NCO/OH molar ratio of 2.5.

Figure 2.8 shows the transitions observed when the molecular weight of the polyol is changed, maintaining the NCO/OH ratio. As observed in the films, decreasing the length of soft segments from 2000 to 1000 increases Tg_{SS} noticeably, from -52 °C to -32 °C. When PPG400 is used, the soft segment transition disappears and a broad peak is clearly visible at around 85 °C, once again associated with a transition within hard domains. The fact that in impregnated paper this transition is shifted toward higher temperatures by more than 10 °C, in relation to free-standing polymer films, is due to physical and covalent interaction of polyurethane hard segments and cellulose fibres.

Mechanical properties of impregnated paper

After the impregnation and hot-pressing process, all the sheets show homogeneous colour and appearance. However, the materials obtained with

PPG 2000 and PPG 1000 resins exhibited some tack, more evident in the first case. PPG 400, on the other hand, yielded no tack.

Figure 2.9 shows representative examples of tensile stress–strain curves obtained for décor paper impregnated with different polyurethane moisture-curable resins. Figure 2.10, Figure 2.11 and Figure 2.12 summarize the mechanical properties computed from the stress–strain data, as a function of NCO/OH ratio and PPG molecular weight.

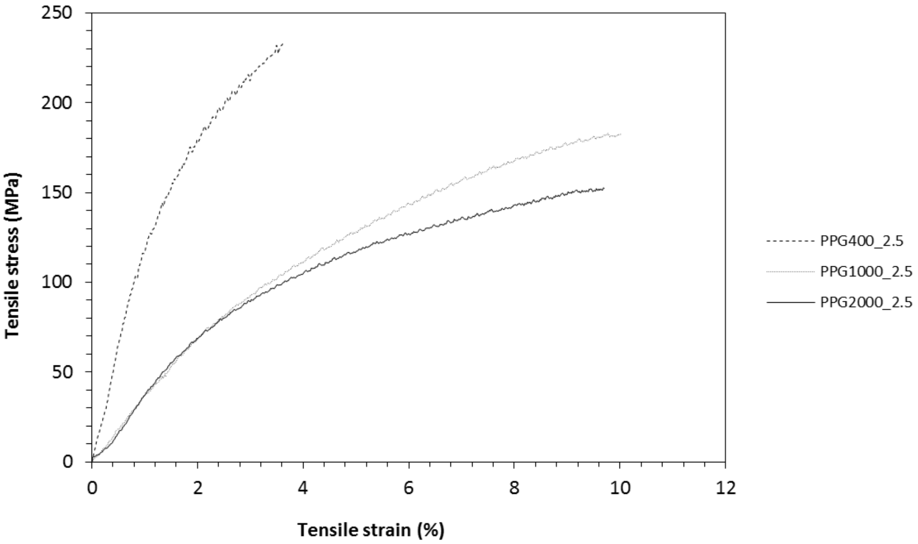


Figure 2.9. Stress-strain curves of papers impregnated with different polyurethane moisture-curable resins.

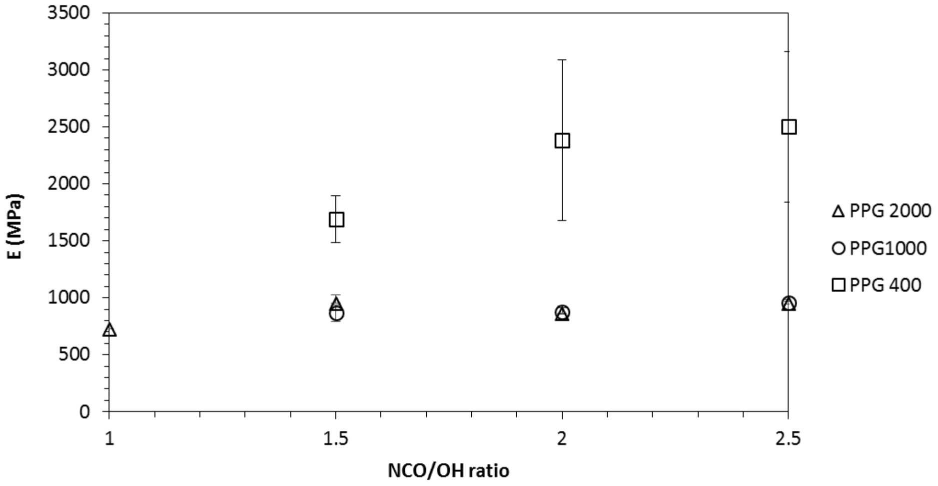


Figure 2.10. Young's modulus of impregnated paper as a function of NCO/OH molar ratio and PPG molecular weight.

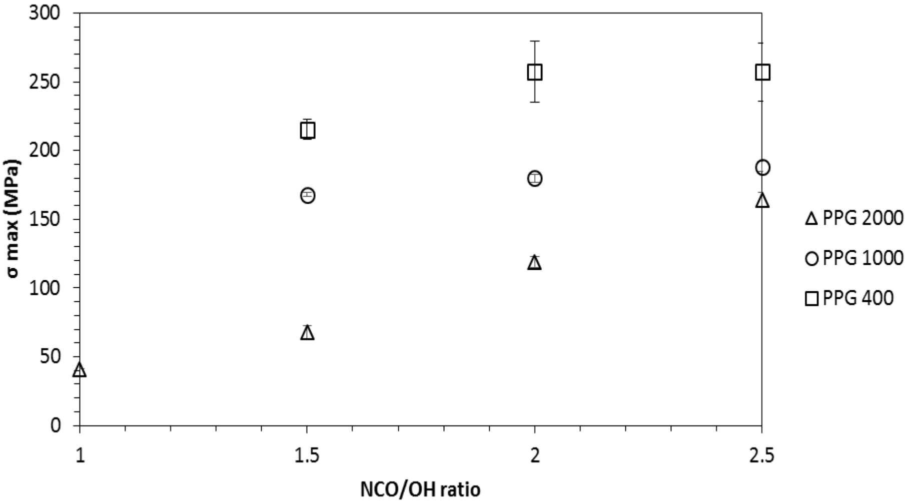


Figure 2.11. Maximum tensile strength of impregnated paper as a function of NCO/OH molar ratio and PPG molecular weight.

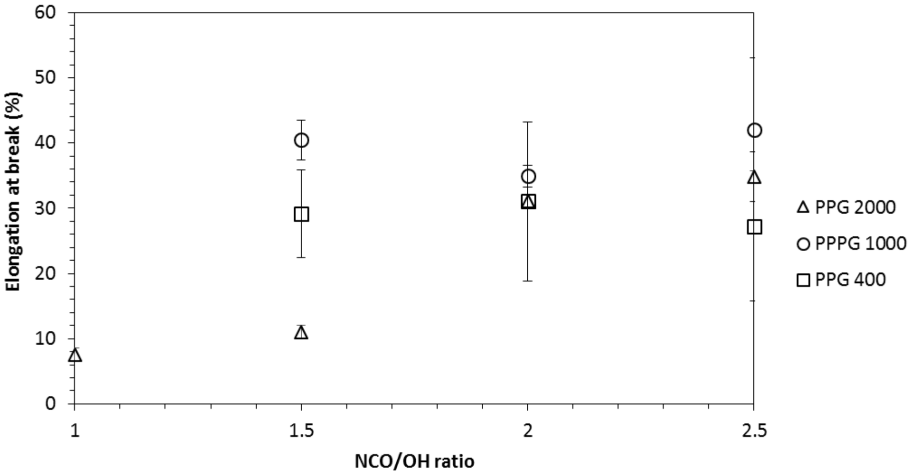


Figure 2.12. Elongation at break of impregnated paper as a function of NCO/OH molar ratio and PPG molecular weight.

As reference, it is noted that dry paper has a Young's modulus of 900±74 MPa, maximum tensile strength of (49 ± 2) MPa, and elongation at break of (7.3 ± 0.3) %. The Young's modulus of the impregnated papers (Figure 2.10) stays similar to that of neat paper, independent of the NCO/OH molar ratio, when PPG1000 or PPG2000 are used. However, PPG400 clearly originates a more rigid material (Figure 2.9 and Figure 2.10), as a consequence of its glass transition temperature being above room temperature, as discussed before. Tensile strength (Figure 2.11) increases with increasing NCO/OH ratio and decreases with molecular weight of PPG. During cure of impregnated paper, available NCO groups in polyurethane resin may react not only with residual water, but also with hydroxyls in paper fibres. This leads to a composite material reinforced by chemical and physical interactions between polymer and paper [18]. Regarding elongation at break (Figure 2.12), no clear trend is evidenced by the results.

Surface resistance and flexibility

The resistance of the impregnated paper sheets to dry heat, cracking, cigarette burn scratching and staining are listed in Table 2.5. Flexibility was also evaluated, taking into account the interest in obtaining a highly postformable material.

In general, surface resistance tends to increase with decreasing polyol molecular weight. The resin based on PPG400 has a performance equivalent to the standard melamine paper, except in terms of dry heat resistance, which is slightly lower, and resistance to shoe polish staining, which remains at level 3 for all polyols, while impregnation with melamine resin leads to level 5 resistance. Resistance to cigarette burn is poor for all materials. In terms of flexibility, impregnation with polyurethane results in a highly flexible paper, while the melamine resin produces a very rigid and brittle foil that breaks under minimal bending (Figure 2.13).

Table 2.5. Evaluation of the produced impregnated papers in terms of surface resistance and flexibility

resin used in impregnation	**dry heat**	**cracking**	**scratching**	**cigarette burn**
Melamine	5	5	3	1
PPG2000_2.5	1	5	1	1
PPG1000_2.5	1	5	1	1
PPG400_2.5	4	5	3	1

Table 2.5. Evaluation of the produced impregnated papers in terms of surface resistance and flexibility *(cont.)*

resin used in impregnation	**staining**					**flexibility**
	shoe polish	**sodium Hydroxide**	**coffee**	**hydrogen peroxide**	**acetone**	
Melamine	5	5	5	5	4	F6
PPG2000_2.5	3	2	2	5	1	F1
PPG1000_2.5	3	3	3	5	2	F1
PPG400_2.5	3	5	5	5	4	F1

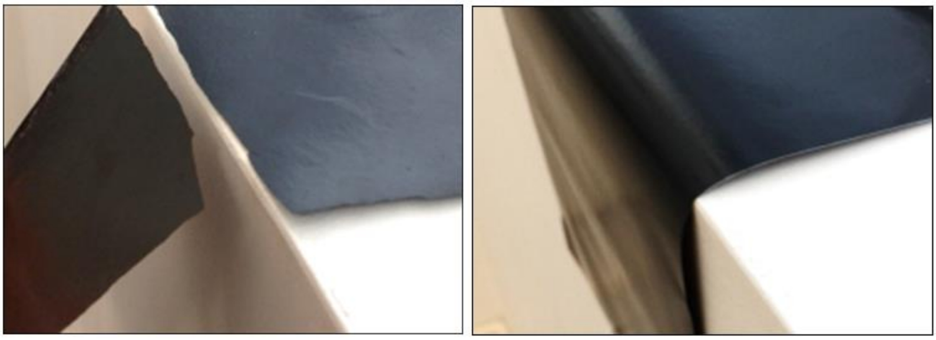


Figure 2.13. Standard melamine cured paper without postforming ability (left) and polyurethane paper with postforming ability (right).

2.3.3. FTIR of polyurethane moisture-curable resins, polyurethane films and impregnated paper

According the literature [12], [31], the characteristic absorptions bands of PU are observed at 3500-3150 cm^{-1} (N–H stretching frequency), 3000-2800 cm^{-1} (CH stretching vibrations: antisymmetric and symmetric stretching modes of methylene groups), 2270 cm^{-1} (–NCO stretching vibration), 1800-1700 cm^{-1} (urethane –C=O vibration), 1700-1600 cm^{-1} (urea –C=O vibration), 1520-1530 cm^{-1} (C-N and N-H vibration), 1395-1365 cm^{-1} (CH_3 bending symmetric vibration), 1223-1243 cm^{-1} (coupled C–N and C–O stretching), and 1070-1100 cm^{-1} (C–O–C stretching) [12], [31]. FTIR spectra of polyurethane resins synthesized with PPG2000 are shown in Figure 2.14. All the previously mentioned absorption bands are present in all resins.

Special attention may be given to the band at 2270 cm^{-1}, associated with stretching band of unreacted –NCO groups, whose intensity decreases as the NCO/OH ratio decreases from 2.5 to 1.0. For a NCO/OH molar ratio of 1.0 all isocyanate groups react during the synthesis and, as expected, that absorption band is inexistent. Resins synthesized with PPG1000 and PPG400 (not shown here) show the same characteristic bands.

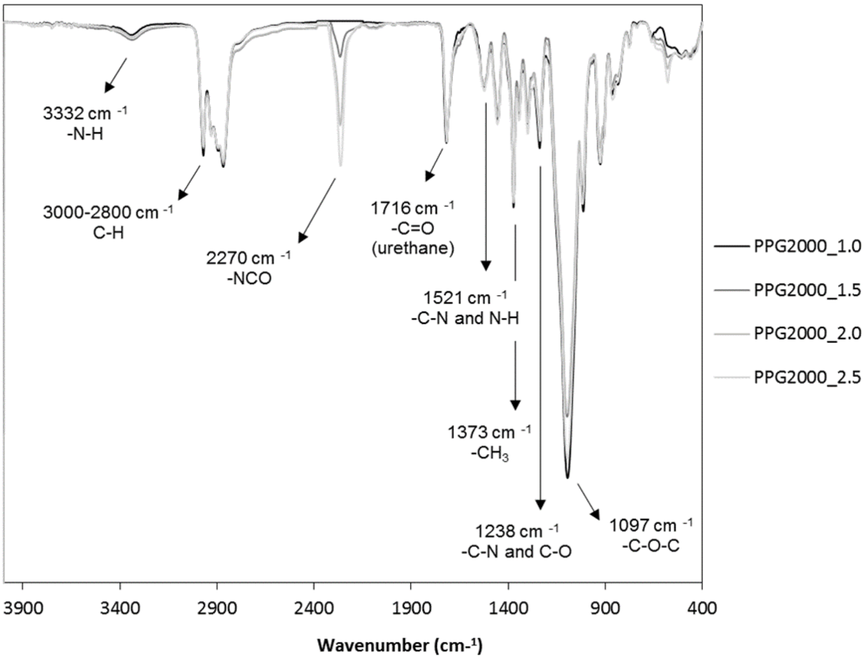


Figure 2.14. IR spectrum of polyurethane moisture-curable resins obtained from PPG2000 with different NCO/OH ratio.

The FTIR spectra of resin, cured polyurethane film and impregnated paper corresponding to the synthesis with PPG400_2.5 are compared in Figure 2.15. The differences between cured and uncured polyurethane are visible. The spectrum of the uncured resin shows an intense peak at 2270 cm^{-1}, due to the presence of unreacted excess isocyanate groups. In the cured film and impregnated paper, this band is absent, indicating complete cure. Additionally, the cured materials show a new band at 1770 - 1600 cm^{-1} (indicated in the figure by a gray bar). This is associated with –C=O vibration in the urea linkages [12], [31] formed during reaction of free isocyanate with atmospheric moisture or, in the case of décor paper, possibility also with hydroxyl groups present in cellulose structure.

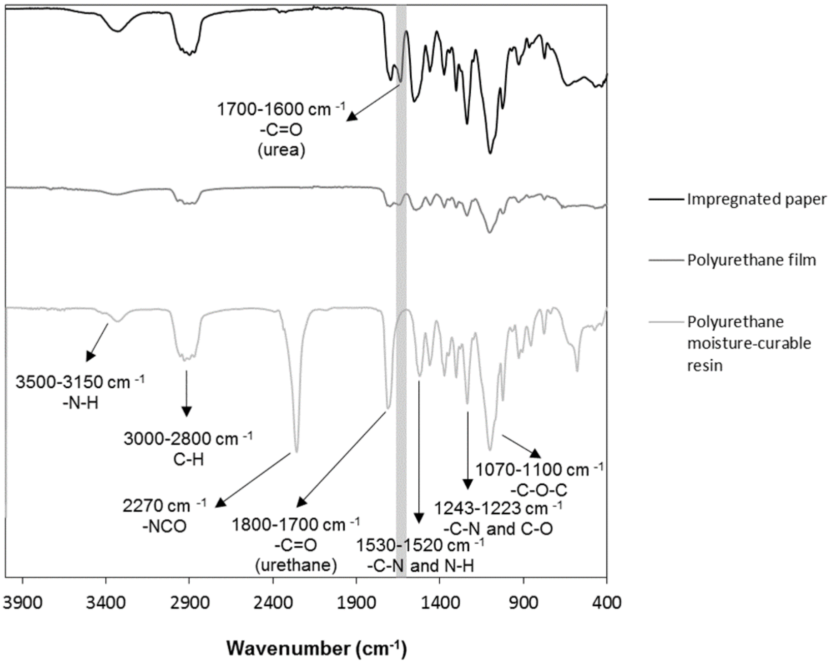


Figure 2.15. IR spectrum of PPG400_2.5: moisture-curable polyurethane (light gray), polyurethane film (dark gray) and impregnated paper (black).

Similar features were observed in the spectra of polyurethane films and impregnated paper synthesized with PPG2000 and PPG1000.

2.3.4. Self-healing

Cured paper impregnated with polyurethane moisture-curable resins PPG400_2.0 and PPG400_2.5 exhibited glass transitions above room temperature in DMA experiments (Figure 2.8). This allows the polymeric surface to exhibit self-healing properties when heated above T_g. The molecular mobility combined with attractive interactions between urethane groups lead to polymer reflow to repair surface damage [7]. As the temperature lowers, the surface regains rigidity.

Results for blade-induced damages are shown in Figure 2.16, in terms of the recovery index, based on measurement of Rz roughness parameter (Eq. 2.7) along heating time. For both resins, maximum healing it attained after 60 s. Surface recovery was almost total for paper impregnated with PPG400_2.0 with 0.98 recovery index. PPG400_2.5 shows lower final recovery, with an index of 0.79. This a consequence of the higher concentration of rigid segments in PPG400_2.5, which results in lower chain mobility. Nonetheless, in both cases, at the end of the recovery process the surfaces showed no perceptible damage to the naked eye.

Damage caused with steel wool could not be evaluated in terms of surface roughness, since the roughness profiles of the damaged surfaces were not clearly distinct from the pristine cured foil surface. The evaluation of damage recovery was therefore performed visually and with the help of a digital camera. Figure 2.17 shows the aspect of the damaged surfaces before and after activating the self-healing process. For both polymer impregnations, the surfaces showed no damage visible to the naked eye after recovery. In addition, there were no discernible differences between the surfaces impregnated with the two polyurethane resins.

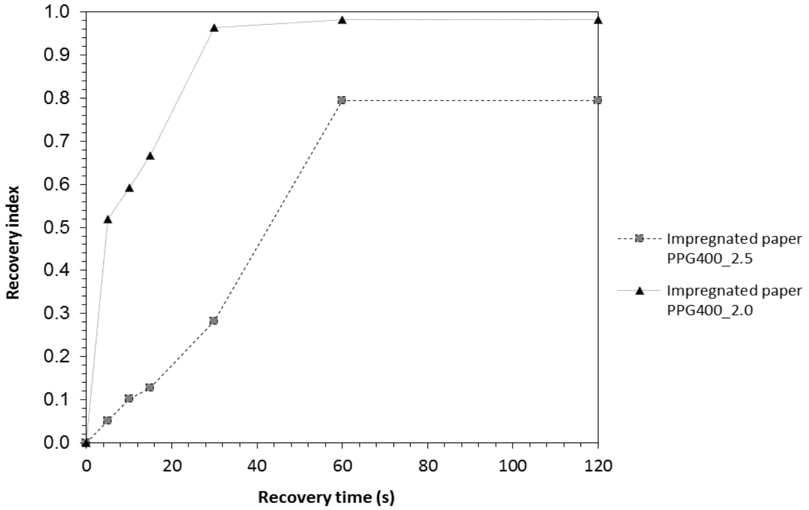


Figure 2.16. Recovery index of PPG400_2.0 and PPG400_2.5 impregnated papers, during heating with hair dryer. Damage was produced with steel blade.

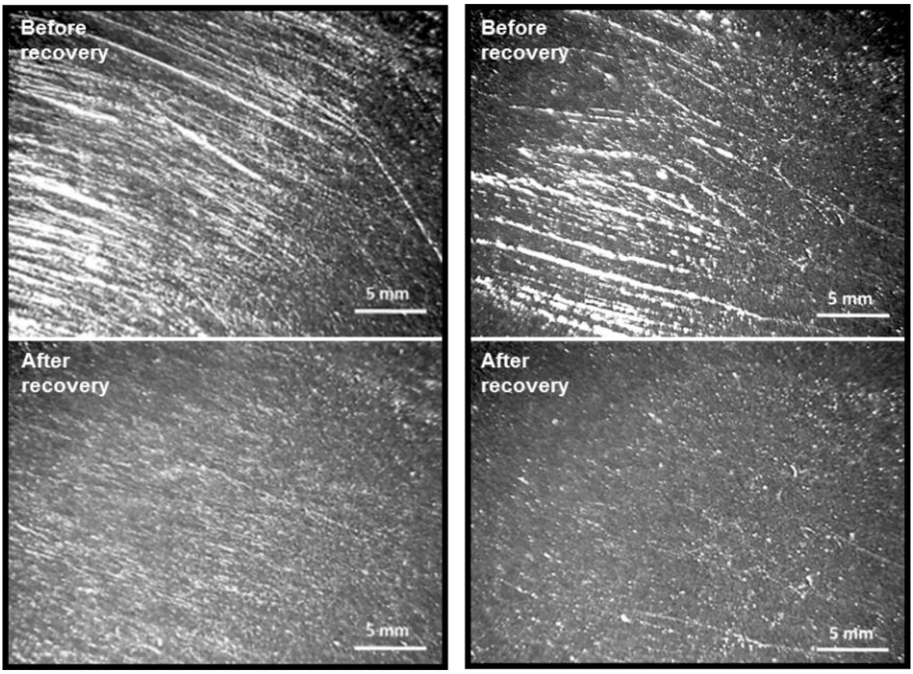


Figure 2.17. Close up photos of surfaces before and after the recovery process, for PPG400_2.0 (left) and PPG400_2.5 (right) impregnated paper. Damage was produced with steel wool.

2.4. Conclusions

The use of polyurethane moisture-curable resins for impregnation of decorative paper was studied. Even though the penetration and saturation times increased considerably, the resins were able to saturate the paper uniformly. Higher amount of free isocyanate and lower polyol molecular weight result in better mechanical strength and adhesive surface properties of the finish foil. From the several syntheses carried out, it was found that surface resistance increases with decreasing polyol molecular weight. The best performances were obtained with paper impregnated with polyurethane moisture-curable resin based on polyol with molecular weight 400 g/mol and NCO/OH ratio 2.5. Despite slightly lower performance in terms of dry heat resistance and resistance to shoe polish, this finish foil showed chemical, cracking, and cigarette burn resistances equivalent to conventional melamine paper, according to EN 438-2. In addition, unlike melamine paper, it exhibited very high flexibility and self-healing performance with fast recovery of superficial damages upon moderate heating. These postformable and self-healing finish foils are promising for use in furniture applications.

2.5. Supporting Information

Table 2.6. Physical properties of resins and films

Polyurethane moisture-curable resins	**Viscosity at 25 °C (cP)**	**Pot-life (h)**	**Visual appearance of film**	**Film tack**	**Film flexibility (1)**
PPG2000_2.5	4050	> 90	Transparent, glossy and colourless	Low	F1 ***
PPG2000_2.0	6580	> 90		Low	F1 ***
PPG2000_1.5	24950	89		High	F1 ***
PPG2000_1.0	600000	0		No film formation	–
PPG1000_2.5	6490	> 90	Transparent, glossy and colourless	None	F1 ***
PPG1000_2.0	12640	> 90		None	F1 ***
PPG1000_1.5	45140	> 90		Low	F1 ***
PPG400_2.5	45240	65	Transparent, glossy and colourless	None	F1 *
PPG400_2.0	216000	65		None	F1 **
PPG400_1.5	600000	0		None	F1 **

(1) - Even though all films passed the F1 mandrel test, a subjective distinction can be made in terms of perceived flexibility. This evaluation goes from * (least flexible) to *** (most flexible).

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CHAPTER 3

Effect of resin nature and content on mechanical properties of cork-based panels

3. Effect of resin nature and content on mechanical properties of cork-based panels [2]

Abstract

The properties of agglomerated cork panels bound with melamine-urea-formaldehyde (MUF) and polyurethane (PU) resins were investigated. Tensile strength, Young's modulus, elongation at break, mandrel flexibility, and resistance to boiling water were evaluated. The resins' wettability on the cork surface was also evaluated.

The results showed that adhesive's nature and content influenced significantly the physical-mechanical properties of the agglomerated cork panels. At the same resin content, panels bound with MUF resin present considerable higher stiffness and tensile strength when compared to panels bound with PU. On the other hand, PU resin lends resilience and water resistance to the panels, and is the only binder that can be used when panel flexibility is desired.

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[2] Submited to European Journal of Wood and Wood Products: A. Antunes, J. Pereira, N. Paiva, J. Ferra, J. Martins, L. Carvalho, Ana Barros-Timmons and F. D. Magalhães "Effect of resin nature and content on mechanical properties of cork-based panels".

3.1. Introduction

Cork is a natural cellular suberous material covering of the species *Quercus suber L.*, commonly known as the cork oak and harvested from the tree periodically, usually every 9–12 years, depending on the country [1]. Cork oak forests spread in the western Mediterranean areas of southern Europe (Iberian Peninsula, south of France and Italy) and North Africa [2]. Cork is a recyclable and renewable source raw material characterized by an interesting combination of properties: low density (120 to 190 kg/m^3), low thermal conductivity, fire retardant, impermeability to liquids and gases, elastic, resilient and chemically stable material [1]–[3]. This natural material presents an alveolar cellular structure similar to honeycombs, formed by small regular hexagonal prismatic closed cells as schematized in Figure 3.1 [2]–[5]. The nomenclature used for directions and sections of this material are axial, tangential and radial [2]–[5]. Chemically, it is mostly composed by suberin (45%), lignin (27%), polysaccharides (12%), ceroids (6%) and tannins (6%) [2]–[5].

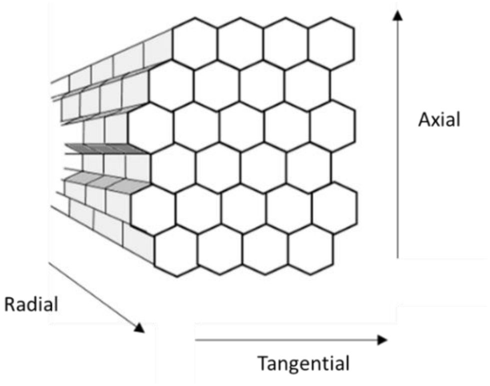

Figure 3.1. Schematic representation of cork cells (adapted from [6]).

Cork is used in a variety of products as wine bottling stoppers; design and fashion items; construction products as surfacing, flooring and insulation purposes [7]. In many applications, composition cork is used. This material is made from a mixture of natural cork and an organic adhesive. The process is carried out under moderate pressure and heating adequate for the specific polymer curing and bonding [8]. Production of agglomerated stoppers at industrial level can be made through individual molding process or continuous extrusion process [9]. The flooring and surfacing agglomerates are produced from rectangular prismatic blocks or cylindrical blocks. To obtain the final product, the blocks are laminated into boards or subjected to rotary lamination yielding a continuous cork sheet or roll, respectively [10]. The binders include thermosetting resins, such as urea–formaldehyde (UF), melamine-urea-formaldehyde (MUF), phenolic adhesives (PF) and polyurethanes (PU) [11]. A specific property just obtained with polyurethane is the higher flexibility of the final panel. However, formaldehyde based resins are three times cheaper and show equality high performance.

The agglomerated cork can be considered a special kind of “wood” based panel and few studies have been focused on the behavior of different binders and process variables for its production. Investigations on agglomerated cork composites as the effect of density on the mechanical behavior of final product [3] and the moisture content and contact angle of polyurethane in cork surface have already been studied [9], [12]–[14]. However, several industrial challenges still exist such as: the influence of nature of the adhesive in cork surface and the impact of resin content on mechanical properties of composite are some pertinent questions. Furthermore, there are no reports regarding the use of melamine-urea-formaldehyde resins.

In case of common wood-based panels, as particleboard or OSB, there are several studies relating resin content and other process parameters with the physico-mechanical properties of the final boards [15]. One example is Ayrilmis et al. (2012) [16] who studied two types of formaldehyde resins, UF and PF, to investigate the effect of resin type and content (8, 10 and 12 wt. %) on the dimensional stability and mechanical properties of particleboards. Authors concluded that increasing resin content, water absorption and thickness swelling decreased for both resin. However, UF particleboard had thickness swelling two times higher than the PF resin bonded particleboard and PF resin shows better mechanical properties. Another one is Ozsahin, 2013 [17] who developed a model for predicting the effects of some production factors such as adhesive ratio, press pressure and time, and wood density and moisture content on some physical properties of oriented strand board (OSB). The results show an useful model for predicting some physical properties of the OSB produced under different manufacturing conditions [17]. Also castor oil based polyurethane resin was tested as an alternative to formaldehyde based resins in particleboards. The aim of research of Ferro et al. (2014) [18] was to evaluate the influence of castor-oil based polyurethane resin formulation in modulus of elasticity and modulus of rupture of particleboards. Results showed significant improvements in the modulus of elasticity with increasing the pre-polymer component and the modulus of rupture property was not affected providing equivalent results for the different proportions of the components of the resin [18]. Similar work using cork was done by Santos et al. (2017) [19] who determine the influence of the production parameters such as binder type (three different diisocyanate based pre-polymers), its quantity, grain size and agglomerate density on the mechanical properties and design requirements of the agglomerated cork.

Agglomerated cork composites are a complex cellular material with high impact in Portuguese economy. Few studies focused on different adhesive systems for agglomerated cork panels were published until now. Neither the application of MUF resins nor their performance comparison with PU resins are reported. This way, the influence of thermosetting resins of distinct nature were investigated at same process conditions. The studied parameters were: resin content at production conditions, contact angle of adhesives, flexibility and mechanical properties of panels.

3.2. Materials and Methods

3.2.1. Materials

Melamine-urea-formaldehyde (MUF) resin and green dye were provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal). Physical characteristics of MUF are: 18 % de melamine; 64 % solid content; pH range of 9.00-10.00 and viscosity range of 200-300 cP (using Brookfield viscosity method – spindle S64).

The conventional adhesives for low-density cork agglomerates are isocyanate terminated reactive prepolymers with a polyether backbone and an average of three functional groups. It was provided by Amorim Cork Composites, S.A. (Santa Maria da Feira, Portugal). Also, the cork granules and pure cork was provided by Amorim Cork Composites, S.A.

3.2.2. Resin distribution

A mixture of resins and green dye was added to granulated cork at a proportion of 6 wt. % of resin content (based on resin solid content). Manual blending during 5 min was done at ambient temperature. Resin distribution was observed at optical microscopic and photographic camera.

3.2.3. Contact angles

Contact angles were measured in a DataPhysics Contact Angle System OCA20, a video-based measuring device equipped with software for image analysis, using the sessile drop method. The droplet volume was 4 µl. Contact angles of resins on pure cork surface were measured during approximately 80 s, at room temperature, allowing the droplets to reach equilibrium. MUF and PU resin were the liquids tested.

3.2.4. Production of agglomerated cork panels

Agglomerated cork was produced blending cork granulate with resin (MUF or PU) as described in section “Resin distribution”. The amount of solid resin was 3.8, 5, 6, 12 and 17 wt. % based in oven dry cork. After blending, a cork panel was hand formed in a deformable aluminum mold of (2 x 450 x 250) mm. The cork amount was determined in order to obtain boards with target densities of 600 kg/m^3. Panels were pressed in a laboratory batch press equipped with both heating and cooling systems, with a set-point in temperature of 150 °C, a pressure of 12 bar, a pressing time of 5 min and a cooling time until to achieve 25 °C. After production, boards were hermetically conditioned until performance evaluation at (23 ± 2) °C and a relative humidity of (50 ± 5) % for 48 h.

3.2.5. Physical-mechanical characterization of agglomerated cork panels

Determination of tensile strength, Young’s modulus and elongation at break of cork panels

Stress-strain tests were carried out adapting the International Standards ISO 7322:2000 (E). Three samples with dimensions of (100 x 15 x 2) mm^3 were tested for each production condition at a crosshead speed of 300 mm/min under room temperature. At least three replicas were made for each measurement.

Resistance boiling water of cork panels

The resistance to boiling water was done according ISO 7322:2000(E). Three samples with dimensions of (50 x 50) mm^2 were tested for each resin. The procedure was to place the specimens into boiling water for 3 h. After test, samples were visually examined and classified as disaggregated or not.

Flexibility of cork panels

The flexibility of agglomerate cork panels was evaluated following a cylindrical mandrel bending test, according to ASTM F147-87. The method consists in bending the specimen on cylindrical mandrels with different diameters ranging from 3 to 48 mm. The flexibility of the specimen corresponds to the minimum diameter about which the specimen could be flexed without exhibiting any signs of failure.

3.2.6. Scanning electron microscopy of agglomerated cork panels

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM 35C-Noran Voyager equipment, at CEMUP – Centro de Materiais da Universidade do Porto, Portugal. Agglomerated cork panel was fractured during mandrel test and the cut section of specimens were observed. Samples were coated with a gold/palladium alloy before analysis.

3.3. Results and Discussion

3.3.1. Contact angles and resin distribution

The adhesion of a polymer on cork depends, among other factors, on the wetting of the cork surface by the glue.

After blending cork granulate with MUF or PU, resin distribution on the cork granulate surface was observed by optical microscopy (Figure 3.2). The resins were mixed with a green pigment prior to blending with the cork granules. When resin contacts with cork, PU resin disappears immediately but MUF drops roll between cork particles. This difference is evident to the naked eye.

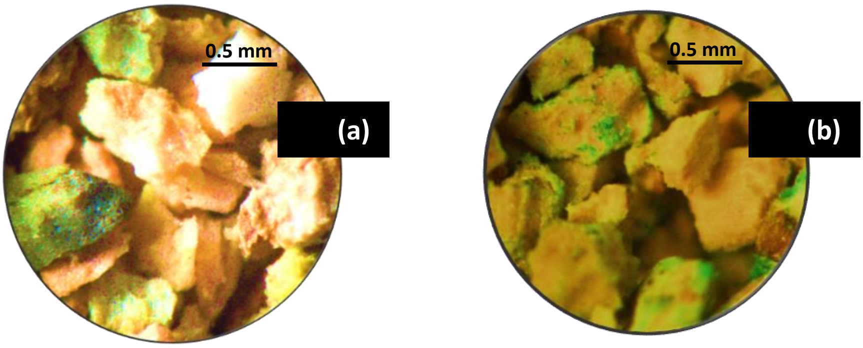

Figure 3.2. Optical microscopy photograph of resin distribution in dry cork surface for (a) PU and (b) MUF resins.

Figure 3.2 (a) shows PU performance when it is mixed with cork particles. Only a few pigmented particles appear in the photo, but these are completely colored, due to the high wettability of PU on the cork surface. MUF resin, on the other hand, does not wet the cork surface easily, which is translated in a nonuniform distribution of resin on the particles' surface – Figure 3.2 (b).

To understand this behavior, the contact angles of MUF and PU resins were measured for drops deposited on the radial, tangential and transverse sections of cork samples. Figure 3.3 shows the dynamic contact angle results obtained during the first 80 s after drop deposition of MUF or PU resin on cork substrates.

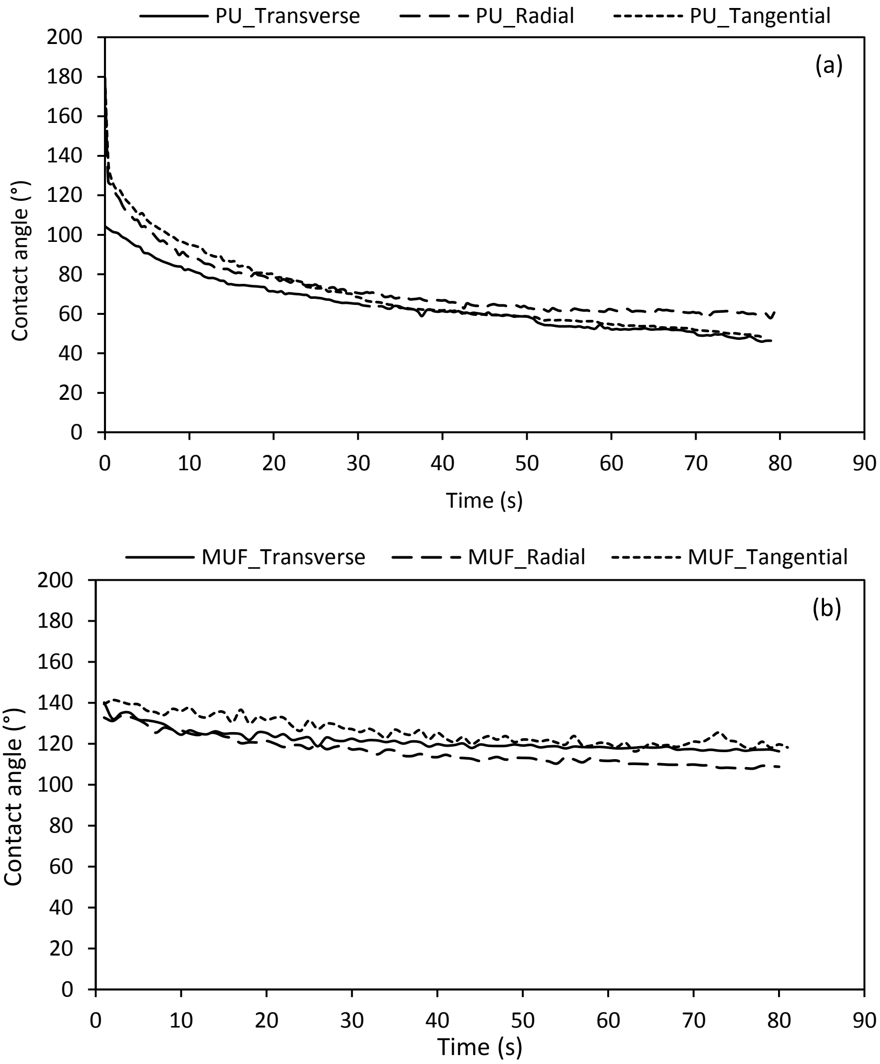

Figure 3.3. Contact angles recover over time for three cross sections of cork and two different adhesive systems: (a) PU and (b) MUF.

The contact angles measured on the three sections were indistinguishable for polyurethane adhesive. The average contact angles are similar (close to 60°). This indicates that PU resin has good wetting properties on cork surfaces.

MUF adhesive shows a distinct performance. MUF is a water-based resin and the drops deposited on cork sections show higher contact angles than polyurethane. Cork is hydrophobic due to the presence of suberin and wax compounds. The reported contact angles for water on all sections are close to 100° [20]. For MUF, the contact angles on three sections were also indistinguishable, but being close to 120°, showing that cork is not easily wet by MUF. This is not, however, a negative factor for the resin's performance as a binder in cork composites. When mixed with cork granules, PU drops will immediately wet the surfaces where they land, covering them uniformly. However, since the volume of binder is much lower than the volume of cork, as a consequence the resin will be deposited on only a few granules during the binder/granule mixing process. On the other hand, since MUF does not wet cork as easily, the resin drops tend to roll between the granules during mixing, leaving small fractions deposits in several particles. The binder is therefore more uniformly dispersed throughout all granules. A higher amount of PU resin may therefore be necessary to insure that all granules receive sufficient adhesive.

3.3.2. Physical-mechanical characterization of agglomerated cork

The results of tensile strength, Young's modulus, elongation at break and mandrel for MUF and PU resins are shown in Figure 3.4, Figure 3.5, Figure 3.6 and Figure 3.7, respectively.

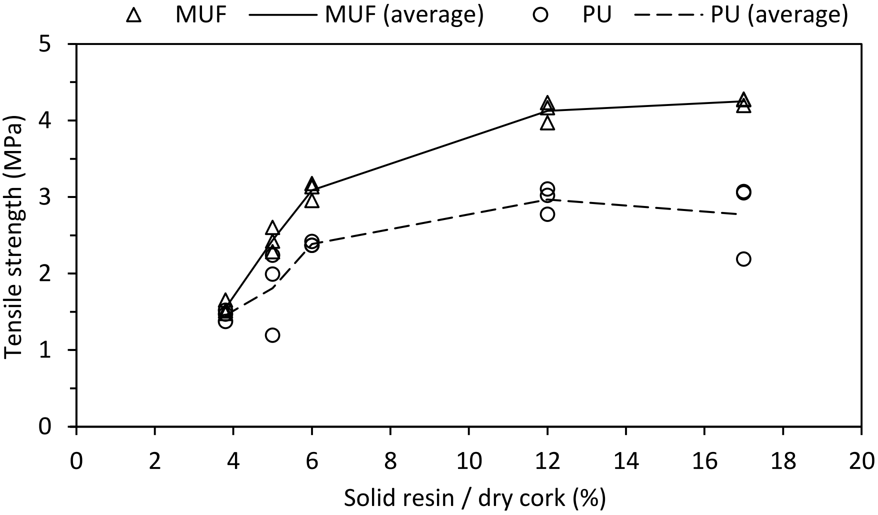

Figure 3.4. Tensile strength results for MUF and PU cork based panels for different resin contents. The lines join the average values for each content value.

As expected, the addition of higher resin content to cork granules increases the tensile strength of all composites. A more noticeable increase is observed between 3.8 and 6 wt.% resin content. For higher resin content there is a less pronounced increase. MUF resin presents considerable higher tensile strength compared to PU specimens. One possible explanation for the lower tensile strength with PU is its higher wettability. As discussed above, this may lead to nonuniform distribution because the resin it immediately retained on the surfaces that it contacts during the mixing process.

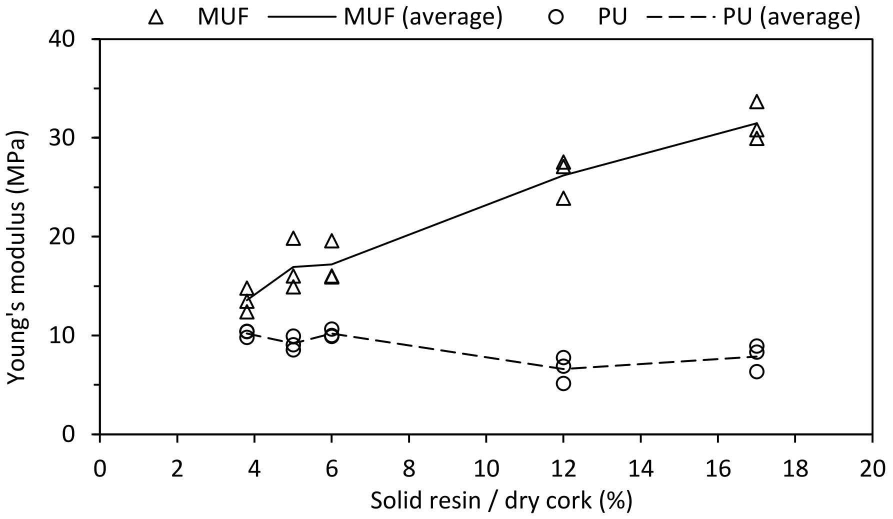

Figure 3.5. Young’s modulus results for MUF and PU cork based panels for different resin contents. The lines join the average values for each content value.

As the MUF content increases, the stiffness of the panel increases, resulting in higher Young’s modulus. The highly crosslinked structure of the cured MUF resin causes this behavior. On the other hand, with PU the Young’s modulus remains essentially constant. PU is a much softer material with low crosslinking, and its elasticity facilitates the relative mobility of the cork granules in response to the imposed deformation.

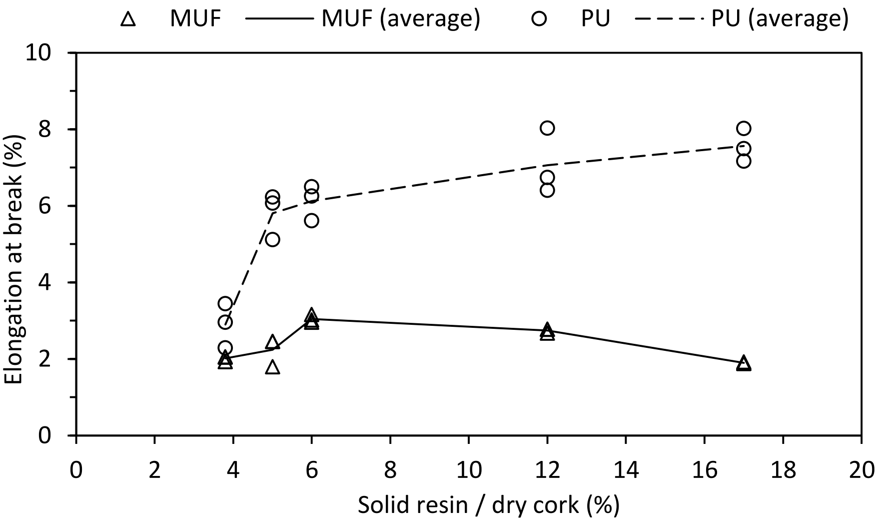

Figure 3.6. Elongation at break results for MUF and PU cork based panels for different resin contents. The lines join the average values for each content value.

Elongation at break results (Figure 3.6) show the effect of the increase of MUF and PU content in final product. When MUF is used, elongation at break increases until 6 % of solid resin, because the resin provides better cohesion between the cork granules. When resin content is greater than 6%, the elongation at break decreases. This is a consequence of the stiffness of cork panel with higher MUF content. With an increase of PU resin content, the elongation at break increases. This is more pronounced on the composites prepared with PU content between 3.8 and 5%. Above 5% of PU content, the elongation at break results show a slight increase followed by stabilization, as happens with Young’s modulus. This indicates that PU content greatly contributes to the toughness of the composites.

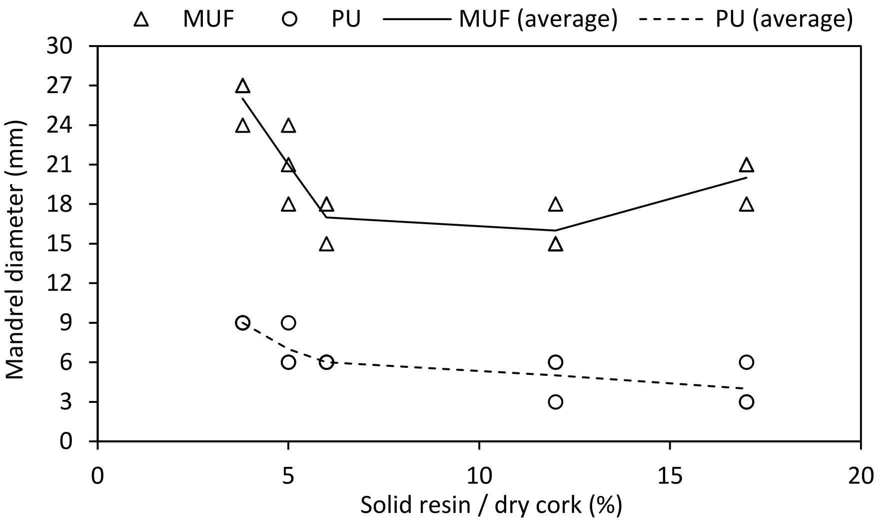

Figure 3.7. Mandrel results for MUF and PU cork based panels for different resin contents. The lines join the average values for each content value.

Panel flexibility results (mandrel tests) show the same trend observed in the elongation at break behavior with different solid MUF and PU content (Figure 3.7). When using MUF resin, between 3.8 and 6 wt.% solid resin content the panel is mechanically weak and it breaks at a relatively high mandrel diameter. Between 6 and 12 wt.% the panel flexibility is better. In this range the panel cohesion is sufficiently high to insure integrity during bending. When solid resin content is higher than 12 wt.%, the rigidity and low resilience of the MUF resin become dominant factors and the panel flexibility is again reduced.

On the other hand, with the increase of PU resin content, the limit mandrel values always decrease. Cohesion improves with resin content and since this is a flexible and resilient binder, there is no detrimental counter effect. It is interesting to note that the tendencies observed in Figure 3.7 for the limit mandrel values are qualitatively symmetrical in relation to those of the elongation at break results, both for MUF and PU.

The water resistance of glued cork composites is an important criterion to determine the suitability of the final product for use in humid conditions. Of all specimens, using MUF and PU resins, only the one with lower MUF content (3.8 wt.%) did not pass the boiling water resistance test, having disaggregated.

3.3.3. Scanning electron microscopy of agglomerated cork panels

Cross sections of cork panels obtained after rupture in mandrel tests were observed. Figure 3.8 presents the differences between the cross section of a panel produced with low and high MUF or PU content.

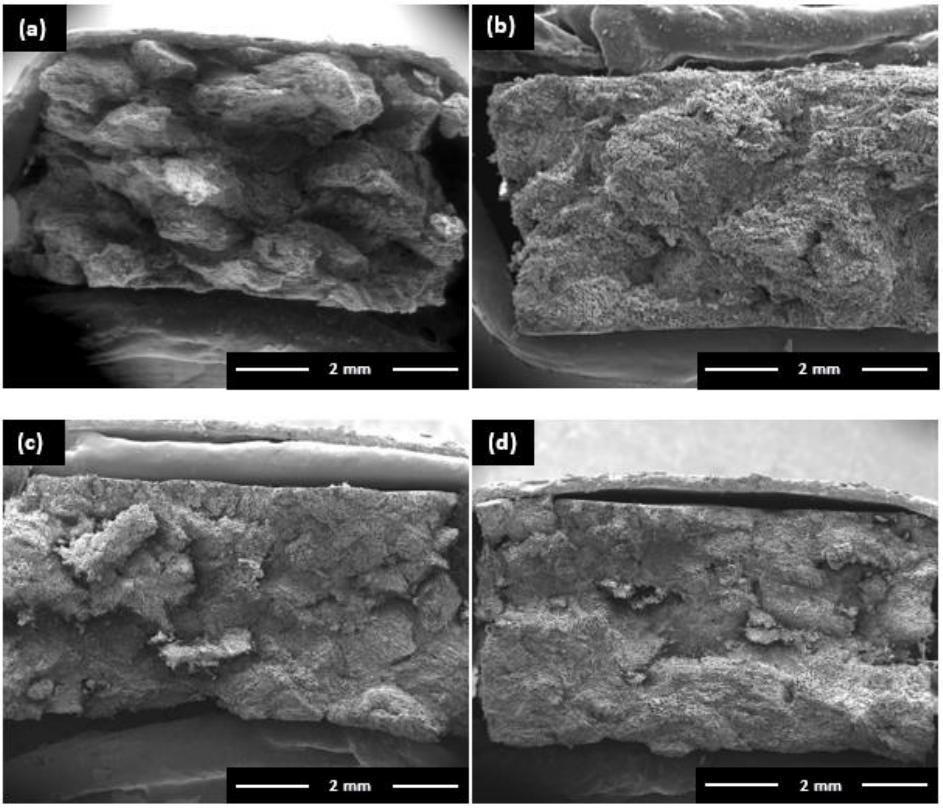

Figure 3.8. Cross section of cork panels observed under microscope when broken in mandrel test: (a) 3.8 wt. % of MUF content; (b) 17 wt. % of MUF content; (c) 3.8 wt. % of PU content and (d) 17 wt. % of PU content.

As previously mentioned, 3.8 wt. % of MUF content in cork panel is not sufficient to produce a cohesive panel. As a result, upon bending, the individual granules separate and the panel breaks along the granules' interface (glue line). The cross section results in an irregular surface as shown in Figure 3.8 (a). However, when high resin content is used (17 wt. %), the glue line between granules becomes much stronger and rupture occurs across the cork granules. This resulting cross section is a homogeneous surface as seen in Figure 3.8 (b). Using PU resin, both low and high adhesive contents lead to homogeneous cross sections – Figure 3.8 (c and d).

It can be concluded that use of a standard MUF resin as binder in agglomerated cork panels at 6 wt. % resin content leads to good mechanical performance. Ultimate tensile strength is actually 55 % higher than when using PU resin at the same content, which has a cost roughly three times higher. However, panel flexibility remains a limiting factor for MUF resin. The lower mandrel value is 18 mm, while with PU a value of 6 mm can be attained.

Results corroborate previous studies [19], [21]–[23] which shown that mechanical properties of cork composites are dependent of type, amount and compatibility between polymeric matrix and cork.

3.4. Conclusions

The use of melamine-urea-formaldehyde and polyurethane resins for the production of agglomerate cork composites were studied. Polyurethane shows the same wetting behavior independently on the cork section, the average contact angles being close to 60°. MUF resin, being waterborne, presents higher contact angles, close to 120°.

For both adhesive types, tensile strength of agglomerate cork panels increases with resin content. MUF resin yields considerable higher stiffness and tensile strength than PU. On the other hand, panels bound with PU have higher elongation at break, flexibility, and water resistance.

Use of MUF resin as binder are a more economical alternative than PU, capable of providing good mechanical performance. However, if panel flexibility is paramount, PU may be the only valid option.

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CHAPTER 4

Blocked melamine-urea-formladehyde resins and their usage in agglomerated cork panels

4. Blocked melamine-urea-formladehyde resins and their usage in agglomerated cork panels [3]

Abstract

Caprolactam and o-p-toluenesulfonamide are tested as chain-growth blockers for melamine-urea-formaldehyde (MUF) resins, in an attempt to reduce the crosslinking density of the cured resin, and hence improve flexibility of the final product. Agglomerated cork panels, where flexibility is a technical demand, were produced with the modified resins and tested.

The blockers were added at three different steps in the synthesis process: methylolation, condensation, and at the end of the synthesis. Besides evaluation of standard properties, resins were characterized using GPC and FTIR. Blocked resins showed better storage stability and improved water tolerance, especially when caprolactam was employed. When used as binders in agglomerated cork panels, the blocked resins allowed for significantly better flexibility, evaluated in terms of mandrel bending test. The tensile resistance of the panels remained well within the desired limits for this type of material.

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4.1. Introduction

Melamine-urea-formaldehyde (MUF) resins have widespread industrial used as adhesives for substrates like paper, wood and cork [1], [2]. They are used as a low cost alternative to melamine-formaldehyde (MF) resins, while still exhibiting better hydrolysis resistance than urea-formaldehyde (UF) resins [3].

Cork, the bark of Quercus suber, is used industrially in the manufacture of many products, which can be divided into two groups: natural cork products and composite cork products. The first are mostly intended for the production of wine stoppers. But processing of natural cork generates a significant volume of waste and rejected material [4]. Composite cork products are made from these wastes, combined with other materials according to the properties desired in the final product. The agglomerated cork composite panels, in particular, result from a process of agglutination of cork granules by action of pressure, temperature and a binder material [4]. These composites are used for various purposes, in particular in construction, aerospace, footwear and decoration [4].

Currently, the most used adhesive for production of cork composites is polyurethane (PU) resin. MUF resins, being economically competitive (about three times lower cost), having equally good adhesion properties, and being easier to process and clean (they are water-based), are an interesting alternative to PU. However, they present a major disadvantage, due to the inherent stiffness that results from their highly crosslinked structure. As a consequence, the resulting agglomerated panels become significantly less flexible than those produced with PU. This is a limitation for some applications and even for processing the panels during manufacture. Indeed, cork agglomerate panels are typically produced in a continuous press and rolled up for storage and delivery. The use of MUF resins as binder impairs this procedure, because of the panel’s low flexibility.

Some works can be found in literature dealing with providing formaldehyde-based resins with some flexibility. Strategies involve introduction of plasticizers [5], [6], flexible chain [7]–[9] and thermoplastic fillers [10]–[13]. In the current work a different approach is followed, based on the incorporation of compounds that act as chain growth blockers. The purpose is to decrease the crosslinking density of the final cured resin, allowing for greater chain mobility and thus higher flexibility. This is schematized in Figure 4.1.

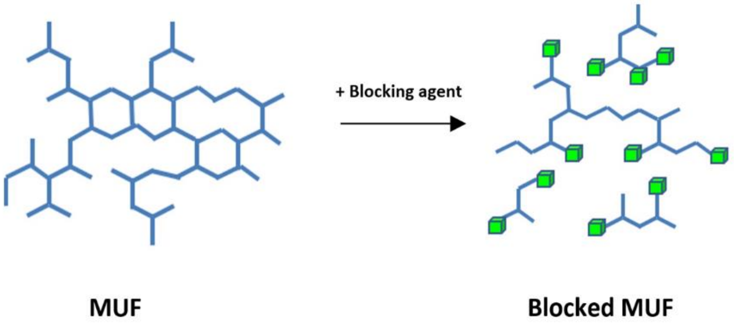


Figure 4.1. Schematic representation of the densely crosslinked MUF resin (left) and the MUF resin with chain growth blockers (right).

Compounds with low functionality, able to react with formaldehyde-based resins, must be used for this purpose. Caprolactam and o-p-toluenesulfonamide (OPTS) were selected in this work. These are mentioned in some existing patents as being able to induce flexibility in formaldehyde-based resins, but the available information is scarce and mostly qualitative [1], [14], [15].

The motivation of this work is therefore to chemically modify MUF resins in order to provide them with the resilience necessary for use in flexible cork-based composite panels. The blockers were added to the resin synthesis at different stages, in order to evaluate implications on the final polymer structure.

4.2. Materials and Methods

4.2.1. Materials

In the preparation of melamine-urea-formaldehyde resins, industrial-grade raw materials provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal) were used, namely: melamine (M), urea (U), formaldehyde (F) solution at 53 wt. %, sodium hydroxide solution at 50 wt. % (NaOH), acetic acid solution at 25 wt. % (CH_3COOH), ammonium sulphate solution at 30 wt. %, caprolactam and OPTS.

The cork granules with 0.5-1.0 mm of diameter were provided by Amorim Cork Composites, S.A. (Santa Maria da Feira, Portugal).

4.2.2. Synthesis of MUF resins

The MUF resins were prepared in a three-necked 2500 ml glass flask under atmospheric pressure, following a procedure based on the so-called alkaline-acid process [16]. Formaldehyde 53 wt. % solution at 50 - 60 °C was charged into the reactor and the pH value was adjusted to 9.0 – 10.0 using sodium hydroxide solution. Urea and melamine were added at equivalent molar ratios F/U = 1.42 and $F/(NH_2)_2 = 1.0$. The methyolation reaction was carried out up to 45 °C. After 50 min of reaction, temperature was increased to 80 °C and the condensation reaction was carried out until water tolerance of a collected sample turns hazy. At this point, pH was adjusted to > 9.0 with NaOH and the reaction was stopped. The solution was cooled to room temperature and final urea was added at 50 °C. Blockers (caprolactam or OPTS) were added to obtain a concentration of 10 wt. % in solution, at three synthesis steps: methyolation, condensation and after the end of reaction.

Table 4.1 shows compositions of the synthesized MUF resins. Samples were named according to the blocker used, percentage applied and synthesis step where blocker was added. For example “Resin Capro_M” signifies MUF resin synthesized with caprolactam at methyolation step.

Table 4.1. Composition of the synthesized blocked MUF resins

Resin	**Blocker**	**Synthesis step**
Capro_M	caprolactam	Methylolation
Capro_C	caprolactam	Condensation
Capro_F	caprolactam	Final
OPTS_M	OPTS	Methylolation
OPTS_C	OPTS	Condensation
OPTS_F	OPTS	Final

4.2.3. Characterization of MUF resins

The solid content (%) was determined by evaporation of volatiles in two grams of resin for three hours at 120 °C in oven. The solid content was determined by the mass ratio of the sample before and after drying.

Dynamic viscosity of MUF resin was determined by Ford Cup number 4 method. The measurements were performed at (25 ± 1) °C.

The resin pH was measured using a combined glass electrode.

Resin density (kg/m^3) was measured using a hydrometer.

Gel time is the time needed for the resin gelification under hot and catalysed environments. This time was measured in a laboratory test tube immersed in boiling water with resin prepared at 3 % of ammonium sulphate solution. Gel time measurements were performed twice and repeated when the results differ by more than 3 s.

The water tolerance of a resin is an indication of the miscibility of the resin with water. Distilled water at 25 °C was gradually added to 5 g resin until the resin solution turns hazy.

Storage stability was evaluated comparing the viscosity of resins until them present viscosity equal or superior to 1 min.

4.2.4. Gel permeation chromatography / Size exclusion chromatography

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 was 1 ml/min and dimethylformamide (DMF) was used as the mobile phase. Samples for analysis were prepared by dissolving a small amount of resin (100 mg) in dimethylsulfoxide (DMSO), followed by vigorous stirring during 1 min. Subsequently, the sample was left to rest (10 min), filtered through a 0.45 µm nylon filter and then the sample was injected.

4.2.5. 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}. The samples were resin films and they were prepared by an evaporation technique. Approximately 50 g of resin was poured into a PTFE-coated mold and then cured in an oven at 120 °C during 3 h.

4.2.6. Production of cork agglomerates

Resins were added to granulated cork and the mixture were prepared by manual stirring during 5 min at room temperature. The solid resin content (RC) was 3.8, 6 and 12 % based on oven dry cork.

After blending, cork panel was hand formed in a deformable aluminium mold (2 x 450 x 250) m^3. The cork amount was determined in order to obtain boards with target densities of 600 kg/m^3. Panels were pressed in a laboratory batch press equipped with both heating and cooling systems, with a set-point in temperature of 150 °C, a pressure of 12 bar, a pressing time of 1.5 min and a cooling time until to achieve 25 °C.

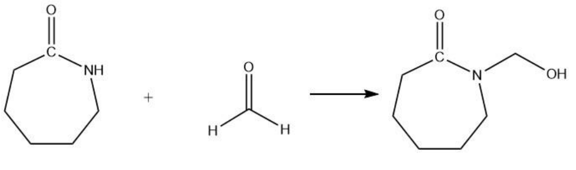
4.2.7. Physical-mechanical characterization of cork agglomerates

After production, boards were hermetically conditioned until performance evaluation at (23 ± 2) °C and a relative humidity of (50 ± 5) % for 48 h. Stress-strain tests were carried out based on ISO 7322:2000 (E). Tree samples with dimensions of (100 x 15 x 2) mm^3 were tested for each production condition in a testing machine Mecmesin MultiTest-1-d equipped with a Mecmesin BFG 1000 dynamometer, at a crosshead speed of 300 mm/min under room temperature.

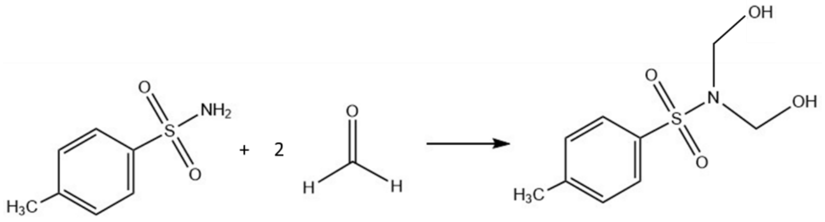
The flexibility of agglomerate cork panels was evaluated following a cylindrical mandrel bending test, according to ASTM F147-87. The method consists in bending the specimen on cylindrical mandrels with different diameters ranging from 3 to 48 mm. The flexibility of the specimen corresponds to the minimum mandrel diameter about which the specimen could be flexed without exhibiting any signs of failure.

4.3. Results and Discussion

As mentioned before, caprolactam and o-p-toluenesulfonamide were selected as blockers taking into account cost and availability for use at an industrial scale. The reaction schemes involving hydroximethylation of each blocker by reaction with formaldehyde are squematized in Figure 4.2. The resulting hydroximethylated species can then react with other monomers or oligomers. Caprolactam acts as a true chain terminator, since it yields only one methylol group after reaction with formaldehyde. OPTS can form two methylols, but their reactivity may differ. In addition, the bulky phenyl group may cause steric hindrance towards chain growth. In both cases, functionality is lower than that of urea, which has four replaceable hydrogen atoms, even though its functionality is effectively 3, due to low reactivity of the fourth.



Caprolactam Formaldehyde



OPTS Formaldehyde

Figure 4.2. Methyolation reaction of caprolactam and OPTS.

Blocker addition was performed at three alternative stages: methylolation, condensation, and after the end of reaction. When the blocker is added in the methylolation stage, part of the formaldehyde and oligomers are expected to react with it and therefore become unavailable for the next stages of polymer growth. On the other hand, blocker addition along the condensation stage should block end groups in the higher molecular weight polymer structure. Finally, blocker addition after the end of reaction is done at room temperature, which does not favour reaction with the formed polymer.

A set of seven resins was synthesized following the same process, but varying the type of blocker and the addition step, as described in Table 4.1. The chemical reaction of caprolactam and OPTS were investigated by FTIR (Figure 4.3 and Figure 4.4). Table 4.3 and Table 4.4 present the final properties of the modified MUF resins.

4.3.1. FTIR analysis of standard MUF and blocked MUF resins

Relevant band assignments for MUF resins, caprolactam and OPTS are shown in Table 4.2 [17]–[19]. The characteristic absorptions bands of MUF resin are observed at 3400–3300 cm^{-1} (NH stretching of primary aliphatic amines and stretching of OH mode of C-OH group), 1650–1630 cm^{-1} (C=O stretching of primary amide), 1560–1540 cm^{-1} (C=N stretching of secondary amines), 1480–1380 cm^{-1} (C-H mode in CH_2 and CH_3), 1380–1330 cm^{-1} (C-N stretching of CH_2-N), 1250-1200 cm^{-1} and 1130-1120 cm^{-1} (C-O stretching of aliphatic ether), 1050–1030 cm^{-1} (C-N or NCN stretching of methylene linkages (NCH_2N), 890-860 cm^{-1} (C-H deformation out of plane), 814-812 cm^{-1} (triazine ring stretching), 750–700 cm^{-1} (N-H bending of secondary aliphatic amines (R_1–CH–NH–CH_2–R_2)) and they are listed in Table 4.2.

Table 4.2. Typical absorption band assignments of FTIR spectrum of MUF resin and characteristic absorptions bands of modified MUF resins (adapted from [17]–[26])

Absorption band (cm^{-1})	**Chemical Structure assignment**	**Observations**
3400-3300	Stretching O–H mode of C–OH group and NH stretching of primary aliphatic amines	
1650-1630	C=O stretching of primary amide	
1560-1550	C-N stretching of secondary amines	
1480-1380	C-H mode in CH_2 and CH_3	
1460-1300	SO_2 asymmetrical stretches of the sulfonyl	OPTS
1380-1330	C-N stretching of CH_2-N	
1240	C-O-C stretching	
1200-1100	SO_2 symmetrical stretches of the sulfonyl group	OPTS
1130-1120	C-O stretching of aliphatic ether	
1050-1030	C-N or NCN stretching of methylene linkages (NCH_2N)	
980-970	Carbon ring in cyclic compounds	Caprolactam
890-860	C-H out of plane	
880	p-substitution of benzene ring	OPTS
814-812	Triazine ring stretching	
750 - 700	N-H bending of secondary aliphatic amines (R_1-CH-NH-CH_2-R_2)	
702	S-N	OPTS

The spectra of MUF resins blocked with caprolactam are compared to the spectrum of the standard resin in Figure 4.3. The spectra are similar. However, one peak is observed in the modified resins, which indicates the presence of caprolactam: the absorption band at 975 cm^{-1}, which is associated to the stretching band of carbon ring in cyclic compounds.

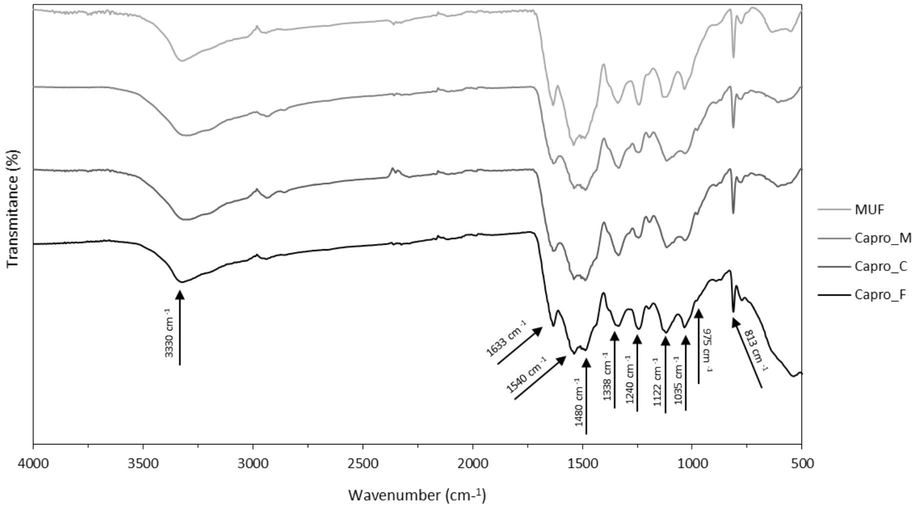


Figure 4.3. Spectra of melamine-urea-formaldehyde resin and resins containing caprolactam.

FTIR spectra of MUF blocked with OPTS are presented in Figure 4.4. All previously mentioned MUF absorption bands are present in all resins containing OPTS. Three new bands can be identified, which show the presence of OPTS in the resin: the absorption band at 1200-1100 cm^{-1} (associated to symmetrical stretches of the sulfonyl group), 880 cm^{-1} (associated to p-substitution of benzene ring) and 702 cm^{-1} (associated with vibration of S-N linkage). Special attention can be given to the changes observed in the range 1460-1300 cm^{-1}, because it corresponds to asymmetrical stretches of the sulfonyl group, which can be masked by MUF spectra.

The FTIR spectra in Figure 4.3 and Figure **4.4** show some differences between 1122 and 1035 cm^{-1} bands. The two bands are more intense for MUF, Capro_F, and OPTS_F resins, because there are more methylene and methylene ether linkages in the resin structure. When blockers are added during the synthesis (resins Capro_M, Capro_C, OPTS_M, and OPTS_C), the degree of crosslinking is decreased and less methylene and methylene-ether linkages are formed.

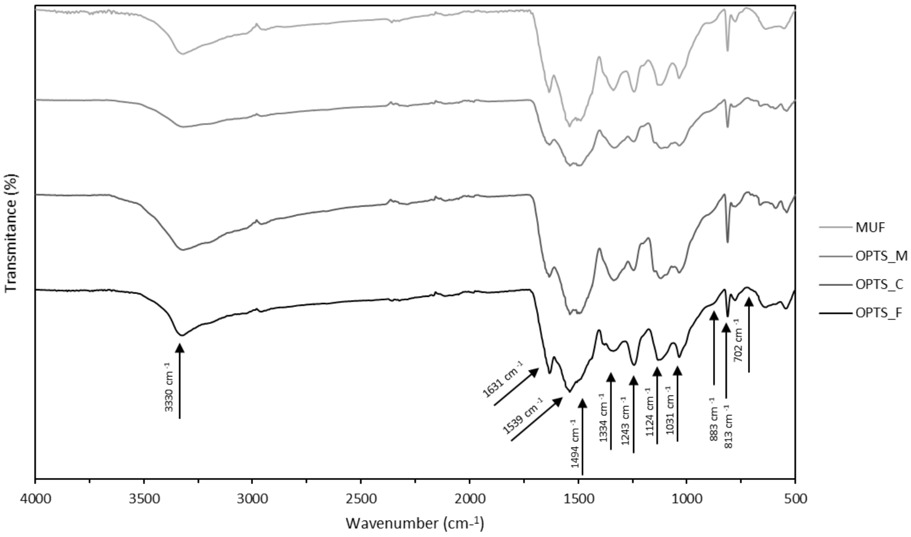


Figure 4.4. Spectra of melamine-urea-formaldehyde resin and resins containing OPTS.

4.3.2. Characterization of standard MUF and blocked MUF resins

Table 4.3 shows the variation of solid content, pH, dynamic viscosity, density, gel time, water tolerance and storage stability of the synthesized MUF resins blocked with caprolactam.

Table 4.3. Properties of MUF resins blocked with caprolactam

Resin	pH	Viscosity (s)	Gel time (s)	Solid content (%)	Density (kg/m^3)	Water tolerance (%)	Storage stability (days)
MUF	8.81	14	90	59.9	1265	140	10
Capro_M	8.28	14	162	59.7	1232	240	75
Capro_C	9.19	13	165	59.6	1230	320	87
Capro_F	8.53	13	154	58.6	1228	180	100

Concerning the final pH, viscosity and solid content, the results are very similar for the three resins blocked with caprolactam, in comparison to the standard MUF. A slight decrease is observed for the density in accordance with the decrease in solid content. Gel time tends to increase with caprolactam addition because of the premature consumption of a significant amount of free formaldehyde, which does not become available for the cure reaction. This effect was more pronounced when caprolactam was added in methylolation and condensation steps.

Water tolerance increases significantly with the introduction of caprolactam in methylolation and condensation steps, which may be a consequence of shorter polymer chains being formed. Also, caprolactam's water solubility (4560 g/l) is higher than melamine's (31 g/l) [27], which may promote the resin's solubility after entering the polymer structure. Water tolerance is highest when caprolactam is added in the condensation step, indicating that incorporation may be more effective in this case. Addition at the end of synthesis does not change water tolerance significantly, indicating that the blocker is not being incorporated in the polymer, as expected.

All MUF resins modified with caprolactam have higher storage stability than the standard resin, *i.e.*, longer shelf-life. Interestingly, resin Capro_F shows the best result, 100 days compared to 10 days for standard MUF. One possible reason is the action of caprolactam as blocker of small oligomers that are present in the final polymer, which are responsible for chemical ageing/gelification. [28] Caprolactam in solution may also act as a colloidal stabilization agent, hindering physical ageing [29].

GPC analysis of amino resins has been shown to be useful for identifying qualitative differences in resin formulations. Under the analysis conditions employed in our works, chromatograms can show the presence of low and high molecular species, corresponding to peaks with retention volumes between 18 and 22 ml, and between 9 and 13 ml, respectively [16], [30], [31]. MUF resins typically have only low molecular weight species, therefore displaying chromatograms with peaks only in the higher volume range. Figure 4.5 shows that the chromatograms are shifted towards lower molecular weight (higher retention volume) when caprolactam is added in the condensation step. This is in accordance with the water tolerance measurements, which were higher for resin Capro_C. Both results are an indication of more effective incorporation of the blocker into the polymer structure. Addition in the methylolation step causes only a slight shift towards lower molecular weight, while addition at the end of synthesis has no effect, also in agreement with the water tolerance results.

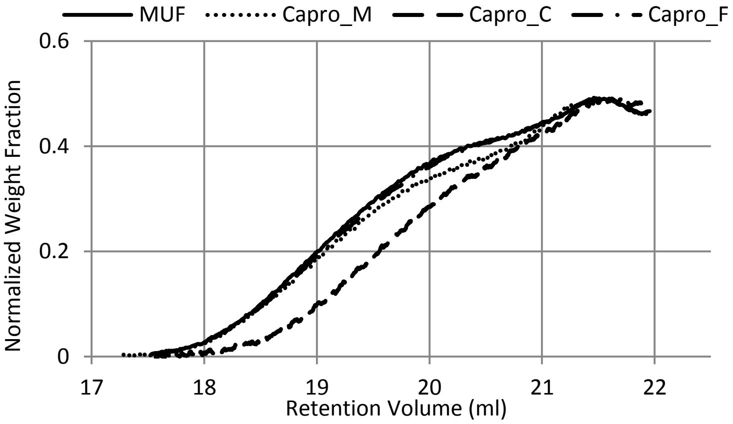


Figure 4.5. Chromatograms of MUF resins blocked with caprolactam.

Table 4.4 shows some physical characteristics of MUF resins blocked with OPTS. The viscosity of the resins (between 12 – 14 s), pH value (8.5-9.5) and solid content (59-60%) are similar independently on the phase of addition of OPTS. All MUF resins modified with OPTS shows similar density.

Table 4.4. Properties of MUF resins blocked with OPTS

Resin	pH	Viscosity (s)	Gel time (s)	Solid content (%)	Density (kg/m^3)	Water tolerance (%)	Storage stability (days)
MUF	8.81	14	90	59.9	1265	140	10
OPTS_M	8.72	12	185	59.7	1253	100	49
OPTS_C	8.72	13	128	59.4	1254	100	55
OPTS_F	8.32	14	156	59.5	1254	80	48

The standard resin shows the fastest cure, followed by the resin with OPTS added in the condensation step, OPTS at the end of the synthesis, and OPTS in the methylolation step. As mentioned above, when the additive is added in methylolation, it consumes formaldehyde which should be available for the reaction. When the additive is added in the condensation step, it will block only a few sites in the already partially developed polymer chain, allowing or continuing growth, but with less branching. When OPTS is added at the end of the synthesis, it just reacts with free formaldehyde and small oligomers present in MUF, due to the much lower mobility of the larger molecular weight species. This blockage of low molecular weight species impairs reactivity during the final cure of the resin, therefore increasing gel time.

As with caprolactam, storage stability increased with OPTS addition, the maximum value obtained being 55 days, for addition in the condensation step. OPTS_M and OPTS_C show similar storage time.

On the other hand, contrary to what happened with caprolactam, slightly lower water tolerance was observed for resins blocked with OPTS, in relation to the standard MUF. This is probably related to its relatively lower water solubility (32 g/l), which is similar to melamine's (31 g/l) [27].

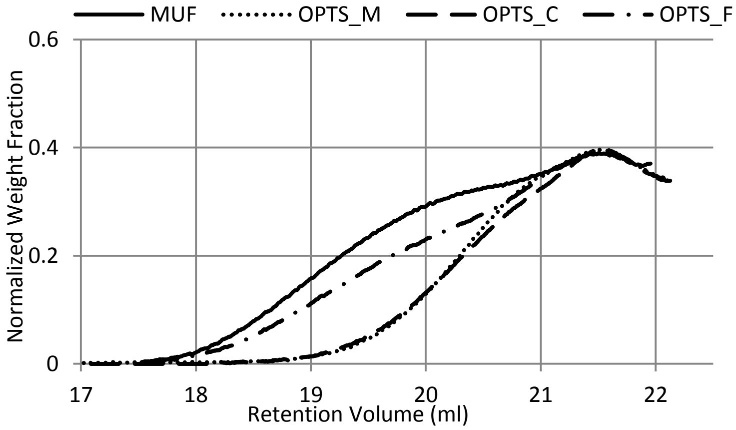


Figure 4.6. Chromatograms of MUF resins blocked with OPTS.

The GPC chromatograms (Figure 4.6) show a significant decrease in molecular weight when OPTS is added both in methyolation and condensation stages. Probably the steric hindrance caused by the large phenyl group plays a relevant role here, hindering chain growth during synthesis. Addition of OPTS at the end of the synthesis also shows a small decrease of molecular weight, for the same reason.

4.3.3. Mechanical characterization of agglomerated cork panels

Mandrel and tensile testing was carried out on agglomerated cork panels using three resin content levels: 3.8, 6 and 12 % of solid resin per mass of dry cork. Three panels were produced for each variable tested. Results are shown in Figure 4.7 and Figure 4.8.

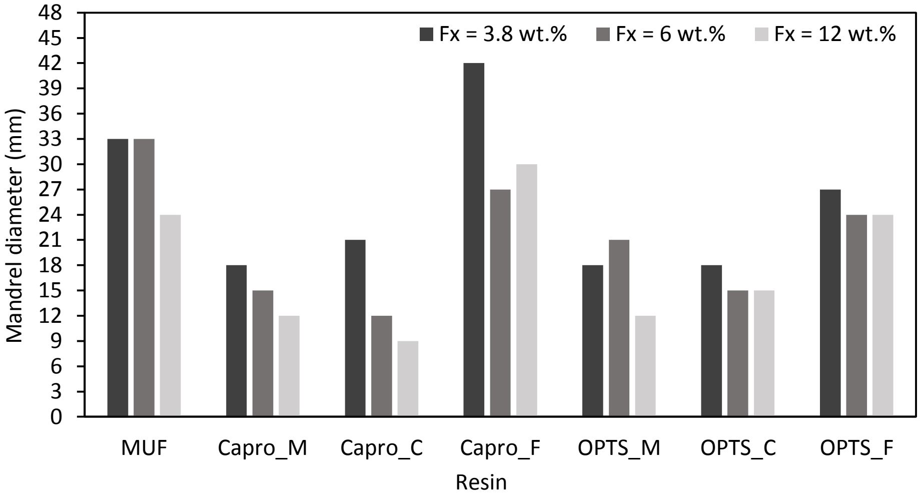


Figure 4.7. Mandrel results (mode) for cork-based panels produced with blocked MUF.

There is a general tendency for a decrease in mandrel value, *i.e.* better flexibility, when RC increases. This is a consequence of better cohesion of the agglomerated grains achieved by higher resin content. Panels produced with standard MUF resin yield a relatively large mandrel values (33 mm for RC = 3.8 wt.% and 6 wt.%, and 24 mm for RC = 12 wt.%).

When MUF resin is modified with blockers, added in the methylolation or condensation steps (resins Capro_M, Capro_C, OPTS_M and OPTS_C), the mandrel value decreases significantly. This confirms that the crosslinking density after curing in these blocked resins is lower than in the standard MUF resin, therefore allowing for greater chain mobility and hence flexibility of the glue line. This improved flexibility of cork panels and decreased the mandrel values as desired. The same does not occur when the blockers were added at the end of the synthesis (Capro_F and OPTS_F), yielding high mandrel values, comparable to the standard MUF. The best mandrel result (9 mm) was obtained for 10 % of caprolactam introduced in the condensation step, with 12 wt.% resin content in the panel.

The resins that yielded the best mandrel performance (Capro_M, Capro_C, OPTS_M and OPTS_C) were selected for evaluation of the tensile properties of the cork-based panels. Figure 4.8 presents these results.

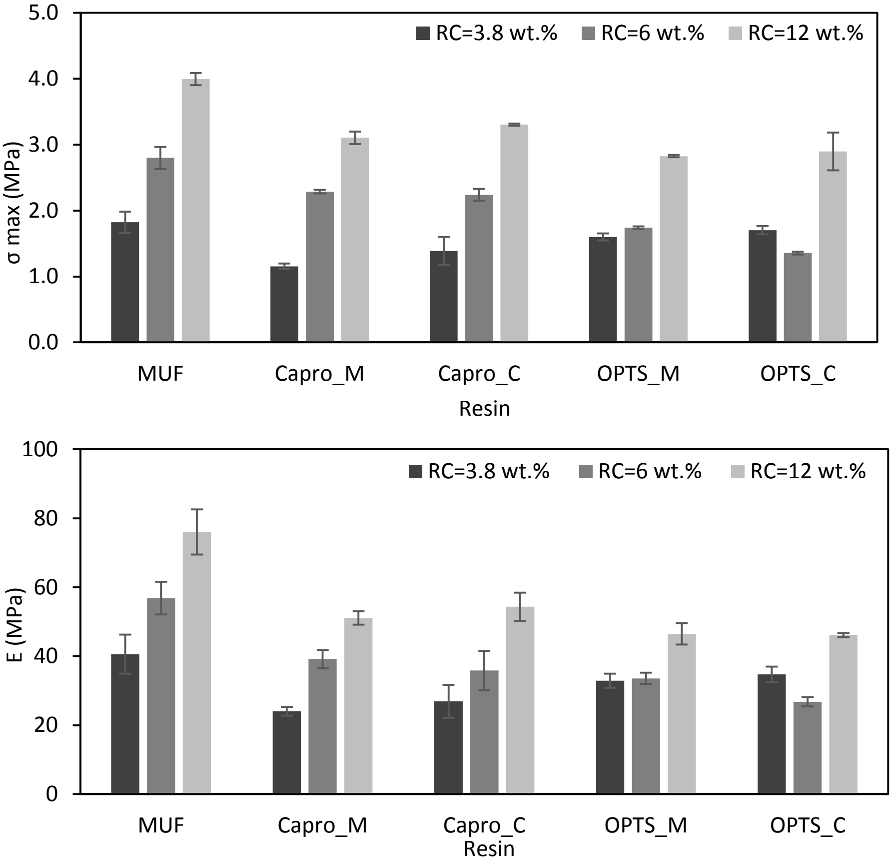


Figure 4.8. Physical-mechanical properties of cork-based panels produced with blocked MUF.

All resins show tensile strength well above the minimum required by APCOR's specification (0.2 MPa for agglomerated cork board for wall cladding and 0.3 MPa for agglomerated cork rolls for wall cladding) [4]. As expected, as the resin content is increased, better tensile resistance is obtained. Concerning Young's modulus, there is a noticeable decrease in the panels' stiffness when the resin is modified with blockers. This again shows the decrease of crosslink density in modified MUF resins. The modulus tends to increase with resin content, as expected.

4.4. Conclusions

Blocked MUF resins were prepared by addition of caprolactam and OPTS at three different stages of the synthesis process. The presence of the blockers in the synthesized resins was confirmed by FTIR analysis. All modified resins show better storage stability than standard MUF resins, the best results being obtained for caprolactam. Water tolerance improved for resins modified with caprolactam in the methylolation or condensation stages. GPC analysis results confirmed that lower molecular weight polymer was obtained when blockers were added in the methylolation or condensation stages. Addition after the end of the synthesis reaction was the less effective approach.

The flexibility of agglomerated cork panels was improved when the blockers were added to the binder resin during synthesis. The best result (mandrel diameter of 9 mm) was obtained for caprolactam added at the condensation step and 12 wt.% resin content. A panel produced with standard MUF resin can only be flexed without rupture on mandrel diameter of 24 mm.

Addition of blockers in the synthesis process proved to be an effective strategy to reduce rigidity of MUF resins. Agglomerated cork panels produced with the modified resins showed improved flexibility, while maintaining appropriate mechanical resistance. Caprolactam proved to be the most effective, yielding the lowest mandrel value and the best storage stability and water tolerance.

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CHAPTER 5

Partial replacement of melamine by benzoguanamine in MUF resins towards improved flexibility of agglomerated cork panels

5. Partial replacement of melamine by benzoguanamine in MUF resins towards improved flexibility of agglomerated cork panels [4]

Abstract

Melamine-urea-formaldehyde (MUF) resins are highly effective adhesives for lignocellulosic materials. However, their high stiffness hinders applications where flexibility is desired. In this work, MUF resins were modified with benzoguanamine by partially replacing melamine in two different steps of the synthesis. The purpose was to obtain a less densely crosslinked, and hence more flexible, structure after cure. All modified MUF resins were characterized using gel permeation chromatography (GPC). Results suggest that benzoguanamine and its derivatives were integrated into the polymer structure. FTIR and ^{13}C-NMR analysis confirmed the presence of benzoguanamine in the modified resins. The addition of benzoguanamine to the MUF resin synthesis significantly improved the flexibility of agglomerated cork panels bound with modified resins. The minimum mandrel diameter on which the panels could be bent by 180° without failure decreased from 18 mm to 12 mm diameter, while the remaining key properties of the panels were maintained (tensile strength and boiling water resistance). The formaldehyde content of the panels (determined according to EN120) correspond to E1 class.

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5.1. Introduction

Melamine-urea-formaldehyde (MUF) resins are thermosetting polymers characterized by high stiffness, absence of color, high gloss, high water resistance, very good adhesive performance, and very low cost when compared to other adhesives for paper, wood and cork [1]–[3]. MUF resins have lower cost than melamine-formaldehyde (MF) resins, while still having better hydrolysis resistance than urea-formaldehyde (UF) resins [1], [2].

The stiffness and brittleness of MUF resins, however, may be a limiting factor when they are used as binders for products where flexibility is desired. Such an example are agglomerated cork panels. These are produced using granulate wastes from the natural cork industry and have applications in a wide variety of areas (construction, decoration, fashion, transportation). The cork granules are mixed with a binder and fed into a mold with parallelepiped or cylindrical shape, which is then closed and heated for curing [3], [4]. The cured product is then laminated into panels with varying thickness, and then stocked. Polyurethane binders, which are highly flexible, easily allow stocking the panels as rolls – the optimal form for storage and transportation. On the other hand, if the panels are bonded with MUF resins, they easily fracture when bending is attempted, due to high stiffness of the cured binder. However, since MUF resins are highly competitive in relation to polyurethanes in terms of cost, it is a pertinent challenge to find an approach to chemically modify these resins, allowing production of sufficiently flexible agglomerated cork panels.

Some general information can be found in the literature suggesting that benzoguanamines can be used as partial substitute of melamine in order to improve some characteristics of MUF resins [5]–[8]. The only work containing detailed information was authored by Henriques, et al. (2017) [7], describing significant improvement of storage stability of a melamine-formaldehyde resin modified with benzoguanamine. The new resin was used to impregnate decorative paper, and the properties of the high pressure laminate produced with it were equivalent to those obtained with the standard resin. Chang (1976) [9] patented the use of benzoguanamine in polyester crosslinking in order to obtain flexible coatings. Benzoguanamine has a similar chemical structure to melamine, but has lower functionality and is less reactive because one -NH2 group is replaced with a benzene ring. By incorporating benzoguanamine in the polymer structure, the resultant resin should present lower crosslink density, resulting in a modified resin with higher flexibility (Figure 5.1) than standard MUF. Replacing melamine with another guanamine raises the price of the adhesive. But the product is still viable when compared to much higher priced polyurethanes.

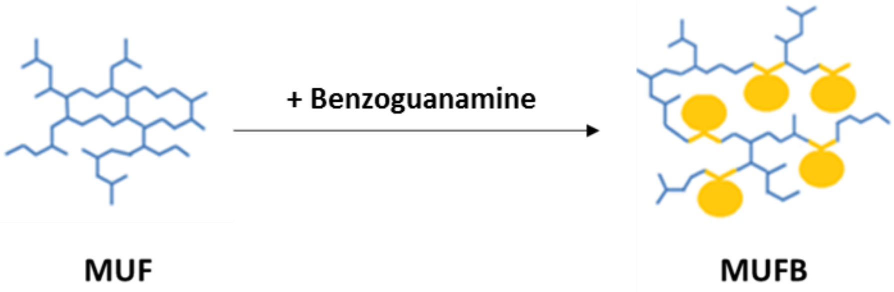

Figure 5.1. Schematic representation of the densely crosslinked MUF resin (left) and the MUF resin containing benzoguanamine (right).

The purpose of this work is to study the most effective approach for introducing benzoguanamine in a standard formulation of melamine-urea-formaldehyde resin, and to evaluate the properties of the resulting adhesive. Agglomerated cork panels are used as an application example, where the flexibility of the final product is not adequate when standard MUF resins are employed.

5.2. Materials and Methods

5.2.1. Materials

For melamine-urea-formaldehyde resins preparation, industrial-grade raw materials were provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal): melamine (M), urea (U), formaldehyde (F) 53 % solution, sodium hydroxide (NaOH) 50 % solution and ammonium sulphate ($(NH_4)_3SO_4$) 30 % solution. Benzoguanamine was purchased from Sigma-Aldrich, USA. Cork oak (Quercus suber) bark granules with 0.5-1.0 mm diameter were provided by Amorim Cork Composites, S.A. (Santa Maria da Feira, Portugal).

5.2.2. Synthesis of MUF and MUFB resins

The MUF resins were prepared in a three-necked 2500 ml glass flask under atmospheric pressure adapting the alkaline process [10]. Formaldehyde 53 % solution at 50 - 60 °C was charged into the reactor and the pH value was adjusted to 7.5 – 9.0 using sodium hydroxide solution. Urea and melamine were slowly added, allowing the heat to rise the temperature from initial temperature up to values between 80 – 90 °C. For the condensation step, a second load of urea and melamine was added and the reaction was carried out until a desired viscosity between 500 and 700 mPa·s was obtained. This reaction was stopped by cooling the subsequent mixture to a temperature of 60 °C. Finally, a given amount of urea was added in order to decrease de $F/(NH_2)_2$ molar ratio to a value between 1.05 – 1.15. The reaction was ended by cooling the mixture to a temperature of 25 °C and pH was adjusted to 8.5-10.0.

The major differences between all produced resins were the amount of benzoguanamine added to the reaction mixture and the reaction step where this was done. A fraction of equivalent moles of the first and/or second melamine load were replaced by benzoguanamine. Table 5.1 describes the synthesized melamine-urea-formaldehyde-benzoguanamine (MUFB) resins. Samples were named according to the fraction of melamine replaced in the synthesis step, and ordered in Table 5.1 according the total amount of benzoguanamine introduced.

Table 5.1. Composition of the synthesized MUFB resins

Resin	**Replaced fraction and addition step**
R_1/4_0	1/4 of first melamine + 0 of second melamine
R_2/4_0	2/4 of first melamine + 0 of second melamine
R_0_1/3	0 of first melamine + 1/3 of second melamine
R_3/4_0	3/4 of first melamine + 0 of second melamine
R_1/4_1/3	1/4 of first melamine + 1/3 of second melamine
R_4/4_0	4/4 of first melamine + 0 of second melamine
R_2/4_1/3	2/4 of first melamine + 1/3 of second melamine
R_0_2/3	0 of first melamine + 2/3 of second melamine
R_3/4_1/3	3/4 of first melamine + 1/3 of second melamine
R_1/4_2/3	1/4 of first melamine + 2/3 of second melamine
R_2/4_2/3	2/4 of first melamine + 2/3 of second melamine
R_3/4_2/3	3/4 of first melamine + 2/3 of second melamine
R_0_3/3	0 of first melamine + 3/3 of second melamine

5.2.3. Characterization of MUFB resins

The solid content (%) was determined by evaporation of volatiles in two grams of resin for three hours at temperature of 120 °C in oven. The solid content was determined by the mass ratio of the sample before and after drying.

Viscosity of MUF and MUFB resins were measured with a Brookfield viscometer at 25 ± 1 °C and it is expressed in mPa·s.

The resin pH was measured using a combined glass electrode.

The density (kg/m^3) of the resins were measured using a hydrometer.

Gel time is the time needed for the resin gelification under hot and catalysed environments. This time was measured in a laboratory test tube immersed in boiling water with resin prepared in a 3 wt.% of ammonium sulphate 30 % solution.

Storage stability was evaluated comparing the pH and viscosity of MUFB at 25 °C until resins present viscosity got equal or superior to 500 mPa·s. Viscosity and pH were measured as described above.

5.2.4. Determination of free formaldehyde of MUFB resins

Determination of free formaldehyde in amino groups was done according to European standard EN 1243. This test takes into account the reaction of the free formaldehyde with sodium sulfite, in the presence of a measured excess of acid, in accordance with the reaction (Eq. 5.1):

$$CH_2O + Na_2SO_3 + H_2O \rightarrow CH_2(OH)SO_3Na + NaOH \qquad \text{Eq. 5.1}$$

and alkaline titration of the unreacted excess acid. The acid-sulfite 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 is calculated using (Eq. 5.2):

$$\text{Free formaldehyde (\%)} = \frac{(\mathrm{V_2\text{-}V_1}) \times \mathrm{M} \times 3.002}{\mathrm{m}}$$

Eq. 5.2

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.

5.2.5. Gel permeation chromatography / Size exclusion chromatography analysis of MUFB resins

GPC/SEC equipped with a Knauer RI detector 2300 and a Knauer injector with a 20 µl was used. The columns used were PSS PolarSil with a pore size 30 Å and a particle size of 100 µm, conditioned at 60 °C using an external oven. The flow rate was 1 ml/min and dimethylformamide (DMF) was used as the mobile phase. Samples for analysis were prepared by dissolving a small amount of resin (100 mg) in dimethylsulfoxide (DMSO), followed by vigorous stirring during 1 min. Subsequently, the sample was left to rest (10 min), filtered through a 0.45 µm nylon filter and then the sample was injected. The universal calibration was done using poly(styrene) standards from PSS, with molecular weight between 162 - 66000 g/mol.

5.2.6. Fourier transform infrared spectroscopy of MUFB resins

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}. Samples were resin films and they were prepared by an evaporation technique. Approximately 50 g of resin was poured into a PTFE-coated mold and then cured in an oven at 120 °C.

5.2.7. ^{13}C-NMR analysis of MUFB resins

About 40 mg of liquid sample was directly mixed with 0.75 ml DMSO-d6 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 Nuclear Overhauser Effect (NOE) 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 h to accumulate. Chemical shifts in DMSO-d6 solution were calculated by defining a ^{13}C chemical shift of DMSO-d6 at 39.5 ppm. All results were discussed after normalized by carbonyl's urea signal.

5.2.8. Thermalgravimetric analysis of MUFB resins

Thermogravimetric analysis (TGA) analysis were performed in a simultaneous thermal analyser STA 449 F3 Jupiter (NETZSCH). Samples masses between 10 and 15 mg were placed in an alumina crucible. The heating rate was 10 K/min, under nitrogen flow (30 ml/min) from room temperature to 500 °C. Samples were cured resin.

5.2.9. Dynamic and mechanical analysis of MUFB resins

Dynamic mechanical measurements of resins were performed using a DMA model Tritec 2000 (Triton Technology) in material pocket support mode, in the temperature range from -100 to 200 °C. The heating rate was 2 °C/min and a gaseous nitrogen stream was used to keep a controlled atmosphere inside of the sample container. The frequencies used were 1, 5 and 10 Hz with maximum dynamic force of 2 N and maximum strain amplitude of 10 μm. Glass transition temperatures were identified as corresponding to the peak on damping coefficient (tan δ) curve. Pocket support was useful because the production of films with the same thickness and without air bubbles could not be achieved with other DMA support.

5.2.10. Production of agglomerated cork panels

Resins were added to granulated cork and the mixture was prepared by manual stirring during 5 min at room temperature. The amount of solid resin was 6 % based on dry cork mass. The catalyst level was 3 wt.% of ammonium sulphate 30 % solution.

After blending, agglomerated cork panel was hand formed in a deformable aluminium mold (2 x 450 x 250) mm^3. The cork amount was determined in order to obtain boards with target densities of 600 kg/m^3. Panels were pressed in a laboratory batch hot-press at 150 °C and 12 bar during 1.5 min. Three panels were produced for each resin tested.

5.2.11. Physical-mechanical characterization of agglomerated cork panels

Tensile strength of panels

After production, boards were hermetically conditioned until performance evaluation at (23 ± 2) °C and a relative humidity of (50 ± 5) % for 48 h. Stress-strain tests were based on ISO 7322:2000 (E), which described cork composites test methods. Three samples with dimensions (100 x 15 x 2) mm^3 were tested for each production condition in a Mecmesin MultiTest-1-d testing machine equipped with a Mecmesin BFG 1000 dynamometer, at a crosshead speed of 300 mm/min under room temperature, as specified in the standard. At least three replicas were made for each measurement.

Resistance to boiling water of panels

The resistance to boiling water was done according to ISO 7322:2000(E). Three samples with dimensions of (50 x 50 x 2) mm^3 were tested for each resin. The specimens were placed in boiling water for 3 h. After the test, the samples were visually examined and classified as disaggregated or not.

Flexibility of panels

The flexibility of agglomerated cork panels was measured according to ASTM F147-87. The method consists in bending the material 180° around a mandrel. The mandrels have diameters ranging from 3 mm to 48 mm, corresponding to designations F1 (3 mm) to F16 (48 mm). The flexibility of the specimen corresponds to the minimum mandrel diameter about which the specimen could be flexed without exhibiting any signs of failure. A flexibility designation of F1 would therefore correspond to maximum flexibility in this test (specimen does not fracture when bent around a 3 mm diameter mandrel).

5.2.12. Formaldehyde content of panels - Perforator method (EN 120)

Formaldehyde content of agglomerated cork panels was determined according to perforator method (EN 120). Perforator method measures the formaldehyde emissions content of the specimen potentially emitted under forceful conditions. Formaldehyde was extracted from 110 g of test pieces by means of boiling toluene and then transferred into distilled or demineralized water. The formaldehyde content of this aqueous solution was determined photometrically by the acetyl acetone method.

5.3. Results and Discussion

The reaction schemes involving urea, melamine, benzoguanamine and formaldehyde are schematized in Figure 5.2 and Figure 5.3.

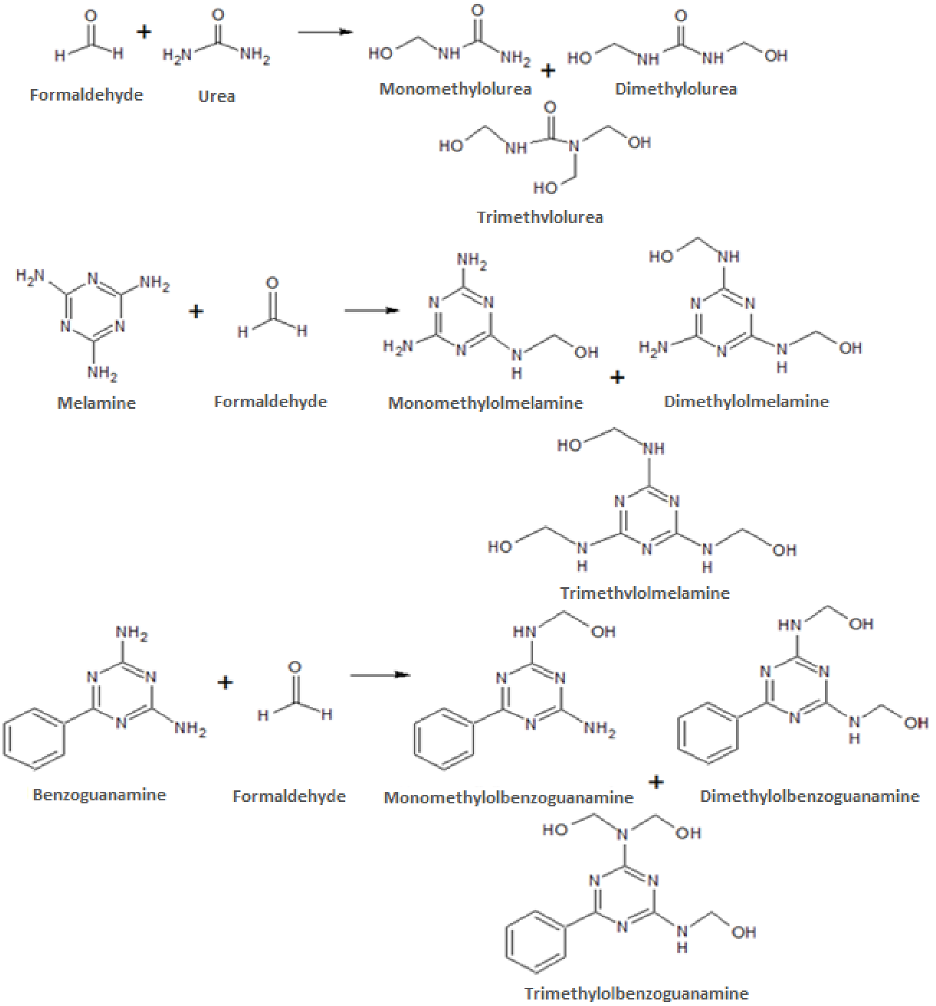

Figure 5.2. Methyolation reaction of urea, melamine and benzoguanamine with formaldehyde, forming methylolureas, methylolmelamines and methylolbenzoguanamines, respectively.

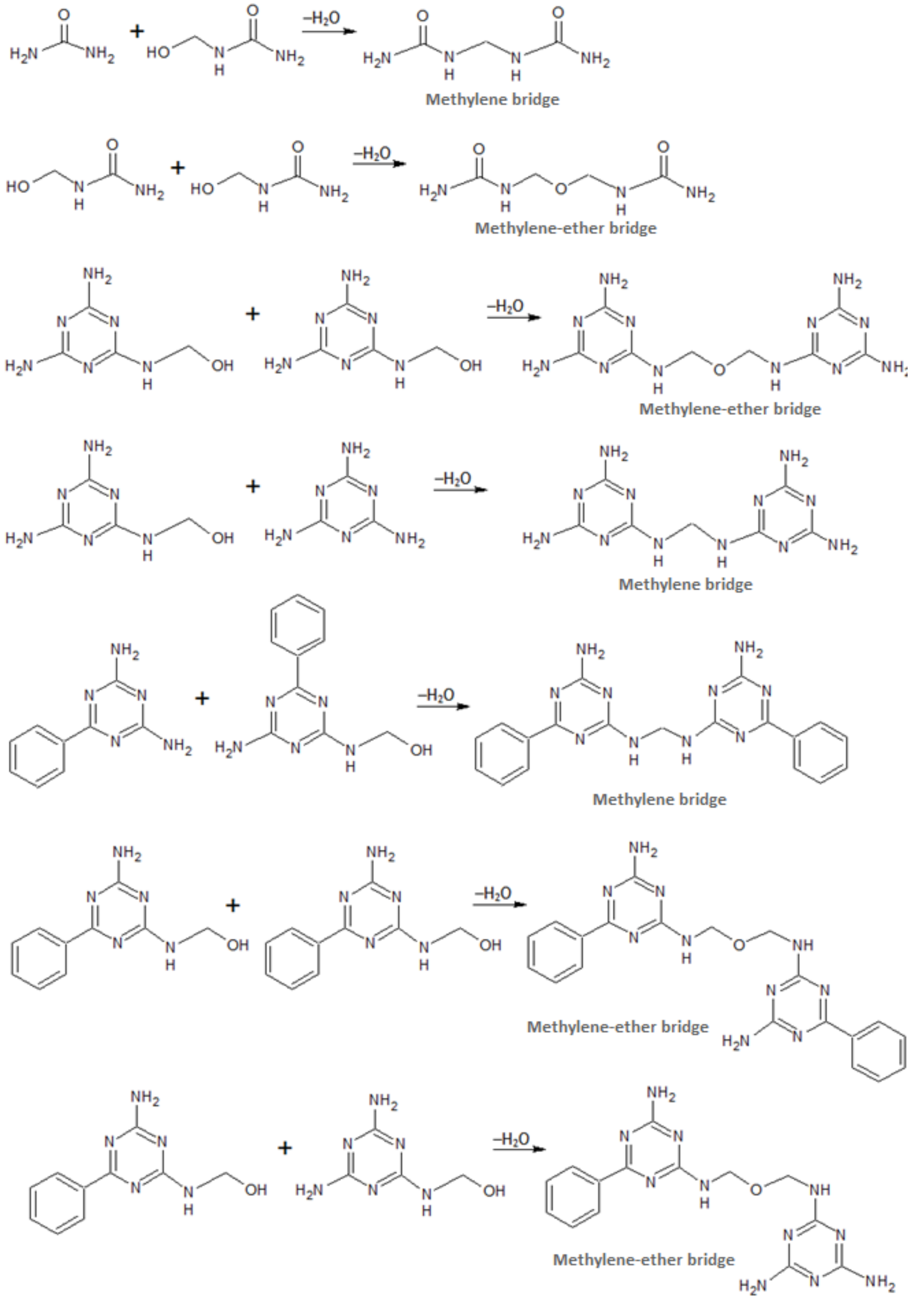

Figure 5.3. Condensation reaction of methylolureas, methylolmelamines and methylolbenzoguanamines forming methylene and methylene-ether bridges.

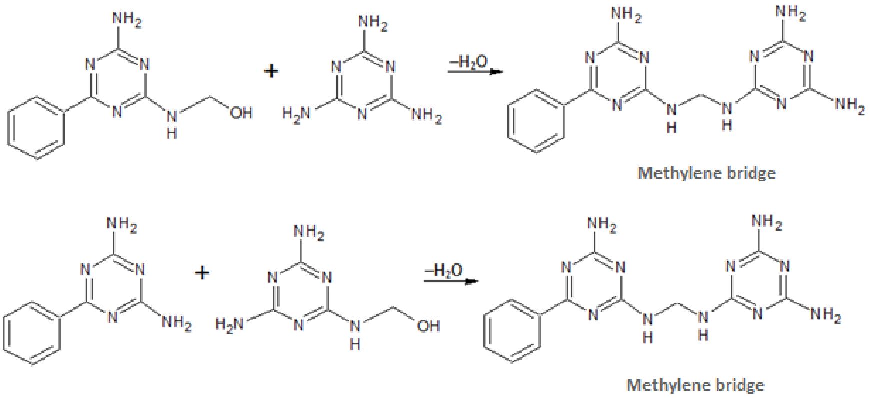

Figure 5.3. Condensation reaction of methylolureas, methylolmelamines and methylolbenzoguanamines forming methylene and methylene-ether bridges *(cont.)*.

5.3.1. General properties

Thirteen resins were synthesized using the same process, but varying the fraction of melamine replaced by benzoguanamine, and the moment of addition during the synthesis. The nomenclature used to describe the formulations was described in Table 5.1. Table 5.2 presents the final properties of the MUFB resins and of the reference MUF resin.

Table 5.2. Properties of the synthesized MUFB resins

Resin	pH	Viscosity (mPa·s)	Gel time (s)	Solid content (%)	Density (kg/m³)	Storage stability (days)	Free formald. (%)
MUF	8.7	235	61	64.4	1.29	19	0.12 ± 0.01
R_1/4_0	9.4	180	80	63.0	1.28	37	0.11 ± 0.01
R_2/4_0	9.9	185	97	63.9	1.28	36	0.07 ± 0.00
R_0_1/3	8.5	185	80	64.3	1.28	29	0.11 ± 0.01
R_3/4_0	8.6	165	70	65.0	1.25	31	0.07 ± 0.01
R_1/4_1/3	9.0	175	81	63.5	1.27	36	0.09 ± 0.01
R_4/4_0				*			
R_2/4_1/3	10.4	170	87	64.5	1.27	45	0.07 ± 0.02
R_0_2/3	9.2	245	73	64.7	1.27	25	0.09 ± 0.01
R_3/4_1/3	10.0	180	**	63.6	1.27	11	0.06 ± 0.00
R_1/4_2/3	9.3	255	75	65.0	1.26	15	0.08 ± 0.01
R_2/4_2/3	9.4	190	68	64.9	1.26	23	0.08 ± 0.01
R_3/4_2/3	8.6	245	**	65.2	1.26	8	0.04 ± 0.01
R_0_3/3				*			

* Resin gelled inside the reactor during synthesis

** The test could not be performed

The synthesis of resins R_4/4_0 and R_0_3/3, involving total substitution of melamine by benzoguanamine in each reaction phase, were not terminated. These resins gelled inside the reactor after the introduction of the final urea load, i.e. there was a very large increase in the viscosity of the reaction medium.

The excessive amount of benzoguanamine used may have resulted in a water-intolerant product [11].

Concerning the final pH, viscosity, solid content and density, the results were very similar for all resins. Incorporation of benzoguanamine increased the storage stability, with the exception of resins R_3/4_1/3, R_1/4_2/3 and R_3/4_2/3, which were less stable than the reference MUF resin. All MUFB resins presented a longer gelling time than MUF. Gel time could not be determined for resins R_3/4_1/3 and R_3/4_2/3 because polymer precipitation occurred after the addition of the aqueous catalyst solution. This was due to the decrease in the water tolerance of resins containing the highest amount of first melamine replaced by benzoguanamine and combined with 1/3 and 2/3 of second melamine (Ross, 1970).

Free formaldehyde content was equivalent or lower than the values observed in the standard resin. This is a surprising result, considering that benzoguanamine was added replacing equivalent moles of NH_2 of melamine, therefore it would be expected that the free formaldehyde content of MUFB would be identical to that of the MUF resin, or actually higher, in case benzoguanamine did not react with it. The lower values obtained may be associated to measurement errors, inherent to the analysis method that is based on visual identification of equivalence point.

5.3.2. Gel permeation chromatography / Size exclusion chromatography analysis

Gel Permeation Chromatography (GPC) has been commonly used for qualitative comparison of MUF resin formulations [10], [12]. Figure 5.4 shows the GPC chromatograms obtained for MUFB resins synthesized in this study, as well as for the standard MUF resin and benzoguanamine.

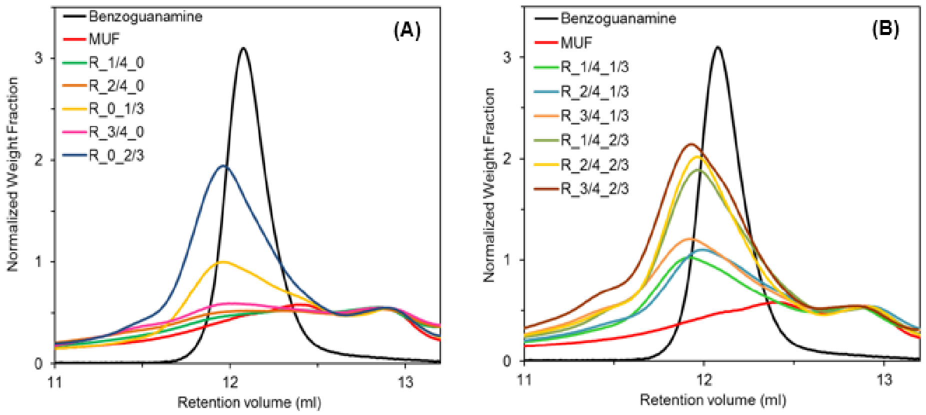

Figure 5.4. Chromatograms of MUFB resins where benzoguanamine was added replacing 1st or 2nd melamine (A) and MUFB resins where benzoguanamine was added replacing 1st and 2nd melamine simultaneous (B).

All synthesized resins, including the standard MUF resin, exhibit a common peak in the retention volume range of 12.5 to 13.0 ml. This range corresponds to low molecular weight compounds and can be assigned to unreacted urea, methylolureas, methylolmelamines, oligomers [10], [12]. The retention volume range between 11.7 and 12.5 ml corresponds to the benzoguanamine peak. Resins with benzoguanamine incorporation present one notorious peak to the left of this peak, between 11.5 and 12.5 ml, which is not visible in the MUF resin. This corresponds to methylolbenzoguanamine derivatives with higher molecular weight than the original monomer. When benzoguanamine was added replacing second melamine (resins R_0_1/3 and R_0_2/3), the peak of the retention volume between 11.5 and 12.5 ml was more intense compared to the resin with benzoguanamine added only in the initial step. Although resin R_3/4_0 had a higher amount of benzoguanamine relative to resin R_0_1/3, the peak was less intense in the retention volume between 11.5 and 12.5 ml. This suggests that the reaction of benzoguanamine and its derivatives occurs to a greater extent when the compound was introduced replacing the first melamine.

All resins presented in Figure 5.4B show a pronounced peak of benzoguanamine derivatives, since in all of them benzoguanamine was added replacing second melamine.

5.3.3. Fourier transform infrared spectroscopy

According to the literature [13], [7], [14] characteristic absorptions bands of MUF resin are observed at 3400–3300 cm^{-1} (NH stretching of primary aliphatic amines and stretching of OH mode of C-OH group), 2970-2950 cm^{-1} (C-H stretching vibration in C-H of methylol group), 1650–1630 cm^{-1} (C=O stretching of urea), 1560–1530 cm^{-1} (C=N stretching of secondary amines in triazine ring), 1500–1380 cm^{-1} (C-H stretching vibration in CH_2 and CH_3), 1380–1330 cm^{-1} (C-N stretching of CH_2-N), 1250-1200 cm^{-1} (stretching of C-N), 1130-1120 cm^{-1} (C-O stretching of aliphatic ether), 1050–1030 cm^{-1} (C-N or NCN stretching of methylene linkages (NCH_2N), 1022-1005 cm^{-1} (C-O stretching aliphatic ether), 890-860 cm^{-1} (C-H deformation out of plane), 814-812 cm^{-1} and 781-771 cm^{-1} (triazine ring stretching) and 750–700 cm^{-1} (N-H bending of secondary aliphatic amines (R_1–CH–NH–CH_2–R_2)).

The two resins with the highest amount of benzoguanamine added in each step (R_3/4_0 – benzoguanamine partially replacing 1st melamine, and R_0_2/3 – benzoguanamine partially replacing 2nd melamine) were analyzed by FTIR. The spectra obtained are shown in Figure 5.5, together with the spectrum for the MUF resin.

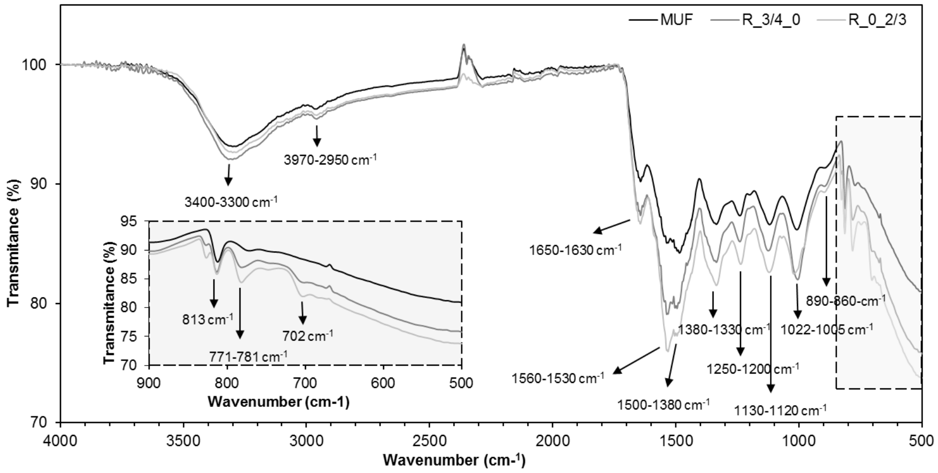

Figure 5.5. IR spectrum of MUF and MUFB resins.

As expected, since the reagents used and the bonds formed are of the same type, the two MUFB resins show spectra very similar to MUF. However, one band can be seen at 702 cm^{-1} only in MUFB resins, corresponding to out-of-plane deformation of C-H of monosubstitued benzene [7]. This indicates the presence of benzoguanamine in these resins.

5.3.4. ^{13}C-NMR analysis

^{13}C-NMR was applied to standard MUF resin and MUFB R_3/4_0 and R_0_2/3. Each signal observed in the spectra was identified according to chemical shifts reported in the literature [7], [15]–[19]. The ^{13}C-NMR spectra and the structural assignments of chemical shifts of standard MUF and MUFB resins are shown in Figure 5.6.

The spectra of analyzed resins can be split into five main areas. The following signal attributions can be made: signals from 160.0 to 170.0 ppm correspond to substituted and unsubstituted benzoguanamine’s and melamine's triazines and urea carbonyl groups, from 138.0 to 128.0 ppm to carbons in benzene ring of benzoguanamine, from 67.0 to 70.0 ppm to methylene-ether linkages, from 64.2

to 63.5 ppm to methylol groups, and from 48.8 to 45.5 ppm to carbons on methylene group.

It should be noted that the three resins have the same functional groups, so the chemical shifts shown are quite similar. The exception is the standard MUF resin, which does not show the signal between 128 and 138 ppm, corresponding to chemical displacement of the benzene ring carbons.

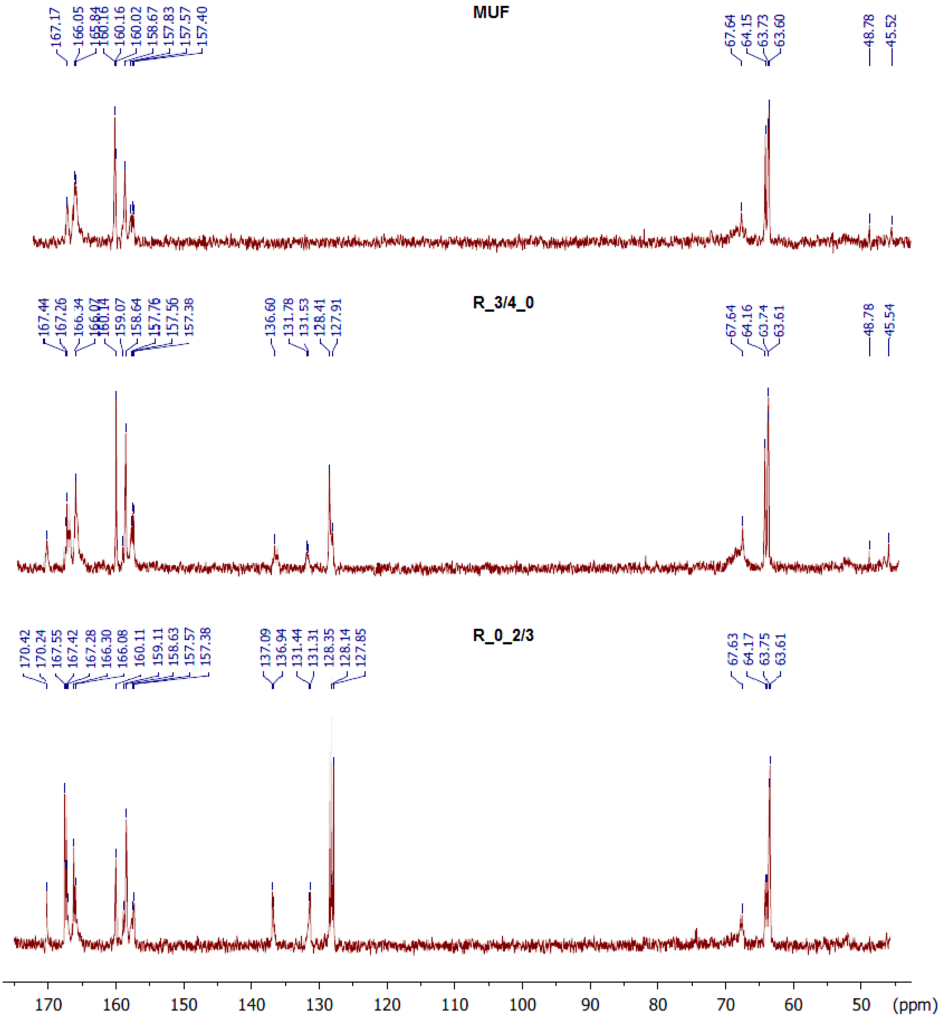

Figure 5.6. ^{13}C-NMR spectra obtained in the region between 200–40 ppm for MUF and MUFB resins.

^{13}C-NMR does not show the presence of free formaldehyde, polyoxymethylene oligomers or trioxane isomers (80 to 90 ppm), corroborating the previous discussion that indicated low free formaldehyde content. When comparing to R_3/4_0, resin R_0_2/3 shows higher amount of carbons from benzene ring, and from the triazine ring bonded to the benzene ring. This is in agreement with the fact that R_0_2/3 has a greater amount of benzoguanamine, and possibly also of methylolbenzoguanamine derivatives, as verified in the GPC/SEC analysis.

5.3.5. Thermogravimetric analysis

The thermal stability of cured resins is shown in Figure 5.7. Three degradation steps can be observed in all the analyzed resins. In stage I, between 30 and 230 °C, weight loss is mainly caused by the escape of the volatile gases like moisture and free formaldehyde. In stage II, between 230 and 380 °C, weight loss is due to breakage of methylene ether bridges into more stable methylene bridges, consequently releasing formaldehyde. In stage III, between 380 and 500 °C, scission of methylene bonds takes place, originating lower molecular weight species [15], [20], [21].

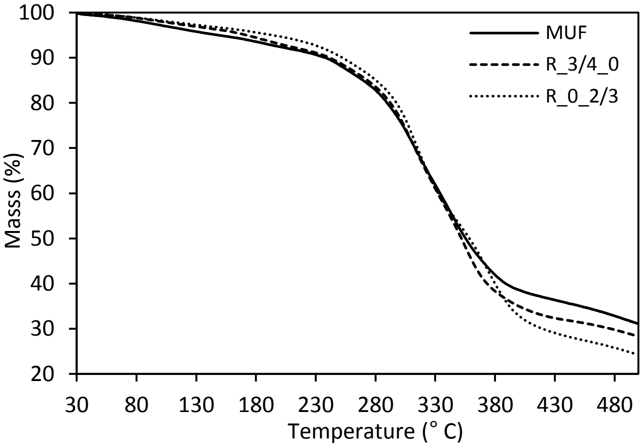

Figure 5.7. Thermogravimetric analysis results of MUF and MUFB resins.

Both MUFB resins present higher final weight loss than MUF. One justification, coherent with GPC results, is the presence of benzoguamine derivatives in resin R_3/4_0 and resin R_0_2/3. These low molecular weight species are more easily decomposed. It is noteworthy that resin R_0_2/3 corresponds to the higher weight loss and has the higher content of benzoguanamine derivatives in GPC analysis.

5.3.6. Dynamic and mechanical analysis

The loss factor (tan δ) of cured R_3/4_0, R_0_2/3 and MUF resins, in powder form, was measured by DMA as a function of temperature, as seen in Figure 5.8.

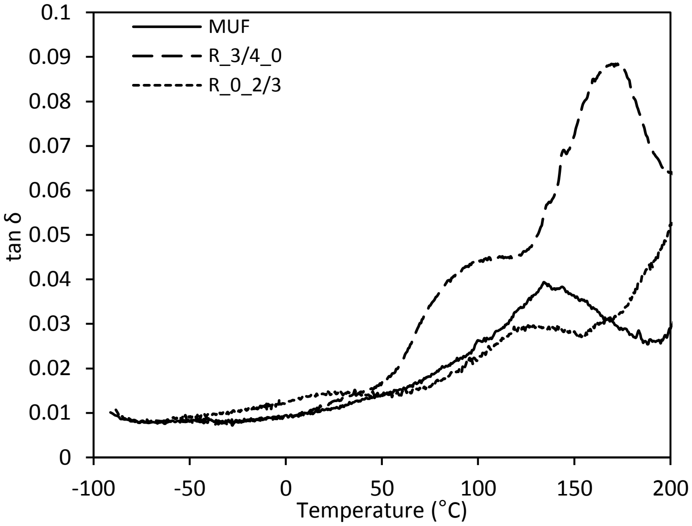

Figure 5.8. Loss factor, tan δ, as a function of temperature for MUF and MUFB resins (1 Hz).

In the thermogram of standard MUF resin it is possible to observe one peak in tan δ approximately centered at 140 °C. This probably corresponds to glass transition of cured MUF, according to the works of Arab and Shokuhfar [22], who identified the *Tg* of cured urea-formaldehyde resin between 150 and

170 °C, and of Hanstrand and Klason [23], who identified the *Tg* of cured melamine-formaldehyde resin between 130 and 180 °C. It is interesting to note that resin R_3/4_0 shows lower Tg (tan δ peak centered at around 100 °C) than MUF and R_0_2/3. This decrease in the glass transition temperature may be a consequence of a less crosslinked, more mobile, polymer structure, obtained when benzoguanamine replaces the first melamine load. A second peak is visible in resin R_3/4_0, centered at 170 °C, which can be attributed to a particular transition in the molecular structure of the MUFB resin, but we cannot identify its origin. Resin R_0_2/3 does not show this peak because benzoguanamine was introduced in the condensation step and the reaction does not occur to the same extension as shown in GPC. Also, resin R_0_2/3 does not show a decrease in glass transition but similar values to standard MUF instead.

Both resins containing benzoguanamine show a small peak between 0 and 50 °C, which probably is a β transition associated with rotation of the phenyl group in benzoguanamine [24].

5.3.7. Physical-mechanical characterization of aglomerated cork panels

Cork panels were produced with all synthesized resins (except resin R_3/4_1/3 and R_3/4_2/3 because of water intolerance as mentioned above). Table 5.3 shows the mechanical properties obtained.

The tensile strength results show that the 0.2 MPa limit required by APCOR specifications [25] for cork agglomerate panels is achieved for all panels. Addition of benzoguanamine does not therefore impair the adhesion strength of the resins. In addition, it must be noted that all specimens produced with MUFB resins passed the required boiling water resistance test, indicating good cohesion even under extreme moisture conditions.

Table 5.3. Mechanical properties of cork-based panels produced with MUF and MUFB resins: maximum tensile strength and higher mandrel value that caused rupture

Resin	**σ max (MPa)**	**Flexibility (mandrel value)**		
		Sample 1	**Sample 2**	**Sample3**
MUF	2.85 ± 0.17	F6	F7	F6
R_1/4_0	3.08 ± 0.20	F5	F4	F4
R_2/4_0	2.35 ± 0.14	F4	F5	F4
R_0_1/3	2.56 ± 0.25	F6	F5	F6
R_3/4_0	2.46 ± 0.15	F4	F4	F4
R_1/4_1/3	2.70 ± 0.23	F5	F4	F4
R_2/4_1/3	2.74 ± 0.25	F5	F5	F6
R_0_2/3	2.38 ± 0.36	F4	F4	F5
R_3/4_1/3	**	**	**	**
R_1/4_2/3	2.95 ± 0.23	F5	F4	F4
R_2/4_2/3	2.31 ± 0.23	F4	F4	F5
R_3/4_2/3	**	**	**	**

** The test could not be performed

The mandrel results presented in Table 5.3 demonstrate that the incorporation of benzoguanamine in the formulation effectively increases the flexibility of the cork panels. The effect is more evident when benzoguanamine replaces the first melamine load (resin R_3/4_0), as the minimum mandrel value decreases from F7 – F6 (21 - 18 mm diameter) to F4 (12 mm diameter) yielding the most consistently flexible cork panel. The small amount of benzoguanamine replacing the first melamine became fully incorporated in the polymer structure, as verified in the GPC results. Furthermore, this modifies significantly the final polymer, as seen by DMA, improving the mobility of the cured resin structure.

However, when benzoguanamine replaces the second melamine, the same effect is not observed as seen by GPC. Resin R_0_1/3 yielded the worst mandrel score (F6) of the modified resins.

Regarding formaldehyde content values, MUF and resin R_3/4_0 present 4.4 and 3.8 mg / 100g oven-dry panel, respectively. These results indicate low formaldehyde content, according to the standard for wood-based panels for construction (EN 13986). The panels can therefore be classified as E1 taking into account the limit value for formaldehyde content (≤ 8 mg / 100 g oven-dry panel).

5.4. Conclusions

Melamine-urea-formaldehyde resins modified with benzoguanamine were successfully synthesized. Benzoguanamine was added at various amounts during the standard synthesis procedure, replacing the first and/or second melamine loads. GPC analysis suggested that incorporation of benzoguanamine in the polymer structure was more effective when the monomer was added to replace first melamine load. FTIR and ^{13}C-NMR analysis confirmed the presence of benzoguanamine in MUFB resins. DMA analysis showed that the replacement of first melamine load by benzoguanamine decreases the glass transition of the cured resin, therefore improving the chain mobility. The modified resins afforded agglomerated cork panels with appropriate mechanical properties, according to current standards. Panels produced using resin with 3/4 of first melamine replaced by benzoguanamine exhibited significantly better flexibility (minimum mandrel of F4) than the standard resin (F6). This work showed that benzoguanamine is a promising compound for the improvement of flexibility of MUF resins, making them appropriate for use as binders in materials where flexibility is a relevant property, like agglomerated cork panels.

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CHAPTER 6

Introduction of linear segments in amino-formaldehyde resins

6. Introduction of linear segments in amino-formaldehyde resins

6.1. Highly flexible glycol-urea-formaldehyde resins [5]

Abstract

Urea-formaldehyde resins are successfully used in many contexts, but their tightly crosslinked thermoset structure impairs some applications, due to stiff and brittle behavior. In this work we show that copolymerization of urea and formaldehyde with glycols introduces linear flexible segments in the polymer structure, thus increasing the resilience and flexibility of the resin after curing. Glycols with different molecular weights (106, 200 and 400 g/mol) were incorporated in the synthesis in different amounts. The chemical and physical-mechanical properties of the resulting products were investigated in detail, namely using FTIR, ^{13}C-NMR, GPC/SEC analysis, dynamic mechanical analysis, adhesive bond strength, and tensile-strain testing. Use of polyethyleneglycol with molecular weight 200 g/mol yielded the most promising glycol-urea-formaldehyde resin, with remarkable resilience and good adhesion properties. When used for paper impregnation, the modified resins yielded flexible and tough papers, in comparison with a conventional urea-formaldehyde resin, which produced brittle papers that fractured easily upon bending.

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6.1.1. Introduction

Urea-formaldehyde (UF) resins are a type of so-called amino resins. They are currently used on a wide range of products: abrasives, foams, impregnated paper laminates, textiles, molded compounds, and adhesives [1]. After thermal curing they display very good adhesion on many substrates, particularly lignocellulosic, showing high tensile strength and excellent solvent and heat resistance. Their high crosslink density results in high stiffness and brittleness [1], which is a limitation for applications where a final product with flexibility and resilience is desired. One example is resin-impregnated paper, used as finishing foil for wood based panels by the furniture industry [2]. After curing, the UF-impregnated paper becomes extremely brittle, which forbids post-forming over curved surfaces. The same occurs with fabric substrates [1], [3], which cannot be post-formed, and become prone to wrinkling when impregnated with UF resins. In the context of adhesives, it has been argued that improving the flexibility of the crosslinked structure of UF resins would improve the bond quality, since it would allow decreasing internal stresses at the glued joint [4]–[6]. Also foams based on amino-formaldehyde resins would benefit from being less brittle for some applications [7]–[9].

A number of studies can be found in the literature focused on decreasing the brittleness of urea and/or melamine-formaldehyde resins [8], [10]–[20]. All strategies are based in the same principle: decreasing the high crosslink density that characterizes these resins. One approach found in some patents from the 70s and 80s, with limited details, is copolymerization with glycols for production of post-formable laminates based on resin-impregnated paper [13]–[15]. The feasibility of reacting glycols with urea-formaldehyde polymer has been demonstrated before. The hydroxymethyl groups present in an UF resin can be etherified with alcohols in acidic medium [1]. Gresham *et al.* [21] claimed in 1944 the preparation of glycol formals, obtained by reacting ethylene glycol with formaldehyde in the presence of sulfuric acid. Hodgins and co-workers described an urea-formaldehyde-ethylene glycol resin appropriate for coatings, discussing the flexibility of final product as a function of the carbon length of the acetal formed [22] , [23].

In the present work we describe the copolymerization of linear glycols with urea and formaldehyde as a strategy to dramatically increase the flexibility of the cured resins. Being incorporated in the polymer structure, the glycols introduce flexible soft segments and act as spacers between crosslinking sites, therefore decreasing crosslink density. Glycols with different molecular weights are tested, and their effect on different chemical and physical properties of the final product is discussed. The applicability of the resulting resins in paper impregnation and as adhesive systems is demonstrated. To the best of our knowledge, this is the first time that a detailed study of the glycol urea-formaldehyde reactive system is presented in the literature.

6.1.2. Materials and Methods

6.1.2.1. Materials

Urea (U), formaldehyde (F) solution at 55 wt%, sulfuric acid (H_2SO_4) solution at 98 wt%, sodium hydroxide solution at 50 wt% (NaOH), ammonium sulfate ($(NH_4)_2SO_4$) solution at 30 %, diethylene glycol (DEG) and polyethylene glycol with number average molecular weight 200 g/mol (PEG200) were provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal). Polyethylene glycol with number average molecular weight 400 g/mol (PEG400) and hexamethylenediamine ($C_6H_{16}N_2$) were purchased from Sigma-Aldrich, USA. The overlay paper used for resin impregnation was supplied by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal).

6.1.2.2. Synthesis of glycol-urea-formaldehyde resins

The glycol-urea-formaldehyde (GUF) resins were prepared in a three-necked 2500 ml glass flask under atmospheric pressure, adapting the so-called strongly acid process [24], [25]. Formaldehyde 55 % solution was charged into the reactor and the pH value was adjusted with a strongly acid. Urea and glycol (molar ratio F/U=2 and equivalent molar ratios F/(U+G) = 1.41, 1.26 or 0.93) were added in equal parts over a time span of 120 min. The reaction was carried out at 80 °C. After 60 min of reaction, the pH was adjusted to > 9.0 with sodium hydroxide solution at 50 % and the solution was cooled to room temperature. Solid content of all resins was adjusted to 50 %. The hypothetical chemical reaction scheme is depicted in Figure 6.1.

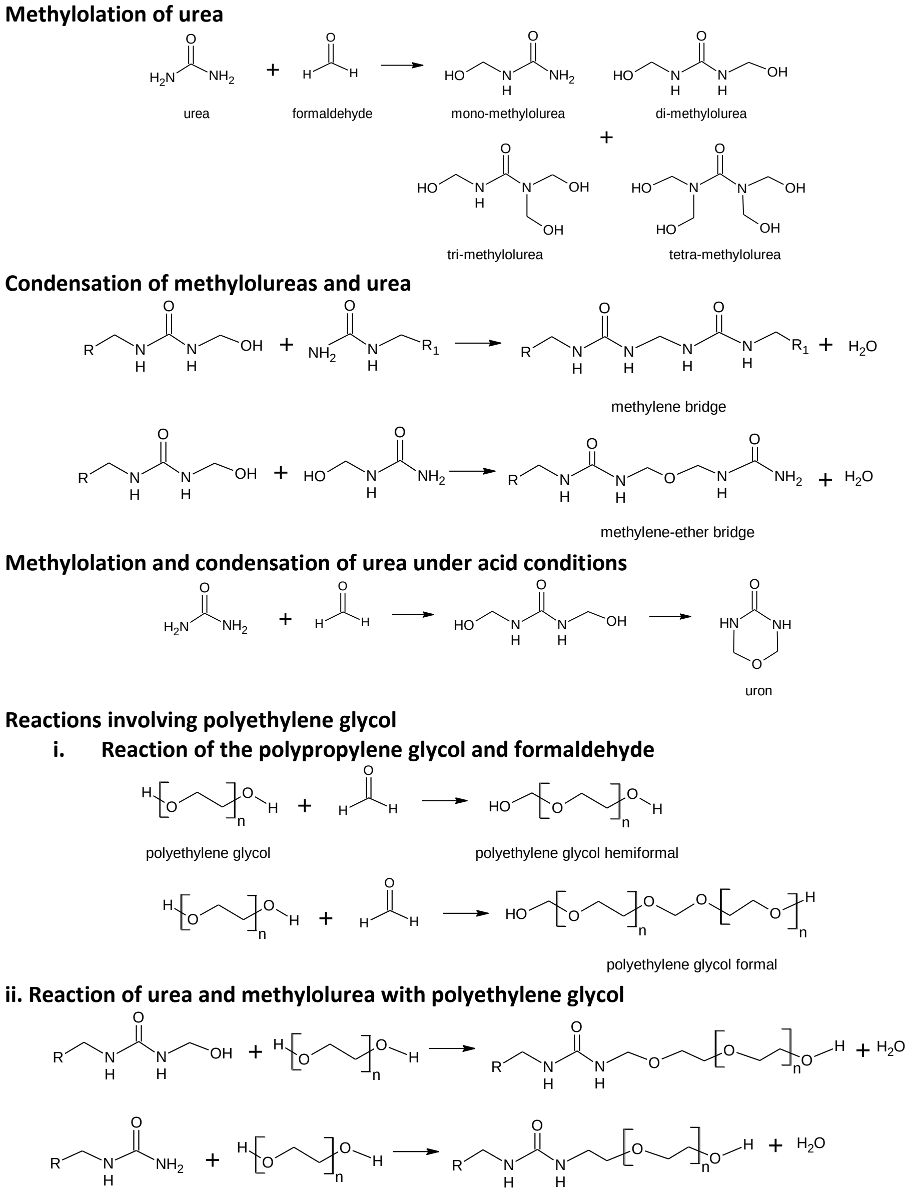

Figure 6.1. Chemical reactions of urea, formaldehyde and polyethylene glycol (adapted from [22]–[25]) and suggested chemical reaction between methylolurea and polyethylene glycol.

GUF resins were synthesised with different glycols (DEG, PEG200 and PEG400) and different molar ratios. F/(U+G) refers to the equivalent molar ratio, defined as the number of reactive groups present in formaldehyde over the number of reactive groups present in urea and glycol. It is considered that formaldehyde has one carbonyl group that allows two reactive sites, urea has two NH_2 groups, and glycol has two hydroxyl groups available to react. One example if PEG200 is used:

$$\frac{\mathrm{F}}{\mathrm{U+G}} = \frac{\mathrm{F}}{\mathrm{NH_2 + OH}} = \frac{\frac{\text{mass}_{\,\mathrm{F}} \times \text{functionality}_{\mathrm{F}}}{\text{molecular weight}_{\,\mathrm{F}}}}{\frac{\text{mass}_{\,\mathrm{U}} \times \text{functionality}_{\,\mathrm{U}}}{\text{molecular weight}_{\,\mathrm{U}}} + \frac{\text{mass}_{\,\mathrm{G}} \times \text{functionality}_{\,\mathrm{G}}}{\text{molecular weight}_{\,\mathrm{G}}}} = $$

$$= \frac{\frac{\text{mass}_{\,\mathrm{F}} \times 2}{30\ \text{g/mol}}}{\frac{\text{mass}_{\,\mathrm{U}} \times 2}{60\ \text{g/mol}} + \frac{\text{mass}_{\,\mathrm{G}} \times 2}{200\ \text{g/mol}}}$$

Eq. 6.1

Samples were named according to the type of glycol used in the synthesis and the F/(U+G) ratio. For example, “PEG200_1.26” means: GUF resin synthesized with PEG with molecular weight of 200 g/mol and a F/(U+G) ratio of 1.26.

In contrast with the conventional alkaline-acid process, in the strongly acid process it is difficult to control the condensation step at molar ratio F/U < 2, because resin gelification often occurs inside the reactor [25]. For this reason, the corresponding reference UF resins without glycol with F/U = 1.41, 1.26 or 0.93 were not synthesized.

6.1.2.3. Generic characterization of UF resins

The solid content (%) was determined by evaporation of volatiles in two grams of resin for three hours at 120 °C in an oven. The experimental solid content was determined by the mass ratio of the sample after and before drying.

The kinematic viscosity was determined by Ford Cup nº 4 method. The measurements were performed at (25 ± 1)° C.

The pH was measured using a combined glass electrode.

The density (kg/m^3) was measured using a hydrometer.

Gel time is the time needed for the resin gelification under hot and/or catalysed conditions. It was measured using a laboratory test tube immersed in boiling water or oil at three conditions: neat resin at 120 °C, resin with 3 % of ammonium sulphate at 100 °C, and resin with 3% of hexamethylenediamine at 100 °C. The purpose was to evaluate the reactivity of the polymer under acid and alkaline conditions.

The storage stability was evaluated comparing the pH and viscosity of the resins after 0, 60 and 240 days of shelf time. pH and viscosity were measured as described above.

6.1.2.4. Fourier transform infrared spectroscopy

FTIR measurements were performed with a Bruker Vertex 70 spectrophotometer. The samples were scanned using a Platinum-ATR single reflection diamond ATR module. Spectra were recorded in the wavenumber range 4000-500 cm^{-1} by signal averaging of 64 scans at a resolution of 4 cm^{-1}. The samples were resin films prepared as described above.

6.1.2.5. Liquid ^{13}C NMR experiments

About 40 mg of liquid sample was directly mixed with 0.75 ml deuterated water 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 Bruker Avance III (75.47 MHz for ^{13}C) using a repetition delay of 1.5 s, 536 scans and about 30 min for accumulate. Chemical shifts are expressed as parts per million.

6.1.2.6. GPC/SEC analysis

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 was 1 $ml \cdot min^{-1}$ and dimethylformamide was used as the mobile phase. Samples for analysis were prepared by dissolving a small amount of resin (100 mg) in dimethylsulfoxide (3 ml), followed by vigorous stirring during 1 min. Subsequently, the sample was left to rest (10 minutes), filtered through a 0.45 µm nylon filter and then the sample was injected [26].

6.1.2.7. Film flexibility

Free standing films were prepared by the casting-evaporation process. Approximately 20 g of resin was prepared and poured into a PTFE coated mold. This was then kept at 60 °C for 12 h, until water evaporated and film was formed. To cure the resins, temperature was increased to 80 °C for 4h, 120 °C for another 4h and 1h at 150 °C to ensure complete cure. The films obtained were about 1 mm thick and 100 mm in diameter. The flexibility of the films was subjectively evaluated by bending manually and checking for the occurrence of fracture or fissures.

6.1.2.8. Mechanical properties of resins supported in overlay paper

The mechanical properties of the resins were quantitatively evaluated after curing on a substrate, since it was not possible to produce defect-free films. The substrate chosen was overlay paper (grammage 20 g/m^2). Sheets of this paper (dimensions 21 x 30 cm^2) were impregnated with the synthesized resins by soaking with a foam roller. The paper sheets were oven-dried at 150 °C during 5 min. Finally, the impregnated overlay papers were submitted to hot pressing at 140 bar and a temperature of 150 °C during 1 hour. The cured impregnated papers had 80-85 % of resin content.

The tensile strength, Young's modulus and elongation at break of the cured papers were evaluated using a Mecmesin MultiTest-1-d equipped with a Mecmesin BFG 1000 dynamometer, at a crosshead speed of 10 mm/min at room temperature. The dimension of the test specimen was 75 mm x 15 mm x 1 mm. At least three replicas were made for each measurement.

6.1.2.9. Atomic force microscopy measurement

A Veeco Multimode Microscope interfaced with a NanoScope IVa (both from Digital Instruments, Santa Barbara, USA) was used for the atomic force microscopy (AFM) measurements. Each sample was imaged with a 16 x 16 μm^2 piezoscanner. Images were obtained in tapping mode, in air and at room temperature. A silicon cantilever (RTESP, Veeco) was used, with a spring constant 20-80 N/m. The NanoScope v6.13 software was used to measure several parameters.

6.1.2.10. Dynamic and mechanical analysis

Dynamic mechanical measurements of cured resins in powder form were performed using a DMA model Tritec 2000 (Triton Technology) in material pocket support mode, under a temperature range from -80 to 150 °C. The heating rate was 2 °C /min and a gaseous nitrogen stream was used to keep a controlled atmosphere inside of the sample container. The frequencies used were 1, 5 and 10 Hz with maximum dynamic force of 2 N and maximum strain amplitude of 10 μm. Glass transition temperatures were identified as corresponding to the peak of the damping coefficient (tan δ) curve. The material pocket option was adopted because films with uniform thickness and without air bubbles could not be obtained.

6.1.2.11. Automated bonding evaluation system

The bond strength of the resins was measured using Automated Bonding Evaluation System (ABES), Adhesive Evaluation Systems Inc. [27], [28]. Two beech veneer strips measuring 0.5 mm thick, 20 mm wide and 117 mm in length stored at 25 °C and 65% of relative humidity were glued together with an overlap of 5 mm. The veneers were prepared using a die cutter supplied by Adhesive Evaluation Systems Inc. (Corvallis, Oregon). Adherent pairs were mounted in the system with an overlapping area of 100 mm^2, pressed together at 1.2 N/mm^2, during 300 s at 150 °C. After that, the system was cooled to room temperature. The amount of adhesive system used for each test was 10 mg. The bond strength was tested almost instantaneously in shear mode (the system is digitally controlled and pneumatically driven). The results provided are the average of three measurements.

6.1.3. Results and Discussion

6.1.3.1. Generic properties

Nine resins were synthesized using different glycol molecular weights and F/(U+G) ratios of 1.41, 1.26 and 0.93, using an adapted form of the so-called strongly acid process. Formaldehyde/urea molar ratio was kept constant: F/U = 2. As mentioned before, in the strongly acid process it is difficult to control the condensation step at molar ratio F/U < 2, due to the tendency for gelification inside the reactor [25]. For this reason, standard resins (without glycol) could not be synthesized for comparison. The solids content of the synthesized resins was around 50%.

Table 6.1 shows the variation of pH, kinematic viscosity, density, and gel time of the produced resins. The cure reactions were performed under three conditions, for comparison of gel times: without catalyst, with ammonium sulfate (acid catalysis), and with hexamethylenediamine (curing agent).

Table 6.1. Characteristics of the synthesized PEA-UF resins

					Gel time		
Resin	**Glycol content (wt.%)**	**pH**	**Viscosity (s)**	**Density (kg/m^3)**	**Without catalyst (min)**	**With ammonium sulfate (min)**	**With hexamethylene-diamine (min)**
DEG_1.41	20	9.35	58	1.190	10	0.50	0.62
DEG_1.26	25	9.81	14	1.162	34	1.58	0.72
DEG_0.93	29	10.88	14	1.150	> 240	3.02	1.27
PEG200_1.41	30	9.96	15	1.166	32	0.75	0.60
PEG200_1.26	35	10.75	26	1.154	38	1.00	1.17
PEG200_0.93	44	9.31	13	1.134	> 240	3.67	1.87
PEG400_1.41	40	9.28	15	1.142	27	1.12	2.90
PEG400_1.26	44	9.19	16	1.140	31	1.38	3.28
PEG400_0.93	51	11.47	14	1.124	> 240	1.68	4.52

Liquid density and kinematic viscosity were similar for all synthesized resins. The final pH was above 9.00 as desired.

Gel time is significantly longer for resins cured without catalyst, as expected. Resin DEG_1.41 starts gellifying after 10 min at 120 °C. As the relative amount of DEG increases, gel time also increases, resulting in more than 240 min for resin DEG_0.93. This can be explained in terms of the lower amount of free formaldehyde present for the cure reaction. The same behavior is observed for the other glycols. Gel time is also observed to increase as the glycol molecular weight increases, because higher molecular weight glycol decreases the proximity of crosslinking sites [2].

The gel time is significantly lower under acid conditions. Ammonium sulfate catalyst changes the gel time of DEG_1.41 resin from 10 min to 0.5 min. Again, an increase in molecular weight of glycol at same molar ratio causes an increase in gel time from 0.5, 0.75 and 1.12 min on DEG_1.41. PEG200_1.41 and PEG400_1.41 resins, respectively. Maintaining molecular weight in acid conditions, gel time increases as molar ratio decreases: PEG200_1.41. PEG200_1.26 and PEG200_0.93 show gel times of 0.75, 1.0 and 3.67 min, respectively. The same trends were observed when hexamethylenediamine was used. However, gel time is always a bit lower than for ammonium sulfate.

The stability under storage conditions of resins modified with glycols was also evaluated. All resins showed at least 8 months of storage stability. The pH of all resins decreased during storage. This is a consequence of Cannizarro reaction between free formaldehyde and the NaOH that was used to stop the synthesis process [29]. This creates an acid medium, favoring the cure reaction.

6.1.3.2. Fourier transform infrared spectroscopy

According to the literature [30] the characteristic absorptions bands of a UF resin are observed at 3350–3340 cm^{-1} (NH stretching of primary aliphatic amines), 2962–2960 cm^{-1} (-OCH_3 aliphatic ethers), 1654–1646 cm^{-1} (C=O stretching of primary amide), 1560–1550 cm^{-1} (C-N stretching of secondary amines), 1465–1440 cm^{-1} (C-OH bending in NCH_2N, CH_2O, OCH_3), 1400–1380 cm^{-1} (C-H mode in CH_2 and CH_3), 1380–1330 cm^{-1} (C-N stretching of CH_2-N), 1320–1300 cm^{-1} (=C-N or =CH-N of tertiary cyclic amides), 1260–1250 cm^{-1} (C-N and N-H stretching of tertiary amides), 1150–1130 cm^{-1} (C-O stretching of aliphatic ether), 1050–1030 cm^{-1} (C-N or NCN stretching of methylene linkages (NCH_2N)), 1020–1000 cm^{-1} (C-O stretching of methylol group), 900–650 cm^{-1} (N-H bending of primary aliphatic amines) and 750–700 cm^{-1} (N-H bending of secondary aliphatic amines (R_1–CH–NH–CH_2–R_2)).

FTIR spectra of urea-formaldehyde resins modified with DEG are shown in Figure 6.2. All previously mentioned UF absorption bands are present in all resins. Some bands show the presence of DEG in the GUF resin: the absorption band at 1126 cm^{-1} (associated with the stretching of the C-O bond), the absorption band at 892 cm^{-1} (associated with the O-CH_2-CH_2 linkages) and at 1062 cm^{-1} (associated with the stretching of the C-O-C bond) [31]. The intensity of these bands increases as F/(U+G) ratio decreases from 1.41 to 0.93. Special attention may be given to the band at 920 cm^{-1}, associated with the stretching of the C-OH bond [31]. This band may correspond to unreacted hydroxyl groups from DEG. Even though it is clearly visible for DEG_0.93, for DEG_1.26 only a subtle peak can be seen, while for DEG_1.41 it seems absent. This may be an indication that there is little or none unreacted PEG when the lowest amount was used in the synthesis.

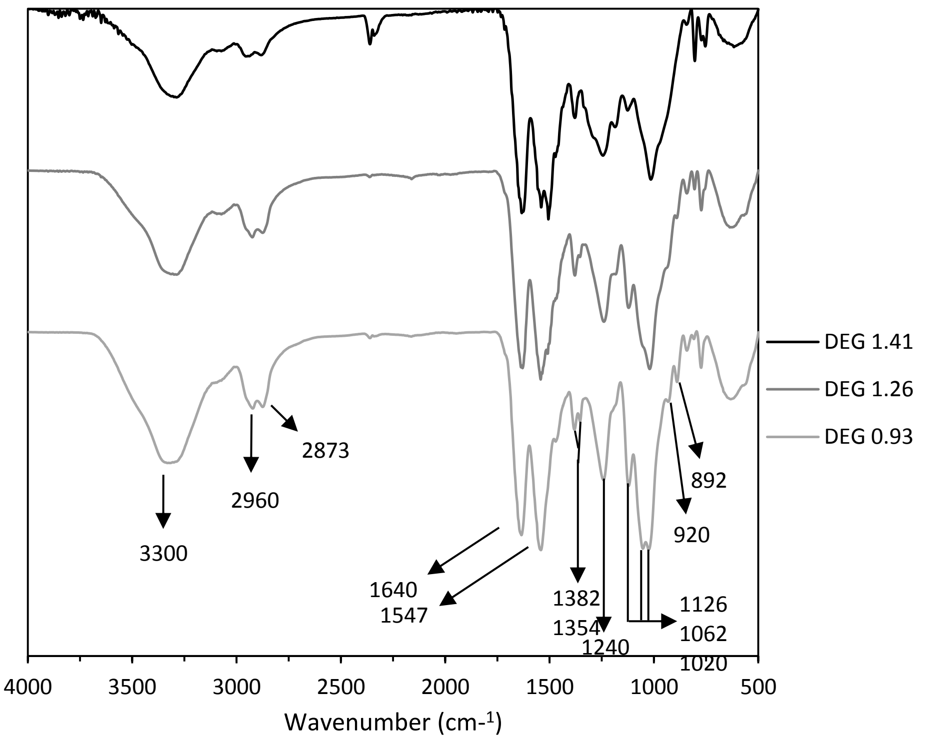

Figure 6.2. IR spectrum of GUF resin film synthesized with DEG.

FTIR spectra of UF resins modified with PEG200 corresponds to the Figure 6.3. Similarly to the previous results, all characteristic UF and PEG200 absorption bands are present in all resins, but some of PEG200 absorption bands may be overlapped with UF bands.

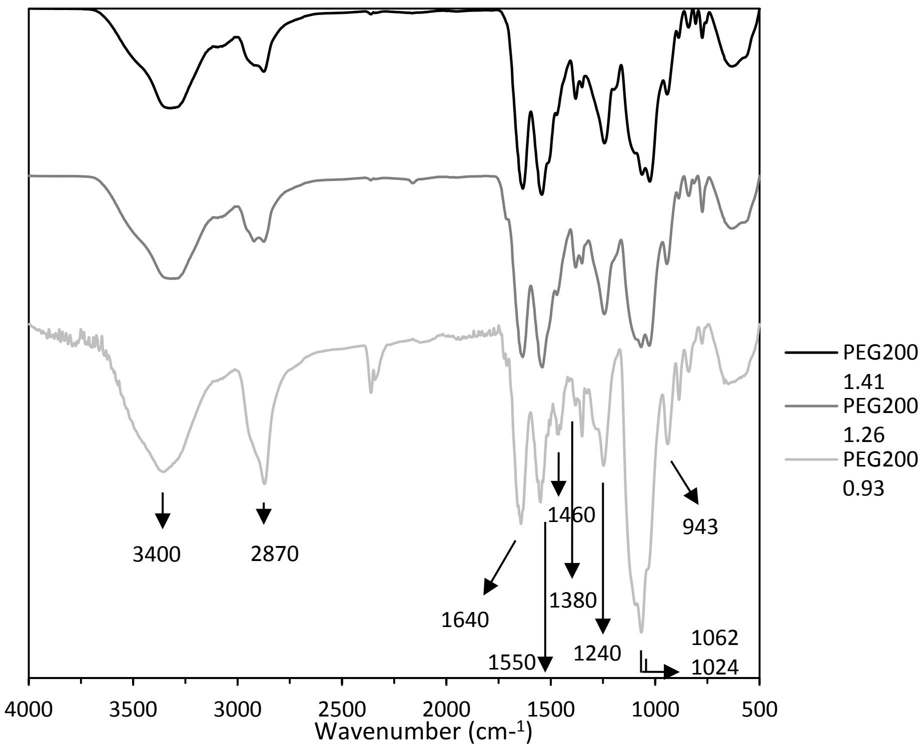

Figure 6.3. IR spectrum of GUF resin film synthesized with PEG200.

The band at 1060 cm^{-1} is associated with the stretching of C-O-C group in PEG200 [32], [33]. Absorption bands at 1460 and 1240 cm^{-1}, associated with vibration of C-OH group [32], [33], show that there is unreacted PEG200 in the final product. These bands are observed for all UF resins modified with PEG200, indicating that free PEG is always present in the resins. This may be related to the lower reactivity of a glycol with more than five carbon atoms [1]. Additionally, the presence of some free glycol in the final resin solution may also be due to the reverse reaction when glycol formal reacts with dimethylolurea [22].

Similar features were observed in the spectra of UF films synthesized with PEG 400 (not shown here).

6.1.3.3. Liquid ^{13}C-NMR spectroscopy

The structural assignments of chemical shifts of the standard UF resin, PEG, and the new GUF resin synthesized with PEG200 are summarized in Table 6.2.

Table 6.2. Structural assignments of chemical shifts of standard UF resin, PEG200 and flexible GUF resin synthesized with PEG200

	Samples		
	UF	**PEG200**	**UF modified with PEG**
Functional groups	**δ (ppm)**	**δ (ppm)**	**δ (ppm)**
Urea			
$NH_2\underline{C}ONH_2$	160.11		
Carbonyl group of unsubstituted and substituted uron			
HN-$\underline{C}$O-NH | | CH_2-O-CH_2	158.36		
N-$\underline{C}$O-N | | CH_2-O-CH_2	156.92 156.72 156.38		156.87
Poly(oxymethylene glycols)			
-CO-N-$CH_2O(\underline{C}H_2O)_nCH_2OH$			92.35
-CO-N-$CH_2O(CH_2O)_n\underline{C}H_2OH$			85.96
Methylene ether group of unsubstituted and substituted uron			
N-CO-N | | $\underline{C}H_2$-O-$\underline{C}H_2$	79.76		79.15
Methylene and methyle-ether glycols species			
$HOCH_2\underline{C}H_2(OCH_2CH_2)_nOH$		69.11 69.00	69.09 68.98
$HO\underline{C}H_2CH_2(OCH_2CH_2)_nOH$		57.84 57.75	57.83 57.75
$HOCH_2CH_2(O\underline{C}H_2\underline{C}H_2)_nOH$		67.06 66.97 66.93 66.85	67.03 66.95 66.90 66.82

Table 6.3. Structural assignments of chemical shifts of standard UF resin, PEG200 and flexible GUF resin synthesized with PEG200 *(cont.)*

	Samples		
	UF	**PEG200**	**UF modified with PEG**
Functional groups	δ (ppm)	δ (ppm)	δ (ppm)
$HO\underline{C}H_2CH_2(OCH_2CH_2)_nOH$		57.84 57.75	57.83 57.75
Methylene ether linkages			
$-NHCH_2O\underline{C}H_2OH$			
$-NHCH_2O\underline{C}H_2NH-$	68.04		68.50
$-N(CH_2-)\underline{C}H_2OCH_2NH-$			67.91 67.10
Methylol groups			
$-NH\underline{C}H_2OH$	65.96		64.67 64.11 63.87 63.68
$-N(CH_2)-(CH_2O)_nCH_2OH$	72.76		
Methylene linkages			
$-N(CH_2)\underline{C}H_2N(CH_2)-$	61.55 61.30 61.17		61.54 61.16
$-N(CH_2)\underline{C}H_2NH-$	50.59 50.09		50.08
$-NH\underline{C}H_2NH-$	46.27 43.96 43.49		
Undefined			
Contaminant	_	59.92	59.92

The spectra of GUF resin synthesized with PEG can be split into six main areas, in agreement with previously reported works [34]–[37]. The 156-160 ppm region corresponds to the substituted and unsubstituted urea and uron carbonyl groups. The signal observed from 67 to 68 ppm corresponds to carbons in methylene-ether linkages. The methylol groups show signals from 63 to 66 ppm, and methylene groups from 40 to 62 ppm. The signals from PEG's are seen 57 ppm and 66 to 69 ppm, in GUF resin. A signal at 59.92 ppm is observed in GUF and PEG200, which probably corresponds to some undefined contaminant present in industrial grade PEG.

As expected, GUF resin displays the same functional groups as UF resin. However, at 92.35 ppm and 85.96 ppm GUF resin displays signals from poly(oxymethelene glycol) linkages, which are not seen in UF. This could evidence that PEG has been incorporated in the resin structure.

6.1.3.4. GPC/SEC analysis

The effectiveness of Gel Permeation Chromatography (GPC) for qualitative comparison of urea-formaldehyde resin formulations has been demonstrated before [24]–[26]. Figure 6.4 shows the GPC/SEC chromatograms collected for the three resins synthesized with DEG, as well as for diethylene glycol monomer and for a standard UF.

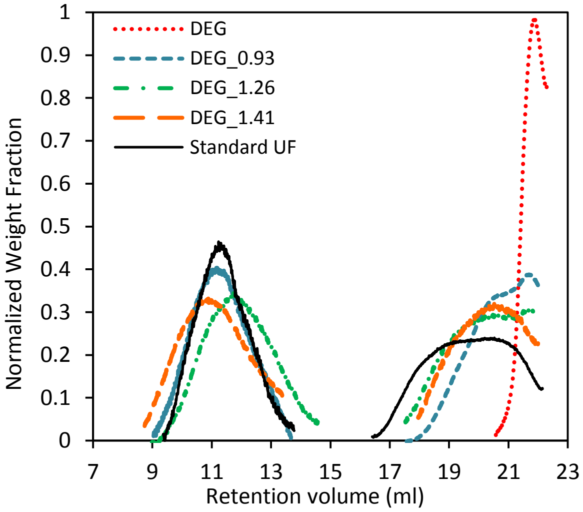

Figure 6.4. Chromatograms of synthesized GUF resins with DEG.

Resin DEG_1.41 shows the presence of low and high molecular weight species, corresponding to peaks with retention volumes between 22 and 18 ml, and between 13 and 9 ml, respectively. In the case of resins DEG_1.26 and DEG_0.93, one additional peak is visible with retention volume roughly between 21 and 22 ml, which coincides with diethylene glycol. This indicates that unreacted DEG is present in these resins, but apparently not in DEG_1.41. This is consistent with the FTIR spectra analysis described above.

GPC chromatograms of GUF resins synthesized with PEG200 are shown in Figure 6.5. The three resins present a notorious peak with retention volume around 21.5 ml, indicating presence of unreacted PEG200 in all resin solutions.

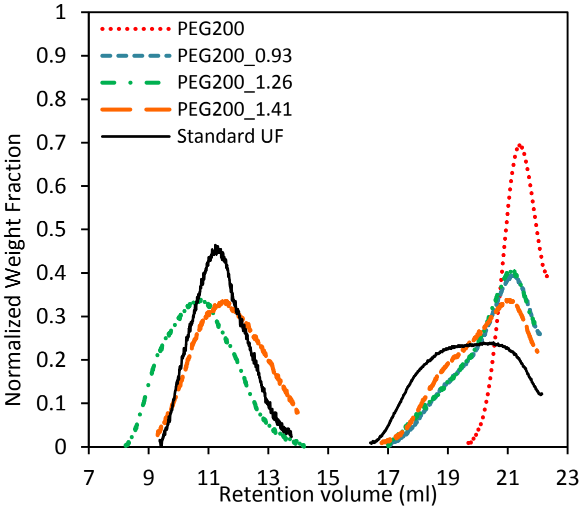

Figure 6.5. Chromatograms of synthesized GUF resins with PEG 200.

Samples PEG200_1.41 and PEG200_1.26 exhibit one peak at high molecular weights with retention volume of 12 and 11 ml, respectively. These products could evidence that part of the PEG200 reacted with UF resin and is also incorporated in the polymeric matrix as in UF resins modified with DEG and the species formed during condensation reaction have higher molecular weight.

Figure 6.6 presents a simplified hypothetical structure for GUF resins synthesized with PEG200 at different molar ratios of F/(U+G). As the relative amount of PEG200 is increased, the crosslinking density decreases and more low molecular weight material is formed, because glycol blocks the development of a high molecular weight network.

Similar features were observed in the chromatograms of UF films synthesized with PEG 400 (not shown here).

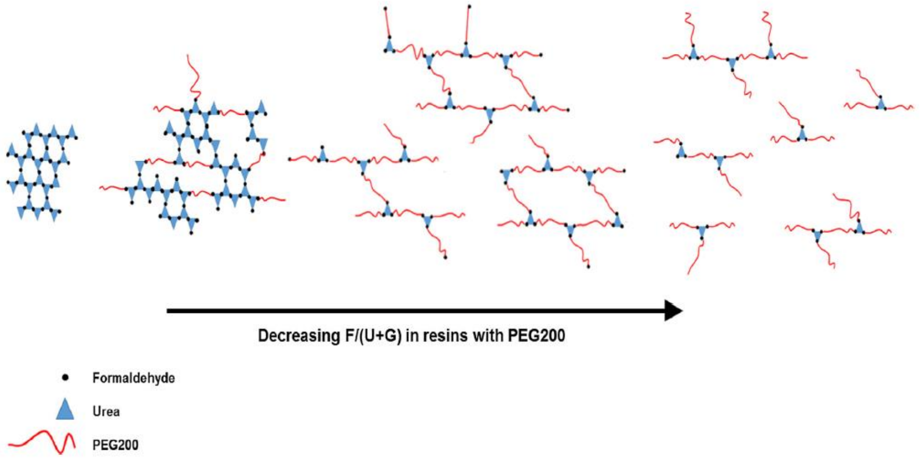

Figure 6.6. Simplified structure of GUF resins with different amounts of PEG200.

6.1.3.5. Film flexibility

The term flexibility describes here the ability of a cured resin film to bend without breaking. It is well known that amino-formaldehyde resins are extremely brittle, undergoing fragile fracture when deformation of a cured film is attempted. Neat films of each modified UF resin were made and their flexibility was evaluated by sensory analysis. Table 6.4 summarizes the results. Films cured with ammonium sulfate and hexamethylenediamine were also tested.

Table 6.4. Subjective characterization of films flexibility

Resin	Without catalyst	With ammonium sulphate	With hexamethylenediamine
DEG_1.41	Very hard	Very hard and oily	Very hard
DEG_1.26	Very hard	Very hard and oily	Very hard
DEG_0.93	Hard	Hard and oily	Hard
PEG200_1.41	Slightly flexible	Very hard and oily	Slightly flexible
PEG200_1.26	Flexible	Very hard and oily	Flexible
PEG200_0.93	Tacky gel	Oily wax	Tacky gel
PEG400_1.41	Wax	Oily wax	Wax
PEG400_1.26	Oily wax	Oily wax	Wax
PEG400_0.93	No film formation	Oily wax	Wax

All films obtained from neat resins modified with DEG and PEG200 are transparent, colorless and glossy, but films obtained from resins modified with PEG400 are white mat. Film tack tends to increase with decreasing molar ratio of F/(U+G) to GUF resins synthesized with PEG200 and PEG400.

Film flexibility increases with the increase of glycol molecular weight, and increases with decrease of F/(U+G) ratio. Longer glycol chains introduce more flexible segments and increase the distance between crosslinking sites, both factors contributing to a more flexible and less tightly crosslinked polymer, thus less brittle. In the limit when the crosslinking density becomes too low, tacky and waxy films are obtained.

Introduction of ratio PEG200 modification at a 1.26 F/(U+G) yielded the best result, translated into a consistent and flexible material, with no oily or wax character. Figure 6.7 shows the difference when films made from standard UF resin and PEG200_1.26 are bent. Standard UF resin breaks under very low strain, displaying brittle fracture, while the resin modified with PEG200 shows very high flexibility.

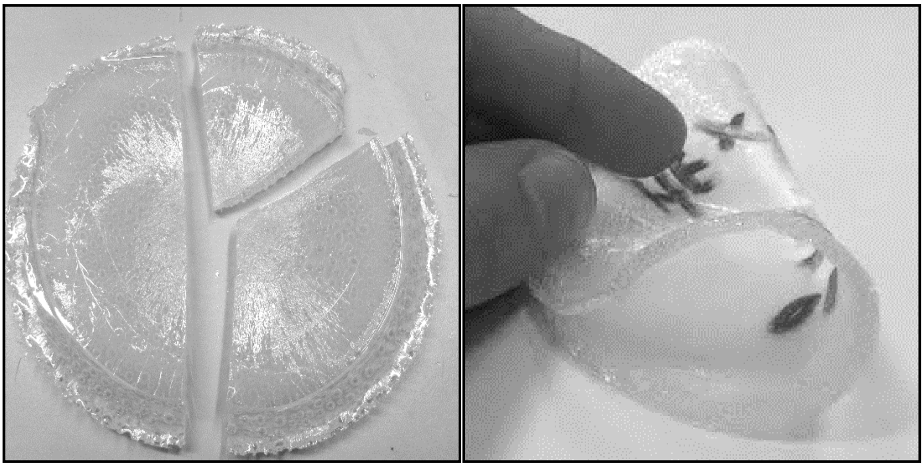

Figure 6.7. Film flexibility comparison for standard UF resin (left) and GUF resin synthesized with PEG200 at F/(U+G)=1.26 (right).

Films produced with hexamethylenediamine present the same behavior as neat films. On the other hand, all films prepared with ammonium sulfate show distinct behavior. No flexibility is observed and all films appeared oily to the touch. This is probably a consequence of the reaction between formaldehyde and glycol being reversible under acidic environment which results in hydrolysis of the produced acetal to the corresponding aldehyde [38]. Thus, ammonium sulfate is not appropriate for catalyzing UF resins modified with glycols, since it leads to an incomplete cure.

6.1.3.6. Atomic force microscopy

The surfaces of cured standard UF resin and flexible GUF resin synthesized with PEG200 were investigated by AFM phase imaging. Figure 6.8 shows the differences between both films.

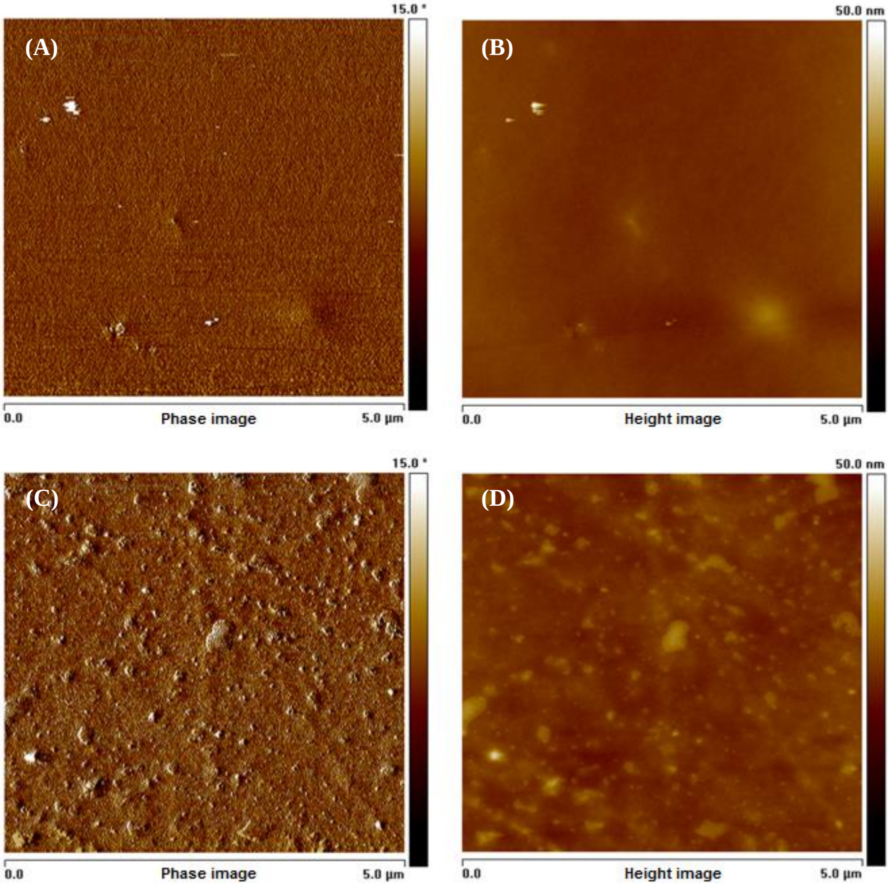

Figure 6.8. AFM images of the surface of the standard UF resin (A and B) and GUF resin synthesized with PEG200 (C and D): phase images (A and C) and height images (B and D).

Cured standard UF resin shows relatively uniform topography. By contrast, resin modified with glycol has a heterogeneous surface. The standard UF resin forms a densely crosslinked structure, resulting in a uniformly hard surface. On the other hand, the heterogeneity of the modified resin seen in Figure 6.8, may be a consequence of a multiphase character, with soft and hard domains, similarly to polyurethanes adhesives exhibiting microphase separation structures. Others authors [39]–[41] have defended that surface morphology of polymer films can be related to the extent of crosslinking, rougher surfaces being observed for lower crosslinking.

6.1.3.7. Dynamic mechanical analysis

Due to the impossibility of producing homogeneous cured films, the DMA tests were performed using a material pocket, after granulating the films. Only the loss factor (tan δ) can therefore be analysed. This is shown in Figure 6.9 and Figure 6.10, as a function of temperature for the resins synthesized with DEG and PEG200. All samples were tested at 1, 5 and 10 Hz, but only results obtained at 1 Hz are shown here.

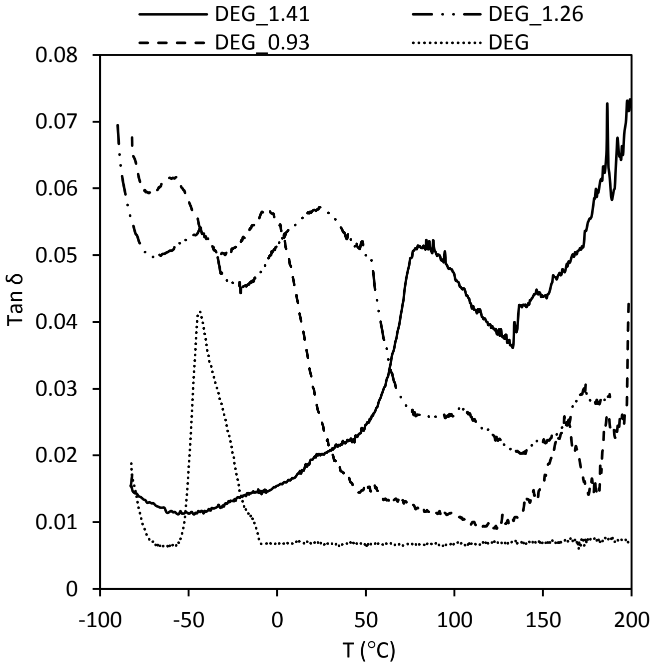

Figure 6.9. Loss factor, tan δ, as a function of temperature for GUF films synthesized with DEG and different F/(U+G) ratios.

Figure 6.9 shows tan δ for the resins with different values of F/(U+G) ratios and for DEG monomer. The latter displays only one tan δ peak, located between -50 and -10 °C. This is assigned to the melting transition of DEG. This peak also seems to be present in the loss factor plots for DEG_1.26 and DEG_0.93, but not for DEG_1.41. This is consistent with the FTIR results, which did not show free DEG in resin DEG_1.41. All resins synthesized with DEG present another relevant peak, which shifts in temperature as the F/(U+G) ratio changes. DEG_0.93 shows this peak in the range -5 to 5 °C, DEG_1.26 at 25 to 70 °C and DEG_1.41 at 80 to 100 °C. This corresponds to the glass transition of the cured polymers. As F/(U+G) decreases, *i.e.* more DEG is present in the synthesis, the peak in tan δ moves towards lower temperatures. This decrease in T_g is a consequence of two factors. On one hand, as more DEG in incorporated in the polymer structure, the crosslinking density decreases and the polymer network gains mobility. On the other hand, free DEG may also be present, which may act as a plasticizer and therefore also decrease T_g.

The DMA thermograms obtained for the other frequencies showed similar features. For each resin, the tan δ peak attributed to the T_g was observed to shift towards higher temperature as the frequency of analysis increased, as expected for the glass transition.

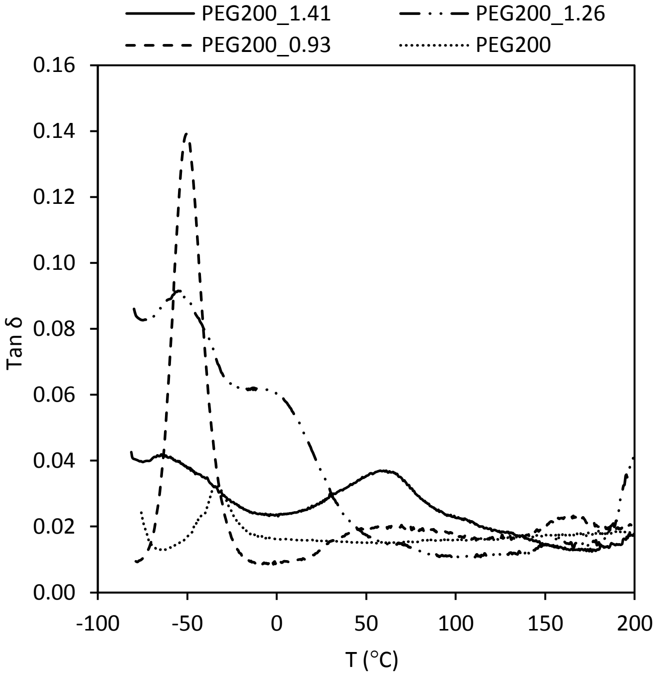

Figure 6.10. Loss factor, tan δ, as a function of temperature for GUF films synthesized with PEG200 and different F/(U+G) ratios (1 Hz).

DMA runs of PEG200 and resins synthesized with it are shown in Figure 6.10. PEG200 has a melting transition at around -40 °C. As in the case of DEG-modified resins, the resins that contain higher amounts of PEG (PEG_1.26 and PEG_0.93) show a distinct low temperature peak in tan δ, which is assigned to free PEG. Only a very small peak is seen at low temperature in PEG200_1.41, probably indicating that most glycol has been incorporated in the polymer structure. The glass transition peak of PEG200_1.41 is visible roughly between 50 and 70 °C. PEG200_1.26 shows the transition at lower temperature, between -10 and 10 °C, as expected. For PEG200_0.93 this transition seems to be superimposed with the free PEG200 melting transition, which may explain the high intensity of this peak.

It is also interesting to note that when considering the same F/(U+G) ratio, increasing the glycol molecular weight leads to a decrease in the glass transition temperature range. For instance, for F/(U+G)=1.41, when the molecular weight of the glycol increases from 100 to 200 g/mol (DEG and PEG200, respectively) the glass transition range shifts from 80-100 to 50-70 °C. Longer glycol segments introduce higher mobility in the network structure and are more effective spacers between crosslinking sites, therefore lowering the glass transition temperature.

6.1.3.8. Shear strength

ABES tests were carried out to evaluate the adhesion of the synthesized resins to beech veneer substrate. Figure 6.11 shows the results of maximum shear strength for press temperatures of 150 °C as a function of F/(U+G) ratio and type of glycol.

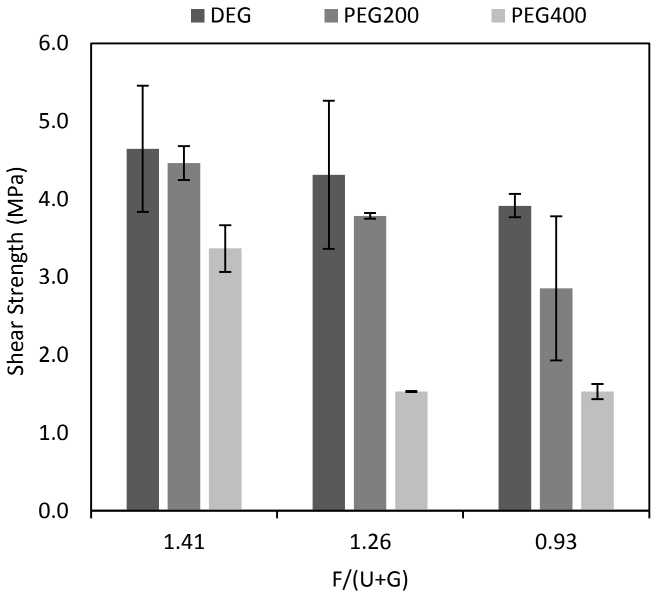

Figure 6.11. Shear strength of synthesized GUF resins.

Resins modified with either DEG of PEG200 have adhesive strength similar to the standard resin (5.2±0.5 MPa) for F/(U+G) ratio of 1.41. Adhesion seems to be somewhat hindered for PEG200_0.93. When PEG400 was used the shear strength decreased significantly, as the reduced crosslinking density impairs adhesion strength. Addition of hexamethylenediamine caused some improvement in shear strength values (not shown here). This, as discussed before, this does not interfere with the flexibility of the final product.

6.1.3.9. Mechanical properties of resin-impregnated paper

As discussed above, the resin synthesized with PEG200 yielded interesting results in terms of high strength combined with good flexibility. The performance of this resin was evaluated when impregnated on paper. Amino resins are widely used for producing finishing foils based on impregnated papers, in the furniture and construction industries. Introducing flexibility in resin-impregnated papers would allow new uses for these materials [2]. Figure 6.12 shows the differences observed when one attempts to bend a cured overlay paper, impregnated with a standard UF and with resin PEG200_1.26. The first readily breaks, while the second bends up to 90° without any visible damage.

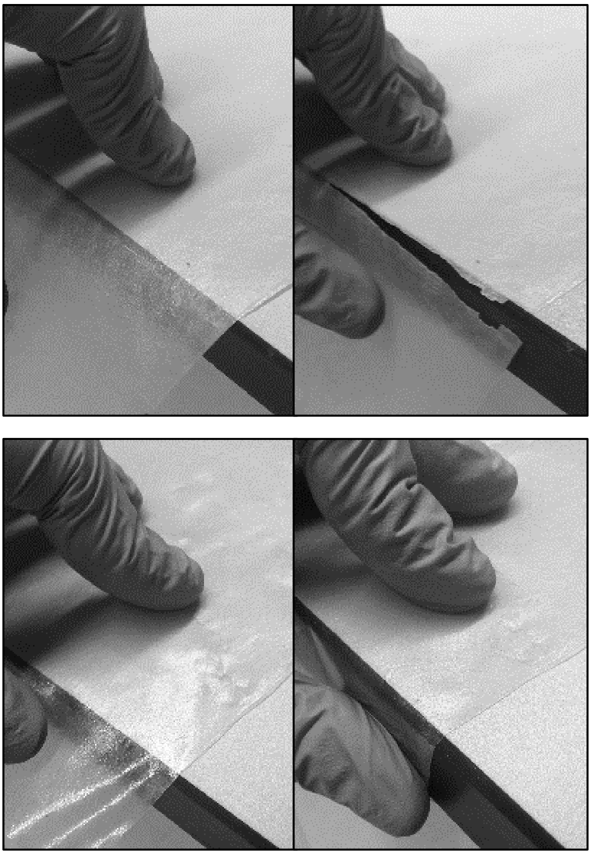

Figure 6.12. Standard rigid UF resin (left) and flexible GUF resin synthesized with PEG200 F/(U+G)=1.26 (right) in impregnated paper.

The cured impregnated papers were subjected to tensile stress-strain tests. Only the resins modified with DEG and PEG200 were evaluated, since the ones modified with PEG400 had waxy characteristics. Figure 6.13 depicts typical curves. Table 6.5 summarizes the mechanical properties computed from the stress–strain data, as a function of F/(U+G) ratio and glycol molecular weight.

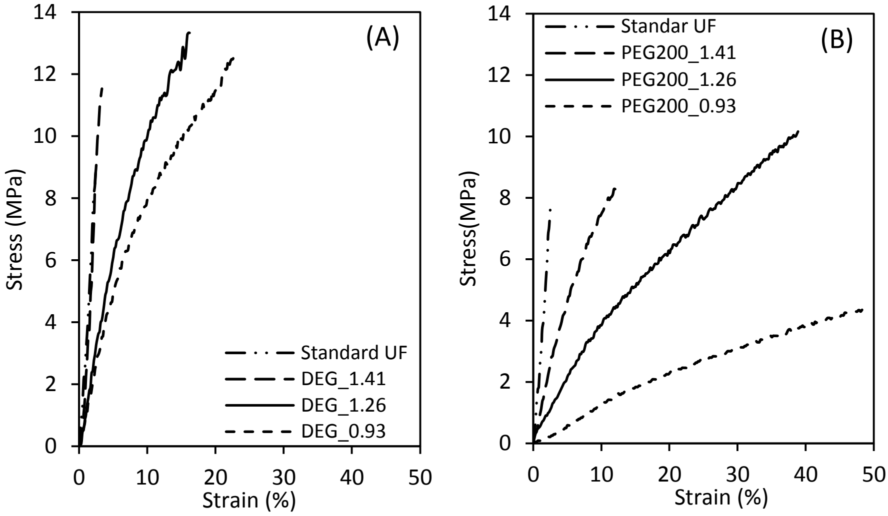

Figure 6.13. Representative stress-strain curves obtained for papers impregnated with different GUF resins synthesized with glycol: (a) DEG and (B) PEG200.

Table 6.5. Mechanical properties of impregnated paper as a function of F/(U+G) ratio and glycol molecular weight

Resin	**σ_{max} (MPa)**	**E (MPa)**	**ε_{max} (%)**	**Toughness (MPa %)**
Standard UF	8.4 ± 0.7	304.6 ± 33.9	2.5 ± 0.0	9.7 ± 1.0
DEG_1.41	10.5 ± 0.8	364.1 ± 26.9	3.0 ± 0.4	14.5 ± 1.6
DEG_1.26	12.7 ± 0.5	128.5 ± 3.2	15.7 ± 0.4	121.8 ± 6.2
DEG_0.93	13.1 ± 0.5	99.3 ± 3.5	21.4 ± 1.4	168.2 ± 15.9
PEG200_1.41	8.5 ± 0.1	93.8 ± 4.2	12.4 ± 0.4	60.5 ± 1.23
PEG200_1.26	10.2 ± 0.1	38.5 ± 2.9	39.8 ± 1.7	241.1 ± 14.8
PEG200_0.93	4.5 ± 0.1	14.4 ± 0.8	48.3 ± 0.7	125.6 ± 3.9

When the UF resin is modified with both DEG or PEG200, the elongation at break increases and the Young's modulus decreases as glycol content increases (lower

F/(U+G) ratio), clearly departing from the brittle behavior shown by the standard UF resin. This is expected, in view of the abovementioned influence of the glycols on the resins' crosslinked structures. However, PEG200 leads to a much more pronounced effect, yielding a much softer and resilient material. Tensile strength tends to increase with glycol content, as the higher mobility of the crosslinked structure allows adapting to higher strain without chains breaking. However, at the highest PEG200 content tensile strength ends up decreasing significantly. As a result, the material with higher toughness (computed as the area under the curve) corresponds to PEG200_1.26. Indeed, considering all the tests performed in this work, this resin showed the better overall performance.

6.1.4. Conclusions

A highly flexible amino resin has been developed by introducing polyethylene glycol with molecular weight 200 g/mol in the synthesis of a urea-formaldehyde resin. In addition to not being brittle after cure, contrary to conventional UF resins, this resin maintains good adhesion strength on wood and displays very high resilience, toughness and flexibility when impregnated on a paper substrate.

It has been shown that the molecular weight and amount of glycol used in the synthesis affects key properties like reactivity, glass transition temperature, flexibility, and toughness. Reaction of glycol with the urea-formaldehyde polymer was demonstrated by ^{13}C-RMN. However, evidence of unreacted glycol being present in the final resin was found by FTIR and GPC-SEC, when it was added in excessive quantity. The reactivity of the modified resin can be improved by adding hexamethylenediamine, an additive commonly used polymer industry, to allow acceptable curing times. On the other hand, catalysis with ammonium sulphate must be avoided, since the reaction between formaldehyde and glycol is reversible under acidic conditions, and the cure reaction becomes incomplete.

This new resin has potential applications in areas where the good adhesion strength and ease of use of amino resins are welcome, but brittleness, low toughness, and lack of flexibility are undesired.

6.2. Cork based panels produced with highly flexible glycol-urea-formaldehyde resin [6]

Abstract

This work studies the performance of six urea-formaldehyde resins modified with glycols (diethylene glycol and polyethylene glycol with molecular weight 200 g/mol) in the production of agglomerated cork panels. The mechanical properties of each panel were evaluated as function of: quantity of binder, molecular weight of glycol and F/(U+G) ratio. The flexibility of each panel was also observed using a mandrel test. Formaldehyde content was measured using the perforator method and three formaldehyde scavengers were applied to decrease its content in the final product.

Urea-formaldehyde resin modified with PEG with molecular weight 200 g/mol and F/(U+G) ratio of 1.26 yielded the most promising agglomerated cork panel, with remarkable resilience, good adhesion properties and low formaldehyde content when jeffamine was used as scavenger.

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[6] This sub-chapter is content from submitted paper to International Wood Products Journal: A. Antunes, N. Paiva, J. Ferra, P. Pereira, A. Ferreira, F. Magalhães, A. Gomes, J. Pereira, C. Coelho, J. Martins, L. Carvalho, “2GAR Project”.

6.2.1. Introduction

The most used adhesive for the production of cork composite is polyurethane (PU). However, amino-formaldehyde resins, as urea-formaldehyde (UF), melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF) are also used [1].

Formaldehyde-based resins are applied in a large industrial products: abrasives, foam structures, foundry sand core binders, paper impregnation and laminates, textile industry, leather tanning, molding compounds and adhesives industry [2], [3]. Wood-based panels industry is the major consumer of amino resins also due to their competitive price, reactivity and performance [4], [5].

The main disadvantage of the use of amino-formaldehyde reins in agglomerated cork is the logistics of the final product. The cork agglomerate panels produced with PU resins are typically stored rolled up on themselves. This procedure becomes impossible with panels produced with MUF resins because thermosetting resins exhibiting high stiffness after cure.

However, from the economic point of view, formaldehyde resins are competitive when compared with the PU because these resins present three times lower price. Thus, there is an industrial interest in chemically modifying formaldehyde resins and giving them the elasticity and resilience non-existent in this category of polymers, allowing their use in cork-based composites. Some works can be found in literature dealing with providing formaldehyde-based resins with some flexibility. Strategies involve introduction of plasticizers [6], [7], flexible chain [8]–[10] and thermoplastic fillers [11]–[14].

Nevertheless formaldehyde is a carcinogenic compound and several attention must be applied in the formaldehyde content of the final product during the development of new resin. Different monomers present different reactivity and could present reversible reactions. Thus, some reactive agents are used as formaldehyde scavenger to decrease free formaldehyde content, examples are urea, melamine, alkyl amines, porous materials and sodium sulphites [15], [16].

The present work is focused on the production and characterization of cork based panel with urea-formaldehyde resins modified with linear chain compounds that act as flexible segments into the UF structure. The linear segments chosen were diethylene glycol (DEG) and polyethylene glycol (PEG) with molecular weight of 200 g/mol. Resins were tested under prepared F/(U+G) ratios: 1.41, 1.26 and 0.93. The aim of this work is identify the mechanical properties of agglomerated cork panels (tensile strength, Young’s modulus, elongation at rupture and mandrel flexibility) when different amounts of modified flexible UF polymers are used as adhesive.

6.2.2. Materials and Methods

6.2.2.1. Materials

Urea-formaldehyde resin modified with diethylene glycol and polyethylene glycol with molecular weight of 200 g/mol (PEG200) were used at three F/(U+G) molar ratio. Resins were named according to the type of glycol used in the synthesis and the F/(U+G) ratio. For example, “PEG200_1.26” means: UF resin modified with PEG with molecular weight of 200 g/mol and a F/(U+G) ratio of 1.26. All resins present solid content around 50 %, a pH range between 9.3 and 10.1, kinematic viscosity between 58 and 13 s, and gel time without catalyst between 10 min and more than 240 min.

Hexamethylenediamine, sodium metabisulphite and jeffamine D230 were purchased from Sigma-Aldrich, USA.

The cork granules with 0.5-1.0 mm of diameter were provided by Amorim Cork Composites, S.A. (Santa Maria da Feira, Portugal).

6.2.2.2. Production of agglomerated cork

Resins were added to granulated cork and the mixture were prepared by manual stirring during 5 min at room temperature. The solid resin content (RC) was 3.8, 6 and 12 % based on oven dry cork.

After blending, cork panel was hand formed in a deformable aluminium mold (2 x 450 x 250) mm^3. The cork amount was determined in order to obtain boards with target densities of 600 kg/m^3. Panels were pressed in a laboratory batch press equipped with both heating and cooling systems, with a set-point in temperature of 150 °C, a pressure of 12 bar, a pressing time of 5 min and a cooling time until to achieve 25 °C.

6.2.2.3. Physical-mechanical characterization of agglomerated cork panels

Tensile Strength of Panels

After production, boards were hermetically conditioned until performance evaluation at (23 ± 2) °C and a relative humidity of (50 ± 5) % for 48 h. Stress-strain tests were carried out adapting the International Standards ISO 7322:2000 (E). Three samples with dimensions of (100 x 15 x 2) mm^3 were tested for each production condition at a crosshead speed of 300 mm/min under room temperature. At least three replicates were carried out for each measurement.

Resistance to boiling water of panels

The resistance to boiling water was done according to ISO 7322:2000(E). Three samples with dimensions of (50 x 50 x 2) mm^3 were tested for each resin. The specimens were placed in boiling water for 3 h. After the test, the samples were visually examined and classified as disaggregated or not.

Flexibility of Panels

The flexibility of agglomerate cork panels was evaluated following a cylindrical mandrel bending test, according to ASTM F147-87. The method consists in bending the specimen on cylindrical mandrels with different diameters ranging from 3 to 48 mm. The flexibility of the specimen corresponds to the minimum mandrel diameter about which the specimen could be flexed without exhibiting any signs of failure.

Formaldehyde Content of Panels - Perforator Method (EN ISO 12460-5)

Formaldehyde content of agglomerated cork panels was determined according to perforator method (EN ISO 12460-5). Perforator method measures the formaldehyde emissions content of the specimen potentially emitted under forceful conditions. Formaldehyde was extracted from 110 g of test pieces by means of boiling toluene and then transferred into distilled or demineralized water. The formaldehyde content of this aqueous solution was determined photometrically by the acetylacetone method [54].

6.2.3. Results and discussion

6.2.3.1. Physical-mechanical characterization of agglomerated cork produced with UF resin modified with glycols

The agglomerated cork panels were subjected to tensile stress-strain tests. The results of tensile strength, Young’s modulus and elongation at break are shown in Figure 6.14, Figure 6.15 and Figure 6.16, respectively. Also flexibility measurements were done at cork panel in mandrel test and results are shown in Figure 6.17.

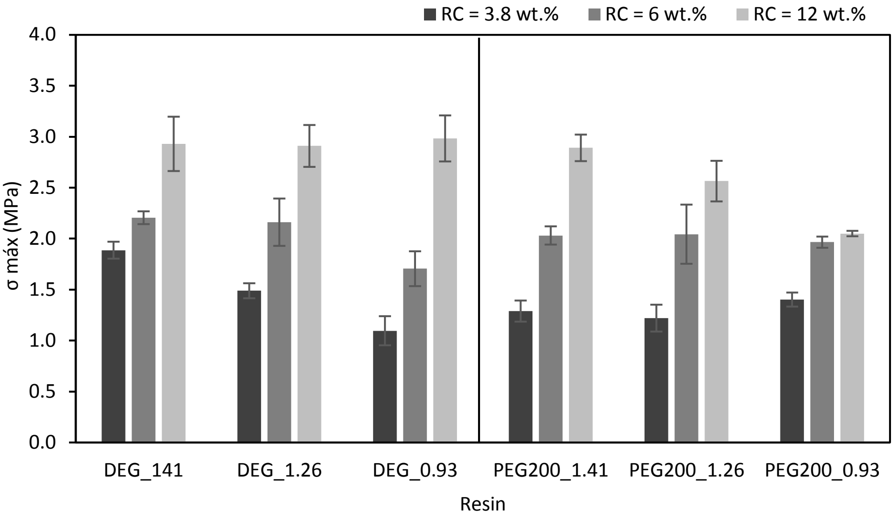

Figure 6.14. Tensile strength of agglomerated cork produced with UF resin modified with DEG or PEG200 as a function of MR F/(U+G) and solid resin content.

As expected, addition of higher resin content to cork granules increases the tensile strength of composites produced with UF resins modified with DEG or PEG200. Tensile strength decreases as F/(U+G) decreases when UF modified with DEG is present at 3.8 and 6 wt.%. To decrease F/(U+G) ratio means increase DEG content and therefore increase separation between crosslinking sites in each polymer. Typically, less crosslinking density results in lower tensile strength observed in composites with UF modified with DEG. In the limit, the tensile strength is noticeably lower, as the reduced crosslinking density impairs adhesion of cork granules. Regarding the low crosslinking density of these resins, high resin content (12 wt. %) originates an interfacial bonding where resin has little impact on the tensile strength, what could be seen to the composites DEG_1.41, DEG_1.26 and DEG_0.93 with 12 wt.% of binder.

There seems to be an optimum amount of each resin for obtaining the best composite. When PEG200 is used, the decrease is not observed as function of F/(U+G) and similar results were observed for 3.8 and 6 wt. % instead of 12 wt. %. This shows that PEG200_0.93, PEG200_1.26 and PEG200_1.41 applied at low content in cork composite production have little influence on tensile strength as long as the resin content is sufficient to produce a cohesive panel. Just at high resin content is possible register the different mechanical properties of cork composite as function of PEG200 content. The results of 12 wt. % of PEG resins are in accordance with those observed in DEG 3.8 and 6 wt. %, where tensile strength tends to increase with increasing of F/(U+G).

Anyway, all produced agglomerated cork panels show tensile strength results that attain the 200 kPa limit required by APCOR (Associação Portuguesa da Cortiça) specifications [18].

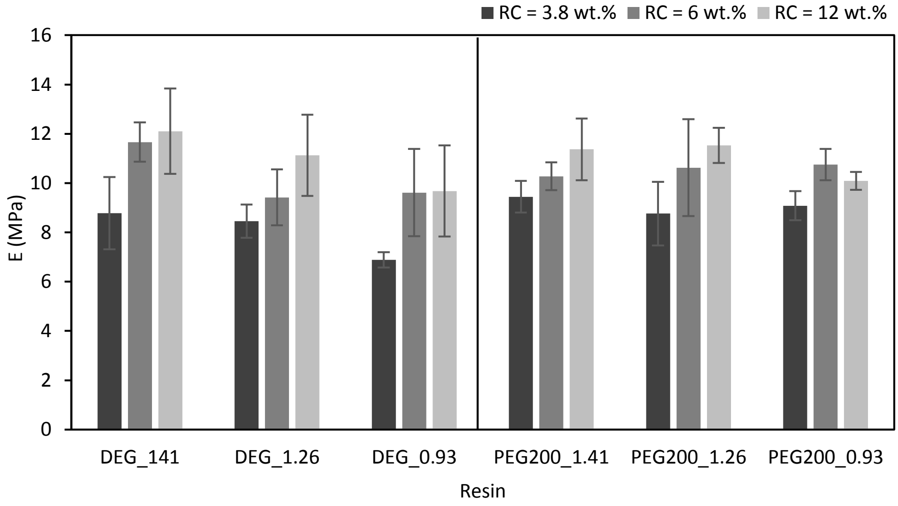

Figure 6.15. Young's modulus of agglomerated cork produced with UF resin modified with DEG or PEG200 as a function of MR F/(U+G) and solid resin content.

As the resin content increases, the stiffness of panel increases, resulting in a slight increase of Young's modulus. However, Figure 6.16 does not show any trend about the differences between crosslinked structure of the six tested resins. Each composite shows similar value at the same resin content apart of resin applied what could mean that composite's stiffness is constant. Bigger differences are observed in elongation at break results.

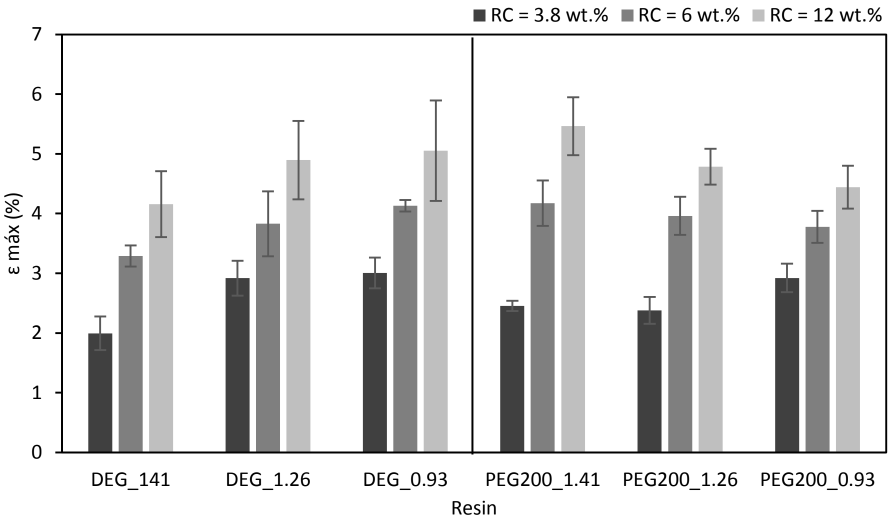

Figure 6.16. Elongation at break of agglomerated cork produced with UF resin modified with DEG or PEG200 as a function of RM F/(U+G) and solid resin content.

Figure 6.16 that as resin content increases, elongation at break of agglomerated cork clearly increases due to the flexible behavior of UF resins modified with linear segments. Elongation at break tends to increase with DEG content, as the higher flexibility of the crosslinked structure allows chain stretching, which corresponds to higher elongation at break. The elongation at break ends up decreasing significantly at higher PEG200 content due to lower cohesion, as discussed for the tensile strength results.

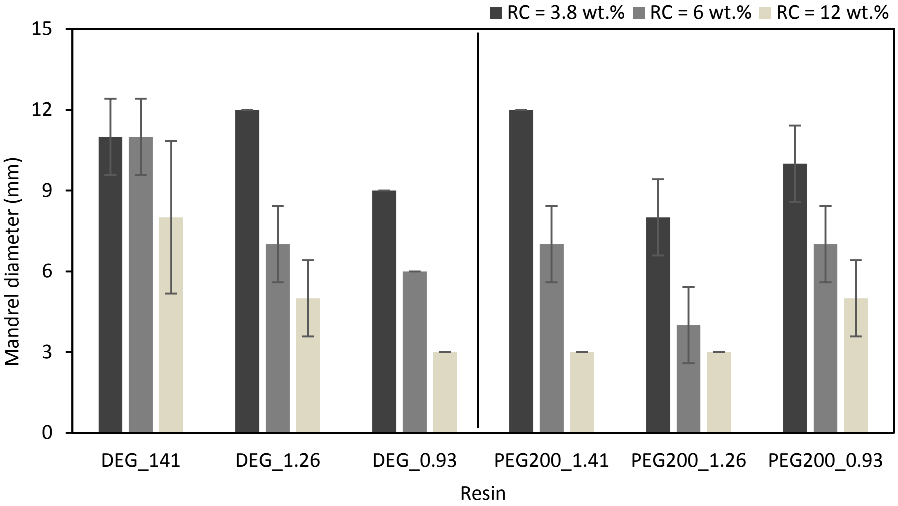

Figure 6.17. Mandrel of agglomerated cork produced with UF resin modified with DEG and PEG200 as a function of MR F/(U+G) and solid resin content.

It is possible to observe a significant difference in the mandrel results of the composites with different quantity of binder agent. There is an optimum solid content to produce panels with better mandrel.

When DEG is used to modify UF resin, higher resin content is favorable to produce a cohesive panel with flexible properties. Agglomerated cork flexibility increases with decrease of F/(U+G) ratio because more soft segments are present in brittle UF matrix.

When replacing DEG with PEG, longer linear chains are introduced in polymeric matrix, increasing the distance between crosslinking sites. This contributes to a more flexible polymer and composite. This could be the reason for the different values of DEG_1.41 and PEG200_1.41, at same resin content. However, in the limit when the crosslinking density becomes too low, waxy panel is obtained and this is the reason why mandrel results worsen with PEG200_0.93. These results are in accordance with elongation at break.

Agglomerated cork panels produced with PEG200_1.26 resin show lower mandrel value, reaching a limit mandel with diameter of 3 mm, allowing for production of cork panels stocked as rolls. The differences between flexible UF resin and rigid standard UF resin are illustrated in Figure 6.18.

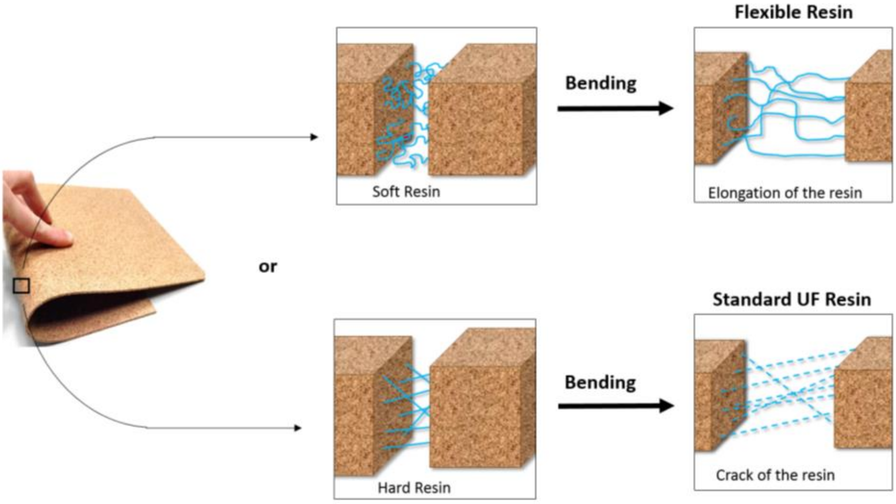

Figure 6.18. Proposal schematic representation of the deformation of cork panel produced with (a) flexible UF resin and (b) rigid standard UF resin.

Flexible UF resin can accommodate the mechanical strain of the panel without breaking because it presents hard and soft segments that allow physical-mechanical deformation of the panel. Standard cured UF resins are characterized by high stiffness and low tenacity.

All agglomerated cork panels produced with these resins disaggregated during the test of boiling water resistance, as expected in UF resins.

6.2.3.2. Formaldehyde emissions of panels produced with UF resin modified with glycols according EN ISO 12460-5

Cork panels produced with PEG200_1.26 were available to regard formaldehyde content. Cork panels show very high formaldehyde content value, 33.1 mg / 100 g oven-dry panel. These result indicate that free formaldehyde in liquid resin is not totally consumed during resin cure and panels present formaldehyde content superior than E2 classification (8 mg/100 g < E2 ≤ 30 mg/100 g oven dry board). The performance of different formaldehyde scavengers were tested to decrease formaldehyde content of agglomerated cork. Hexamethylenediamine and sodium metabisulphite were used before as formaldehyde scavengers [19] [15] but it is the first time of jeffamine used with this purpose.

The amount of each scavenger added to resin was 20 wt.%. Table 6.6 shows the measured values of formaldehyde content for these formulations.

Table 6.6. Formaldehyde content according EN ISO 12460-5 of agglomerated cork produced with PEG200_1.26 (at 6 % of solid resin content/ dry cork)

Aditive	Resin	Additive (wt. %)	Content (mg/100 g oven-dry panel)	Class (EN 13986)
_	PEG200_1.26	_	33.1	> E2
Hexamethylenediamine	PEG200_1.26	20	12.4	E2
Sodium metabisulphite	PEG200_1.26	20	12.2	E2
Jeffamine D230	PEG200_1.26	20	4.0	E1

As expected, the addition of each scavenger decreases formaldehyde content due to its consumption in the cure process. However the addition of hexamethylenediamine and sodium metabisulphite was not sufficient to classify the cork panel board as emission class E1, taking into account the limit value of ≤ 8 mg / 100 g oven-dry panel for formaldehyde content.

The reduction in formaldehyde content was significant when jeffamine D230 was applied and mechanical properties were maintained. Agglomerated cork panels present 4.0 mg /100g oven-dry panel and can therefore be classified as E1 (EN 13986). The jeffamine D230 yielded a promising monomer to modified formaldehyde-based flexible adhesive polymer.

6.2.4. Conclusion

Urea-formaldehyde resins modified with glycols have been applied in the production of agglomerated cork panels. Six resins, three resin contents and three molar ratios were tested, in order to conclude about the best way to produce agglomerated cork panels with the best mechanical and flexible properties.

More adhesive in agglomerated cork panel results in better mechanical performance for all tested adhesives. The tensile strength decreases as DEG content increases. However, UF resins modified with PEG200 show similar results apart of value of F/(U+G) ratio. As the resin content increases, the stiffness of panel increases, resulting in higher Young's modulus. Elongation at break tends to increase with glycol content and resin content because the flexible properties of UF modified with linear segments. When DEG is used to modified UF resin, higher resin content is favorable to produce a cohesive panel with flexible properties. Agglomerated cork flexibility increases with decrease of F/(U+G) ratio according with mandrel evaluation.

Cork agglomerated panels produced with PEG200_1.26 resin show very low mandrel value, allowing for stocking the cork panels in roll form. Also the 200 kPa limit required by APCOR specifications is achieved for all panels produced with this resin. However, these cork panels show very high formaldehyde content, which indicates that free formaldehyde in liquid resin is not totally consumed during resin cure and it is necessary to apply scavengers to decrease this value. Jeffamine D230 proved to be an excellent scavenger, allowing for producing agglomerated cork panels with classification E1.

6.3. Introducing flexibility in UF resins: copolymerization with polyetheramines [7]

Abstract

Adhesives obtained by copolymerizing urea, formaldehyde and difunctional polyetheramine with different molecular weights (230, 600, 900 and 2000 g/mol) are presented as a more resilient alternative to conventional urea-formaldehyde resins. Urea and polyetheramine contents were varied and the resulting resins characterized by FTIR, ^{13}C-NMR and TGA. These resins were used for production of agglomerated cork panels, an application that demands that the binder system is flexible. Polyetheramine with molecular weight 900 g/mol yielded the most promising agglomerated cork panel, with remarkable flexibility, good tensile strength and with the E1 formaldehyde content specification for wood-based panels used in construction, according to European Standard EN 12460-5.

These new thermoset adhesives have demonstrated to be capable of being used in systems where conventional formaldehyde-based resins do not perform well due to inherent high rigidity.

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[7] A. Antunes, M. Rêgo, N. Paiva, J. Ferra, J. Martins, L. Carvalho, A. Barros-Timmons and F. D. Magalhães, “Introducing flexibility in UF resins: copolymerization with polyetheramines”, *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 56 (16), pp. 1834-1843, 2018.

6.3.1. Introduction

Amino-formaldehyde resins are thermosetting polymers that have been used for decades on a wide range of uses. Urea and/or melamine-formaldehyde resins have been applied as adhesives for wood substrates and for paper impregnation [1]. After cure, these resins form a strong bond with lignocellulosic substrates, and have excellent solvent and heat resistance. However, their high crosslink density results in high stiffness and brittleness. This may be undesirable when a tough and flexible final product is desired which may occur in different contexts, like post-formable impregnated finishing foils, wrinkle-resistant fabric finishes [1], [3], resilient foams [7]–[9], low internal stress glued joints [4]–[6], etc. Flexibility is one of the biggest challenges in the development of new generation amino-formaldehyde resins. One possible strategy to increase the flexibility of amino-formaldehyde resins is by decreasing crosslinking density, through introduction of long linear segments. Some examples are patents from the 70s and 80s, where authors copolymerize glycols with formaldehyde-based resins for production of post-formable laminates based on resin-impregnated paper [13]–[15]. These segments may also be provided by linear diamines, which are able to react with formaldehyde. Following this concept, Ebewele *et al.* (1991 and 1993) [4]–[6] modified an urea-formaldehyde resin by incorporating di- and trifunctional amines, with the goal of decreasing the internal stress developed during resin cure on solid wood joints and particleboards. The authors observed that direct addition of some amines produced a violent reaction that resulted in a large amount of insoluble material. Therefore, they have opted to abandon direct amine addition and produced urea-capped derivatives as percursors to the copolymerization. These modifications were shown to be effective in enhancing cyclic stress resistance and fracture toughness. However, the flexibility of the final products was not directly evaluated. In different context, linear amines are used as curing agents for obtaining flexible epoxy adhesive systems [57]–[59].

This work describes the synthesis and characterization of a new type of flexible urea-formaldehyde resins, modified with polyetheramines (PEA). Production of agglomerated cork panels was selected as an example of the applicability of these resins. Flexibility is a key property in cork panels, since after production they must be rolled for storage and transport. Traditional urea-formaldehyde resins cannot be used for this purpose, since they produce stiff panels that crack upon bending. Our work shows that the PEA-modified urea-formaldehyde resins, on the contrary, confer flexibility to the agglomerated cork panels, while maintaining good tensile strength.

6.3.2. Materials and Methods

6.3.2.1. Materials

In the preparation of polyetheramine-urea-formaldehyde (PEA-UF) resins, industrial-grade raw materials were used, namely: urea (U) and formaldehyde (F) solution at 53 % were provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal). Jeffamines D230, ED600, ED900 and ED2003 (polyetheramines), of average MW 230, 600, 900 and 2000 g/mol (oligomers with unspecified dispersity), respectively, were provided from Huntsman (Osnabrück, Germany).

The cork granules was provided by Amorim Cork Composites, S.A. (Santa Maria da Feira, Portugal).

6.3.2.2. Synthesis of PEA-UF resin

The polyetheramine-urea-formaldehyde (PEA-UF) resins were prepared by reaction of polyetheramines (Jeffamine with molecular weight 230, 600, 900 or 2000 g/mol), formaldehyde and urea in presence of water in a three necked 250 ml glass flask, under atmospheric pressure. The system was kept at 80 °C during 90 min and mechanically stirred at 200 rpm. The reaction is terminated by cooling the mixture to a temperature of 25 °C.

Different molar ratios (MR) of formaldehyde to amino groups were chosen for the formulation, i.e., $F/(NH_2)_{2\ Urea}$ of 6.5, 4.7 and 2.3 and $F/(NH_2)_{2\ Final}$ of 1.2 and 1.0. The molar ratio $F/(NH_2)_{2\ Final}$ include amino groups of urea and polyetheramines. Solid content of all resins were adjusted to (50±2) % and final pH was not adjusted.

Table 6.7 shows the compositions of the synthesized resins. Three sets are defined: set I, for analysing the effect of the presence or absence of urea; set II, for analysing the effect of polyetheramine and urea content, and set III, for analysing the effect of molecular weight of polyetheramine.

Table 6.7. Composition of synthesized resins

Set	**Resin**	**MR $F/(NH_2)_2$ Urea**	**MR $F/(NH_2)_2$ Final**	**Polyetheramine molecular weight (g/mol)**
I	A	-	1.2	230
	B	4.7	1.2	230
II	C	6.5	1.2	230
	B	4.7	1.2	230
	D	2.3	1.2	230
	E	2.3	1.0	230
III	E	2.3	1.0	230
	F	2.3	1.0	600
	G	2.3	1.0	900
	H	2.3	1.0	2000

6.3.2.3. Characterization of PEA-UF resin

The solid content (%) was determined by evaporation of volatiles in two grams of resin for three hours at 120 °C in oven. The solid content was determined by the mass ratio of the sample before and after drying. Viscosity of resins was measured with a Brookfield viscometer at (25 ± 1) °C and it is expressed in mPa·s. The resin pH were measured using a combined glass electrode. Storage stability was evaluated comparing the differences of pH and viscosity of resins at 25 °C during 30 days.

6.3.2.4. ^{13}C-NMR analysis

About 40 mg of liquid sample was directly mixed with 0.75 ml DMSO-d6 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 h to accumulate. Chemical shifts in DMSO-d6 solution were calculated by defining a ^{13}C chemical shift of DMSO-d6 at 39.5 ppm. All results were discussed after normalized by signal of urea's carbonyl.

6.3.2.5. Films production

Free standing films were prepared by the casting evaporation process. Approximately 20 g of resin was prepared and poured into a PTFE coated mould. This was then kept at 60 °C for 12 h, until water was evaporated and the film was formed. To cure the resins, temperature was increased to 80 °C for 4 h, 120 °C for another 4 h and 1h at 150 °C to ensure complete cure. The films obtained were about 1 mm thick and 100 mm in diameter.

6.3.2.6. Flexibility, Tack, and Elasticity Evaluation

All films were subjectively evaluated after cure. Flexibility was evaluated by bending the films manually and observing whether fracture occurred. To assess tackiness, light pressure was applied on the film surface with a clean finger. Elasticity was evaluated by manually performing applying a small tensile force and observing strain recovery. This qualitative evaluation was considered sufficient for the purpose of the discussion presented here.

6.3.2.7. 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}. Samples were resin films prepared by the evaporation technique described above. The intensities were normalized by FTIR intensity for C–H stretching of methyl and methylene groups of jeffamine around 2986-2868 cm^{-1}.

6.3.2.8. Thermal gravimetric analysis

Thermogravimetric analysis were performed in a simultaneous thermal analyser STA 449 F3 Jupiter (NETZSCH). Samples masses between 10 and 15 mg were placed in an alumina crucible. The heating rate was 10 K/min, under nitrogen flow from room temperature to 500 °C. Samples were films prepared as described above.

6.3.2.9. Production of agglomerated cork panels

Resins were added to granulated cork and the mixture were prepared by manual stirring during 5 min at room temperature. The amount of solid resin was 6 % based on oven dry cork. After blending, cork panel was hand formed in a deformable aluminium mould (2 x 450 x 250) mm^3. The cork amount was determined in order to obtain boards with target densities of 600 kg/m^3. Panels were pressed in a laboratory batch press equipped with both heating and cooling systems, with a set-point in temperature of 150 °C, a pressure of 12 bar, a pressing time of 5 min and a cooling time until to achieve 25 °C. Three panels were produced for each variable tested.

6.3.2.10. Physical-mechanical characterization of agglomerated cork panels

Tensile strength

After production, boards were hermetically conditioned until performance evaluation at (23 ± 2) °C and a relative humidity of (50 ± 5) % for 48 h.

Stress-strain tests were carried out adapting the International Standards ISO 7322:2000 (E). Three samples with dimensions of (100 x 15 x 2) mm^2 were tested for each production condition in a testing machine Mecmesin MultiTest-1-d equipped with a Mecmesin BFG 1000 dynamometer, at a crosshead speed of 300 mm/min under room temperature. At least three replicas were made for each measurement.

Resistance to boiling water

The resistance to boiling water was done according ISO 7322:2000(E). Three samples with dimensions of (50 x 50) mm^2 were tested for each resin. The procedure was to place the specimens into boiling water for 3 h. After test, samples were visually examined and classified as disaggregated or not.

Flexibility of panels

The flexibility of agglomerated cork panels was evaluated following a cylindrical mandrel bending test, according to ASTM F147-87. The method consists in bending the specimen on cylindrical mandrels with different diameters ranging from 3 to 48 mm. The flexibility of the specimen corresponds to the minimum diameter about which the specimen could be flexed without exhibiting any signs of failure.

6.3.2.11. Formaldehyde content of panels - Perforator method (EN 12460-5)

Formaldehyde content of agglomerated cork panels was determined according to perforator method (EN 12460-5). Perforator method measures the formaldehyde emissions content of the specimen potentially emitted under forceful conditions. Formaldehyde was extracted from 110 g of test pieces by means of boiling toluene and then transferred into distilled or demineralized water. The formaldehyde content of this aqueous solution was determined photometrically by the acetylacetone method [54].

6.3.3. Results and discussion

The proposed chemical reactions schemes involving urea, jeffamine and formaldehyde are depicted in Figure 6.19 and Figure 6.20.

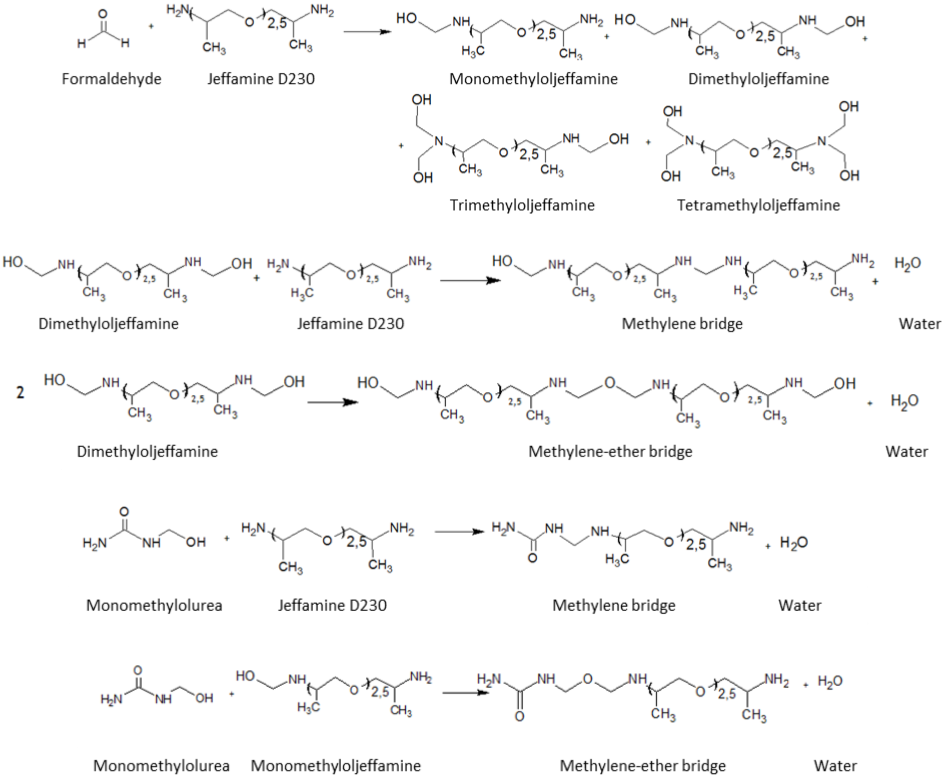

Figure 6.19. Methylolation and condensation reaction of urea, formaldehyde, polyetheramine (Jeffamine D230) and respective derivates forming methylene and methylene-ether bridges.

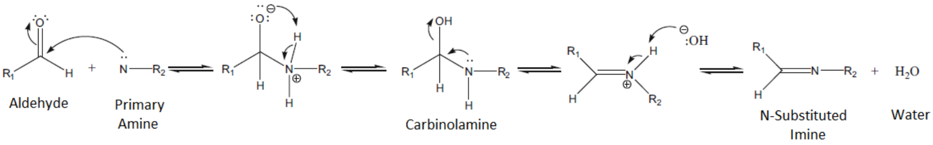

Figure 6.20. Reaction mechanism for formation of imine-containing coumpound [60].

6.3.3.1. Generic properties of liquid resins and cured films

Nine resins were synthesized according to the same process, but differing in terms of urea content, PEA content and PEA molecular weight. Table 6.8 shows the final pH, viscosity, solid content and storage stability of the liquid resins, and a qualitative description of the cured films obtained with each resin.

Table 6.8. Physical properties of resins and films

Set	**Resin**	**pH**	**Viscosity (mPa·s)**	**Storage time (days)**	**Cured film properties**
I	A	12.0	8600	>30	Flexible film
	B	11.9	220	>30	Flexible film with some elasticity
II	C	12.4	220	>30	Flexible film with some elasticity
	B	11.9	110	>30	Flexible film with some elasticity
	D	11.5	100	>30	Tacky and flexible film
	E	12.3	80	>30	Tacky and highly viscous mass
III	E	12.3	80	>30	Tacky and highly viscous mass
	F	12.5	40	>30	Tacky and highly viscous mass
	G	13.1	110	>30	Tacky and highly viscous mass
	H	12.5	115	>30	Tacky and highly viscous mass

The final pH was always above 9.00, as expected considering the alkaline character of polyetheramines. The viscosities of the liquid resins decrease as the F/U ratio is decreased, for the same molecular weight PEA. Reacted urea promotes polymer branching and free urea acts as a solvent [61], therefore decreasing viscosity. When MR F/$(NH_2)_2$ $_{\text{Urea}}$ is constant, increase of polyetheramine molecular weight results in approximately constant viscosities, between 80 and 120 mPa·s. The pot-life all resins is always higher than 30 days.

All cured films were transparent and glossy, with a yellow tint. A preliminary subjective evaluation was made in terms of flexibility, tack, and elasticity, as seen in Table 6.8. The film obtained from Resin B is shown in Figure 6.21, as an example of the film flexibility obtained.

Figure 6.21. Flexibility of cured film obtained with Resin B.

Comparing resins A and B, in Table 6.8, it is observed that the presence of urea in Resin B improves the elasticity of the cured film. Urea increases the crosslinking density, promoting elastomeric properties. Unlike Resin B, Resin A, which has no urea, shows thermoplastic behavior, melting at 120 °C and solidifying back at room temperature. This indicates that the degree of crosslinking is very low. As more urea is added (*i.e.* as MR F/$(NH_2)_2$ $_{\text{Urea}}$

decreases), the crosslinking density probably increases, but no significant changes are observed in the subjective evaluation of the cured films. When MR F/(NH$_2$)$_2$ $_{\text{Final}}$ decreases, the concentration of crosslink sites decreases because of higher polyetheramine content and film tack tends to increase, as shown in Table 6.8. Increasing PEA molecular weight results in no clear trend aside from all cured resins becoming a tacky and viscous polymeric mass.

6.3.3.2. FTIR analysis of PEA-UF resins

Figure 6.22 shows the FTIR spectra obtained for the cured Resins A and B, as well as for Jeffamine D230.

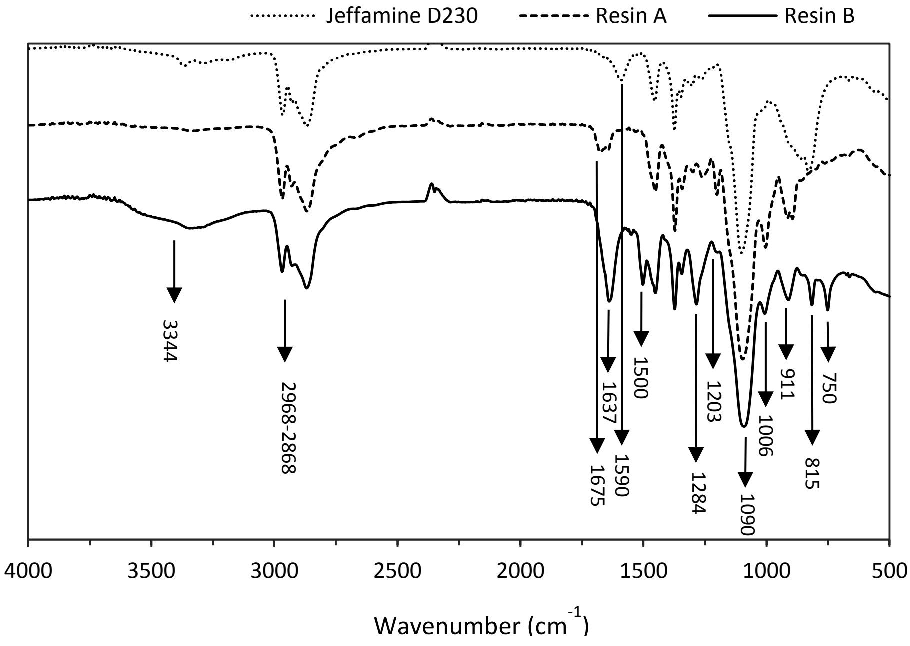

Figure 6.22. Normalized IR spectra of Jeffamine D230; Resin A and Resin B.

According with the literature [60], [62], the characteristic absorptions bands of Jeffamine D230 are observed at 3350–3340 cm^{-1} (NH stretching of primary aliphatic amines), at 2968-2868 cm^{-1} (C-H stretching of methyl and methylene groups of polyetheramine), at 1284 and 1203 cm^{-1} (multiple C-C stretching mode), at 1090 cm^{-1} (C-O-C stretching vibrations) and at 1590 cm^{-1} the characteristic band of primary amines (-NH$_2$ bending mode). All these absorption bands are present in the spectrum of Resin A except those associated with the stretching and bending vibrations of N-H bond of primary aliphatic amines at 3350–3340 cm^{-1} and 1590 cm^{-1}, respectively. This indicates the absence of unreacted polyetheramine in the cured films. Special attention should be given to the bands at 1675 cm^{-1}, which suggests the formation of imine bonds (C=N), and at 1010–1000 cm^{-1} which indicates the formation of methylol groups (C-O stretching mode) [30].

Resin B presents a different spectrum due to the presence of urea. The main differences are observed at 1500, 815 and 750 cm^{-1}, ascribed to secondary amines [30], [63], and C-N and N-H bending of methylene bridges, respectively. Special attention should be paid to the band at 1637 cm^{-1} which indicates the presence of urea (C=O stretching of primary amide). The imine bonds at 1675 cm^{-1} may also be present in Resin B, but it may be overlapped with the characteristic absorption band of urea.

FTIR spectra of resins modified with different molecular weights of polyetheramines are shown in Figure 6.23. All previously discussed characteristic absorption bands are present in these resins. For this reason, only the bands that show significant variations are discussed here.

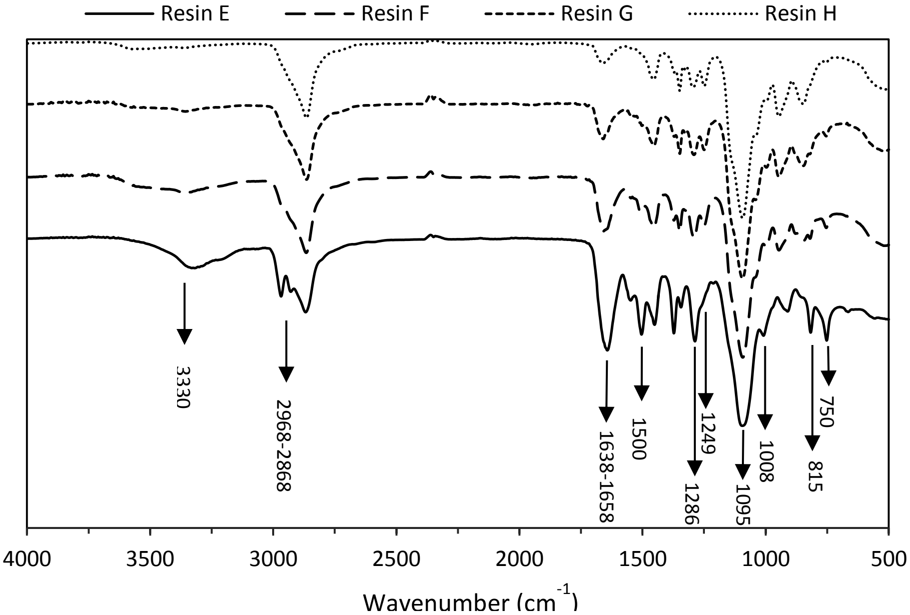

Figure 6.23. Normalized IR spectra of films of Resin E (MW 230 g/mol), Resin F (MW 600 g/mol), Resin G (MW 900 g/mol) and Resin H (MW 2000 g/mol).

Increasing the molecular weight of polyetheramine causes the reduction of the intensity of the absorption band of primary aliphatic amines (3330 cm^{-1}). Also, the intensity of the bands corresponding to C=O (around 1638-1658 cm^{-1}) decreases. This is attributed to the decreasing amine and ureaconcentration in the resin as the molecular weight of polyetheramine increases [60].

6.3.3.3. Liquid ^{13}C-NMR spectroscopy of PEA-UF resins

Figure 6.24 shows the ^{13}C-NMR spectra of Resin A (polyetheramine-formaldehyde) and Resin E (polyetheramine-urea-formaldehyde). Each signal observed in the spectra was identified according to chemical shifts reported in the literature [64]–[69]. The structural assignments of chemical shifts are listed in Table 6.9.

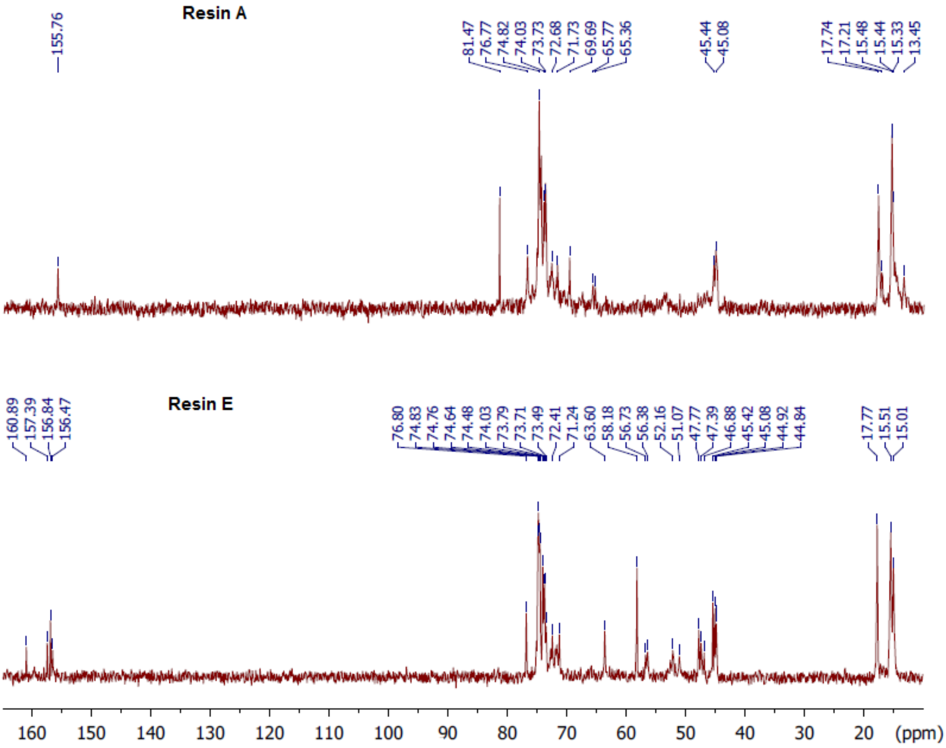

Figure 6.24. ^{13}C-NMR spectra of Resin A and Resin E.

Table 6.9. ^{13}C-NMR assignment for Resins A and E

Structures		**δ (ppm)**		
		Literature [64]–[69]	**Resin A**	**Resin E**
Free urea	$NH_2\underline{C}ONH_2$	160	-	160.89
Mono substituted urea	$-NH-\underline{C}O-NH_2$	158	-	-
Di and tri substituted urea	$–NH-\underline{C}O-NH-$	157	-	157.39
Imine	$=C=N-$	155-156	155.76	156.84 156.47
Ether	$-N(CH_{2-})-\underline{C}H_2-O-CH_3$	79-81	81.47	-
Monomethylol group	$HO-\underline{C}H_2-NH-$	64-66	65.77 65.37	63.60
Dimethylol group	$HO-\underline{C}H_2-N(-CH_2-OH)-$	71-72	71.73 72.68	71.23 71.66 72.41
Methylene-ether bridges I	$-NH-\underline{C}H_2-O-CH_2-NH-$	68-70	69.69	-
Methylene-ether bridges II	$-NH-\underline{C}H_2-O-CH_2-N(CH_2-)-$	53-56	-	56.73 56.38
Methylene bridges I	$-NH-\underline{C}H_2-NH-$	46-48	-	47.76 47.40 46.87

Table 6.9. ^{13}C-NMR assignment for Resins A and E *(cont.)*

Structures		**δ (ppm)**		
		Literature [64]–[69]	**Resin A**	**Resin E**
Methylene bridges I	$-N(CH_2-)-\underline{C}H_2-NH-$	52-55	-	52.16
Ether from polyetheramine	$-C(CH_3)H-O-\underline{C}H_2-C(CH_3)H-$ $-CH_2-\underline{C}(CH_3)H-O-$ $-CH_2-O-\underline{C}H_2-C(CH_3)H-$	71-77	73.76 74.02 74.47 74.82 76.77	73.50 73.71 74.03 74.48 74.63 74.75 76.80
Free and mono substituted polyetheramine	$-CH_2-\underline{C}(CH_3)H-NH_2$ $-CH_2-\underline{C}(CH_3)H-NH-$	44-45	45.41 45.09	45.41 45.08 44.92 44.83
Terminal methyl group from polyetheramine	$-CH_2-C(\underline{C}H_3)H-NH-$ $-CH_2-C(\underline{C}H_3)H-NH_2$	17-18	17.74 17.21	17.77 17.23
Central methyl group from polyetheramine	$-CH_2-C(\underline{C}H_3)H-CH_2-$	15	15.48 13.44	15.50 15.02

As expected, Resin A shows no evidence of the presence of urea in its structure. The methylene-ether linkages type I (68-70 ppm - resulting from reaction of two primary amines) are more evident in Resin A, while methylene-ether linkages type II (53-56 ppm - resulting from reaction between one primary and one secondary amine) are seen in Resin E. Furthermore, the peaks associated with methylene bridges (-NH-CH_2-NH-) between 46 and 55 ppm are not detected in the spectrum of Resin A, indicating that methylene-ether bridges and imine groups are favoured in the absence of urea.

The presence polyetheramine in the resins is detected in both spectra by the peaks between 71 to 77 ppm corresponding to ether from polyetheramine, the peaks from 44 to 45 ppm ascribed to mono substituted polyetheramine, and the peaks from 15 to 18 ppm attributed to terminal and central methyl groups from polyetheramine. Likewise, the presence of the peaks between 155 to 156 ppm, associated with the imine group is observed in both resins. These results indicate that polyetheramine effectively originated a new type of linkage with formaldehyde regardless of the presence of urea in agreement with the FTIR analysis.

The ^{13}C-NMR results confirm that all the reactions described in Figure 6.19 and Figure 6.20 occur during the synthesis of PEA-UF polymers. Whilst urea promotes a crosslinked structure with flexible chains from polyetheramine, the presence of methylol and free amino groups are useful for the cure of the resin during the production of agglomerated cork panels.

6.3.3.4. Thermogravimetric analysis of cured films

The thermal stability of cured films of Resins A and B (without and with urea, respectively) is shown in Figure 6.25 in terms of mass loss, and in terms of first derivative of mass loss in relation to temperature. Figure 6.26 shows the corresponding results for cured films of Resins E (MW 230 g/mol), F (MW 600 g/mol), G (MW 900 g/mol) and H (MW 2000 g/mol).

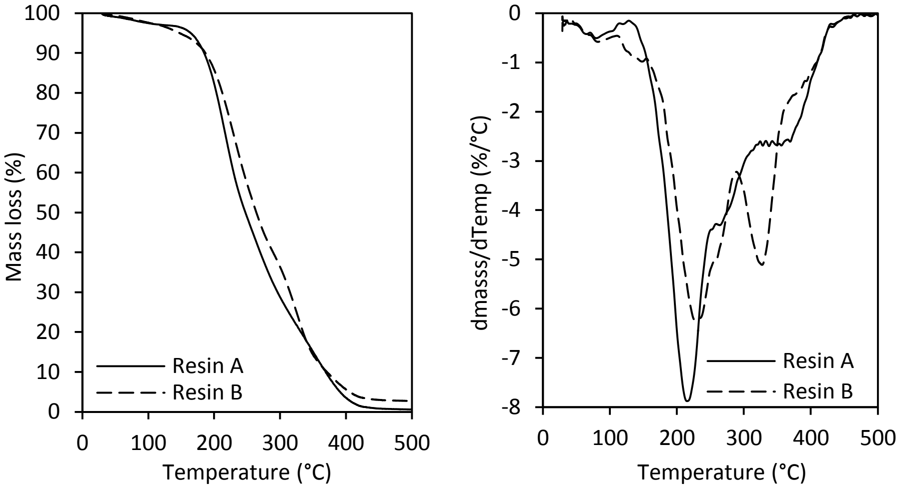

Figure 6.25. TGA thermograms (left) and first derivatives of mass loss (right) of the cured resins synthesized in the presence and in the absence of urea.

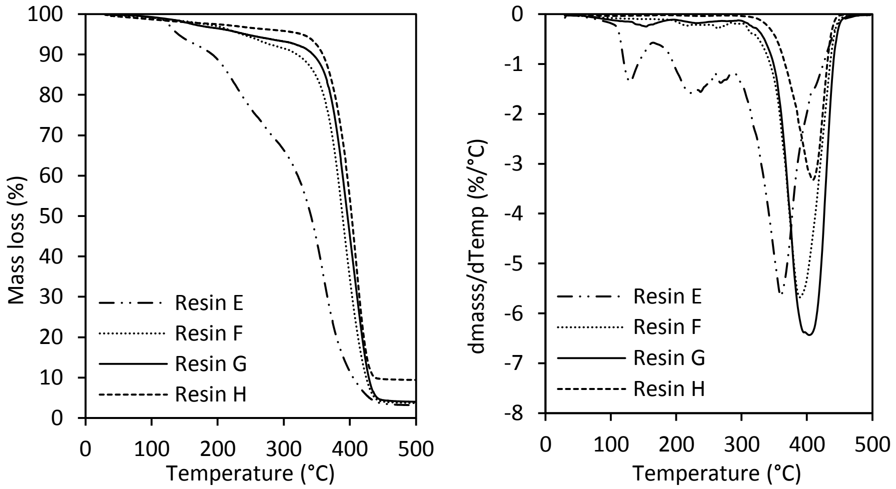

Figure 6.26. TGA thermograms (left) and first derivatives of mass loss (right) of the cured resins synthesized using with polyetheramines with different molecular weight.

In Figure 6.25, the weight loss observed at lower temperatures, up to 160 °C, is mainly caused by escape of volatile gases, namely moisture and free formaldehyde, from incomplete cure or released from linkage reversion [60], [70]–[72]. In the temperature range 160-250 °C, the weight-loss is attributed to formaldehyde released from conversion of methylene-ether bridges into more stable methylene bridges [71]. The presence of urea induces a slight shift of this degradation step towards higher temperature, probably due to higher crosslinking density [73]. From 250 and 350 °C, a new degradation step occurs: chain scission forms radicals which induces extensive fragmentation of the polymer chains [72]. This is more pronounced for the resin containing urea. Indeed, this degradation step is typically pronounced in urea-formaldehyde polymers, as observed by Esmaeili et al. [71]. At even higher temperatures (350-450 °C), degradation can be attributed to breaking of methylene bridges from polyetheramine [62].

The effect of PEA molecular weight on thermal stability of the cured polymer is shown in Figure 6.26. Except for Resin E the mass loss steps up to 350 °C discussed above can barely be identified whilst the one corresponding to polyetheramine degradation (350-450 °C) is much more pronounced, as a result of higher contents of this compound. In addition, this decomposition step shifts towards higher temperatures with increasing PEA molecular weight, in agreement with the known thermal stabilities of these polyetheramines [60], [62].

6.3.3.5. Physical-mechanical characterization of cork agglomerates

Tensile strength and mandrel tests were performed on cork agglomerates produced with the synthesized resins. Figure 6.27 shows the results for the three sets defined in Table 6.7: (I) influence of the presence of urea, (II) influence of urea and polyetheramine content and (III) influence of molecular weight of polyetheramine.

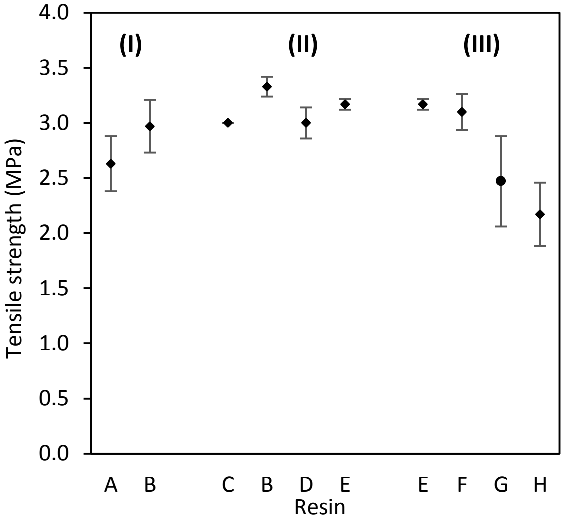

Figure 6.27. Physical-mechanical properties of cork-based panels produced with PEA-UF resins: (I) influence of the presence of urea; (II) influence of urea and polyetheramine content and (III) influence of molecular weight of polyetheramine.

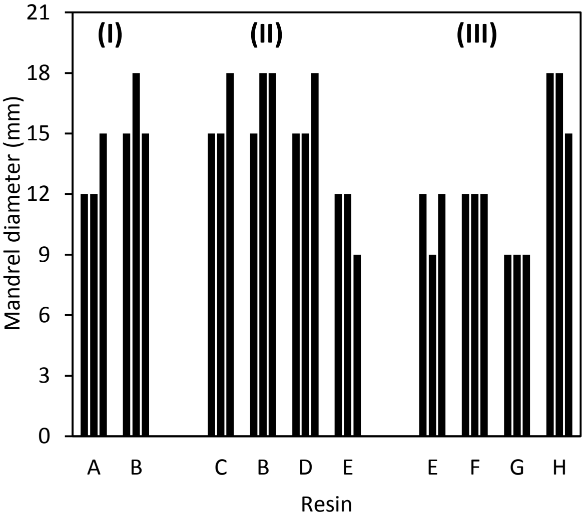

Figure 6.28. Mandrel flexibility results of cork-based panels produced with PEA-UF resins: (I) influence of the presence of urea; (II) influence of urea and

polyetheramine content and (III) influence of molecular weight of polyetheramine. Three measurement are shown for each resin.

The panels’ tensile strength does not differ significantly for the different resins. The only tendency that can be identified is the decrease in the tensile strength as the molecular weight of PEA increases (set III in in Figure 6.27) as a consequence of the lower crosslink density in the cured resins [2]. As expected, this also causes the minimum mandrel value to decrease, indicating higher flexibility of the panel (Figure 6.28). The best mandrel diameter obtained is 9 mm, for Resin G (PEA with molecular weight of 900 g/mol) which is significantly lower than that of a standard UF resin, which is 18 mm. Longer PEA (2000 g/mol) causes a decrease in flexibility (higher mandrel value) due to the penalizing effect of the binder having lower mechanical strength [2].

The tensile strength results show that the 200 kPa limit required by APCOR specifications [55] for cork agglomerate panels is achieved for all panels. Addition of polyetheramine does not therefore impair the adhesion strength of the resins. In addition, all specimens produced with PEA-UF present better mandrel test results than a standard UF resin, which cannot reach values below the mandrel diameter of 18 mm.

The performance of the panels produced with the new resins was also validated in terms of resistance to boiling water, a test decisive for industrial approval of cork binding systems. Only agglomerated cork panels produced with Resin A and Resin H did not pass the test, having disaggregated in less than three hours. This was expected, since Resin A is not a crosslinked polymer and Resin H presents very low crosslink density, due to the high molecular weight of the polyetheramine used.

The formaldehyde content was measured for the panels with best mandrel performance, obtained with Resin G. The result was 0.4 mg/100 g oven dry cork panel. This value satisfies the specification for wood-based panels used in construction (EN 13986:2004+A1:2015). The panel would be classified as E1, taking in account the limit value for formaldehyde content of 8 mg/100 g oven dry board. Resin G has demonstrated to be capable of being used in systems where conventional formaldehyde-based resins do not perform well due to inherent high rigidity showing remarkable flexibility, good adhesion properties and very low formaldehyde content.

6.3.4. Conclusion

Polyetheramine-urea-formaldehyde (PEA-UF) resins were synthesised using difunctional polyetheramines with different molecular weights, and different contents of urea and polyetheramine. The chemical characterization of the ensuing polymers was performed by FTIR and ^{13}C-RMN, demonstrating the presence of polyetheramine in the urea-formaldehyde structure. Thermal decomposition of PEA-UF was also studied showing higher thermal stability for resins synthesized with increasing molecular weight of PEA.

Agglomerated cork panels produced with the synthesized resins displayed tensile strength, mandrel flexibility and boiling water resistance results that could be directly related to the expected lower crosslinking density of the cured polymer. A good compromise between bond strength and flexibility was obtained for PEA/UF resin produced with polyetheramine 900 g/mol. The minimum mandrel flexibility value was 9 mm, which is significantly lower than that of a standard UF resin, which is 18 mm. The panels showed very low formaldehyde content according to European Standard EN 12460-5. These new PEA-UF resins show potential applications as binders for composite systems where flexibility is needed, which cannot be achieved by the conventional formaldehyde-based resins, due to excessive brittleness.

6.4. References

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CHAPTER 7

Conclusions, Economic Feasibility and Future Work

7. Conclusions, Economic Feasibility and Future Work

7.1. General conclusions

The objective of this PhD thesis was the development of resins with improved performance for paper impregnation and agglomerated cork applications: polyurethane resins with enhanced properties were studied for post-forming applications; formaldehyde-based resins with improved toughness were developed for use in the production of agglomerated cork. This work was co-founded and developed in close cooperation with the Portuguese company EuroResinas – Indústrias Químicas S.A., one of the major producer of formaldehyde-based resins.

The first study of this thesis was focused on the use of polyurethane moisture-curable resin to impregnate décor paper, replacing the traditional melamine-formaldehyde resin. The main conclusions of this work were:

- The NCO/OH molar ratio and polypropylene glycol molecular weight have significant influence on the physical properties of the resultant polymers and composite foils (higher amount of free isocyanate and lower polyol molecular weight result in better mechanical strength and better surface properties of the finish foil);
- The best performances were obtained with paper impregnated with polyurethane moisture-curable resin based on polyol with molecular weight 400 g/mol and NCO/OH ratio 2.5 which finish foil showed chemical, cracking and cigarette burn resistance equivalent to conventional melamine paper, according to EN 438-2 and exhibited self-healing properties;

- These post-formable and self-healing finish foils developed are promising for use in furniture applications.

Before the development of new formaldehyde-based resins for use in cork composites, the effect of resin content and nature (polyurethane and melamine-urea-formaldehyde) on the mechanical properties were studied. The principal conclusions were:

- The adhesive’s nature and its wettability are factors that greatly influence the physical-mechanical properties of the agglomerated cork composites;
- Higher adhesive load in agglomerated cork panel results in higher mechanical performance for both adhesives;
- For the same resin content, MUF resin presents considerable higher stiffness and tensile strength when compared with PU specimens, however, PU resin has higher elongation at break, while MUF resin reveals a brittle behavior and lower mandrel results.
- Use of MUF resin as binder is a more economical alternative than PU. However, if panel flexibility is paramount, PU may be the only valid option.

Some strategies were suggested and tested to improve the flexibility of the amino-formaldehyde resin, in order to make it appropriate for use in agglomerated cork panels. The first one was to decrease the high crosslinking density of amino-formaldehyde resins using chain growth blockers. Caprolactam and o-p-toluenesulfonamide were added at three different steps in the synthesis process of MUF resin from which resulted the following main conclusions:

- Caprolactam showed the best performance as chain growth blocker when it was added at the condensation step;
- Caprolactam-blocked resins showed better storage stability and improved water tolerance, as well as were able to provided agglomerated cork panels with a significantly better flexibility. The panels' tensile strength results were within the desired limits for this type of material.

Another approach was the development of MUF resins with a voluminous substituent, in order to reduce crosslinking density. Melamine-urea-formaldehyde resins modified with benzoguanamine were produced. The principal conclusions were:

- DMA analysis showed that the replacement of the first load of melanine by benzoguanamine decreases the glass transition by improving the chain mobility of cured resins;
- Resins synthesized with 3/4 of the first melamine replaced by benzoguanamine produced cork panels with physical-mechanical properties according to required legislation and improved flexibility properties.

The third strategy developed to obtain more flexible agglomerated cork panels was the introduction of linear flexible segments in the amino-formaldehyde structure. Ethylene glycols with different molecular weights (106, 200 and 400 g/mol) were used and added to the reaction mixture in different amounts. The principal conclusions were:

- Molecular weight and amount of glycol used in the synthesis affects key properties of the product, like reactivity, glass transition temperature, flexibility and toughness;
- A highly flexible amino resin was developed by using polyethylene glycol with molecular weight 200 g/mol which displayed very high resilience, toughness and flexibility when impregnated on a paper substrate;
- The developed resin has potential applications for agglomerated cork panels with good adhesion strength and flexibility, however, poor water resistance and high formaldehyde content was observed.

The last approach was the development of a new UF resin with introduction of polyetheramines, also functioning as linear flexible segments, which lead to the following main conclusions:

- Polyetheramine-urea-formaldehyde resins produced high flexibility films;
- The characterization of this new polymer by FTIR and ^{13}C-RMN showed the reaction of polyetheramine with the urea-formaldehyde structure;
- A good compromise between bond strength and flexibility was obtained for cork composites made with PEA-UF resin;
- Cork agglomerated panels produced with jeffamine 900 g/mol presented very low formaldehyde content according to European Standard EN 12460-5, water resistance and the lower mandrel value, which allows production of rolled panels.

The strategies followed to decrease the high crosslinking density of formaldehyde-based resins and improve flexibility of agglomerated cork panels bound with the modified resins were successful. However, the major objective outlined, was successfully achieved with just one of the developed solutions: a PEA-UF resin.

The major challenge found during this PhD was the significant change of the main goal during the first year of work. Following the strategic interests of the industrial sponsor, the initial focus on polyurethane resins shifted towards flexible amino-formaldehyde resins. The lack of existing information about these resins was another challenge. Similar limitations were also faced in the research about agglomerated cork panels. The studies found in the literature reported several trials to produce agglomerated cork panels, but most of them used polyurethane adhesive and the performance of amino-formaldehyde resin was not reported.

Beyond the importance of these studies and innovative developments, this work was mainly focused on competitive solutions that could be directly introduced on the market. Nevertheless, this work provided an important scientific contribution for both understanding synthesis of flexible formaldehyde-based adhesives and production of agglomerated cork panels. This work provides a solid support for new projects within the research group on flexible formaldehyde-based resins (e.g. for paper impregnation).

7.2. Economic feasibility and cost comparison

Melamine-urea-formaldehyde resins are highly competitive in relation to polyurethanes, since their price (500 €/ton) i.e. three times cheaper than the commonly used polyurethane adhesives'. The most promising resins developed in this work are presented in Table 7.1. Considering the cost of electrical energy used in the synthesis process of a standard resin is the same in new formulation, a cost estimation of the final price of the new products can be obtained (Table 7.1).

Table 7.1. Main characteristics and price of best performing amino-formaldehyde resins developed in this work

	Mandrel diameter	**σ max at 6 wt.% of binder content**	**Formaldehyde content**	**Price**
	(mm)	**(MPa)**	**(mg/100 g oven-dry panel)**	**(€/ton)**
Standard MUF	18	3.1 ± 0.1	4.4	500
MUF + caprolactam	12	2.3 ± 0.1	< 4.0	612
MUF + benzoguanamine	12	2.5 ± 0.2	3.8	1088
PEA-UF	9	2.9 ± 0.4	0.4	3179
Polyurethane	6	2.4 ± 0.1	0	1500

Polyetheramines were the most interesting chemical used in this work, however, these were also the most expensive. Comparing the price estimates, the MUF resin modified with caprolactam and benzoguanamine demonstrated to be the most cost effective solutions for producing more flexible cork composites.

7.3. Future work

Although formaldehyde-based resins have been questioned over the last years due to the formaldehyde emissions, they have always had an exceptional positioning in the market because of availability and price of raw materials, being solvent free, and having low production costs and good performance. Furthermore, nowadays it is possible to produce low formaldehyde-emitting resins, complying with today's stringent regulations. Thus, there is no reason to believe that this class of adhesives will be replaced in the near future of industrial wood-based products production. Furthermore, there is a continuous market demand for improving properties of formaldehyde-based resins, such as flexibility.

Regarding the synthesis processes of developed work, some optimization could be done to achieve a cheaper product. Table 7.2 shows some resin formulation that could be tested.

Table 7.2. Optimization of formulations

	Price (€/ton)
Synthesis of UF_PEA with 1/3 of the amount of PEA900 used in Resin G	1175
Synthesis of UF_PEA with 1/3 of the amount of PEA900 used in Resin G + 10 wt. % caprolactam	1270
To combine resin UF-PEG200_1.26 as additive during MUF synthesis	780

First strategies is based in synthesis of UF-PEA resins with lower PEA900 content to decrease the final price of the product. The second proposal is the use of caprolactam blocker with previous formulation. Third suggestion consist in combining resin UF-PEG200_1.26 as additive during MUF synthesis.

During the development of this work some possible routes were not followed due to time limitations. Further studies should be performed testing the use of dicarboxylic acids. These compounds may be used to produce a pre-condensed mixture by strongly acid process which after alkalization would be added to a standard MUF resin formulation. Another additional approach could be to combine MUF resin with a flexible polymer to promote flexible micro domains within the MUF structure in order to reduce the high crosslinking density – two examples are latex and polyurethane dispersions.

Finally, it is also important to apply all developed resins in paper impregnation because this is another EuroResinas business area and there is a huge industrial interest in high flexibility post-forming paper. Therefore, it would be interesting to evaluate these resins as additives or as core impregnation resins.