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THÈSE

Developpement d'adhésifs industriels à base de biomatériaux et de mélamine sans formaldéhyde

Présentée devant l'université de Lorraine

pour l'obtention du titre de

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Résumé

Dans cette recherche, il y a deux parties principales : la première est basée sur la résine mélamine-glyoxal sans utilisation de formaldéhyde, et sa modification pour qu'elle soit utilisée comme adhésifs pour bois. La deuxième partie concerne la préparation d'adhésifs écologiques et de polyuréthane non isocyanate (NIPU) à partir de biomasse (sucre, protéines, tanins, etc.).

Dans notre vie quotidienne, un grand nombre de produits industriels en bois sont utilisés, par exemple la table, les chaises et les armoires en panneaux de particules, les sols d'intérieurs en panneaux de fibres, etc. Tous sont généralement liés avec des résines synthétiques à base de formaldéhyde (comme l'urée formaldéhyde, la mélamine-urée-formaldéhyde). Cela pose un problème d'émission de formaldéhyde toxique lors de la production et de l'utilisation, ce qui affecte gravement la santé publique car le formaldéhyde est cancérigène. Par conséquent, il est très important et urgent de trouver une substance appropriée pour remplacer le formaldéhyde dans les adhésifs utilisés pour le bois. Ainsi, le glyoxal tiens notre attention le fait qu'il est un aldéhyde non toxique, qui possède deux sites actifs (groupes aldéhyde) pour participer à la réaction. En fait, le formaldéhyde a été remplacé par glyoxal dans la préparation de la résine urée glyoxal qui trouve des applications dans l'industries du papier et du textile. Par contre elle n'est pas utilisée comme adhésif pour bois, car la réactivité du glyoxal est inférieure à celle du formaldéhyde et les propriétés de liaisons des résines sont médiocres.

La mélamine est un réactif chimique plus réactif que l'urée, qui modifiait la résine urée-formaldéhyde et améliorerait ses performances de liaison. Certes, l'utilisation de la mélamine et du glyoxal pour préparer des résines MG pour panneaux à base de bois qui répondent aux exigences de la production est devenu un bon choix. Cependant, en comme la réactivité du glyoxal n'est pas la même que celle de formaldéhyde, l'agent de durcissement conventionnel pour la résine UF tel que le chlorure d'ammonium, le sulfate d'ammonium ne fonctionne pas avec la résine MG. L'un des premiers travaux importants consiste à explorer un nouvel agent de durcissement adapté aux résines MG. Le liquide ionique N-méthyl-2-pyrrolidone-hydrogénosulfate ([HNMP] HSO₄⁻) s'est révélé efficace en tant que durcisseur de résine MG. Lorsque la quantité ajoutée atteint 10% (sur la base de la résine solide), la résistance au cisaillement à l'eau froide pendant 24 heures du

contreplaqué lié à la résine MG était de 0,63 MPa. Bien que cela soit très proche des exigences standard (≥ 0.7 MPa), mais pas assez. Par conséquent, il a été nécessaire de mener des études de modification sur les résines MG afin d'améliorer ses performances. Comme le montre la figure ci-dessous, deux méthodes de modification différentes ont été étudiées :



L'une consiste à remplacer le glyoxal par du glutaraldéhyde pour synthétiser des résines mélamine-glyoxal-glutaraldéhyde (MGG'). Depuis, le glutaraldéhyde améliore les performances des adhésifs au tanin ou même des résines synthétiques MUF. Les propriétés des résines de MGG avec différents rapports de substitution du glutaraldéhyde ont été étudiées et évaluées par la force de liaison du contreplaqué. Les résultats montrent que l'augmentation de la proportion de glutaraldéhyde, augmente viscosité de la résine MGG'. Le rapport molaire glyoxal / glutaraldéhyde qui donne les meilleures performances est égal à 4, en particulier la résistance à l'eau (2h de résistance au cisaillement dans l'eau bouillante (0,7 MPa). L'analyse structurale de la résine par MALDI TOF et FTIR a confirmé que le glutaraldéhyde a participé à la réaction et avait formé une résine copolycondensée mélamine-glyoxal-glutaraldéhyde meilleur que la résine glyoxal-mélamine.

Une autre modification consiste à améliorer les performances des résines MG avec du 5-hydroxyméthylfurfural en tant que modificateur pour obtenir une résine HMFMG. Comparée aux résines MG non modifiées, la résine HMFMG préparée en ajoutant 5% de HMF présente une meilleure force de liaison et une meilleure résistance à l'eau. Bien que la performance de liaison humide de celui-ci ne soit pas conforme à la norme, mais de manière prévisible, continuer à augmenter la quantité de HMF permettra à la résistance à l'eau des résines HMFMG de satisfaire aux exigences de la norme.

Une autre recherche importante dans cette étude est la préparation d'adhésifs pour bois à base de matières premières issues de la biomasse. Bien que les résines synthétiques MMG décrites ci-dessus ou la résine HMFMG additionnée de HMF aient obtenu de bons effets de liaison, elles devraient être utilisées comme adhésifs pour le bois dans la production industrielle du bois, mais des produits pétrochimiques

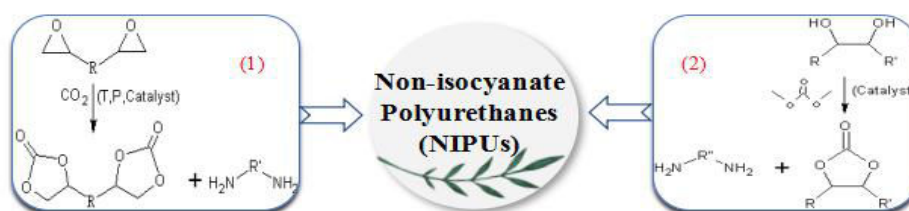
non Ressource renouvelable. Par conséquent, la préparation d'adhésifs pour bois à partir de ressources de biomasse renouvelable est un sujet de recherche important.

Il existe actuellement de nombreuses études sur la préparation des adhésifs pour le bois à partir de matières premières issues de la biomasse, les plus courantes d'entre elles étant les adhésifs pour le bois à base de tanins, de lignine, de protéines et d'amidon. Cependant, en tant qu'adhésifs pour bois à base de biomasse, ils ont un problème commun à résoudre, à savoir une faible résistance à l'eau. La grande majorité des rapports de recherche sur les adhésifs à base de biomasse ont également pour but de résoudre ce problème. Dans la présente étude, sur la base de l'étude précédente sur les résines synthétiques MG, il a été noté que l'alcool furfurylique est issue de la biomasse renouvelable, pour cela des résines synthétiques à base d'alcool furfurylique et le glyoxal (FAG) ont été préparées en faisant réagir de l'alcool furfurylique avec le glyoxal, les résines alcool furfurylique-formaldéhyde (FAF) et alcool furfurylique-glutaraldéhyde (FAG') ont été également synthétisées simultanément. Le contreplaqué a été préparé pour évaluer la performance des résines. Comme prévu, les résines FAF ont la meilleure adhérence et la meilleure résistance à l'eau, cependant le formaldéhyde reste toxique. La résine FAG présente également de bonnes performances de liaison et de résistance à l'eau (résistance au cisaillement à sec de 1,02 MPa, résistance à l'eau froide à l'eau de 1,36 MPa, résistance à l'eau de 1,46 MPa de 2h), bien qu'elles soient plus faibles que la résine FAF, mais assez répond aux exigences de la norme. Etant donné que le glutaraldéhyde a la réactivité la plus faible parmi les trois aldéhydes, les propriétés de liaison de la résine FAG synthétisée ne sont pas satisfaisantes.

Une autre matière de la biomasse, la protéine de blé a été réagie avec le glyoxal, puis la polyéthylèneimine a été ajoutée en tant qu'agent de réticulation et avoir un adhésif à base de protéine et respectueux de l'environnement. La résine a montré de bonnes propriétés de liaison et de résistance à l'eau, mais la viscosité est élevée, et elle ne peut être utilisée que pour le contreplaqué. De plus, cet adhésif doit être mélangé avec du PEI avant utilisation, ce qui est peu pratique à utiliser. Par conséquent, un adhésif de résine synthétique à base de protéines a été préparé. Adhésifs à base de protéines de résine polyamides obtenus par réaction de la protéine de soja avec l'anhydride maléique, puis avec l'hexaméthylènediamine. Le contreplaqué collé obtenu présente une excellente performance, la résistance à sec atteint 1,09 MPa, la résistance à l'eau froide pendant 24h était 0,85 MPa et la résistance après 2h d'eau bouillante

est de 0,78 MPa, qui sont déjà supérieures aux exigences de la norme.

Récemment, un sujet très intéressant sur la préparation de polyuréthanes non isocyanates (NIPU) pour remplacer les polyuréthanes largement utilisés à base d'isocyanates qui sont très toxique. En ce qui concerne la synthèse des NIPU, il existe deux méthodes courantes : **1)** l'une consiste à faire réagir le dioxyde de carbone avec un groupe époxy sous pression et dans des conditions de catalyseur afin d'obtenir un carbonate cyclique, puis à réagir avec des amines. **2)** L'autre méthode consiste à réagir des espèces de groupes o-hydroxy avec le carbonate de diméthyle, puis avec le diamine également.



Dans mon étude, cette dernière méthode sera utilisée pour explorer la synthèse de NIPU avec du glucose et du saccharose et tentera de l'appliquer en tant qu'adhésif pour bois, revêtement bois / fer et mousses rigides NIPU moussantes.

Les résines NIPU ont été utilisés comme revêtements et pour le collage le bois. Les NIPU à base de glucose ont donné des meilleures performances que les NIPU à base de saccharose. La résine NIPU à base de saccharose utilisée pour la préparation de panneaux de particules a donné des résultats intéressants. Une force de cohésion interne (IB) de 1.01 MPa et une excellente résistance à l'eau. On peut supposer que si des NIPU à base de glucose étaient utilisées pour la préparation de panneaux de particules ou de contreplaqué, donnera de meilleurs résultats que les NIPU à base de saccharose. Et l'agent de couplage au silane KH560 a été utilisé pour réduire la température de durcissement des NIPUs, ce qui a été confirmé.

De plus, des NIPU à base de glucose ont utilisé pour préparer des mousses rigides. En utilisant un agent de couplage au silane KH560 en tant qu'agent de réticulation et de l'hydrogénocarbonate de sodium en tant qu'agent moussant et dans des conditions de température élevée (200 °C), on a obtenu une mousse rigide de g-NIPU. Cette mousse a une bonne résistance à la pression et son comportement aux contraintes est plus caractéristique. Bien que la compression aplatisse effectivement les parois cellulaires, la structure cellulaire est maintenue et les parois cellulaires n'ont pas été détruites, ce qui indique un certain niveau d'élasticité dans les parois

cellulaires. Un problème sérieux dans ces travaux de recherche est la température élevée de moussage nécessaire. Par conséquent, une méthode de préparation de mousses NIPU à base de glucose auto-soufflantes dans des conditions de basse température (même à la température ambiante) a été étudiée. L'acide maléique a été utilisé comme initiateur, le glutaraldéhyde comme agent de réticulation, très bien mélanger, puis rapidement soufflé et transformé en mousse à température ambiante. Les mousses humides obtenues sont ensuite séchées à l'étuve pour obtenir une mousse dure NIPU. Il convient de souligner que les mousses obtenues présentent de deux manières une résistance au feu très limitée, ce qui indique que, comme pour les mousses de polyuréthane synthétiques, l'utilisation éventuelle d'un retardateur de flamme apparaît nécessaire.

Mots-clés: résine, mélamine-glyoxal, composites de bois, tanin, protéines de soja, polyuréthannes non isocyanates (NIPU), colle à bois

Abstract

In this research, there are two main parts works, first is based on melamine glyoxal resin without formaldehyde used, and the modification of it use for wood industry adhesives. The other part is the preparation of environmentally friendly adhesives and non-isocyanate polyurethane(NIPU) from biomass-based (sugar, protein, tannin, etc.). Wood composites such as plywood and particleboard were used for easuring the performance of adhesives, and more possibilities applications of them such as coating and foams were tried also. ^{13}C -NMR, Fourier Transform Infra-Red (FTIR), Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF), thermomechanical analysis(TMA), Differential scanning calorimetry(DSC) and other instruments help to analyze structures and thermodynamic properties of adhesives. The descriptions of specific works are as follows:

- 1) Synthetic melamine-glyoxal resin without use toxic formaldehyde and a suitable hardener was found for it. By the modification of glutaraldehyde, a melamine-glyoxal-glutaraldehyde(MGG') resin with good performance was prepared and used for plywood production, which can replace the industrial Urea-formaldehyde resin wood adhesive. In addition, 5-hydroxymethylfurfural as a chemical reagent derived from biomass material was also used to modify MG resin to improve its bonding performance and water resistance.
- 2) The biomass material furfuryl alcohol was used to react with aldehydes (formaldehyde, glyoxal, glutaraldehyde) to prepare plywood adhesives. Among them, furfuryl alcohol-glyoxal(FAG) resin, which was reacted with a non-toxic glyoxal, and with a good bonding propertiesis. It's as an environmentally friendly adhesive for wood bongding. The effect of different acidity of curing agents on bonding performance has also been explored, a self-neutralizing hardener is synthesized and used.
- 3) Proteins, tannins were used to prepare bio-based environmentally friendly wood adhesives, and improved the bonding properties and water resistance by the addition of crosslinking agents (furfuryl alcohol-glyoxal resins, epoxy resins, polyethyleneimine, etc.).
- 4) Biomass materials such as monosaccharide and disaccharide were used to synthesize non-isocyanate polyurethane(NIPU), and used for plywood or particleboard to obtain bio-based NIPU adhesives with excellent performance. The

effect of several crosslinkers on the curing temperature and bonding properties of NIPU was also studied. Research on more application about NIPU have also been conducted, for example, coating and rigid foams.

Key words: Resin, Melamine-glyoxal, Wood composites, Tannin, Soy protein, Non-isocyanate polyurethanes(NIPU), Wood adhesive

Présentation des publications

I -Les résines à base de mélamine- glyoxal

1. **Xi X**, Pizzi A*, Amirou S. Melamine-Glyoxal-Glutaraldehyde Wood Panel Adhesives without Formaldehyde[J]. Polymers, 2018, 10(1): 22.
2. **Xi X**, Liao J, Pizzi A*, Gerardin C, Amirou S, Delmotte L. 5-Hydroxymethyl furfural modified melamine glyoxal resin[J]. The Journal of Adhesion, 2019: 1-19.

II -Les résines à base de furannique- glyoxal

1. **Xi X**, Wu Z, Pizzi A*, Lei H, Du G. Furfuryl alcohol-aldehyde plywood adhesive resins[J]. The Journal of Adhesion, 2018: 1-25.

III-Adhésifs écologiques à base de matériaux de biomasse tels que des protéines et des tanins

1. Zhang J, **Xi X**, Liang J, et al. Tannin-based adhesive cross-linked by furfuryl alcohol-glyoxal and epoxy resins[J]. International Journal of Adhesion and Adhesives, 2019,94:47-52.
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3. **X.Xi**, A.Pizzi, C.R.Frihart, L.Lorenz, C.Gerardin. Tannin plywood bioadhesives by non-volatile aldehydes generation by specific oxidation of mono- and disaccharides. International Journal of Adhesion and Adhesives, submitted
4. **Xuedong Xi**, Antonio Pizzi *, Christine Gerardin, Xinyi Chen, Siham Amirou. Soy Protein Isolate based Polyamides as Wood Adhesives. Wood Science and Technology, 2019, submitted

IV-Résine NIPU à base de biomasse utilisée comme adhésif, revêtement, rigide mousse

1. **Xi X**, Pizzi A*, Delmotte L. Isocyanate-Free Polyurethane Coatings and Adhesives from Mono-and Di-Saccharides[J]. Polymers, 2018, 10(4): 402.
2. **Xuedong Xi**, Zhigang WU, Antonio Pizzi*, Christine Gerardin, Hong Lei*, Bengang Zhang, Guanben Du. Non-Isocyanate Polyurethane Adhesive from sucrose used for particleboard[J]. Wood Science and Technology, 2019: 1-13.
3. **Xi X**, Pizzi A*, Gerardin C, Du G. Glucose-biobased Non-Isocyanate Polyurethane Rigid Foams[J]. J Renew Mater, 2018: 1-11.

1. INTRODUCTION

1.1. Generalites

1.1.1. History of adhesives and thermosetting resins

Adhesives are in general one-component or multi-component materials with bonding characteristics, which under certain conditions which can bond the two surfaces (such as wood, metal, glass plastic, etc.) to be tightly held together by surface adhesion. The materials used as adhesives can be generally divided into two categories: natural high molecular substances and synthetic resins. The use of adhesives has a long history. As early as more than 2,000 years ago, natural starch gels and bone glues (based on animal protein glue) have already been used. However, the adhesives based on natural high-molecular materials, which are also water-soluble often present an unsatisfactory bonding performance. Especially since the beginning of the 19th century, after the industrial revolution, the adhesives prepared from natural polymer materials cannot adapt to industrial production requirements. Before 1800, animal and vegetable adhesives such as gelatin, fish gelatin or starch adhesive were used. This situation changed with the advent of industrial synthetic resin adhesives in the 20th century.

1895/1917: industrial manufacture of casein and gelatin, and first use of casein adhesives for manufacturing airplanes and interior carpentry;

1905/1910: Synthesis and application of phenolic resin;

1926: Adhesives for plywood panels made from soybeans;

1930: First urea-formaldehyde and resorcinol adhesives ;

1940s: Polyvinyl acetate, neoprene, polyurethane, etc;

1960s-1970s: application of acrylates and modified acrylates;

It is from this dates that the adhesive industry has gradually entered a stage of further perfectioning.

1.1.2. Adhesives and resins for the wood industry

Adhesives are one of the most important raw materials in the wood industry, as they are indispensable for most of wooden products such as plywood, particleboard, fiberboard, laminated veneer lumber(LVL), decorative veneers and so on. The most widely used thermosetting adhesives today in the wood industry are the following

resins:

- Phenol formaldehyde (PF);
- Urea – Formaldehyde (UF), Melamine –Formaldehyde (MF) and Melamine – Urea – Formaldehyde (MUF)
- Isocyanate (PMDI, polymeric diphenyl methane diisocyanate)
- Tannins and other natural polyphenols

PF resin adhesives have good bonding performance and water resistance. They are exterior application adhesives and have many applications in North America, Northern Europe, Germany, China, etc. However, in France, Italy and Spain, their application is rather limited due, among others, to the law governing the release of toxic phenol.

UF resins are the most commonly used resins for indoor applications, due to their low cost, short hot press time and good performance[1]. The problem of UF resins is related to their poor water resistance and formaldehyde emission, although in some cases of E1 rated resins, this problem has been greatly reduced with the reduction of formaldehyde emission, but it is still not completely eliminated. Much work has been done around the modification of UF resins and much is still ongoing [2-5].

MUF resins are an adhesives synthesized by modifying UF resins with melamine, which is superior in performance to UF resin and has better water resistance[6,7]. they are the most widely used outdoors or semi-outdoors adhesives in Europe, especially in France, Italy and Spain. However, the cost of melamine is very high, which limits its application. More research on how to reduce the cost of MUF is still ongoing. Pure MF resins are usually not used to bond wood, generally used to produce impregnated paper, veneer, etc. And the price is higher than MUF resins.

Polymeric 4,4'-methyldiphenyl diisocyanate(PMDI) is the most recent synthetic product in the field of thermosetting resins[8,9], and has important applications for insulation (thermo-insulating foams) as well as for wood-metal and wood-plastic bonding in combination with polyvinyl acetate PVA resins or other polyhydroxy materials. As an adhesive for wood panels it guarantees good external performance and short pressing times, and without formaldehyde emission, but the presence of free radicals $-N=C=O$ is dangerous to public health. For the application of PMDI, the plant installation must be adapted and modified to avoid sticking problems with the press platens. . The PMDI consumption for particleboard, medium density fibreboard(MDF) and Oriented Strand Board(OSB) manufacturing is constantly increasing in countries

like France, Germany and Italy despite the high cost of the product (1500-2300 euros /ton), this being considered as a disadvantage.

Tannin is a natural chemical compounds of mainly phenolic nature, which has a phenolic character and thus can react with aldehydes for wood bonding or as a substitute for phenol and synthetic natural phenolic resins. Tannin adhesives are well known and used in Australia, South America, South Africa, and their use is also growing in Europe. They provide short hot press times and low or no formaldehyde emissions and acceptable bonding performance for interior or exterior panels according to the formulation used.

1.1.3. Wood-based panels.

With the development of science and technology, the application of wood in different environments has become more and more demanding, with the boards obtained by cutting natural wood having difficulties to meet the ever more stringent application requirements, leading, thus, to the development of wood-based panels. The panels made from wood are mainly of four types:

1. particle boards
2. Fibre boards (high density fibre board- HDF, or medium density fibre board- MDF)
3. OSB (Oriented Strand Board)
4. Plywood panels, LVL(Laminated Veneer Lumber) and Glulam(Glued Laminated Timber)

Particleboard and medium density fiberboard are the most widely used and they are used often to make furniture. The boards commonly used for indoor applications are bonded with UF resins or conversely with MUF resins for outdoor or semi-external applications. Due to the use of formaldehyde-based adhesives, the inescapable problem presented by these panels is their emission of formaldehyde, harmful to human health. Thus, there are already applications of environmental friendly adhesives such as soy protein based and tannin based adhesives for the preparation of these boards, but they are not universal. Large market usage demands on the production efficiency of the boards, and a continuous press with a large capacity can be used instead of the powerful multi-stage press installation. In Europe, the panels industry has been working on the manufacture of particleboard for high-volume (4,000,000 m³/year) continuous press installation.



Figure 1.1. Pictures of particleboard(left) and medium density fiberboard(right)

Production of oriented strand board(OSB) and glulam is increasing in worldwide, especially in the United States and Europe. Their application is mainly as external and structural boards, and they can compete with plywood and laminated wood panels for such a market sector.. Usually, OSB and Glulam are bonded with high-performance adhesives, such as PF and/or PMDI for OSB, and PRF (Phenol-Resorcinol-Formaldehyde) or one component polyurethane resins for glulam. This also makes this type of boards with a higher price. The OSB manufacturing process is similar to that of particle board with electrically heated continuous presses. Glulam are produced in large single-stage presses and either not heated or heated by radiofrequency heating due to their large thickness.



Figure 1.2. Picture of oriented strand boards

In general, plywood is produced by a sequential process: rotary cutting veneers, veneers drying, applying the adhesive, assembling, and finally hot pressing. The production of it is difficult to automate, and its hot pressing efficiency is not satisfactory as for particle board. Moreover, even the most efficient equipment can only at a pressing time greater than 30 s/mm of panel thickness. Most plywood panels are used for semi-outdoor or outdoor use and are bonded with PF or MUF resins. The production of plywood is more oriented to special products with high added value as, for example, using a precious wood veneers with beautiful wood grain on the surface layer to produce “mimic” of expensive plates, thus a decorative role. Here too a lot of

research has been carried out trying to optimize the process and products to have:

- Low or no formaldehyde emission, especially for indoor products;
- Low thickness swelling in water for any outdoor application;
- Compliance with European standards of quality and environmental safety (ISO 29000 and ISO 14000)
- Fire retardant characteristics.

This can make plywood more efficient and competitive than those previously described.



Figure 1.3. Picture of plywood

1.2. Melamine-formaldehyde (MF) resins

Melamine formaldehyde resins are obtained by condensation polymerization of melamine and formaldehyde catalyzed by either an acid or a base. Their industrial production began in the early 1930s. The MF resin is white or transparent like a UF resin. Due to their adaptability, effectiveness and clear color, notwithstanding their high price, MF resins are also used for the production of decorative papers for board surfaces finishing.

MF resins have good bonding properties, as well as very good boiling water resistance (in newer formulations almost comparable to phenol formaldehyde resins). They cure fast even at lower temperatures, an additional advantage. Although the cured MF resins are hard and have good wear resistance, this hardness and brittleness makes it easy for them to crack and hence it does affect their service life.

1.2.1. Synthesis of melamine- formaldehyde resins.

Melamine and formaldehyde react in much the same way as urea and formaldehyde as shown in Figure 1.4, but here also with a few differences in the reaction mechanism. Compared to urea, melamine has a lower solubility in water, but

because of the very high reactivity of melamine with formaldehyde, the addition and condensation reactions are faster and more complex, and a hydrophobic condensation product is formed more quickly than urea. Unlike the polycondensation reaction of urea-formaldehyde resin, condensation of a MF resin can occur under alkaline, neutral and acid conditions, while for a urea-formaldehyde resin it is only carried out under acid conditions[10-13].

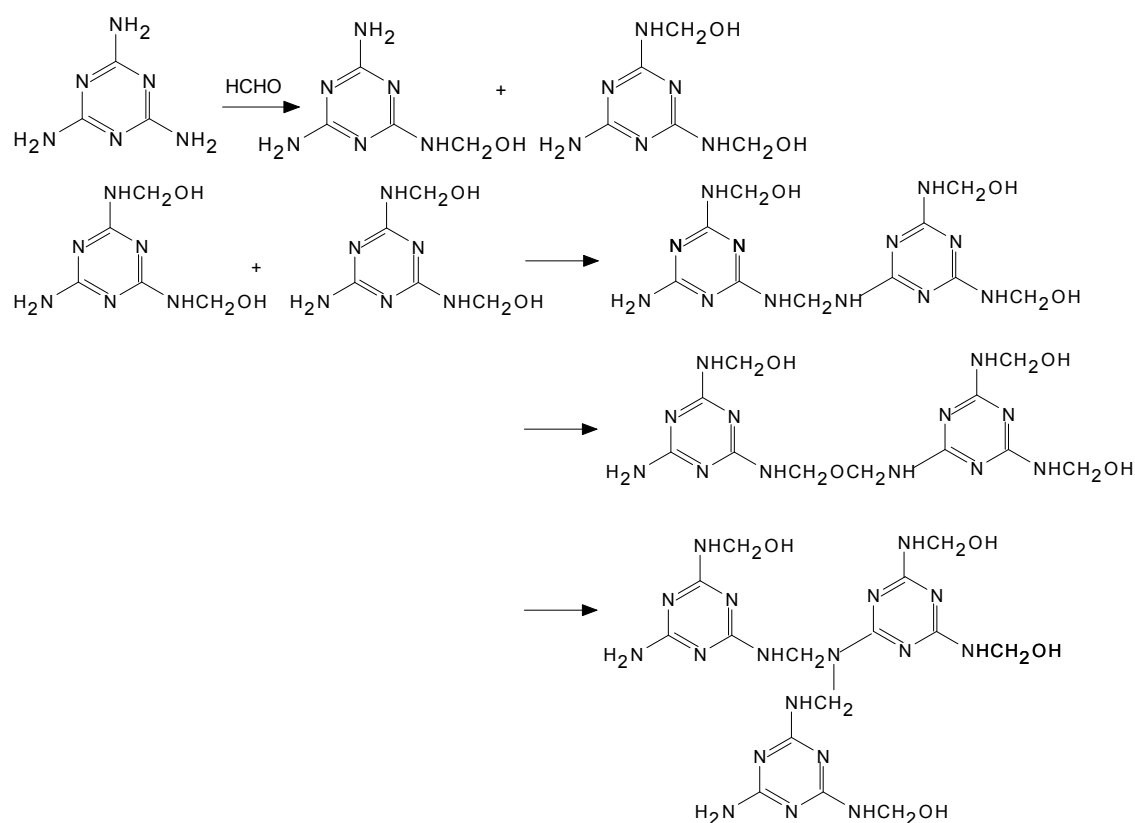


Figure 1.4. Synthesis reaction of an MF resin [10].

During their hardening MF resins do not produce as much formaldehyde as UF resin, so in MF resins there is a high proportion of residual methylene-ether bridges. Tomita and Ono (1979) [10] have proposed a theory on the kinetics of reactions between melamine and formaldehyde. They found that the initial F/M ratio has a great influence on the distribution of methylolated products: with an F/M ratio of less than 3, a mixture of monomethylol, dimethylol and trimethylol melamine had been obtained. But, if the F/M ratio is higher (10 or more), hexamethylol melamine be formed. The crosslinking reaction of the MF resins requires a minimum temperature of 65 ° C. In reality, MF resins can polymerize at lower temperatures by catalysis with a strong acid, but the bond is then very brittle and the shear strength of the panels bonded with it is also poor.

Furthermore, in the crosslinked structure of the MF resin, the melamine cores are

bonded to each other by methylene bridges or dimethylene-ether bridges. The proportions of these two types of bonds depend on the ratio of F/M molar ratio. A high ratio promotes the formation of dimethylene ether linkages as well as higher the degree of branching.

1.2.2. Synthesis of melamine- glyoxal(MG) resins.

Despite that the MF resins have a lower formaldehyde emission problem than UF resins, it is still inevitable that formaldehyde is used during their preparation and thus that emission occurs during the bonded products life, which is unacceptable as the formaldehyde is now classed as toxic and carcinogenic. Glyoxal is nontoxic (LD50 rat $\geq$ 2960 mg/kg; LD50 mouse $\geq$ 1280 mg/kg when compared to formaldehyde LD50 of 75 mg/kg) and non-volatile[14,15]. Because of advantages such as its mature production technology, low cost and easy biodegradation, G has been widely used as a green environmentally friendly additive in the papermaking and textile industries[16]. The non-volatile and non-toxic aldehyde glyoxal (G) was used to substitute formaldehyde to react with urea to synthesize Urea-glyoxal(UG) resins and its uses for textiles are well known[17], However, these are low condensation resins not adaptable for wood. Successful preparation of urea-formaldehyde-glyoxal resin by partial substitution of formaldehyde with glyoxal use for bonding plywood have been the subject of several articles that showed that such resins have a good performance[18]. The problem of these latter resins is that formaldehyde, although much less, is still there. The first important success in the bonding of plywood with absolute UG resins has been achieved, and some initial acid-catalytic reactions involved in the synthesis of the UG resin were theoretically investigated by quantum chemistry using density function theory[18,19]. Furthermore, as UG resins are slower curing than UF resins, ionic liquids were shown to even solve this drawback and to be the ideal hardeners for UG resins[20].

Because of the higher reactivity than urea, melamine was used to react with glyoxal to prepare melamine-glyoxal(MG) resin and use for particleboard[21]. It was found that surprisingly the MG resin did not gel at 100 ° C even in presence of a hardener(NH₄Cl), Even a fast hardener, namely chrome nitrate, when used still only yielded a poorer internal bond (IB) strength for the panels can be obtained. The best IB strength result is just 0.28 MPa, far below the minimum of 0.35 MPa required by relevant standards. Nonetheless, with ¹³CNMR and MALDI-TOF-MS analysis, the

reaction between melamine and glyoxal was confirmed and interpreted as:

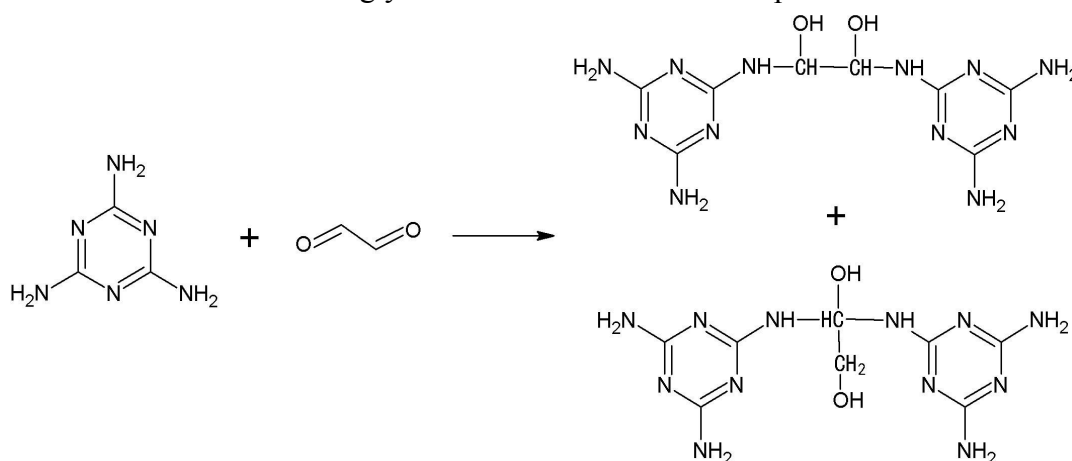


Figure 1.5. Reaction of melamine with glyoxal

Then, the further polycondensation reaction to obtain large molecular weight and branched structures as:

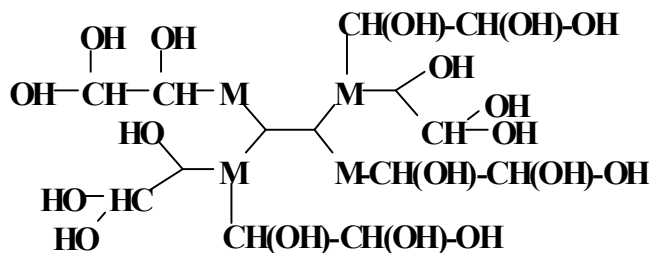


Figure 1.6. Branched structure reaction product of melamine with glyoxal(M is melamine)

1.3 Furfuryl alcohol

Furfuryl alcohol as an important biosourced chemical raw material, which is mainly used in producing furfural and furan resins. In addition, it is also widely used in industrial production of dyes, synthetic fibers, rubber, pesticides and casting. This chemical is usually obtained from hemicelluloses of different types from agricultural waste such as sawdust, wheat or corn and is therefore considered a natural product (Figure 1.7).

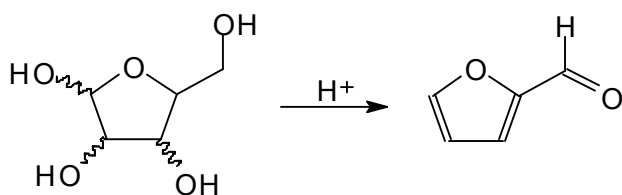


Figure 1.7: Examples of natural products for producing furfuryl alcohol: corn, oats and wheat.

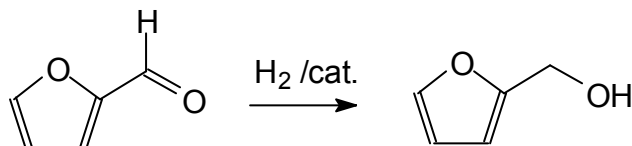
The furfuryl alcohol of agricultural origin is obtained mainly from two reactions:

- 1) Hydrolysis of pentosans of hemicelluloses.

Several processes and starting materials are described in the literature for the production of furfural [22,23].

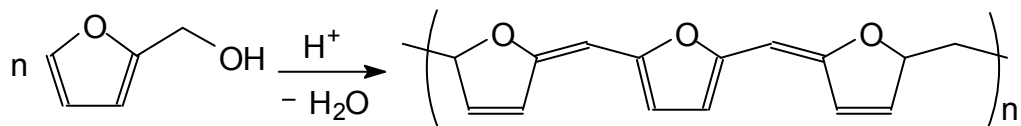


- 2) Catalytic hydrogenation at high pressure of furfural.



The catalysts generally consist of metals. Recent studies have shown the effectiveness of mixtures Co-Mo and B [24] and Cu-MgO [25].

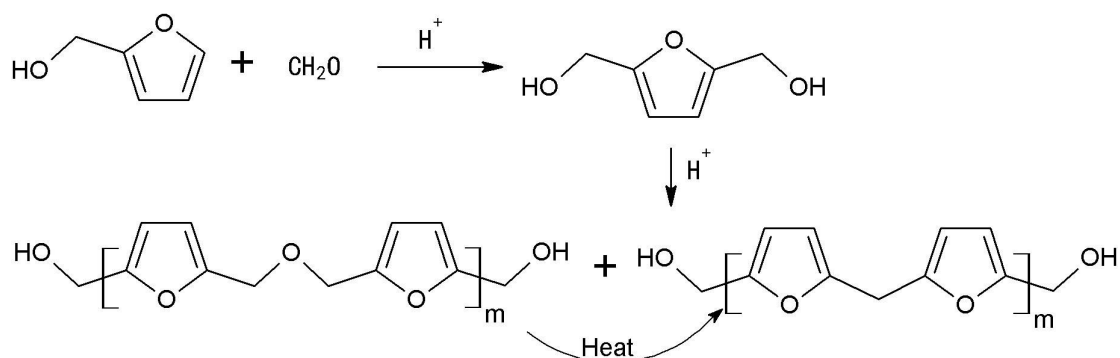
Furfuryl alcohol is well known for undergoing a very exothermic self-condensation reaction in an acid medium in the following way:



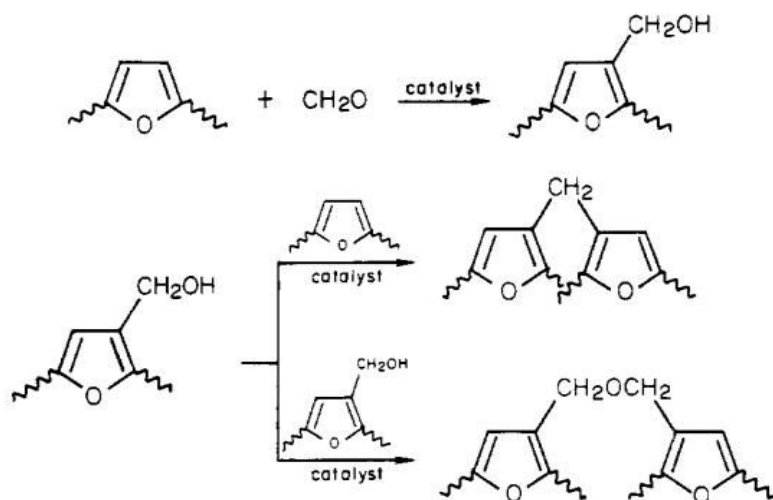
Under strong acidic conditions, the reaction proceeds violently and releases heat, so that the process becomes self-sustaining and all furfuryl alcohol is rapidly converted to poly-furfuryl alcohol, and cured.

Furfuryl alcohol can also be converted to 2,5-bis (hydroxymethyl) furan by reaction with formaldehyde to continue the polycondensation reaction to synthesize

furfuryl alcohol- formaldehyde resins[26]:



There is even research proposing that in the curing process with strong catalysts or at higher temperatures, formaldehyde can react at the 3,4 positions of the furan rings of the resin to form methylene or oxydimethylene bridges as follows[27]:

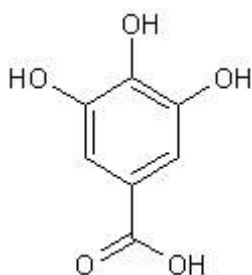


Furan polymers prepared in a solvent and in a nitrogen atmosphere was helped to analyze the mechanism of polymerization of furfuryl alcohol[28]. The polycondensation reaction yielded linear and branched polymers and even to three-dimensional structures according to the applied catalysis conditions applied. Many research works have been conducted on these materials to evaluate their resistance to heat and corrosion, and their strong non-flammable nature. Because of these characteristics, these products of are widely used in the foundry industry and in anti-corrosion metal painting. The furanic resins and phenol-furanic resins are known and used commercially, for example to bind foundry cores sand. However, furanic resins alone have not been used as wood adhesives, probably, among, others for their dark/black colour, not with standing the fact that they tend to have excellent water and weather resistance. Their main drawback, in the case of furfuryl alcohol, is the

necessity to have a very acid pH for curing. While this is acceptable for certain applications it is not suitable for wood adhesives, where too low a pH and too high a residual acidity would hydrolyse the holocellulose of wood at the interface. This would cause, eventually, interfacial failure of the bonded wood joint or panel.

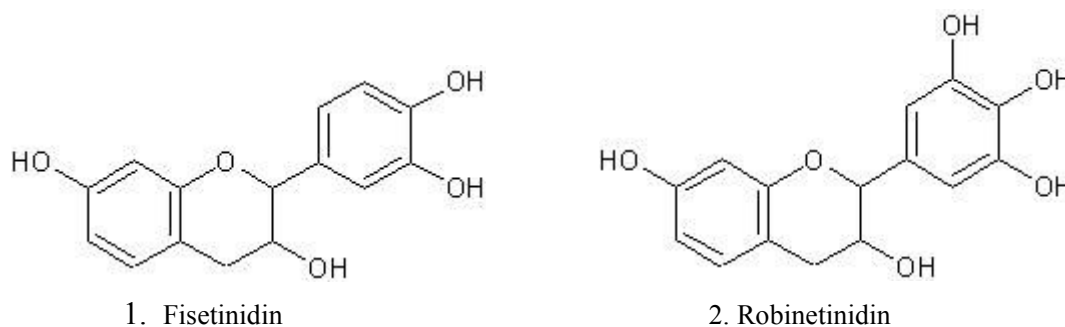
1.4 Tannins and tannin adhesives

Tannins are natural polyphenolic substances used by plants to protect themselves from insects and fungi. They are widely distributed in the plant kingdom [29], therefore they are considered as the fourth most abundant material of plant-based compounds, just after cellulose, hemicelluloses and lignins [30]. The chemical structure of tannins is very variable, but always presents polyphenolic moieties. From the point view of their chemical structure, there are two main classes of tannins: hydrolyzable tannins and condensed tannins. The hydrolyzable tannins consist of polyphenolic derivatives of gallic acid esters:



They have already been used as partial substitutes for phenol in the preparation of phenol formaldehyde resins [31,32], but this use is limited by their low reactivity with formaldehyde and other aldehydes.

Condensed tannins are made up of flavonoid units and are more than 90% of the world's commercial tannins production. They have proved to be much more interesting for the preparation of adhesives and resins due to their higher reactivity. In general, they always consist of a mixture of four types of linked flavonoid monomer units (Figure 1.8) in varying proportions.



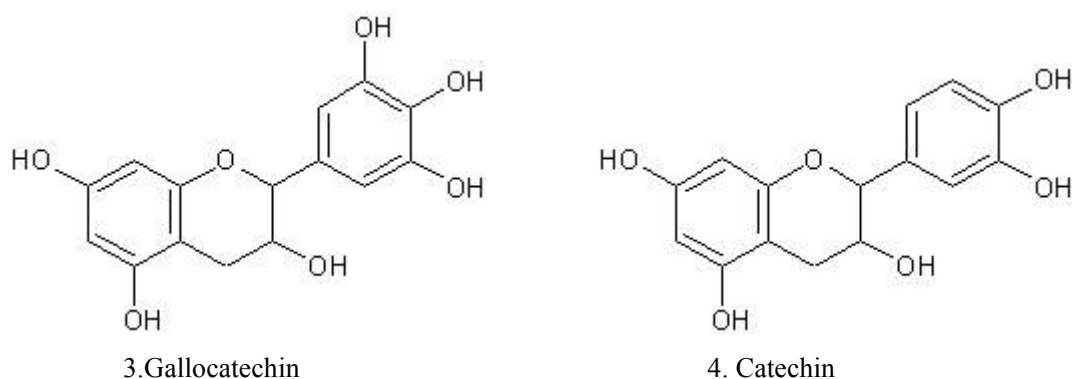
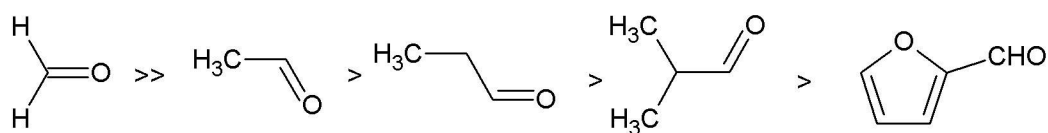
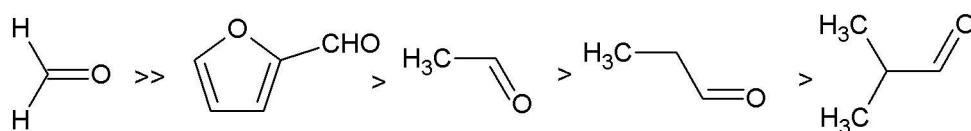


Figure 1.8 Four possible representations of mono flavonoid type structures [29]

These compositions in different proportions affect the viscosity and reactivity of tannins. A considerable amount of research work has been conducted on the application of these condensed tannins [33,34]. They are used in many industrial applications such as: wood adhesives or leather dyes and many others [29]. Since tannins are phenolic in nature, they can react in the same way as phenols and also react well with aldehydes. Notable differences were observed in the reaction rates of resorcinol and phloroglucinol tannins A-rings with various aldehydes. In the case of procyanidins, phloroglucinol A-rings tannins, the reaction rates with various aldehydes are thus classified [35]:



For resorcinol A-rings tannins, the reactivity scale is as follows:



1.5 Protein based adhesives

Protein-based adhesives are natural adhesives using substances containing proteinaceous as the main raw material. They can be distinguished as plant proteins and animal protein adhesives. At present, the most popular research is on soy protein adhesives, because of the abundant raw material reserves and its low prices. However, their poor water resistance and high viscosity (due to secondary forces within the protein chain and between different protein chains, as figure 1.9) still severely restricts their industrial applications. A lot of research work has been carried out to solve these problems.

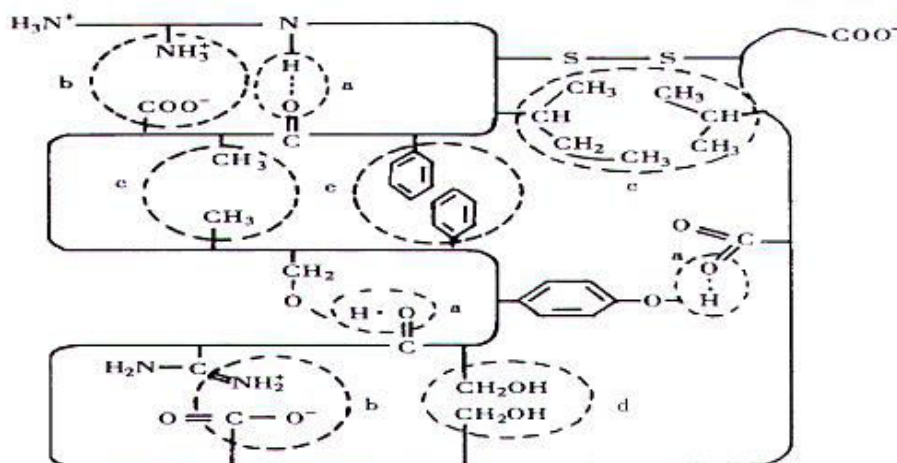


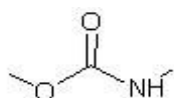
Figure1.9 Chemical bonds in soy protein

a. hydrogen bond; b. salt bond; c. hydrophobic bond; d. Van der waals force.

Generally, The preparation of soy protein adhesives is mainly done first through protein denaturation or hydrolysis under acid and alkali as catalyst, then by adding some modifiers or crosslinking agents to react with it. Soy protein is easy hydrolyzed into small molecules under acid conditions, resulting in unstable bonding properties of soy protein adhesives[36]. The performance of alkali-modified soy protein adhesive is relatively reproducible and presents the best bonding effect between pH 9 to 11[37,38]. Unfortunately, the performance of protein adhesives are not up to standard when soy protein only undergoes such a degradation treatment. Therefore, the application of some modifiers to improve the bonding performance has become a necessity. There are common cross-linking modifiers: epoxy resin, pMDI, synthetic resins (such as melamine-formaldehyde, melamine-urea-formaldehyde, phenol-formaldehyde, melamine-glyoxal), etc[39-50]. Graft modification has also been shown to be an effective method to improve the performance of protein adhesives, but the usual reaction conditions for it are very harsh. Thus, to prepare protein adhesives that do not use toxic substances such as formaldehyde, are moreover simple to prepare and also have good performance constitutes an important area of research.

1.6 Polyurethanes(PU) and non isocyanates polyurethanes(NIPU)

Polyurethanes are macromolecular polymers containing repeating urethane groups as follows:



They are obtained by polymerizing isocyanates and polyols. They have excellent performance as adhesives, such as chemical resistance and bonding properties. Their use has grown rapidly since their discovery in the 1930s. There are many types of polyurethane products such as semi-rigid and soft foams, and rigid plastic, coatings, adhesives, elastic fibers, etc. so that they are very widely used in industrial production and in daily life.

Polyurethanes can and have already been prepared for various potential applications from polyols of renewable materials, including materials such as tannin [51-54] and lignin [55-58]. However, polymeric isocyanates must always be used in the industry to prepare polyurethanes, even if they are associated with biosourced polyols. This has already been the case with oxypropylated flavonoid tannins [59,60], as with many other natural polyols. In order to solve this problem, non-isocyanate polyurethanes (NIPU) which did not use toxic isocyanate as a raw material have been developed and attracted much attention. Research on this topic has also become a hot topic. Research on chemical pathways for the preparation of non-isocyanate-based polyurethanes are already available [61], although these have recently involved vegetable oil-derived materials as renewable resources [62].

Even though polyurethanes can and have already been prepared for a number of possible applications using biobased polyols from renewable materials. However, polymeric isocyanates must always be used in the industry to prepare polyurethanes, even if they are associated with biosourced polyols. In order to solve this problem, a non-isocyanate polyurethane (NIPU) which did not use toxic isocyanate as raw material was developed and attracted much attention. Research on this topic has also become a hot topic.

Many research works are available on the different reaction routes for preparing non-isocyanate-based polyurethanes (NIPU). In general, oligomers terminated by five-membered cyclic carbonate groups are used, synthesized by catalyzing an epoxy group with carbon dioxide or by reacting dimethyl carbonate with an adjacent hydroxyl group, and then react it with diamines to form polyhydroxyurethanes, such as [63,64]:

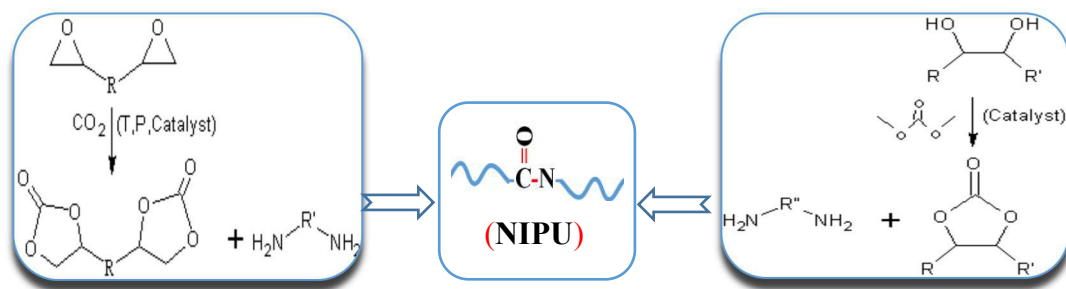


Figure1.10 NIPU Preparation Routes

Several works on this type of approach exist in the literature [65-81]. Some of the most interesting studies among them use biomass materials to prepare NIPUs by inserting an epoxy group on the molecule of the biomass material by reacting it with epichlorohydrin [82], as follow:

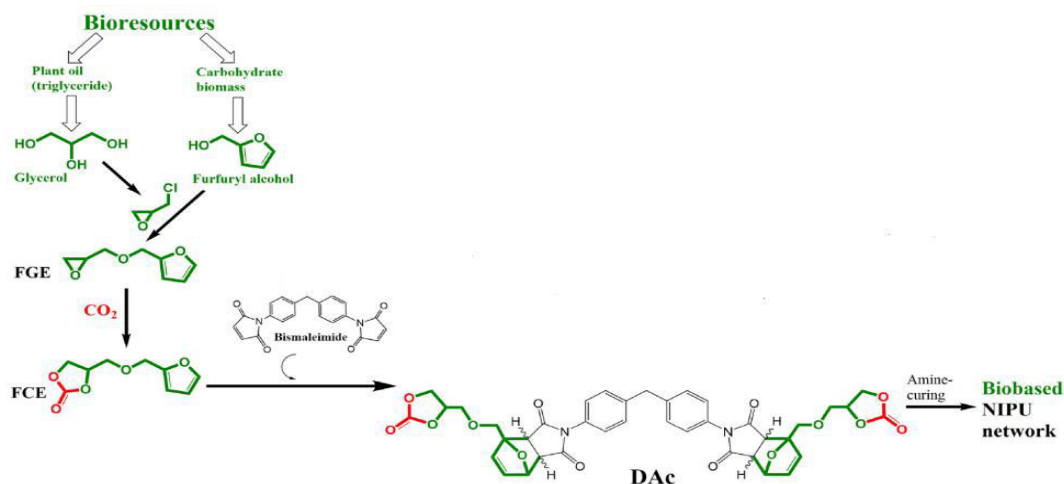


Figure1.11 Preparation of NIPU from biological resources

There is also an approach to form an epoxy functional group from a C = C bond in a biomass oil (soybean oil, rapeseed oil, etc.) by oxidation treatment. This is then reacted with carbon dioxide (with a catalyst) to form a cyclic carbonate, and finally reacted with the diamine to give NIPUs[83,84].

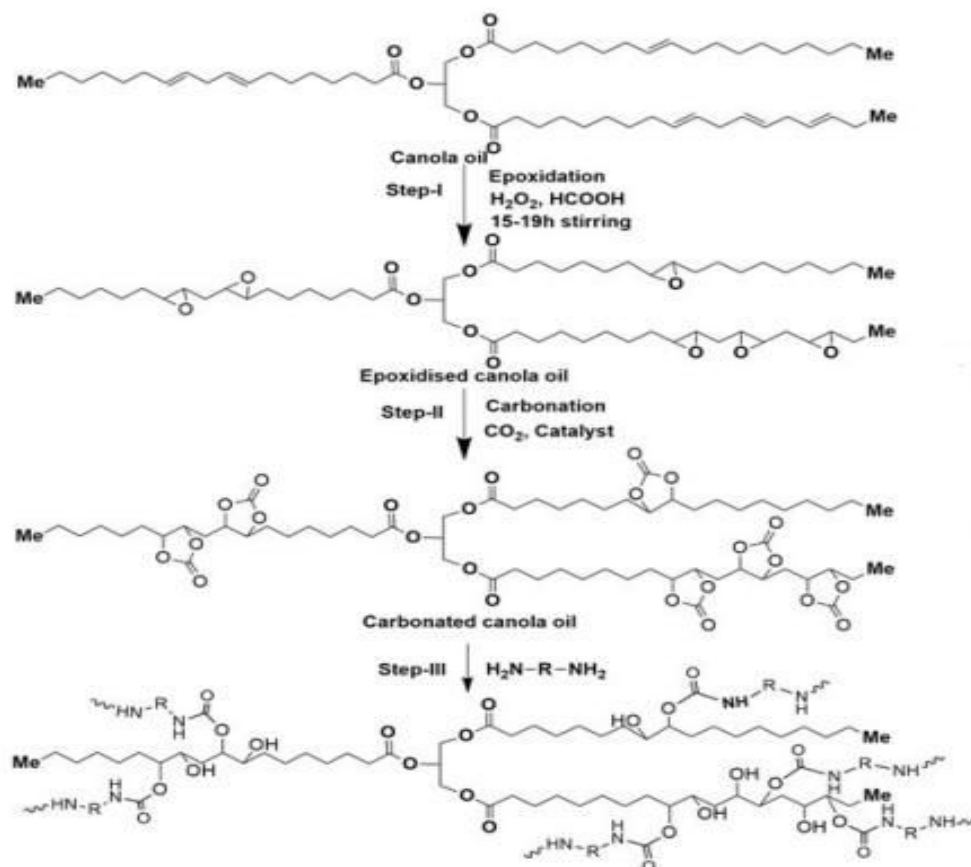


Figure1.12 Preparation of NIPU from canola oil

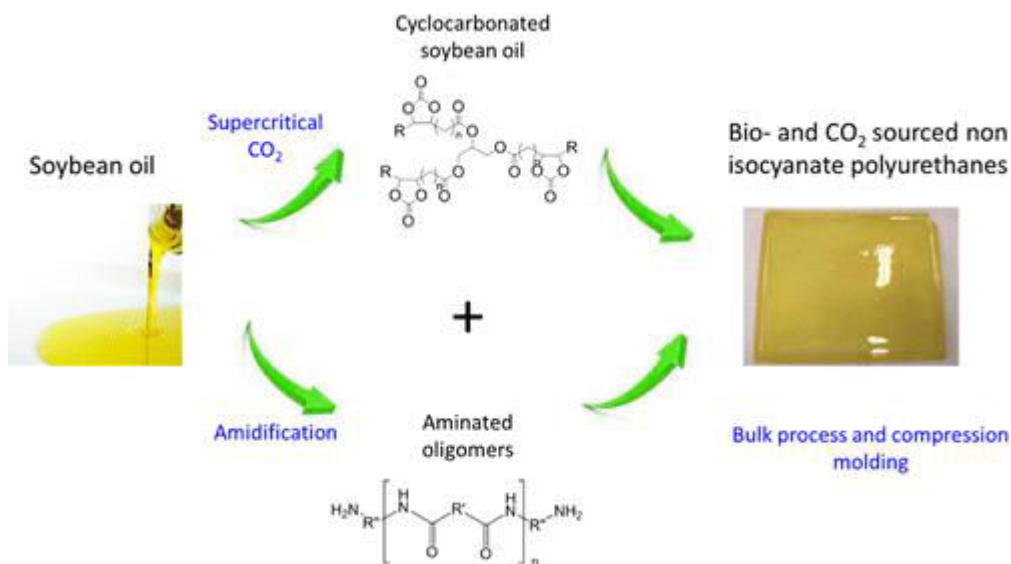


Figure1.13 Preparation of NIPU from soybean oil

Recently, research on the use of biomass to prepare NIPUs has intensified with work on their preparation from tannin or lignin-based preparation, which has shown interesting performance as surface coatings in wood or steel [85-88]. In addition, non-isocyanate polyurethanes from monosaccharides (glucose) and disaccharides

(sucrose) have been prepared and have been proven as surface coatings for wood and steel; as thermosetting wood panel adhesives [89,90], and even with initially encouraging first results as NIPU foams [91].

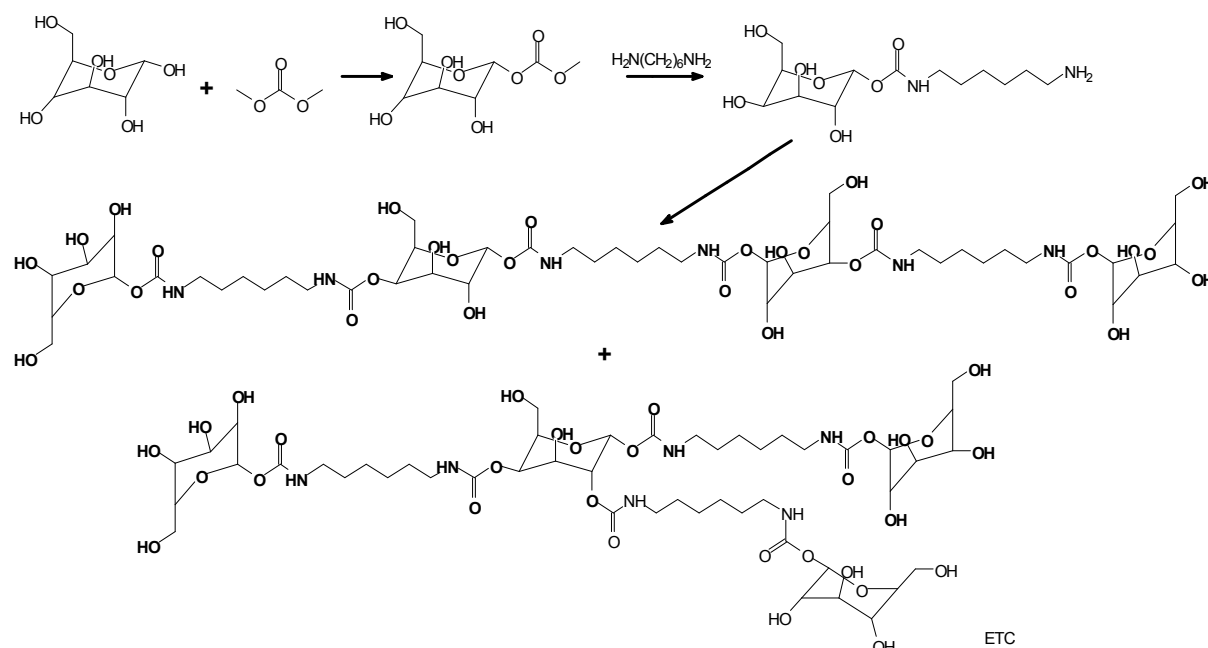


Figure1.14 NIPU preparation pathway based on glucose

1.7 Testing and analysis of adhesives or resins

1.7.1 Viscosity

The viscosity of the adhesive liquid affects its elongation and penetration on the wood surface, thus affecting the bonding properties of wood products prepared with it. Too high or too low viscosity of the adhesive will damage the bonding strength of it, therefore controlling a proper viscosity is important and necessary for the adhesive. The viscosity of adhesives are generally measured by using a rotational viscometer. The test liquid is placed in a beaker or straight cylindrical container with a diameter of not less than 70mm to accurately control the temperature of the liquid to be tested.

1.7.2 Solids content

The solid content of adhesive means the proportion of polymer with bonding ability in the liquid adhesives. The longer hot press time is needed to drain the solvent (usually water) for the adhesives with low solid content, which is unacceptable because it reduces production efficiency and consumes more energy. This is a reason for some synthetic resins (such as Urea-Formaldehyde resin) need to evaporate part of

water before its use.

The measurement of a resin solids content are carried out in accordance with the provisions of the national standard GB/T 14074-2006. The crucible is made of tin foil, the mass is weighed to M1, which is accurate to 0.0001 g; the sample is weighed to M2, and the mass of the sample is almost (1±0.1) g. To 0.0001 g; then, the sample is dried in a constant temperature oven at a temperature of (120 ± 1) °C for 2 hours. After taking the sample out of the oven, it is placed in a desiccator for at least 15 minutes, and immediately its weight is taken to be M, and the result must be accurate to 0.0001 g.

The solid content is then calculated according to the following formula:

$$\omega = \frac{M - M1}{M2} \times 100\%$$

Where: ω is the solid content, %;

M is the mass of the dry pot and the sample after drying, in grams;

M1 is the mass of the dry pot, in grams;

M2 is the mass of the sample before drying, in grams.

1.7.3 Thermal performance analysis

As a thermosetting synthetic resin or biomass-based wood adhesive, it's very important and meaningful to study their thermal properties. In the wood industry fields, commonly used thermal performance analysis are: Differential scanning calorimetry(DSC), Thermogravimetric analysis(TGA), thermomechanical analysis (TMA), Dynamic Mechanical Analysis (DMA). Here we introduce two thermal performance analyzers used in this research work, namely DSC and TMA.

Differential Scanning Calorimetry (DSC)

The principle of DSC is to quantitatively measure the heat absorbed or released of the sample by the detector during the temperature control of the program, thus to study the thermal change of the sample. DSC can be used to analyze glass transitions, melting and boiling points, crystation time and temperature, percent crystallinity, polymorphism, heats of fusion and reactions, specific heat, thermal stability, rate and degree of cure, reaction kinetics, purity of the tested materials. For the wood adhesives, DSC has been used extensively to study the curing process of thermoset adhesives[92-95], as it allows intuitively master the optimum curing temperature of the adhesives, and also quantitative measurement of the heat associated with the process. By this way, the activation energy (E) and reaction rate (k) of the curing process of the adhesives can be noticed. Thus the degree of cure of the adhesives can be clarified, as we all know it's one of the most important variables affecting the

properties of thermosetting resins. Thermosetting resins are crosslinked through the curing process then remarkably physical and mechanical properties changed, and the bonding strength of panels reflected.

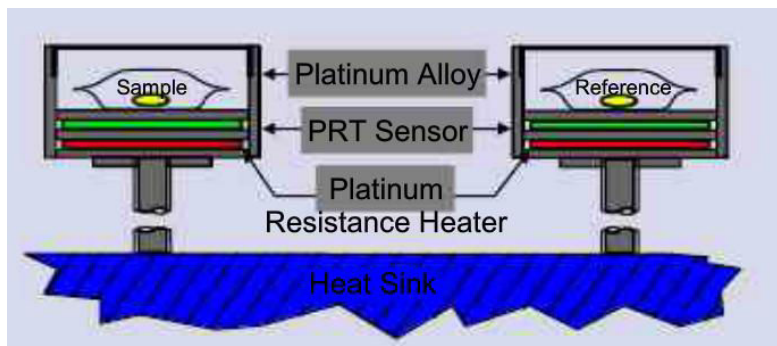


Figure1.15 Schematic diagram of DSC

Thermomechanical Analysis (TMA)

TMA is used to measure mechanical properties of the sample during the program control heating process. It's widely used to characterize materials and determine transition temperatures and thermal expansion coefficients[96]. For the wood adhesives, with two small pieces of veneers(such as figure1.16), TMA allows the calculation of the Young's modulus E for each case tested. Such a measuring system has been introduced and is used to follow the progressive hardening of the adhesive with the increase of temperature and to indicate comparatively if an adhesive system is faster or slower hardening and if it gives stronger joints than another one. This is recognized by the public and widely used in adhesives test analysis[97-101].

The classical mechanics relationship between force F and deflections f

$$E = [L^3/(4bh^3)][F/(f_{\text{wood}} - f_{\text{adhesive}})]$$

E-Young' s modulus

L- sample length(mm)

b- sample width(mm)

h- sample thickness(mm)

$\Delta f(f_{\text{wood}} - f_{\text{adhesive}})$ -difference between defined forces in the method(N)

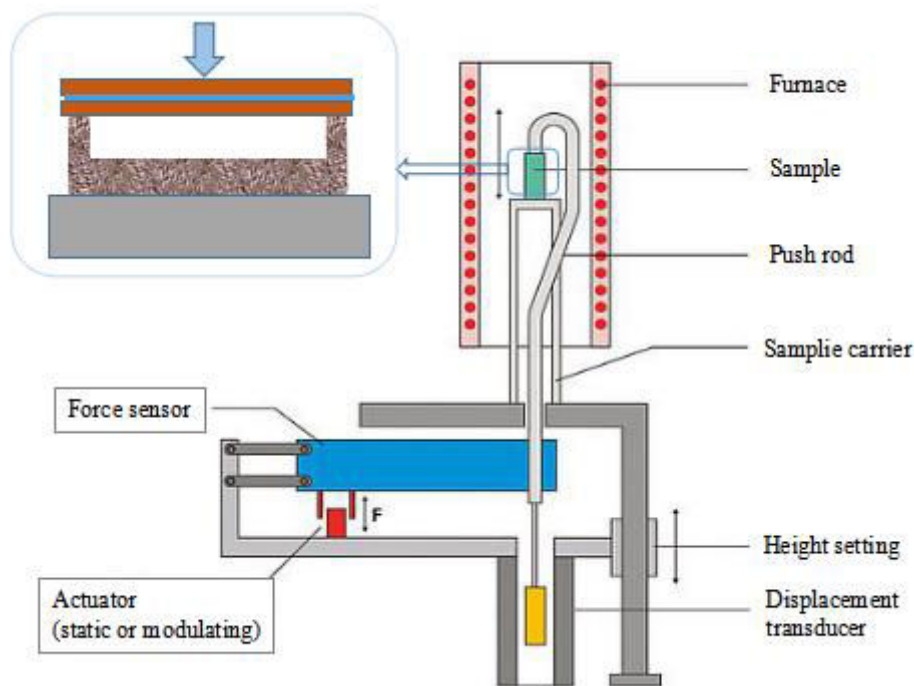


Figure 1.16 TMA operating principle

1.7.4 Structural analysis

Fourier Transform infrared spectroscopy (FTIR) analysis

Fourier transform infrared (FTIR) spectroscopy has a large application range, from the analysis of small molecules or molecular complexes to the analysis of cells or tissues. The design principle of Infrared or FTIR spectroscopy is based on the molecular vibrations, and infrared light energy is absorbed. And a very important point is different functional groups can be associated with characteristic infrared absorption bands, which correspond to the fundamental vibrations of the functional groups [102]. By this way we can probe the properties of chemical groups in the sample.

Normally, two main types of vibrations are observed in the FTIR test: vibrations along chemical bonds, called stretching vibrations, which involve bond-length changes; another is bending vibrations that involving changes in bond angles. These make the same chemical bond possibility with two different infrared absorption bands that are better help us to analyze and confirm the chemical groups.

For the analysis of wood adhesives, FTIR is a very common and effective method. By the presentation of the functional group in a special absorption band, it can be determined whether the reaction proceed, for example, in the preparation of urea-formaldehyde resin, a IR absorption peak at $1130\text{--}1150\text{ cm}^{-1}$ can be attributed -COO-stretching of aliphatic ether. This proves that the condensation reaction of the

methylol urea obtained by the addition reaction of urea with formaldehyde has occurred, and the ether bond be formed[103].

In addition, utilized in conjunction with other analytical techniques, such as MALDI, FTIR can aid in the determination of specific chemical structures[104].

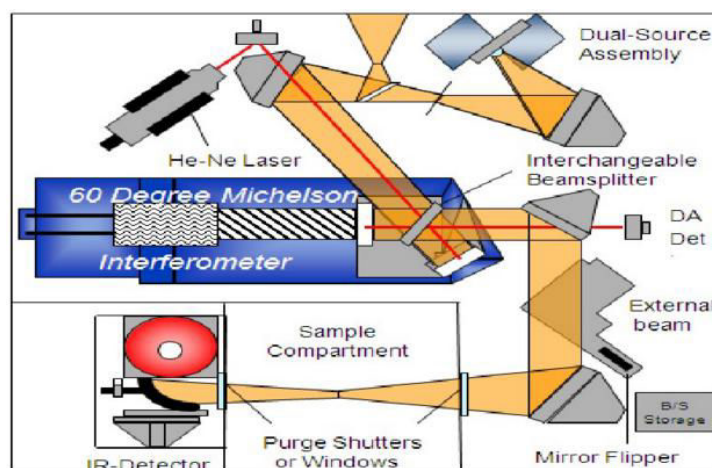


Figure 1.17 Schematic Diagram of an FTIR Spectrometer

Cross Polarisation-Magic Angle Spinning Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR) Spectra

Since Schaefer and Stejskal first reported high-resolution ^{13}C spectra of polymers in the glassy state in 1977[105], significant advances in the development of “highresolution” nuclear magnetic resonance(NMR) techniques for the characterization of molecular properties of solids have occurred, and among them the CP-MAS ^{13}C NMR is one of most rapid developed technique. so far, this spectroscopy has been extended into a diversity of chemical areas. For example, natural as well as synthetic polymers, resins, model membranes, coals, surface-bonded species, organometallics and other organic solids[105]. In the wood industry, it is not only used to analyze wood components such as cellulose[106], but also for chemical analysis of adhesives. Many reports about almost all adhesives including synthetic resins(such as Urea-Formaldehyde, Melamine-Urea-Formaldehyde, Phenolic-Formaldehyde) and natural materials(tannins, lignin,proteins, starch, etc.) based adhesives indicates the practicality of CP-MAS ^{13}C NMR[107-112]. Indeed, CP-MAS ^{13}C NMR technique has already become a common analytical method in the field of wood adhesives.

MALDI-TOF analysis

Since the MALDI TOF instrument first appeared in 1990s, in the past few decade matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

(MALDI-TOF-MS) has become one of the most powerful tools for the analysis of biomolecules[113]. However, MALDI-TOF mass spectrometric tools were not widely considered for routine applications in biological sciences at the beginning. Until Karas and Hillenkamp introduced it as a principle for analysis of large molecules at 1988[114].

MALDI-TOF MS is a “soft” ionization techniques, during the test, the sample is embedded in the crystalline structure of small organic compounds (matrix) and deposited on a conductive sample support plate. The cocrystals are irradiated with a nanosecond laser beam, The energies introduced are causes structural decomposition of the irradiated crystal and generates a particle cloud (the plume) from which ions are extracted by an electric field. Following acceleration through the electric field, the ions drift through a field-free path and finally reach the detector for testing. Based on the time of flight to the detector to detect the mass-to-charge ratio (M/Z). Fragmentation of analyte molecules upon laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result, intact analyte molecules are desorbed and ionized along with the matrix and can be analyzed in a mass spectrometer.

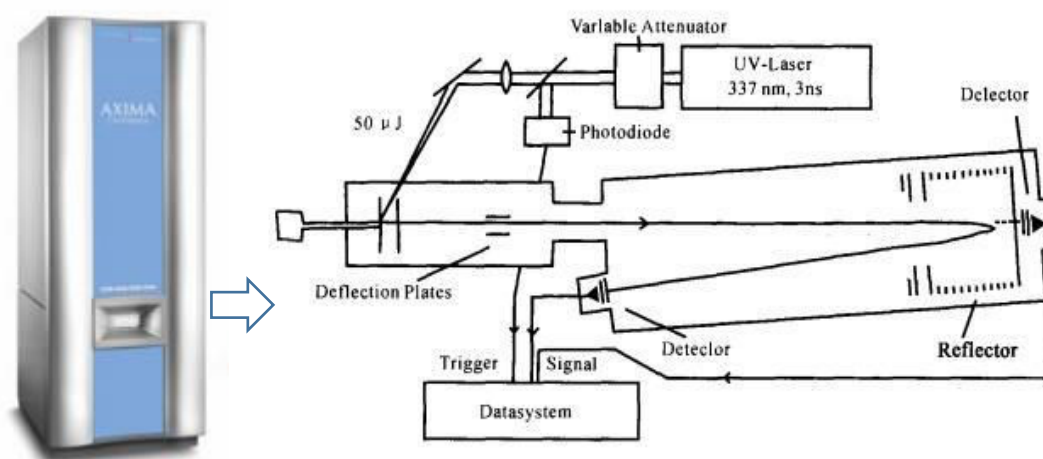


Figure 1.18. MALDI TOF instrument and the working principle

MALDI TOF has revealed itself to be a powerful method for the characterization of both synthetic and natural polymers[115]. MALDI TOF very common applied in wood adhesives, and the literature on this subject is really large enough today, so that too vast to be summarized here. However, it's convinced that MALDI is a reliable method for analyzing wood adhesives.

1.8 Preparation and testing of the panels

1.8.1 Particleboard

Panelboards are generally manufactured from wood particles bonded tightly

together using synthetic polymeric adhesives. The processing includes pressing under heat for sufficient time to allow the adhesive to bond the particle's material through the curing process. The chips are placed in a glue blender and sprayed with the resin for about 1 min to obtain a homogenized mixture. The resin solids loading in particleboard does to-day range between 8% and 12% that is why 10 % based on the dry wood particles weight was used in the laboratory usually.

Particleboard panels are produced to-day in Europe at a target density of 0.68-0.70 g/cm³. The physical properties, water absorption and thickness swelling (EN 317)[116]and mechanical properties, modulus of rupture (EN 310) [117], modulus of elasticity (EN 310)[117] and internal bond strength (EN 319)[118] must also be determined for the produced particleboards. In order to ensure the accuracy of the results, multiple specimens were used to determine the modulus of elasticity and modulus of rupture (MOR), and for the internal bond strength (IB), thickness swelling (TS), and water absorption, then average values were taken for each parameter in each case.

The internal bond (N/mm²) is given by this formula:

$$IB = \frac{F \max}{a \times b}$$

where: Fmax is the tensile strength (Newtons), a, b are the length and width of the sample (millimeter).

1.8.1 Plywood

Laboratory plywood panels are commonly used methods for detecting the performance of adhesives, and evaluated by their dry shear strength, wet shear strength to know the bonding performance and water resistance of the adhesives. Among them, Triplicate three-layer laboratory plywood panels are most favored preparation. The glue spread used was of 250-300 g/m² double glue line, and hot pressing time, temperature and pressure as variables. After hot pressing the plywood was stored under ambient conditions (20°C and 12% relative humidity) for 48 hours before testing according to China National Standard GB/T 14074 (2006) [115], China National Standard GB/T17657 (1999)[119], and European Norm EN 636:2012 (2012)[120].

The shearing strength test pieces were cutted as:

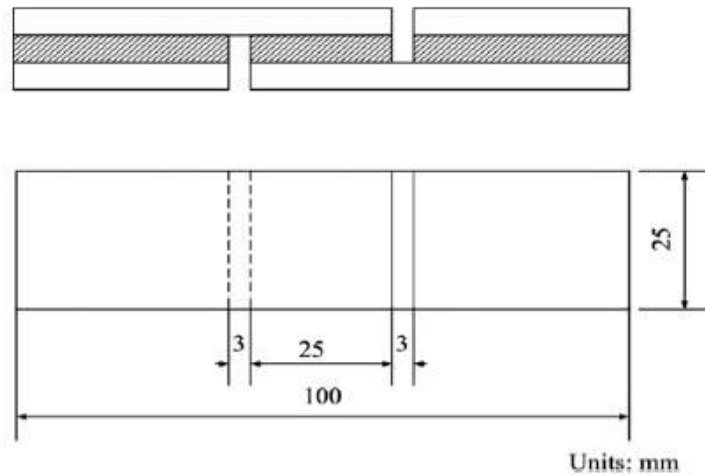


Figure1.19 Dimension of bonding strength test of plywood

The shearing strength (MPa) is given by formula:

$$\sigma = \frac{F_{\max}}{S}$$

where: $F_{\max}$ is the tensile strength (N), S is the bonding area (mm^2).

1.9 The foams and solid foams

Foams are complex materials gathering a lot of bubbles, which are consisting of the dispersion of a gas in a condensed medium[121]. The formation of foams is a process that is regularly observed when in particular gases are mechanically mixed in a liquid. It's worth emphasizing that pure liquids cannot form stable foams, such as pure water, ethanol, benzene, etc. The liquid can forms a stable foam at least with two or more components. Surfactant solutions, proteins, and other water-soluble polymer solutions tend to produce stable, long-lasting foams. Foaming solutions are not limited to aqueous solutions, and non-aqueous solutions also produce stable foams. Depending on the type of condensed medium, the foams may be liquid or solid[121].

Liquid foams are used frequently in daily life: surfactant foams, shaving cream, milk foam, cappuccino or beer are very relevant examples, it seems that foams are everywhere. Solid foams are harder to find in nature. In general, they are produced from the evolution of a gas in a high viscosity liquid medium and this liquid hardened as the gas escapes. There are many solid foams examples around us in everyday life such as bread, cakes as shown in the pictures.



Figure 1.20 Bread and cake solid foams

And also solid foams can be produced by curing a polymer. Latex mattresses, sofas and sports soles(Figure 1.21) made by polyurethane foam are examples of the importance of foams to our lives.



Figure 1.21 Daily applications of foams

Generally, The solid foam we are talking about is a low density foam materials characterized by their lightness and their "honeycomb" structures. In fact, according to the type of foam raw materials, foams can be divided into: organic foams (such as polyurethane, phenolic foams), metal foams, ceramic foams[122].

Foams can also be classified according to the type of cells. Open cell foams have cells that are highly interconnected by pores and their structure is therefore very permeable and light. Closed cell foams have a much higher resistance than the previous ones because the walls are not holed and therefore can withstand greater compressive forces[123]. In general, this type of foam is denser and therefore their price per cubic meter is higher.

Another classification of solid foams is based on physical properties, which can be classified as elastic foams and rigid foams. Elastic foams have the property of being deformable while returning to their original shape when the stress applied to them disappears. Among them, an interesting "memory" foams is a relatively new product and very popular, which has been used properly on the seat and seat back(Figure 1.22).



Figure1.22 Elastic foams for seat and seat back

Rigid foams, on the other hand, are materials that are not deformed and that find as main applications the thermal and acoustic insulation of buildings and insulation pipes. The best selling rigid foams are polyurethanes and phenolics.

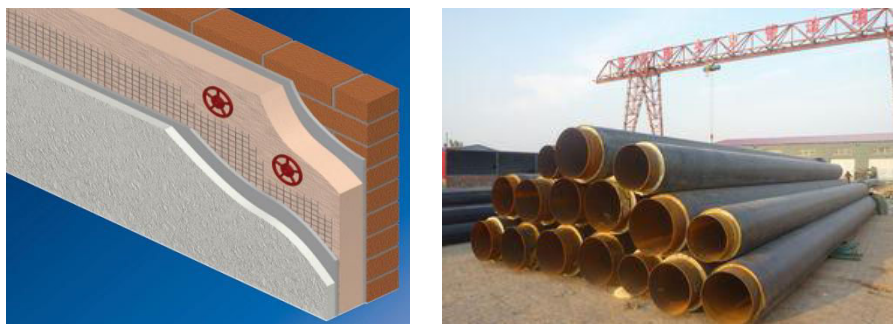


Figure 1.23 Commercial applications of rigid foams

However, toxic chemical materials isocyanates and phenols are required for the preparation of polyurethane foams and phenolic resin foams. Proper solutions that by finding their right alternatives is very necessary and meaningful. For phenolic foams, tannins are well known as a natural phenolic substance and are widely found in plants. So it is very straightforward and convenient mind to prepare phenolics foams by replacing phenol in whole or in part with tannins. Thus a lot of tannin foam research and production work has been going on.

For polyurethane foams, the formulation and preparation of non-isocyanate polyurethanes is an effective solution to the problem of toxic isocyanates being used.

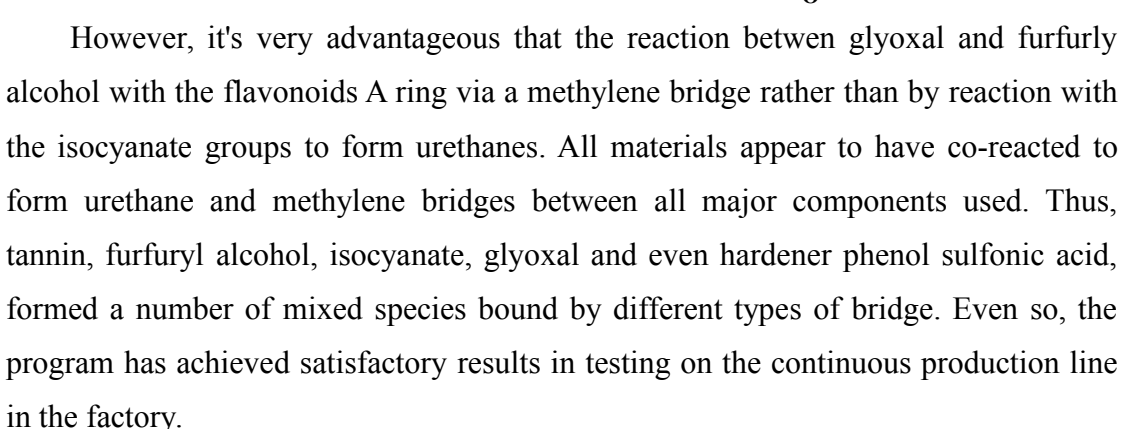
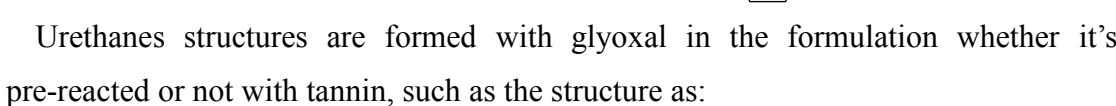
1.10 Tannin foams

In the case of rigid foams, many studies have been initiated to use natural products for wall insulation[124]. Among them, tannin rigid foam is the most advanced technological innovation in this field. The first records of tannin-based foams date from the early 1970s when a basic formulation was developed in South Africa ,but these foams had severe problems, until 1994, a public record of a formulation that appeared to work well.



Figure 1.24 Rigid tannin-based foam

Tannin foams have also many different developments as general rigid foam insulation. One is to imitate synthetic polyurethanes foams, so that try to react it with isocyanate by two main attempts way. The first is by reaction of benzylation or oxypropylation to obtain modified tannins, which are used as a polyol to react with a polymeric isocyanate for preparing the foams[125-128]. This is a universal approach that suitable to another natural polyphenol, lignin [129]. Second way uses a very different strategy based on the reaction of the tannin with the aldehyde and formed the hydroxymethyl(-CH₂OH) groups subsequent react with the isocyanate. According to this second approach, a mixed rigid foams of phenolic-polyurethanes type have been developed by using natural tanin and furfuryl-alcohol co-treated with polymeric isocyanate to form the polyurethane foams[130]. In this system, a variety of different copolymerization oligomers have been detected, as the complex reaction types. Urethanes appear to have been formed with two flavonoid tannin sites, mainly at the C3 flavonoid hydroxyl group, but also, although less, on the phenolic hydroxyl groups of the flavonoid oligomers.



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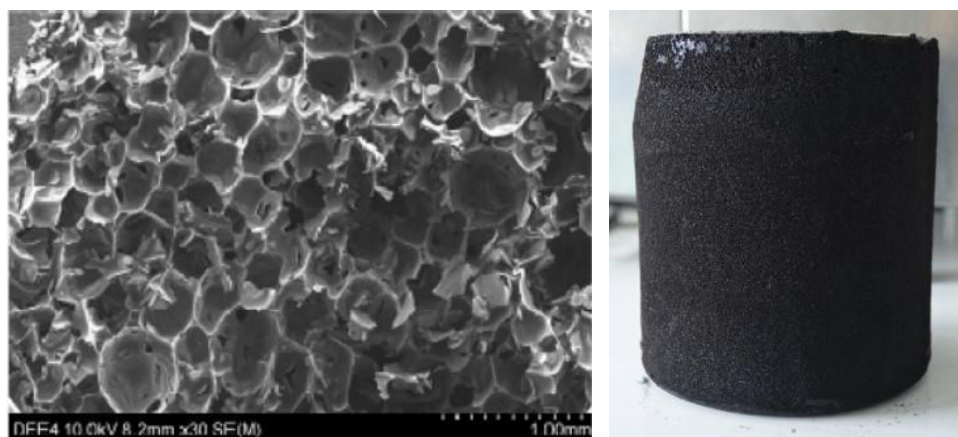


Figure 1.25 Scanning electron microscope image of the structure of a first-generation tannin-furanic foam (left) and macro-appearance of the same (right).

In order to improve and enhance these tannin foams, so far, much research has been conducted to them, formulating them without formaldehyde, organic solvent as swelling agent, furfuryl alcohol[132-134]. Also made it's possible by swelling in an alkaline condition and but only acid[135]. By copolymerizing tannin foaming system with synthetic resins or isocyanates, the shapes of the foams cells can be controlled[136,137]. Grafting on a small proportion of the tannin with the long hydrorepellant chains to improve their resistance to water[138]. More foaming methods have been studied such as heat-swelling, self-swelling or and simply inflated by mechanical agitation for use as projecting foams[139, 140]. In addition to rigid foams, flexible foams have also been developed [141-143].

A number of applications have been developed for these foams. Among others, open cell foams with very good acoustic insulation[144], carbonized foams for a large number of different applications[145], and also more recently for bone repair by osteogenesis with stem cells [146]. All of these shown a large extent beyond the limitations of foam as thermal insulation materials. The foams are used in a variety of ways, so many other applications can be envisioned also, and we believe that more applications will be developed in the future.

1.11 Non isocyanate polyurethanes foams

The first appearance of NIPU was in 1957 year, Dyer and Scott reported that reacted ethylene carbonate with primary diamine to get the bis(2-hydroxyethylcarbamate), then vacuum distilled it at 150 ° C in presence of

cerium oxide or zinc borate as a catalyst[147]. Even though at that time they were called polymeric urethanes, instead of non isocyanate polyurethanes, but truly, this is the original NIPU. Since then, a large number of researchers have explored NIPUs. Commonly, most of them focus on the application of NIPUs as coatings[148-161]. However, only some reports have tried the use of NIPUs as an adhesive[162-165]. Even more scarce is the use of NIPUs for foaming[166-168], for example the following figure from reference[167]:

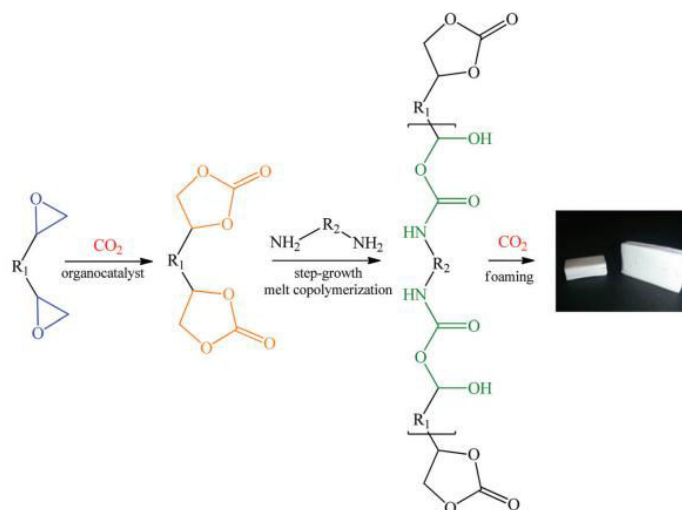


Figure 1.26 CO₂-blown microcellular non-isocyanate polyurethane (NIPU) foams

Therefore, the research and application of NIPU for foams is of particular interest. NIPU foams are, thus, a fairly new topic. Although some reports mentioned previously indicate that NIPU has successfully produced foams, this just remained at laboratory level. There appears to be little doubt that the research and production application of NIPU foams will have a future, especially environmentally friendly biomass-based NIPU foams. Therefore, in this research work, we will focus on the synthesis and foaming preparation of NIPU from biomass materials.

1.12 Objectives of this thesis

Melamine-formaldehyde and melamine-urea-formaldehyde resins and adhesives are widely used, particularly for impregnated paper surface coatings and for plywood or particleboard bonding. The problem of these resins is the presence of formaldehyde and its emission, this chemical being considered as toxic and possibly carcinogenic. In order to solve this problem, there are two approaches that can be taken, which are one of the main objectives for this thesis work.

The first one is to replace formaldehyde in some of formaldehyde based resins

with glyoxal. Because glyoxal is a non-volatile, non-toxic aldehyde, wood panel adhesives based on this aldehyde are nontoxic or of much decreased toxicity. Glyoxal-urea resins and glyoxal-melamine resins have already been developed but their rate of crosslinking is very slow to render impossible their use as wood panel adhesives under industrial conditions. The first task of the thesis was therefore to develop melamine-glyoxal resins (MG) and look for the correct hardener, for example, using ionic liquids that has been reported to have a good hardening effect on urea glyoxal(UG) resins. Then modify the MG resins to improve their performance and to use them as adhesives for plywood or particleboard.

The second objective of the thesis was the preparation of environment friendly adhesives based on biomass (for example sugars, tannins, proteins, etc.). The first task of this objective was to continue the modification of existing biomass adhesives and to improve their performance by addition of a crosslinking agent. The second task in this line was to prepare non-isocyanates polyurethanes (NIPU) from biomass materials. The main application of these NIPU resins was first for wood panels and particle board adhesives, and second for preparing suitable coatings adhering to metal iron surfaces or wood surfaces. Finally, the third task was to try to foam NIPUs to prepare non-isocyanate polyurethane rigid foams to replace polyurethane foams, which are very widely used nowadays. As the NIPUs forms are very new topic, especially based on biomass materials. At present, the research on foams of NIPUs are still at the laboratory level, and they are prepared under harsh conditions, such as organic solvents, pressurization, catalysts. In this work, a simple synthesis process will be used, and effective foaming methods will be probed also.

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3. PRESENTATION DES PUBLICATIONS

3.1 Adhésifs de mélamine-glyoxal-glutaraldéhyde sans formaldéhyde pour panneaux de bois

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Résumé: la résine mélamine-glyoxal-glutaraldéhyde pour le collage de panneaux de bois a été préparée en une seule étape, à savoir la réaction de la mélamine avec le glyoxal et simultanément avec une proportion beaucoup plus faible de glutaraldéhyde (résine MGG'). Aucun formaldéhyde n'a été ajouté. Le durcissement lent de cette résine a été surmonté par l'addition de liquide ionique "hydrogénosulfate de N-méthyl-2-pyrrolidone" dans le mélange de colle. Les résultats de résistance du contreplaqué obtenus étaient comparables à ceux obtenus avec des résines mélamine-formaldéhyde pressées dans les mêmes conditions. L'analyse avec MALDI/TOF (Matrix Assisted Laser Desorption Ionisation/Time Of Flight) et infrarouge à transformée de Fourier (FTIR) a permis d'identifier les principales espèces d'oligomères obtenues et les différents types de liaisons formées, ainsi que le rôle multifonctionnel du liquide ionique. Ces résines sont proposées comme substituant approprié aux résines base de formaldéhyde.

Mots clés: liquides ioniques; les résines de mélamine; adhésifs pour bois; contre-plaqué; rôle des liquides ioniques; MALDI-ToF; FTIR.



Article

Melamine–Glyoxal–Glutaraldehyde Wood Panel Adhesives without Formaldehyde

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Abstract: (MGG') resin adhesives for bonding wood panels were prepared by a single step procedure, namely reacting melamine with glyoxal and simultaneously with a much smaller proportion of glutaraldehyde. No formaldehyde was used. The inherent slow hardening of this resin was overcome by the addition of *N*-methyl-2-pyrrolidone hydrogen sulphate ionic liquid as the adhesive hardener in the glue mix. The plywood strength results obtained were comparable with those obtained with melamine–formaldehyde resins pressed under the same conditions. Matrix assisted laser desorption ionisation time of flight (MALDI ToF) and Fourier transform Infrared (FTIR) analysis allowed the identification of the main oligomer species obtained and of the different types of linkages formed, as well as to indicate the multifaceted role of the ionic liquid. These resins are proposed as a suitable substitute for equivalent formaldehyde-based resins.

Keywords: ionic liquids; melamine resins; wood adhesives; plywood; ionic liquids role; MALDI-ToF; FTIR

1. Introduction

Melamine–formaldehyde and melamine–urea–formaldehyde resins and adhesives are extensively used in particular for impregnated paper surface overlays and for plywood and particleboard panel binders [1]. The problem with these resins is now the presence of formaldehyde and its emission, as this chemical has been reclassified to carcinogenic category 1B and mutagen category 2 according to the “Classification, Labelling and Packaging of substances and mixtures” (CLP) of the EU Regulations.

Glyoxal has been chosen to substitute formaldehyde in some of these resins due to its capacity for giving clear adhesive resins and thus presenting the same appearance as UF-, MF- and MUF-bonded wood panels.

Glyoxal is nontoxic (LD50 rat ≥ 2960 mg/kg; LD50 mouse ≥ 1280 mg/kg when compared to formaldehyde's LD50 of 75 mg/kg) and non-volatile in the conditions in which formaldehyde is volatile when used in panels bonded with formaldehyde-based adhesives [2,3]. Because of advantages such as its mature production technology, low cost and easy biodegradation, glyoxal (G) has been widely used as a green environmental additive in the papermaking and textile industries [4]. In wood adhesive, it is mainly used to substitute formaldehyde (F) partially or totally, in applications as a crosslinking agent or curing agent in natural wood adhesives such as tannin-based adhesives [5,6], lignin-based adhesives [7] and protein-based adhesives [8]. While glyoxal is nontoxic and non-volatile it is also much less reactive than formaldehyde and the presence of two vicinal aldehyde groups partially, but only partially, offsets this drawback. Moreover, the literature about glyoxal-based resins application for wood adhesives and resins is rather scarce.

Recently, much work has been conducted to prepare and study the reaction mechanism and structure of environmentally friendly urea-based aminoresins by choosing glyoxal (G) to substitute formaldehyde (F) partially or totally so as to eliminate or markedly decrease formaldehyde (F) emission [9–12]. Urea–glyoxal (UG) and urea–glyoxal–formaldehyde (UGF) resins have been successfully synthesized and used as wood adhesive for plywood, interior decoration and furniture material [10,11] as well as for particleboard [12]. Equally, melamine–glyoxal resins have been formulated and while they were capable of yielding reasonable bond strength to satisfy relevant plywood standards, they did not yield internal bond (IB) strength results for particleboard to the level needed to satisfy relevant standards [13]. This was shown to be due to the energy of activation of cross-linking of the melamine–glyoxal (MG) resins being higher than formaldehyde–formaldehyde (MF) resins [13]. Acceptable gel times are obtainable only at temperatures higher than 150 °C, thus too high to be able to properly cure the resin in a particleboard core where the max temperature reached is of 110–120 °C. This rendered possible some applications such as MG resins impregnated paper surface overlays where the resin is in direct contact with the hot platen of the press at 180 °C but showed such resins limitations as binders for wood particleboard [13].

Ionic liquids are salts in the liquid state. In general, the term is restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C. They are salts in which the ions are poorly coordinated, this causing these solvents to be liquid below 100 °C. Ionic liquids are largely made of ions and short-lived ion pairs. Ionic liquids are becoming of considerable importance in many applied fields of technology [14–16]. The potential market of ionic liquids is large. Currently, ionic liquids have an estimated market value of 1.3 billion US dollars per year, mainly as replacement for traditional organic solvents in petrochemical and pharmaceutical industries [14]. Their market is expected to increase rapidly, this likely upsurge being attributed to the greener characteristics of these materials and good solubility in water and organic solvents [14].

Recently, the energy of activation of cross-linking of urea–glyoxal resins was effectively and markedly decreased by the use of ionic liquids (IL) as resin hardeners and additives [12,17]. This made it possible to obtain the same performance of UF resins by using UG + IL resins to even bond particleboard. The same approach has then been used in this article for melamine–glyoxal resins with the added variation of using a small proportion of glutaraldehyde (G') further condensed with the MG resin to yield a melamine–glyoxal–glutaraldehyde (MGG') adhesive presenting even better water resistance of the wood panels bonded with it.

2. Materials and Methods

2.1. Preparation of *N*-Methyl-2-Pyrrolidone Hydrogen Sulphate ([HNMP] [HSO₄⁻]) Ionic Liquid

[HNMP] [HSO₄⁻] ionic liquid was synthesized according to the method of Wang et al. [18]. 1.0 mol *N*-methyl pyrrolidone (LERMAB, Epinal, France) was weighed and placed into a 250 mL three-neck flask. Then 1.0 mol sulphuric acid (Carlo Erba, Milan, Italy) was added dropwise into the 250 mL three-neck flask with a dropping funnel under continuous mechanical stirring at room temperature. A considerable amount of white smoke appeared during the dropwise addition of acid. The mixture became a sticky, light yellow transparent liquid after stirring at 80 °C for 4 h. The resultant liquid *N*-methyl-2-pyrrolidone hydrogen sulphate ([HNMP] [HSO₄⁻]) was washed three times with ether and ethyl acetate, respectively, then it was dried under vacuum to remove the ether and ethyl acetate.

2.2. Preparation of MG and MGG' Resins

The MG resins were prepared at M/G molar ratio: 1:6, according to the method of Deng et al. [13]. Glyoxal (40% water solution, Sigma-Aldrich, St. Louis, MO, USA) was placed in the three-neck flask and the pH was adjusted to 4.5 using 33% NaOH. Subsequently, melamine was added, and the mixture was heated to 60 °C for 1 h. The reaction mixture was cooled to room temperature ready for use.

Under the same reaction conditions, different parts of glyoxal were substituted with glutaraldehyde (50% water solution, Sigma Aldrich, St. Louis, MO, USA) to prepare MGG' resins. The relative molar proportions of glyoxal to glutaraldehyde are shown in Tables 1 and 2.

Table 1. Proportions of melamine (M), glyoxal (G) and glutaraldehyde (G') used in the preparation of the MGG' resins.

Resin Type	Relative Mixing Molar Ratio Glyoxal:Glutaraldehyde	Melamine (g)	Glyoxal (40% Solution) (g)	Glutaraldehyde (50% Solution) (g)
MG	100:0	25.2	174	0
MGG'1	95:5	25.2	163.5	12
MGG'2	90:10	25.2	156.6	24
MGG'3	85:15	25.2	147.9	36
MGG'4	80:20	25.2	139.2	48
MGG'4	75:25	25.2	130.5	60

Table 2. Plywood results for melamine-glyoxal-glutaraldehyde (MGG') resins. MG resin of mole ratio M/G = 1:6, pH = 4.5, reacted at 60 °C for 1 h. Three layers plywood were prepared and tested for tensile shear strength. Ten per cent by weight [HNMP] [HSO₄⁻] ionic liquid was used as hardener.

Name of Resin	Relative Mixing Mole Ratio of Glyoxal:Glutaraldehyde	Solid Content /%	Viscosity/m Pa·s	Dry Shear Strength/ MPa	24 h Cold Water Shear Strength/ MPa	2 h Boiling Water Shear Strength/ MPa
MG	100:0	49	390	0.6	0.63	--
MGG'1	95:5	48.9	410	0.6	0.9	--
MGG'2	90:10	48.8	540	0.59	1.02	--
MGG'3	85:15	48.7	1720	0.76	1.39	0.45
MGG'4	80:20	48.5	2890	0.73	1.48	0.7
MGG'4	75:25	solidified in the reactor				

-- means the samples broke.

2.3. Fourier Transform Infrared Spectrometry (FTIR)

To confirm the presence of relevant structures, a Fourier Transform Infra Red (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrophotometer (Kyoto, Japan). A blank sample tablet of potassium bromide, ACS reagent from ACROS Organics (Acros Organics, Geel, Belgium), was prepared for the reference spectrum. A similar tablet was prepared by mixing potassium bromide with 5% *w/w* of the sample powders to be analyzed. The spectrum was obtained in transmission measurement by combining 32 scans with a resolution of 2.0 (Perkin-Elmer, Villebon, France).

2.4. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-ToF) Spectrometry

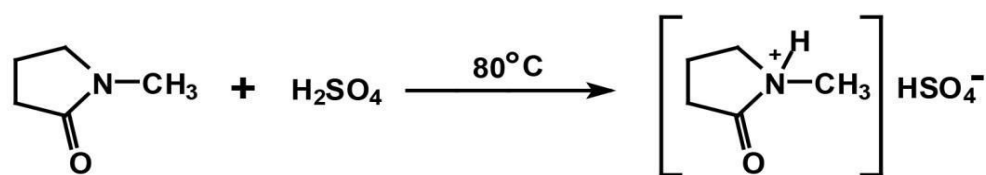
Samples for Matrix assisted laser desorption ionization time-of-flight (MALDI-ToF, AXIMA Performance, Shimadzu, Manchester, UK) analysis were prepared first dissolving 5 mg of sample powder in 1 mL of a 50:50 *v/v* acetone/water solution. Then 10 mg of this solution is added to 10 µL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 µL of a NaCl solution 0.1 M in 2:1 *v/v* methanol/water, and predried. Then 1 µL of the sample solution was placed on its dedicated location and the plaque is dried again. MALDI-ToF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were carried out making 1000 profiles per sample with two shots accumulated per profile. The spectrum precision is of +1 Da.

2.5. Plywood Preparation and Testing

The performance of the MGG' resins was tested by preparing laboratory plywood panels and evaluating their shear strength dry, after 24 h cold water soaking, and after 2 h in boiling water, tested wet. Triplicate three-ply laboratory plywood panels of 450 mm × 300 mm × 5 mm were prepared for each MGG' adhesive resin and 2 mm poplar (*Populus tremuloides*) veneers. To the glue mixes was added 10% by weight [HNMP] [HSO₄[−]] ionic liquid as hardener on total MGG' resin solids. The glue spread used was of 260 g/m² double glue line, and hot pressing time was of 6 min at 150 °C and 1.5 MPa pressure. After hot pressing, the plywood was stored under ambient conditions (20 °C and 12% moisture content) for 48 h before testing according to China National Standard GB/T 14074 (2006) [19] and China National Standard GB/T17657 (1999) [20] which require a minimum average shear strength of 0.7 MPa on five specimens tested, and European Norm EN 636:2012 (2012) [21].

3. Results and Discussion

The same principle of using an ionic liquid as a hardener that has been used for urea–glyoxal resins [12,17] was applied to melamine–glyoxal (MG) and melamine–glyoxal–glutaraldehyde (MGG') resins for which, *N*-methyl-2-pyrrolidone hydrogen sulphate ([HNMP] [HSO₄[−]]) was used as hardener. As this material is relatively expensive it was prepared in the laboratory according to the method of Wang et al. [15] and used with a minimum of purification [12,17] (Scheme 1).



Scheme 1. Preparation of *N*-methyl-2-pyrrolidone hydrogen sulphate ([HNMP] [HSO₄[−]])

The MG resin evolved into the MGG' resins given the better results that were obtained with such a combination. The double reaction, in two successive steps of melamine with glyoxal and glutaraldehyde has led to clear resin with no formaldehyde, each presenting distinct characteristics. These are shown in Table 1 which also reports the strength results of laboratory plywood panels prepared by using the different melamine–glyoxal–glutaraldehyde resins to which had been added 10% of [HNMP] HSO₄[−] ionic liquid. These satisfy the relevant requirements of international standards for both dry strength and strength after 24 h cold water soaking. In the two best cases they also satisfy the requirements for exterior grade bonds as their strength is still acceptable after the boiling water test.

3.1. Adhesives Bonding Performance

The first characteristic that can be noticed from Table 2 is that the proportion of glutaraldehyde increases the viscosity, and more interestingly the dry and wet tensile strengths increase up to a proportion of 20% molar of glutaraldehyde. A higher proportion nonetheless causes the viscosity to increase to such an extent that the resin solidifies in the reactor. Equally remarkable is the finding (Table 2) that the tensile strength increases after 24 h cold water soak. The effect is very marked and becomes more evident as the proportion of glutaraldehyde increases. At first it was thought that the water repellent $-(\text{CH}_2)_3-$ chain of glutaraldehyde caused the effect, but while this contributes to maintaining the dry strength once in water it does not justify the marked increase in strength noticed. It does however, contribute also to the resistance of the bond to boiling water as the bond performance improves as the relative proportion of glutaraldehyde increases.

Thermomechanical analysis experiments has shown that the hardening of the resin occurs in two phases (indicated with two arrows in Figure 1) a second increase in modulus occurring as the temperature, hence the curing time increases. This appeared to indicate that while the two aldehydes have been added simultaneously in the reactor, one is less reactive (glutaraldehyde) and had both

reacted with the melamine in the reactor, one of them was contributing to cross-linking earlier than the other aldehyde. Considering the difference in reactivity of the two aldehydes when the MGG' resins were prepared, this should indicate that a MG resin is formed on to which some glutaraldehyde is also eventually linked. Cross-linking then, will depend first from the more numerous, still reactive hydroxyethyl groups formed by the first addition of glyoxal onto melamine to form bridges. Second from the less reactive hydroxypentyl groups yielded by the grafting reaction of glutaraldehyde onto the MG resin. This would explain the two phases of hardening of the MGG' resin seen in Figure 1. To show that this was the case, matrix assisted laser desorption ionisation time of flight (MALDI-ToF) mass spectrometry analysis of different resins and intermediates was carried out. This presented several points of interest: (i) first of all the composition and oligomers distribution in the MG and in particular the MGG' resin; (ii) second, and of equal interest, was to find out what was the interaction of the ionic liquid with both the two aldehydes, with melamine, with the MGG' resin so as to finally deduce its mechanism of action.

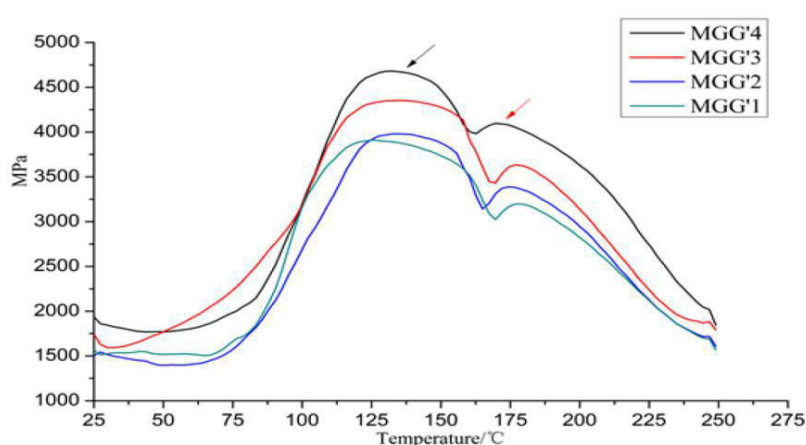


Figure 1. Thermomechanical analysis (TMA) curves showing the Modulus of Elasticity (MOE) as a function of temperature for the hardening of the MGG' adhesives from Tables 1 and 2.

Thermomechanical analysis curves of the MG resin hardening in respect of the hardening of the MG resin + 3% IL and MG resin + 5% IL (Figure 2) shows clearly the rise at a much lower temperature of the MOE of the IL catalysed resins indicating their much faster curing. This confirms the role of IL in lowering of the energy of activation of condensation and hardening of MG resins.

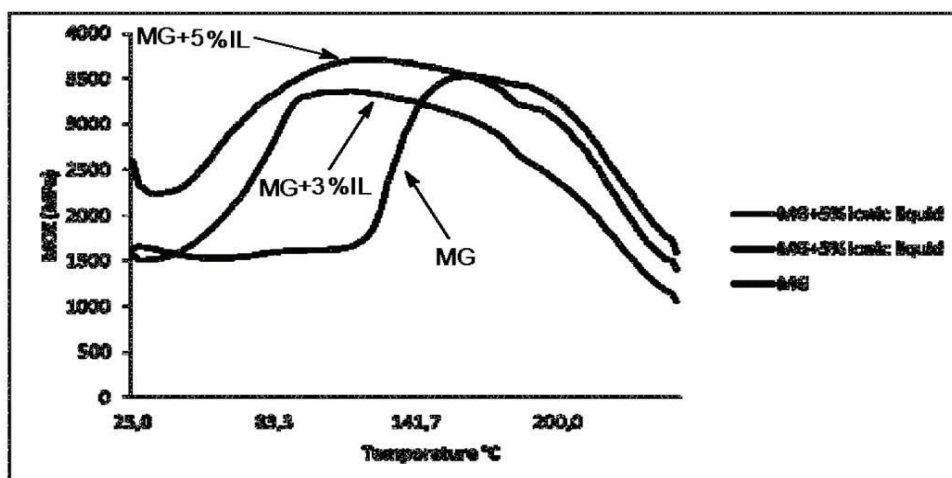


Figure 2. Comparative thermomechanical analysis curves of the rate of hardening of MG resins with and without addition of IL.

3.2. Analysis of Chemical Species Formed in the Reactions Analysed by MALDI-ToF Spectrometry

The MALDI-ToF of the two aldehydes first shown is for just the MALDI spectra of glyoxal and glutaraldehyde after reaction with the ionic liquid (Figures 3a,b and 4a–c). The species identified are shown in Tables 3 and 4. Two main trends are noticeable:

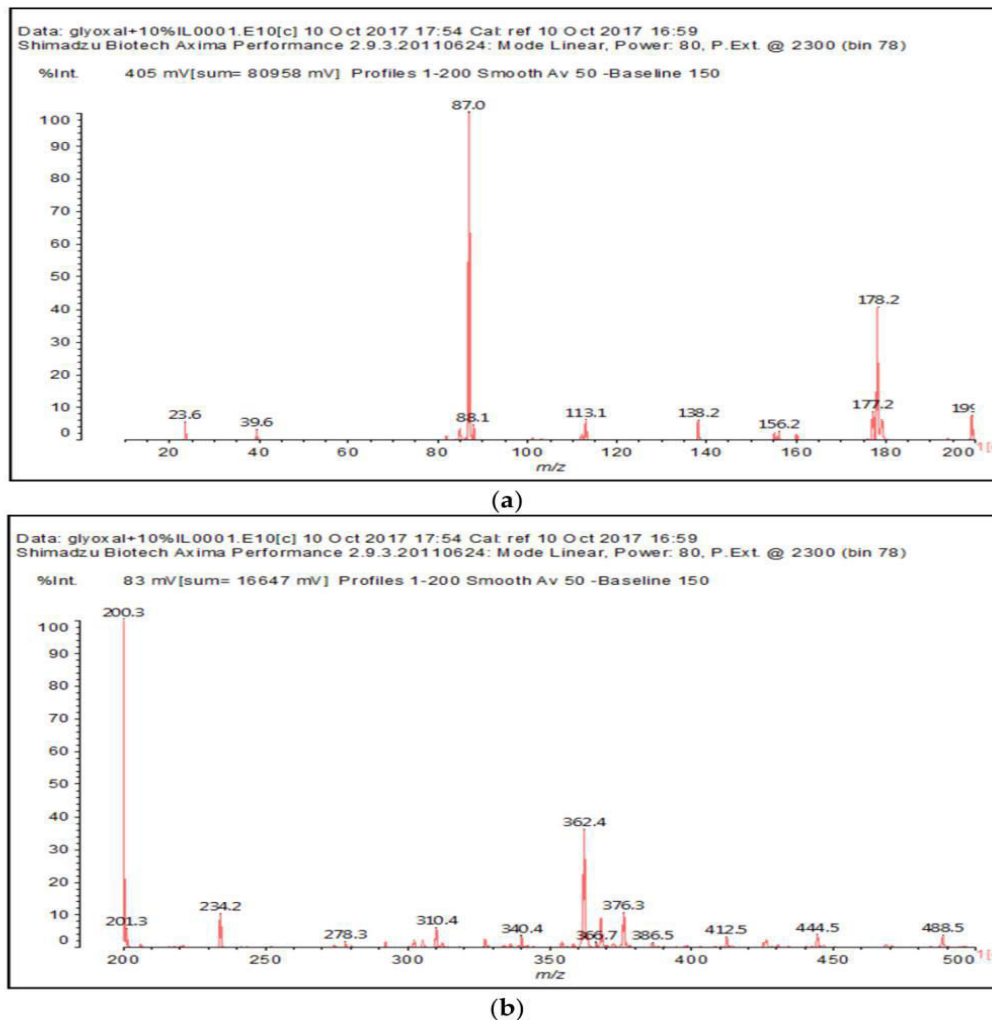
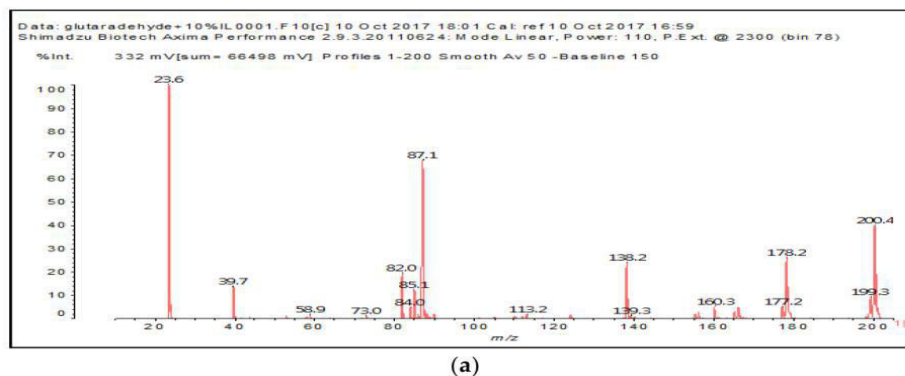


Figure 3. MALDI-ToF spectrum of the interaction between glyoxal and *N*-methyl-2-pyrrolydone hydrogen sulphate ([HNMP] HSO₄⁻) ionic liquid: (a) 20–200 Da range; (b) 200–500 Da range.



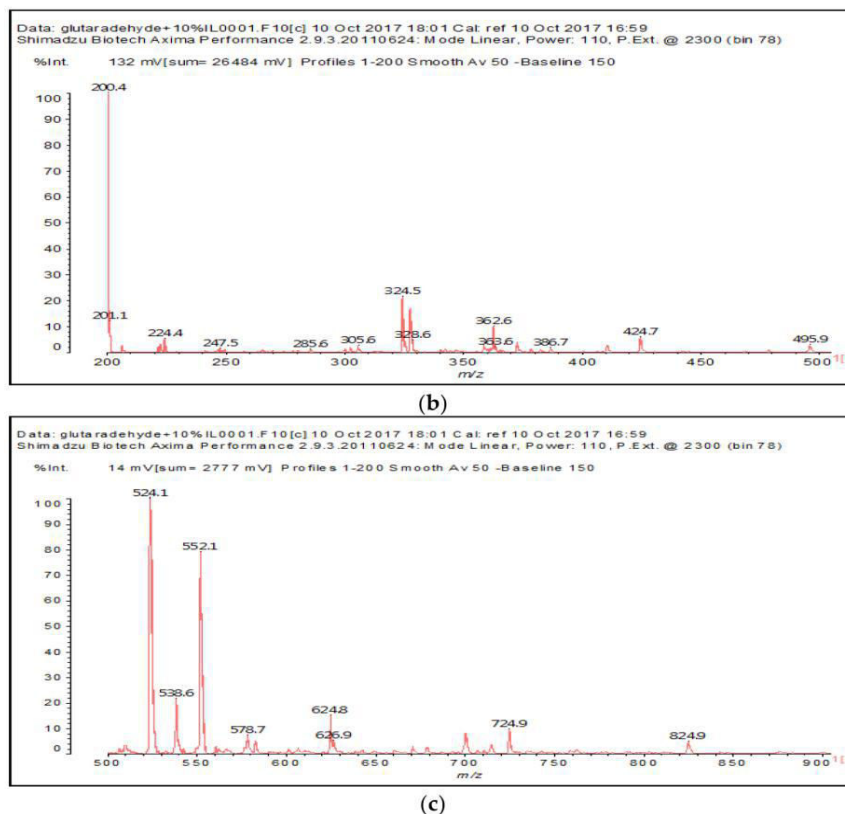


Figure 4. MALDI-ToF spectrum of the interaction between glutaraldehyde and *N*-methyl-2-pyrrolydone hydrogen sulphate ([HNMP] HSO₄[−]) ionic liquid: (a) 20–200 Da range. (b) 200–500 Da range. (c) 500–900 Da range.

Table 3. Species formed by the reaction of glyoxal with IL, by MALDI.

Peak	Chemical Species
199–200 Da = calculated 197 Da, proton = 198 Da	
138 Da = 140 Da, glyoxal dimer by aldol condensation	
By aldol condensation as:	
234 Da = 230 Da calculated, plus protonated, by aldol condensation, with Na ⁺	

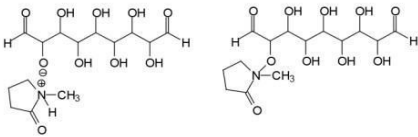
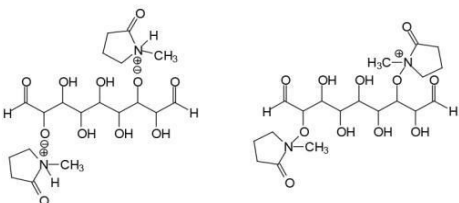
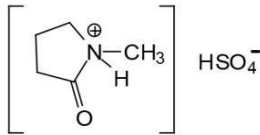
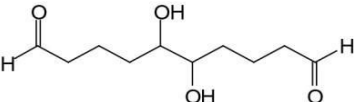
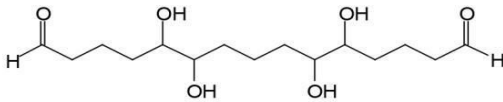
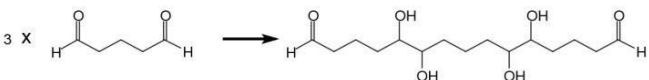
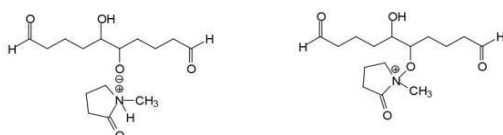
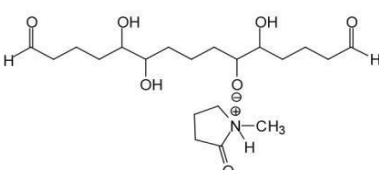
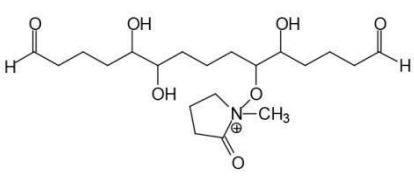
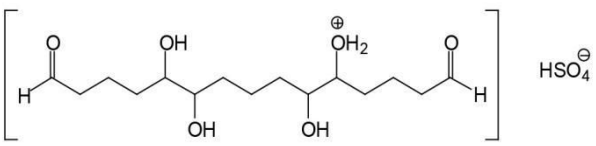
366–367 Da = 366 Da calculated, without Na ⁺	
387 Da = 366 Da + 23 Da = as above but with Na ⁺ 487–488 Da = with Na ⁺	

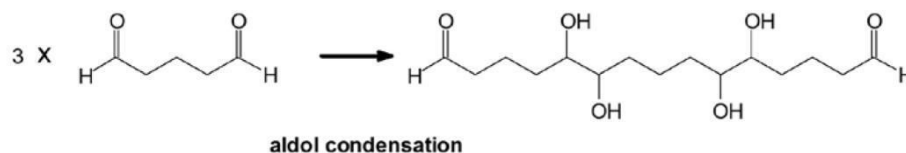
Table 4. Species formed by the reaction of glutaraldehyde with IL, by MALDI.

Peak	Chemical species
199–200 Da = calculated 197 Da, proton = 198 Da without Na ⁺	
222 Da = as 199–200 but with Na ⁺ , however it is also possible 224 Da = 225 Da calculated with Na ⁺ obtained by aldol condensation	
328.6 Da = 304 Da + 23 = 327 Da calculated, glutaraldehyde trimer by aldol condensation with Na ⁺	
by aldol condensation, thus as	
but also at 325 Da (observed 324 Da) thus more probable:	
as well as coupling with HSO ₄ [−] (see example of the 424 Da peak). 424 Da = 426 calculated, glutaraldehyde tetramer by aldol condensation with Na ⁺ but also	

and also	
but also protonated + HSO_4^- such as	
524 Da = glutaraldehyde pentamer by aldolcondensation, with Na^+ but also the alternatives as for the 424 Da peak	---
624 Da = glutaraldehyde hexamer by aldolcondensation, with Na^+ but also the alternatives as for the 424 Da peak	---
724 Da = glutaraldehyde heptamer by aldolcondensation, with Na^+ but also the alternatives as for the 424 Da peak	---

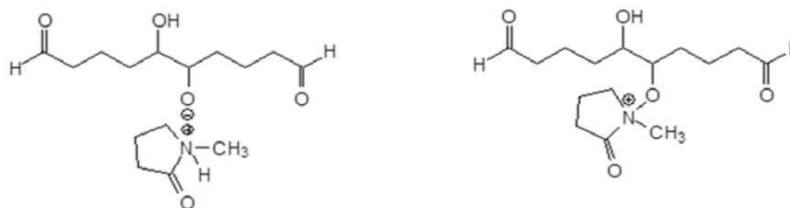
Two main trends are noticeable, as shown below.

1. Linear oligomerization of the aldehyde by aldol condensation, which indicates that IL has some catalytic effect on the autocondensation of the aldehyde (Scheme 2).



Scheme 2. Example of glutaraldehyde aldol condensation

2. Formation of complexes between the aldol-derived oligomers formed with either *N*-methyl pyrrolidone or HSO_4^- , or both (Scheme 3).



Scheme 3. Examples of complexes between aldol condensates and ionic liquid

Figure 5 and Table 5 show the MALDI-ToF of the interaction between melamine and the ionic liquid. Only three peaks could be interpreted, namely the melamine peak, the ionic liquid peak and that of a coordination compound between two ionic liquid molecules and one single melamine at 536–539 Da (Table 4). The rest are fragments either coming from impurities or fragments generated in the MALDI. It is clear that the melamine itself is not affected by the IL, although species like that of 536–539 Da could facilitate reaction with the aldehydes.

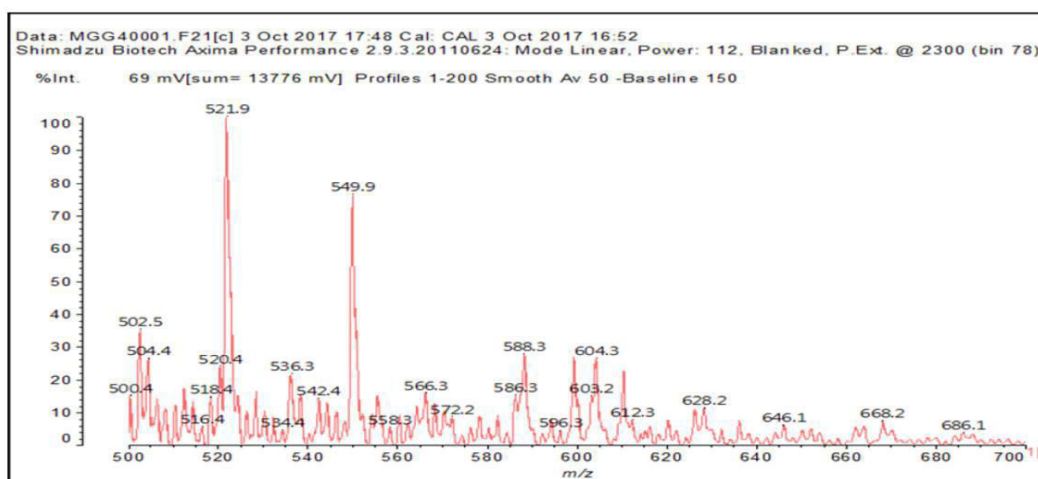
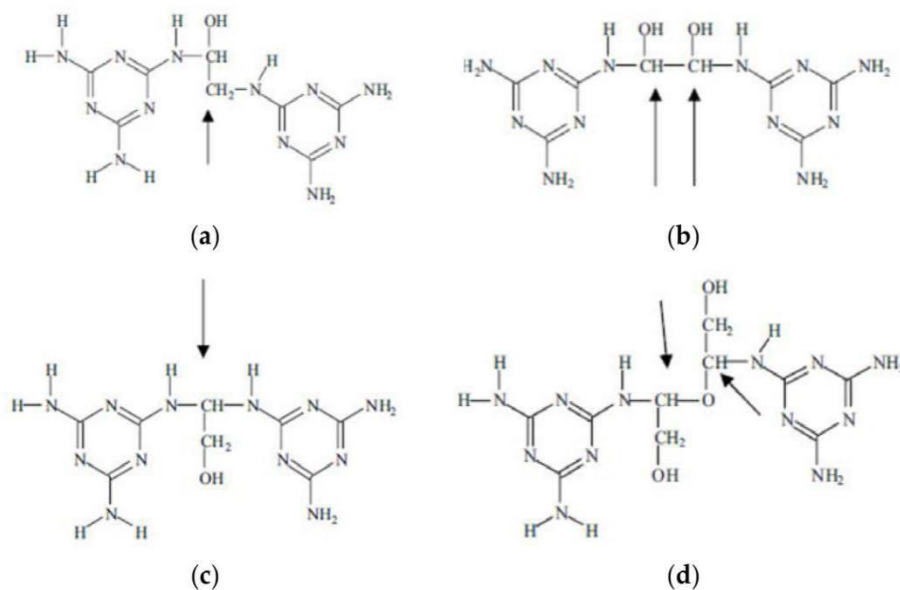


Figure 5. MALDI-ToF spectrum of the interaction between melamine and *N*-methyl-2-pyrrolydone hydrogen sulphate ([HNMP] HSO₄[−]) ionic liquid. 500–700 Da range.

Table 5. Species formed by reaction of IL with melamine alone. Only two peaks could be interpreted. The rest are fragments either coming from impurities or fragments generated in the MALDI. It is clear that the melamine itself is not affected by the IL, although species like the 538 Da could facilitate reaction with the aldehydes.

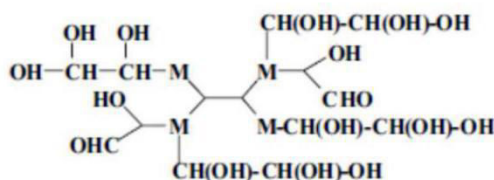
Peak	Chemical species
200 Da = [HNMP] HSO ₄ [−] , calculated 197 Da, + protonation.	
536–539 Da = 539 Da calculated (516 + Na ⁺ = 539)	

In the case of MG resins several types of glyoxal bridges have been shown to form and link melamine molecules [13], such as the following (Scheme 4).



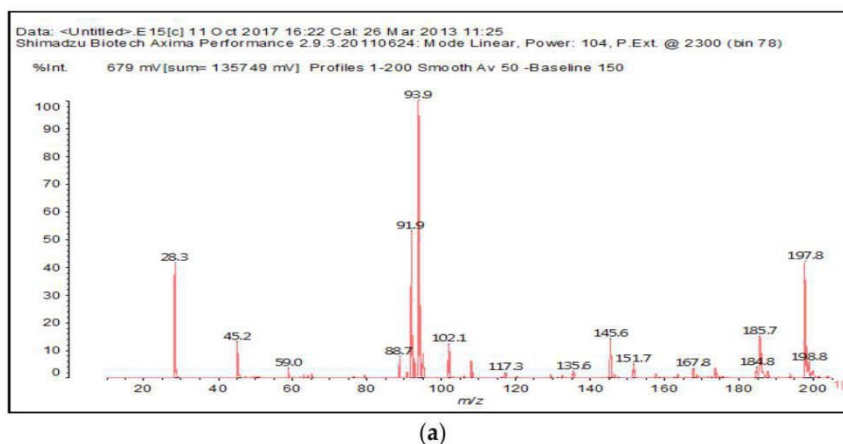
Scheme 4. Type of bridges formed in MG resins

They also form and link very branched resins of structure of the type below (Deng et al. 2017) (Scheme 5).



Scheme 5. Type of branched oligomers formed in MG resins

Table 6 and Figure 6a–c, show what occurs when the resin MGG' resin is formed when IL is added.



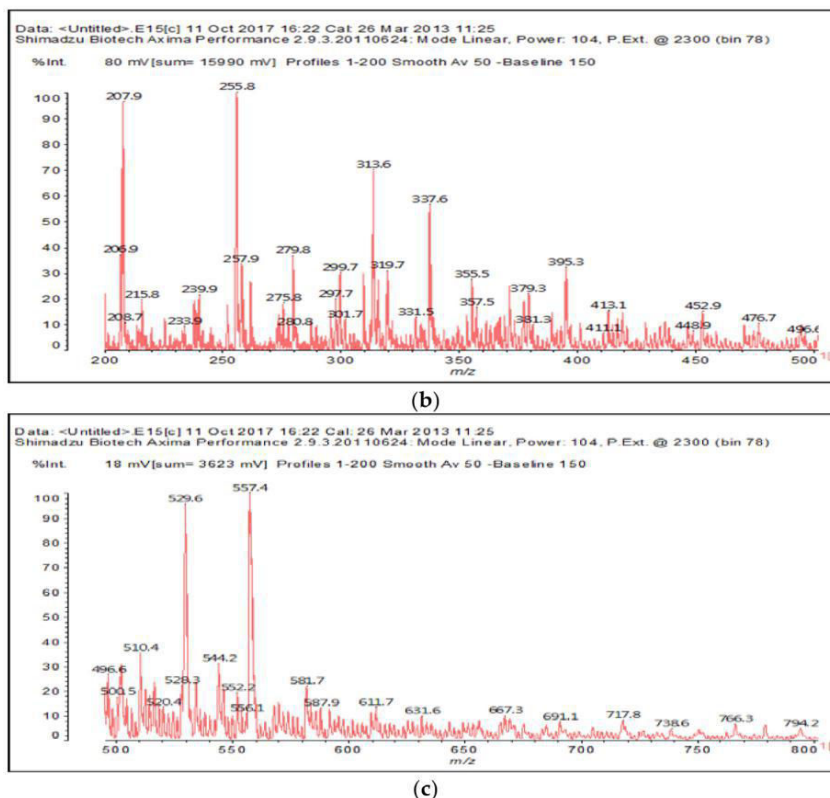


Figure 6. MALDI-ToF spectrum of the formation of the MGG' resin in the presence of *N*-methyl-2-pyrrolidone hydrogen sulphate ([HNMP] HSO_4^-) ionic liquid: (a) 20–200 Da range. (b) 200–500 Da range. (c) 500–800 Da range.

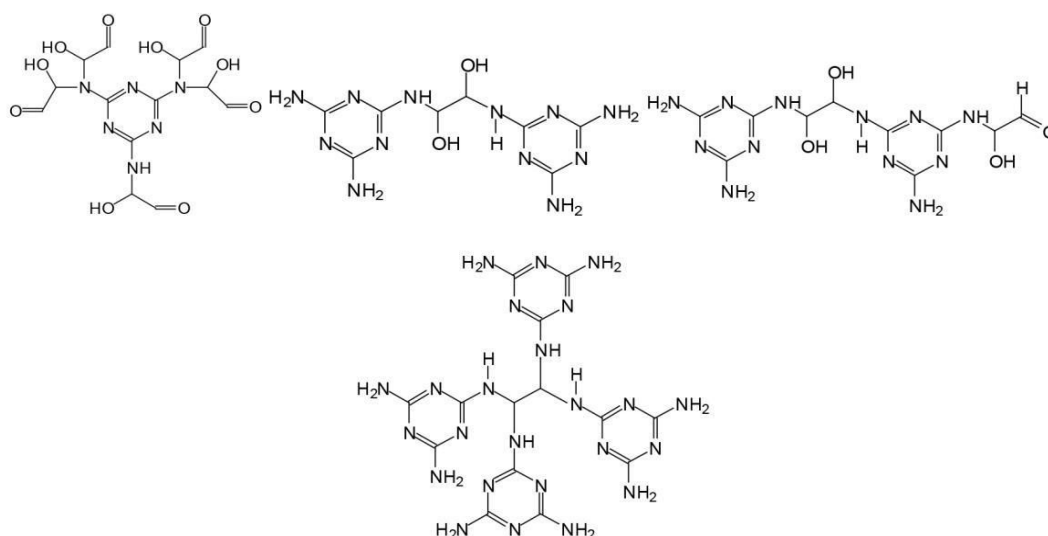
Table 6. Oligomers formed by the reaction of MGG' with and without IL.

Peak	Chemical species
149–151 Da = Melamine + 23 Da (Na^+) with and without IL	
159 Da = G + G' by aldol condensation with and without IL. Small with IL	
184–185 Da = $\text{M}(\text{Glyox})_1$ without Na^+ in MGG' with IL	
197.8 Da = [HNMP] HSO_4^- (only present in MGG' with IL)	
234 Da = aldol condensation of glyoxal + Na^+ exists only in MGG'+IL	
331.5 Da = 328.6 Da glutaraldehyde+IL by aldol condensation occurs but is relatively small in MGG'+IL	

But also $331.5 = 310 + \text{Na}^+$ (333 calculated deprotonated = 332) in MGG'+IL	
395 Da = 392 Da (369 + 23) calculated. MGG'+IL with Na^+	
439 Da = MG5 + Na^+ , present in only MGG'	
496 Da = 491 Da (with Na^+), probably multiprotonated, in MGG'+IL (= GMGMG')	
521 Da = 516/518 calculated = MG5G' without Na^+ or MG5G' without Na^+ of MGG'+IL 536–539 Da = MG5G' + Na^+	
557.4 Da = 558 Da calculated = MG4G2' of MGG'+IL without Na^+ 566 Da without Na^+ , in MGG' 581.7 Da = 581 calculated = MG4G2' with Na^+ in MGG'+IL 588 Da with Na^+ . 588 Da in both MGG' and MGG'+IL	

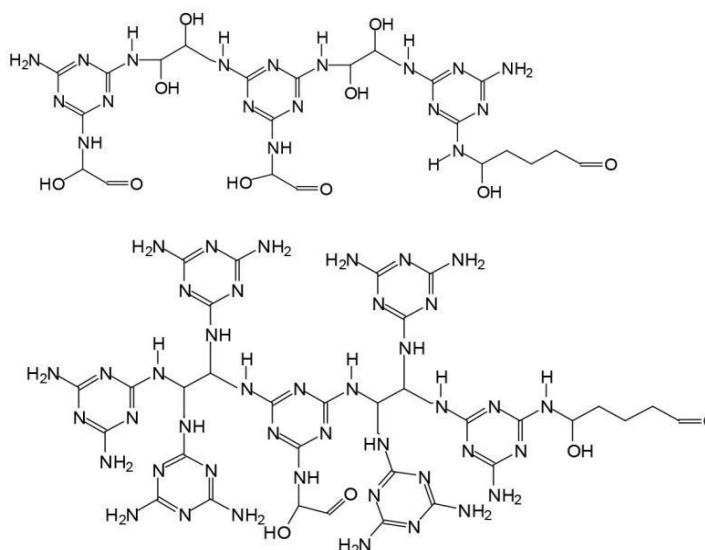
736–738 Da = 738 deprotonated, without Na ⁺ In both MGG' and MGG''+IL	
795–796 Da = without Na ⁺ in both MGG' and MGG'+IL	
993 Da = 992 Calculated + protonated with Na ⁺ , only in MGG'	
1010 Da = 1008 Da calculated + protonated, only in MGG'	
1169 Da = 1168 Da calculated, Without Na ⁺	

In the case of the IL being present aldol condensation of the aldehyde occurs and species in which melamine is linked to aldol condensed aldehydes occur. For both the resin MGG' with and without IL condensation oligomers of melamine–glyoxal and of melamine–glyoxal–glutaraldehyde are present. Thus species such as the following are the result (Scheme 6).



Scheme 6. Oligomers types formed in MG resins

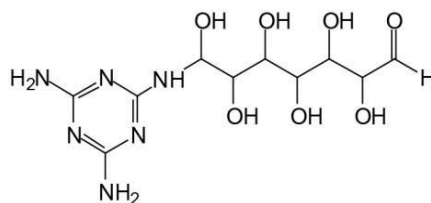
Due exclusively to the condensation of melamine and glyoxal these species are present together with species on which glutaraldehyde is definitely grafted on. Some of these are (Scheme 7):



Scheme 7. Oligomers formed in MGG' resins showing reaction of glutaraldehyde and glyoxal

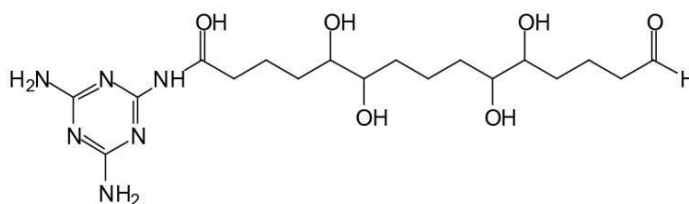
Where a glutaraldehyde is linked to a melamine of a MG resin skeleton.

Also species in which an aldehyde that has undergone aldol condensation has reacted and linked with the melamine are present in the MGG'+IL resins. For example the peak at 356–357 Da ($333 + 23$ Da of Na^+) in Figure 6 represent just one of these species issued by the aldol condensation of three glyoxals linked to a melamine molecule. Aldehydes react readily with melamine, but when a dialdehyde reacts after one of the two aldehyde groups has reacted and before the second one reacts aldol condensation can occur involving this second, still free aldehyde group. Thus either (i) the glyoxal units have condensed by aldol condensation for subsequently the residual aldehyde group to react with melamine; or (ii) one glyoxal molecule has reacted with melamine and the other glyoxals have then reacted on the residual aldehyde function by aldol condensation (Scheme 8).



Scheme 8. Reaction of a glyoxal aldol condensate on melamine.

This is not the only case occurring in the MGG' + IL resin case, as for example the 452–453 Da peak in Figure 6, this being a species formed by aldol condensation of three glutaraldehydes linked to a melamine (Scheme 9).



Scheme 9. Reaction of a glutaraldehyde aldol condensate on melamine.

3.3. Analysis of Reactions by Fourier Transform Infrared (FTIR) Spectrometry

FTIR analysis of the hardened MG and MGG' resins (Figure 7 and Table 7) shows all the main groups of the melamine and reacted glyoxal. These are listed in Table 6. The more interesting feature is the existence of the peak at 1234 cm^{-1} of C–O–C stretching. Its presence indicates that substituted methylene ether-like bridges (–CHR–O–CHR–) are formed in the case of MG resins just as they form in melamine–formaldehyde resins (MF, –CH₂–O–CH₂–). These substituted methylene ether-like bridges (–CHR–O–CHR–) clearly rearrange to substituted ethylene bridges (–CHR–CHR–) by the elimination of water as already shown in a previous study [13].

Table 7. FTIR spectra of hardened MG and MGG' resins.

Wavelength/ cm^{-1}	Group
812	triazine bending vibration
1074.3	C–O stretching vibration
1235	C–O–C (ether group) stretching vibration
1460.1	Methylene C–H bending vibration
1543	Triazine C=N bending vibration
1550.8	Triazine C=N bending vibration
1678	C=O(carbonyl) stretching vibration
1735.9	C=O(ketone) stretching vibration
2739	C–H stretching vibration
2962.7	C–H(aldehyde) stretching vibration
3100–3200	N–H, O–H stretching vibration

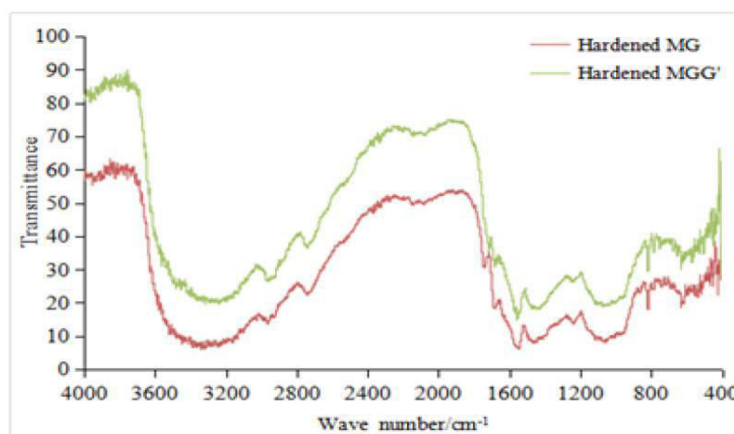


Figure 7. FT-IR spectra of hardened MG and MGG' resins.

In Figure 8 there is a comparison of the FTIR spectra of IL, MG+IL and MGG'+IL. Other than small peaks corresponding to the addition of the small amounts of IL the two resin spectra show the same peaks as shown in Figure 7. The probable presence of ethers in the structure is supported also by the existence of MALDI-ToF peaks such as those at 395 Da ($371 + 23 \text{ Da Na}^+$) and at 355 Da (without Na^+) and 379 Da (with Na^+) in Figure 6 which correspond to the two structures below (Scheme 10).

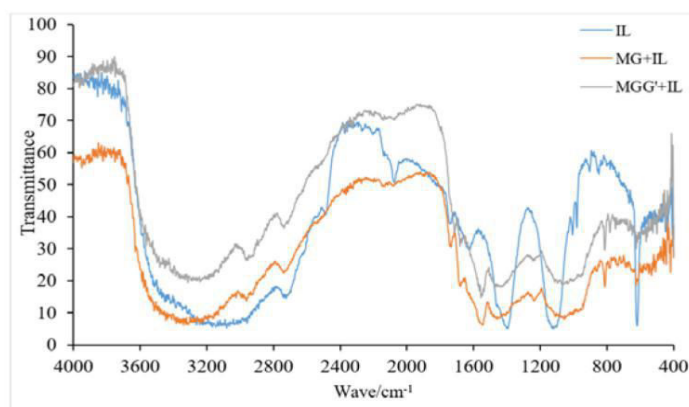
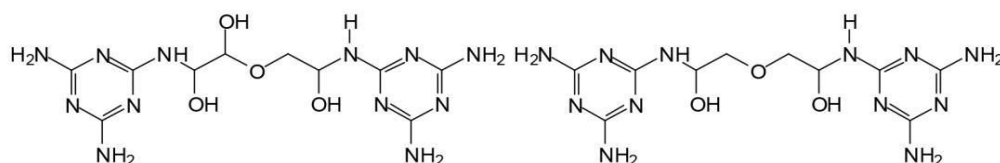


Figure 8. FTIR spectra of IL, MG+IL resin and MGG'+IL resin.

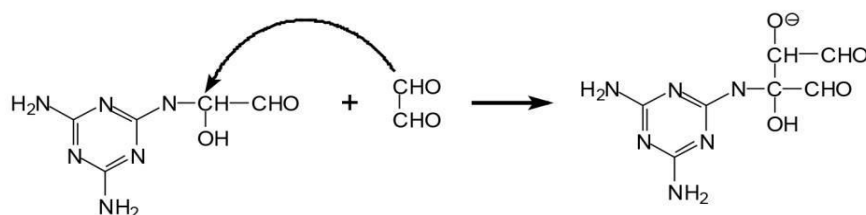


Scheme 10. Glyoxal ether bridges formed by water elimination between two melamine molecules.

3.4. Summary of Effects

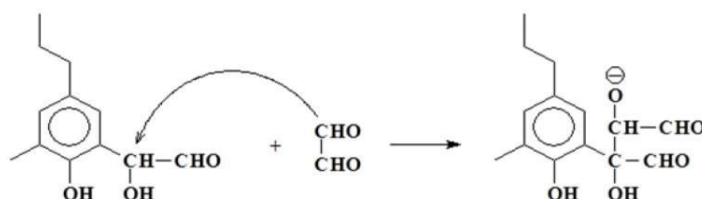
Having identified some of the more relevant of the oligomers that were found and shown that melamine and glyoxal do react and form resins which also cross-link it is of interest to summarize what is then the role of ionic liquids.

1. IL appears to catalyse the reaction of aldehydes, and aldehydes pre-reacted with urea or melamine, to yield aldol condensation. It allows aldol condensation even of aldehydes that have been pre-reacted with melamine or even with wood lignin. An example (Scheme 11):



Scheme 11. Example of aldol condensation on an aldehyde prereacted with melamine

Or even with wood lignin [22–23] (Scheme 12).



Scheme 12. Example of aldol condensation on an aldehyde prereacted with lignin

This latter opens up the possibility of reaction with the lignin in the wood substrate, and thus of some covalent bonding between an aldehyde based adhesive and the substrate. While to advance such a hypothesis is possibly premature, it might also contribute to explain the good bonds obtained with aldehyde adhesives catalysed by ionic liquids.

- IL catalyses the hardening of melamine–aldehyde resins to decrease hardening temperature, energy of activation of the hardening/condensation reaction and thus equally to improve their performance at equal temperature.
- Moreover, IL affects the wood substrate by demethylation of lignin [22–24] rendering the substrate even more receptive to any type of adhesion.

However, it cannot be excluded that also other effects are induced by the presence of ILs.

4. Conclusions

Melamine–glyoxal–glutaraldehyde (MGG') resins which use no formaldehyde have been shown to be capable of bonding interior and exterior grade plywood under industrially significant press conditions when an ionic liquid is used as the hardener. Small proportions of glutaraldehyde improved the water resistance of the panel bonds obtained. These resins showed hardening in two steps due to the different reactivity of the two aldehydes used. The role of the ionic liquid was fundamental in the performance obtained, its role being not just limited to the function of hardener but also: (i) to decrease markedly the energy of activation of hardening of the MGG' resins; (ii) to favour some limited aldol condensation of the aldehydes in the hardening of the MGG' resins, even on aldehyde sites pre-reacted with melamine; (iii) to cause demethylation of lignin and thus rendering the wood substrate more prone to adhesion [23,24]; and (iv) to favour possibly the reaction of aldehyde groups in the resin with the lignin of the substrate.

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Author Contributions: Xuedong Xi and Siham Amirou contributed equally to the preparation of the MGG' resin and the ionic liquid and the performance of the MALDI-ToF analysis. Antonio Pizzi analyzed and interpreted all the MALDI-ToF spectra, and deduced from the data all the reactions occurring and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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3.2 Résine de mélamine-glyoxal modifiée avec du 5-hydroxyméthyl-furfural

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Résumé: Le glyoxal en tant qu'aldéhyde non volatil et non toxique, peut être utilisé dans l'industrie du bois pour substituer le formaldéhyde et préparer des résines comme mélamine-glyoxal (MG). Cependant, en raisons de faible réactivité du glyoxal par rapport au formaldéhyde, les performances de la résine MG ne sont pas aussi satisfaisante. Le 5-hydroxyméthyle furfural (HMF) a été utilisé comme modificateur pour améliorer les propriétés de la résine mélamine-glyoxal (MG) et préparé la résine mélamine-glyoxal-hydroxyméthyle furfural (HMFMG) et testé en préparant de contreplaqué. Le spectromètre MALDI/TOF (Matrix Assisted Laser Desorption Ionisation/Time Of Flight), La RMN du carbone 13 haute résolution dans les solides (rotation à angle magique et polarisation croisée CP/MAS) (CP-MAS 13C), la calorimétrie à balayage différentiel (DSC) et l'analyse thermomécanique (TMA) ont été utilisés pour analyser la structure des oligomères formés et les propriétés thermomécaniques des résines. La résine HMFMG a montré une meilleure performance de liaison du contreplaqué et une meilleure résistance à l'eau qui peut être expliqué par une énergie d'activation de durcissement de la résine HMFMG inférieure à celle de la résine MG.

Mots clés: hydroxyméthyle furfural; Résine mélamine-glyoxal; Adhésif pour bois; Analyse structurelle; Problèmes environnementaux; Santé et sécurité



5-Hydroxymethyl furfural modified melamine glyoxal resin

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ABSTRACT

Glyoxal as a nonvolatile and nontoxic aldehyde, which can be used as a substitution of formaldehyde in wood industry to prepare novel melamine-glyoxal (MG) resins. However, for the reason of the lower reactivity of the glyoxal compared with formaldehyde, the performances of the MG resin is not as good as expected. 5-Hydroxymethyl furfural (HMF) was used as a modifier to improve the properties of melamine-glyoxal (MG) resins to prepare a hydroxymethyl furfural modified melamine-glyoxal (HMFMG) resin. This was tried as a plywood adhesive. Matrix-assisted laser desorption ionization time of flight (MALDI-TOF), Cross Polarisation-Magic Angle Spinning Nuclear Magnetic Resonance (CP-MAS ¹³C NMR), Differential Scanning Calorimetry (DSC), and thermomechanical analysis (TMA) were used to analyze the structure of the oligomers formed and the thermomechanical properties of the resins. The curing activation energy of HMFMG resin was found to be lower than MG resin, and it also significantly with a better plywood bonding performance and water resistance.

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structural analysis;
environmental issues; health
and safety

1. Introduction

Formaldehyde-based resins such as urea-formaldehyde resin, phenol-formaldehyde resin, melamine-formaldehyde resin or melamine-urea-formaldehyde resin, are widely used in the wood industry to produce plywood, medium density fiberboard, particleboard, and impregnated paper surface overlays.^[1,2] The use of formaldehyde for these resins, and its emission from bonded panels, has now become problematic as this chemical is considered toxic and possibly carcinogenic. In order to overcome this problem, the use of other aldehydes to replace formaldehyde is an effective method.^[3,4,5,6]

Compared to formaldehyde, glyoxal is less volatile (boiling point 51°C) and is non-toxic. Moreover, also its mature production technology, low cost, and easy biodegradation render it widely used in the clothing and paper industry as a wet-resistance enhancer and crosslinker.^[7] In wood adhesives, glyoxal has been generally used to substitute partially or totally formaldehyde

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in biosourced adhesives such as tannin adhesives,^[8,9] lignin adhesives and protein adhesives.^[10,11] However, few works in the literature report the use of glyoxal alone for wood adhesives. Recently, glyoxal and urea have been successfully used to synthesize urea-glyoxal (UG) resins used as binders for plywood.^[12] To solve the problem of high activation energy of curing of UG resins, acid ionic liquids have been used as hardeners, thus reducing the curing temperature of UG resins and improve their bonding performance to allow their use as particleboard binders.^[13] However, as UF resins, UG resins still have the defect of presenting a relatively poor water resistance. Melamine is generally used to improve the bonding performance and water resistance of urea-based resins. Moreover, the synthesis and structure characterization of melamine-glyoxal (MG) resin have been studied, and an MG resin used for bonding plywood and particleboard has been developed.^[14] The disadvantages of high curing temperature and poor water resistance are however still present. To obtain a better water resistance the MG resin was modified by reacting it with a small proportion of glutaraldehyde (G') to yield a melamine-glyoxal-glutaraldehyde (MGG') adhesive.^[15] By the use of ionic liquids (IL) as resin hardeners and additives, plywood with good water resistance and bonding properties was prepared with it.^[15] Due to the lower reactivity of glyoxal compared to formaldehyde, the performances of the MG resin alone was not as good as expected.

5-hydroxymethyl furfural is a biosourced material that can be prepared by dehydration of glucose or fructose, it has a highly reactive furan ring, a hydroxymethyl group, and an aromatic aldehyde group. Recently, hydroxymethyl furfural-modified urea formaldehyde resins have been used to bond particleboard and it has been shown that this approach can improve the bond performance and water resistance of UF resins.^[16] In this paper, 5-hydroxymethyl furfural has been used to modify MG resin, to prepare plywood bonded with it and to measure its performance when an ionic liquid (IL) was used as a hardener.

2. Experimental

2.1. Preparation of MG and HMFMG resins

The MG resins were prepared at M/G molar ratio:1:6, according to reference.^[14,15] Glyoxal (40% water solution, by Acros Organics, Geel, Belgium) was placed in the three-neck flask and the pH was adjusted to 4–4.5 using 33% NaOH. Subsequently, Melamine (by Acros organics, Geel, Belgium) was added, and the mixture was heated to 70°C for 1 h. The reaction mixture was adjusted pH to 7 and cooled to room temperature ready for use.

HMFMG resin is synthesized by a two-steps method. Twenty-one-gram Melamine, 6.3 g of 5-hydroxymethyl furfural (by Sigma Aldrich, St. Louis, USA) and 20 g water were placed in a three-neck flask and the pH was adjusted to 8.0–8.5, the mixture was heated to 70°C for 30 min, then the Glyoxal was added, and the pH adjusted to 4–4.5, then kept under the same conditions for another 1 h. The pH of the mixture was adjusted to 7 and the resin cooled to room temperature to be ready for use.

2.2. FTIR

To confirm the presence of relevant structures, a Fourier Transform Infra-Red (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrophotometer. A blank sample tablet of potassium bromide, ACS reagent from ACROS Organics, was prepared for the reference spectrum. A similar tablet was prepared by mixing potassium bromide with 5% w/w of the sample powders to analyze. The spectrum was obtained in transmission by combining 32 scans with a resolution of 2.0 cm⁻¹.

2.3. Thermomechanical analysis (TMA)

The resins were tested by thermomechanical analysis. The samples were prepared by applying each adhesive between two beech wood plies, with dimensions of 21 mm × 6 mm × 1.1 mm. These beech resin-beech sandwich specimens were tested in non-isothermal mode between 25°C and 250°C at a heating rate of 10°C/minute with a Mettler Toledo 40 TMA equipment in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 s (6 s/6 s). The classical mechanics relationship between force and deflection

$$E = [L^3 / (4bh^3)] [F(\Delta f_{\text{wood}} - \Delta f_{\text{adhesive}})]$$

allows the calculation of Young's modulus E for each case tested. Such a measuring system has been introduced and is used to follow the progressive hardening of the adhesive with the increase of temperature and to indicate comparatively if an adhesive system is faster or slower hardening and if it gives stronger joints than another one.

2.4. Differential scanning calorimetry (DSC)

The test was performed on a Perkin-Elmer DSC calorimeter with type DSC 204F1 purchased from Rodgau, Germany. The specimens were heated from 30 to 210°C under a temperature increase rate of 10 K/min, and the thermal changes were recorded. The software used for data analysis was PYRISTM Version 4.0.

2.5. Cross polarization-magic angle spinning ^{13}C nuclear magnetic resonance (CP-MAS ^{13}C NMR) spectra

The resins modified/unmodified were dried in the oven at 103°C for 2 h then analyzed by solid-state CP MAS ^{13}C NMR. Spectra were obtained on a Brüker AVANCE 400 MHz (Brüker, Billerica, MA, USA) spectrometer with a 4 mm probe at a frequency of 125 MHz. The pulse duration at 90° was 4.1 μs , with a contact time of 2 ms and a recycling delay of 4 s. Chemical shifts were determined relative to tetramethyl silane (TMS) used as a control. The spectra were accurate to 1 ppm. The spectra were run with suppression of spinning sidebands.

2.6. MALDI-TOF analysis

Samples for Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared first dissolving 5 mg of sample powder in 1 mL of a 50:50 v/v acetone/water solution. Then, 10 mg of this solution is added to 10 μL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 μL of a NaCl solution 0.1 M in 2:1 v/v methanol/water, and pre-dried. Then, 1 μL of the sample solution was placed on its dedicated location and the plaque is dried again. MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were carried out making 1000 profiles per sample with two shots accumulated per profile. The spectrum precision is of +1 Da.

2.7. Plywood preparation and testing

The performance of the resins was tested by preparing laboratory plywood panels and evaluating their shear strength dry, 2 h in boiling water and after 24 h cold water soaking. Triplicate three-layer laboratory plywood panels of 450x300x5 mm were prepared by bonding with MG and HMFMG resins and 2 mm poplar (*Populus tremuloides*) veneers. To the glue mixes were added 5% by weight on resins solids of [HNMP] HSO₄-ionic liquid as a hardener. The glue spread used was of 260 g/m² double glue line, and hot pressing time was 6 min at 150°C and 1.5 MPa pressure. After hot pressing the plywood was stored under ambient conditions (20°C and 12% relative humidity) for 48 h before testing according to China National Standard GB/T 14074 (2006),^[17] China National Standard GB/T 17657 (1999),^[18] and European Norm EN 636:2012 (2012).^[19]

3. Results and discussion

3.1. Performance of the resins and of the plywood bonded with them

The properties of the plywood panels that were bonded with MG and HMFMG resins, with 5% ionic liquid acid as hardener are shown in Table 1. Their characteristics that can be noticed from Table 1 is that the modified HMFMG resin has a better bonding performance than the MG resin. Thus, the HMFMG-bonded plywood dry shear strength and its 24 h water soaking wet strength show a satisfactory improvement. This is particularly true for the value of the 24 h water soaking wet strength as high as 0.73MPa, showing an improvement of 55% over MG, and satisfying the requirements of China National Standard GB/T 9846.3–2004 (≥ 0.7 MPa).^[20] It has the further advantage that after 2 h in boiling water it presents a strength of 0.51MPa, while the MG-bonded plywood does not resist to such a stringent test. Thus, 5-hydroxymethyl furfural is a good modification of the MG resin, especially constituting an improvement of the cold and hot water resistance. It is also conceivable that the results may improve further with increasing proportions of hydroxymethyl furfural. Equally conceivable is that the improvement due to the addition of hydroxymethyl furfural may be due to an increase in the molar proportions of aldehyde/hydroxymethyl functions in relation to the available melamine. In this regard, this latter contribution is likely to be minor because as the aldehyde/hydroxymethyl functions proportion increases so does also the presence of reactive sites on the added furanic rings.

Figure 1 shows the cured MG and HMFMG resins by a simple way of applying the resins as wood surface then heating at 120°C for 1 h. Many small cracks are observed in Figure 1b (MG resin, Indicated by the red arrow), meaning that the cured resin is very brittle. Conversely, there are no cracks in Figure 1a (HMFMG resin) showing that the HMFMG resin has better toughness or more elastic and distributes better the stresses than the MG one.

Table 1. Performances of plywood bonded with the MG and HMFMG resins with 5% Ionic acid as hardener.

	MG resin	HMFMG resin
Solids content/%	44.3%	46.5%
Viscosity/mPa·s	112	190
Dry shear strength/MPa	0.73 ± 0.05	1.03 ± 0.07
Wood failure/%	55%	80%
24h cold water soak shear strength/MPa	0.47 ± 0.03	0.73 ± 0.07
Wood failure/%	10%	65%
2h boiled water shear strength/MPa	–	0.51 ± 0.1
Shear strength of Standard GB/T 9846.3–2004 requirement	≥ 0.7 MPa	

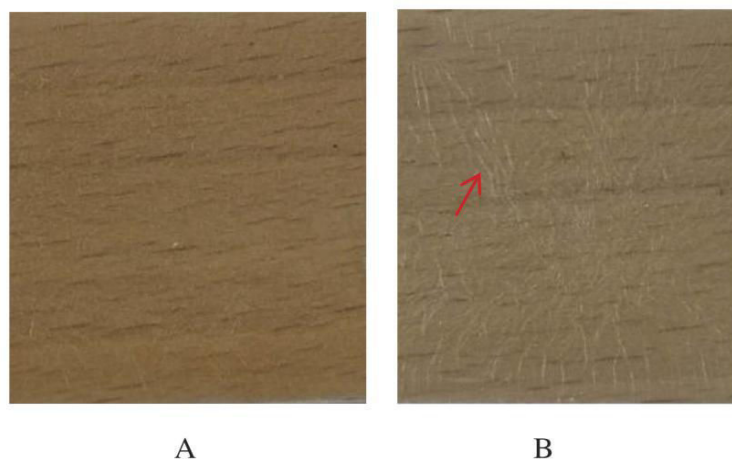


Figure 1. Pictures of the HMFMG resin (A) and MG resin (B) as wood surface finishes after heating at 120°C for 1 h.

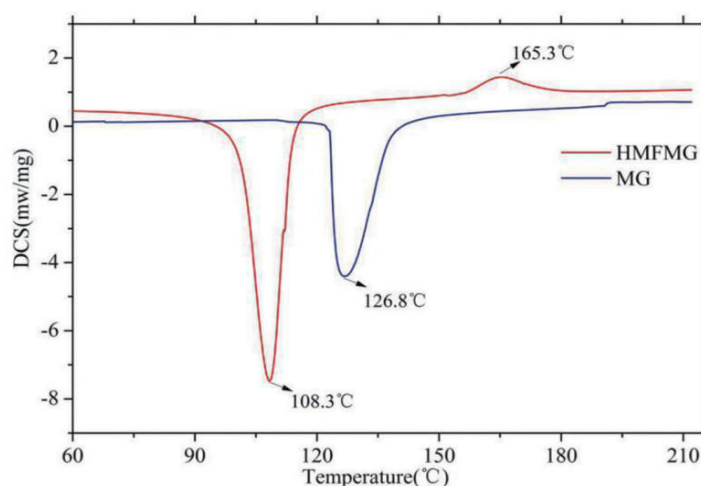


Figure 2. DSC curves of the resins.

3.1.1. Thermal analysis

Differential Scanning Calorimetry (DSC) was used to monitor the curing behavior of the two resins. The test curves shown in Figure 2 indicate that curing of the HMFMG resin starts at a lower temperature, and also presents a lower temperature curing peak (108.3°C) compared to the MG resin (126.8°C). This means that the HMFMG resin is more reactive and has a lower curing activation energy than the MG resin. Thus, when cured under the same plywood pressing conditions, the former will show a better curing behavior and also better bonding. This is a benefit due to the higher reactivity of the resin imparted by the addition of hydroxymethyl furfural. In addition, a distinct endothermic

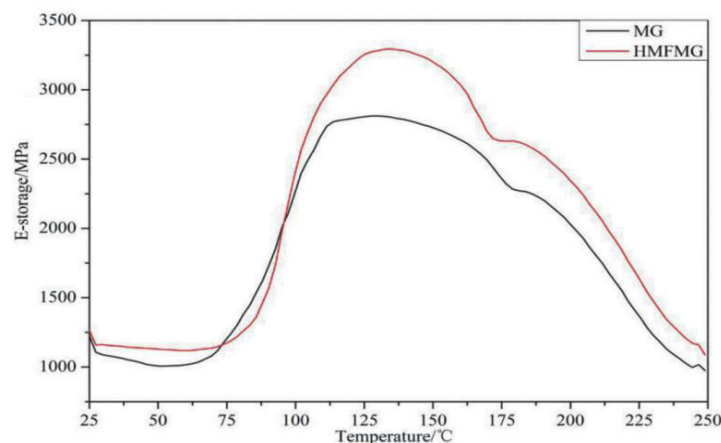


Figure 3. TMA curves of the resins.

peak is found at 165.3°C on the HMFMG resin curve, this possibly caused by the opening of the furan ring.^[21]

The thermomechanical analysis (TMA) results of the MG and HMFMG resins with the ionic liquid hardener are shown in Figure 3. The modified HMFMG resin has a higher storage energy (3300MPa) than the MG resin (2800MPa). This means that the cured HMFMG resin has higher bonding strength, this being consistent with the test results of the plywood shear strength. As the temperature starts to increase the modulus does increase too for both resins. However, the growth rate of the modulus for HMFMG is greater than for MG. This confirms the conclusion from the DSC results that HMFMG has a higher reactivity and a faster reaction rate than MG. It must also be noted that the modulus of the HMFMG resin is almost always higher than that of the MG resin after it is fully cured, even at higher temperatures, meaning that HMFMG has a better heat resistance than MG.

3.1.2. CP-MAS ^{13}C NMR

The peak signal of the aromatic carbons of the triazine ring of melamine is at 173.0 ppm, but both the HMFMG (Figure 4) and MG (Figure 5) resins present no peaks at this shift, that means that all the melamine is involved in the reaction. The peak at 164 ppm is the shift belonging to tri-to multi-substituted melamine, indicating that melamine has formed a tridimensional network in the case of both the two hardened resins.^[14]

The peaks at 158 ppm (Figure 4) and 156 ppm (Figure 5) belong to carbons connecting double bonds and hydroxyl group such as for the structure M-NH-C(OH)=CH_2 . The peak at 153 ppm (Figure 5) may belong to the C2 and C5 of the furan ring,^[22] such as

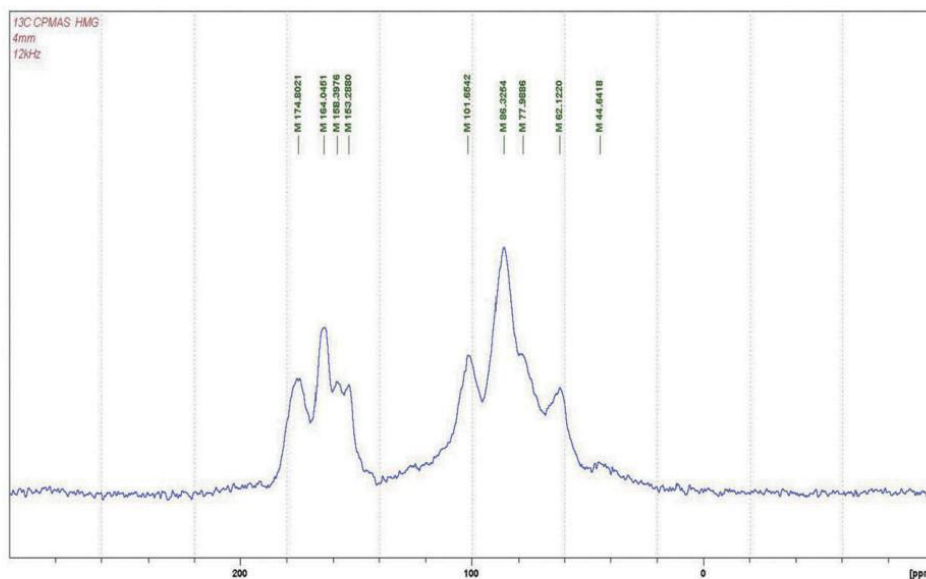


Figure 4. CP-MAS ^{13}C NMR spectrum of HMFG resin.

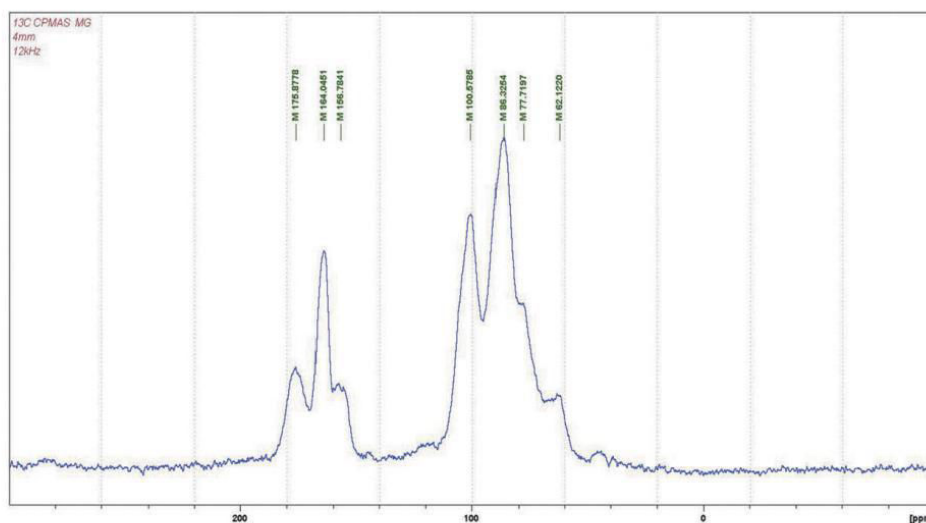
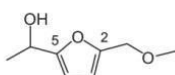
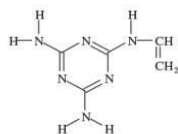


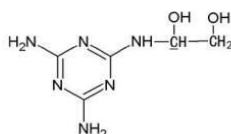
Figure 5. CP-MAS ^{13}C NMR spectrum of MG resin.



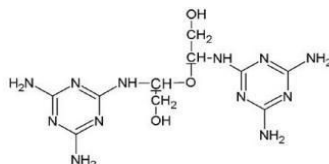
It is proved that the hydroxymethyl furfural has reacted in this system. The group that belongs to the 100.4–101 ppm shift is the one formed by the two carbons in a $\text{C} = \text{C}$ bond in structures like



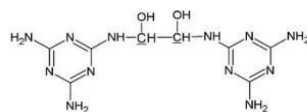
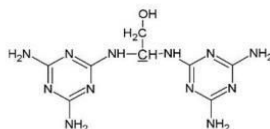
the wide peak centered at 86.3 ppm in two CP-MAS ¹³C NMR spectrum of resins pictures can correspond to the two following structures:



and/or



The peaks present in both the liquid and the hardened resin spectra at 77–79 ppm belong to two possible structures, namely and/or



The peak at 62.1 ppm in the HMFMG resin ([Figure 4](#)) is evidently stronger than for the MG resin ([Figure 5](#)), this peak bonging to the hydroxymethyl carbon (-CH₂OH), which is a reactive functional group and possibly yielding further cross-linking to form macromolecular structure or a tridimensional network, hence with better bonding performance.

3.1.3. FTIR

The FTIR analysis of the product of the reaction of melamine with hydroxymethyl furfural (called here MHMF), hardened MG and HMFMG resins

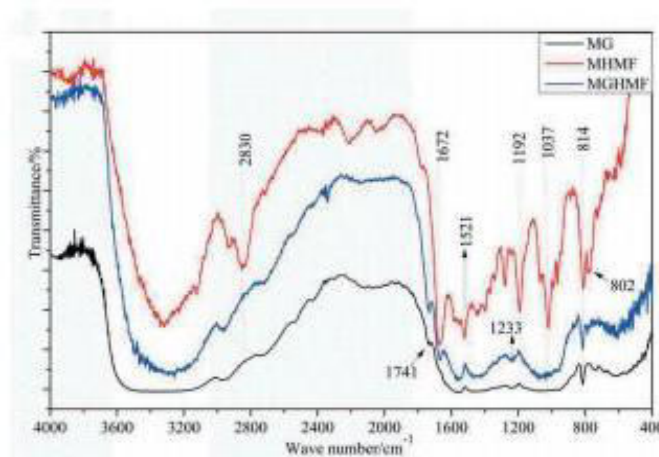


Figure 6. FTIR spectra of the resins.

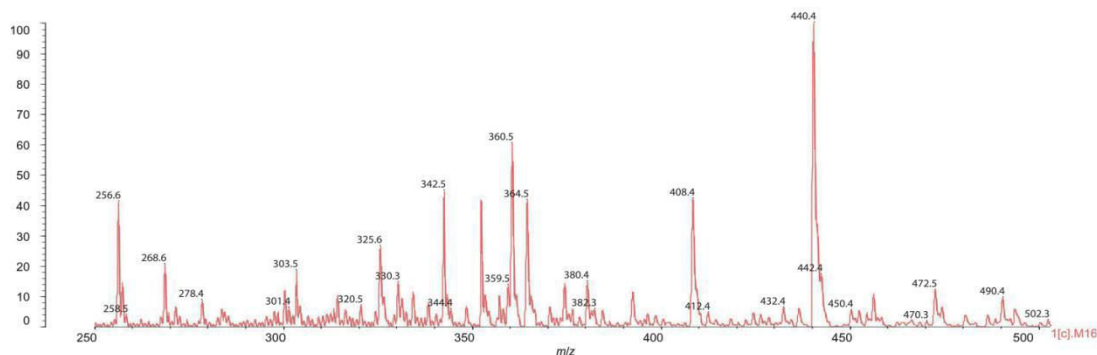
Table 2. FTIR peak assignments.

Wavelength/cm ⁻¹	Group
802	Furan ring characteristic peak
814,1550	Triazine bending vibration
1037	C-O-C stretching vibration
1192	C-O stretching vibration
1233	C-N bending vibration
1280	CH ₂ bending vibration
1521	C = C stretching vibration(aromatic furan ring)
1672	C = O(carbonyl) stretching vibration
1741	C = O(ketone) stretching vibration
2830	C-H absorption peak from O = C-H
2957	C-H stretching vibration
3100–3200	O-H stretching vibration

(Figure 6 and Table 2) shows all the main reactive groups. These are listed in Table.6^[16,21,23] The peak at 1192 cm⁻¹ in the MHMF spectrum belongs to the C-O stretching vibration of the hydroxymethyl group and the 1233 cm⁻¹ one is the C-N bending vibration, proving that reaction between melamine and hydroxymethyl furfural has occurred. The peak at 1672 cm⁻¹ is attributed to the carbonyl (C=O) stretching vibration, and the 2830 cm⁻¹ one is assigned to the C-H absorption peak of the aldehyde (O=C-H) group, showing the presence of aldehyde groups in the reaction product of MHMF. Comparing the MG and HMFMG resins spectra it can be observed that in the HMFMG spectrum (Figure 6), there is a C=O absorption peak at 1672 cm⁻¹. During the curing process, this will proceed further to form ether bonds (C-O-C) or methylene bridges (-CH₂-) thus improving bonding.

Data: HMFMG10001.M16[c] 13 Apr 2018 13:49 Cal: ref 13 Apr 2018 13:46
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 89, P.Ext. @ 2300 (bin 78)

%Int. 104 mV[sum= 20812 mV] Profiles 1-200 Smooth Av 50 -Baseline 150



Data: HMFMG10001.M16[c] 13 Apr 2018 13:49 Cal: ref 13 Apr 2018 13:46
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 89, P.Ext. @ 2300 (bin 78)

%Int. 22 mV[sum= 4384 mV] Profiles 1-200 Smooth Av 50 -Baseline 150

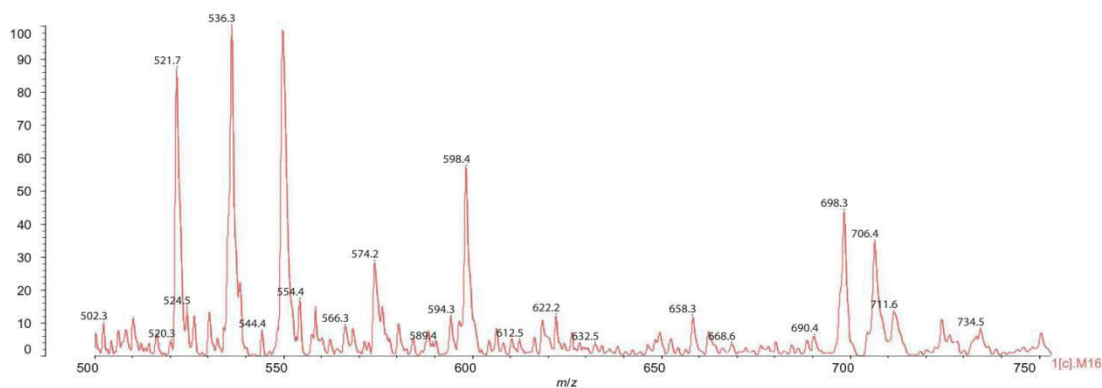
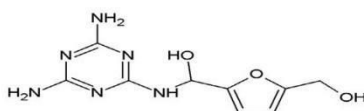


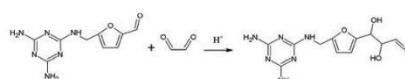
Figure 7. MALDI ToF spectrum of the reaction product of M with HMF: 250Da-750Da range.

3.1.4. MALDI-ToF

The MALDI ToF spectra of the reaction product of melamine with 5-hydroxymethyl furfural showed the formation of a number of reaction products involving the two chemicals (Figure 7, and Table 3). Single or multiple condensations with melamine appear to occur as those of the species at 275Da in Table 3:

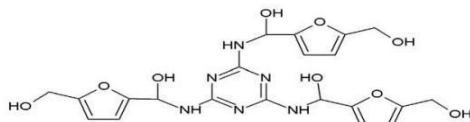


And the structure at 550Da such as:

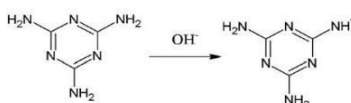


12  X. XI ET AL.**Table 3.** Oligomers identified by MALDI-TOF mass spectrometry of the HMF MG.

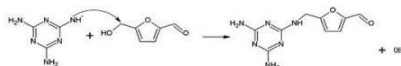
256.6Da = 257Da(calculated), 234Da with 23(Na+)



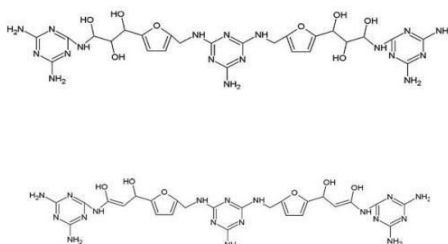
275Da =



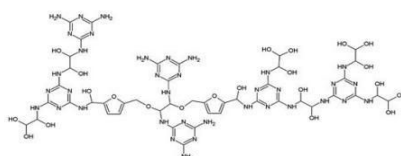
342.5Da = 342Da(calculated) without Na+



The reaction can occur in a step process, as follows:^[24]



to form the structures at 257Da and 342Da in Table 3. This is also confirmed by the carbonyl bond (C = O) found by FTIR for the reaction product of melamine with hydroxymethyl furfural. The carbonyl group (C = O) in these structures may undergo aldol condensation with glyoxal in the second synthesis step yielding structures such as the 374Da (Table 4) one, the forming scheme being as follows:^[15,25,26]

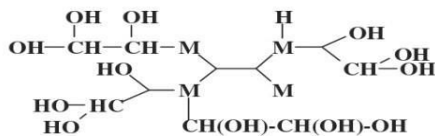


A more stable bond bridge (C-C) is then formed, rather than the ether bridge (C-O-C) that is prone to hydrolysis and cleavage. This is also one of the reasons why HMF MG gives better bonding than the MG resin.

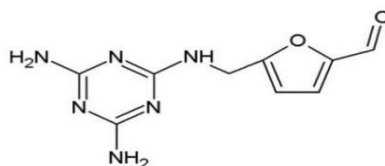


Table 4. Oligomers identified by MALDI-TOF mass spectrometry of the HMFMG.

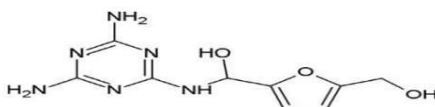
352.5Da = 351Da calculated, with 23Da (Na⁺)



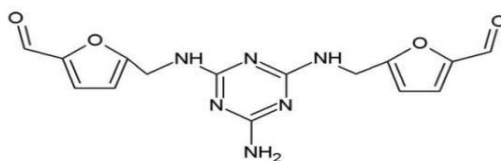
374.4Da = 374Da calculated, with 23Da (Na⁺)



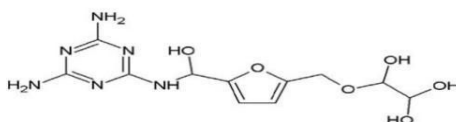
506Da = M-HMF-HMF-M with Na⁺



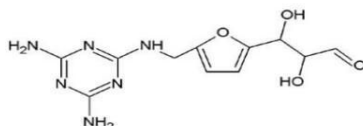
Or = 507Da



550.0Da = 527Da calculated+23(Na⁺)



618.6Da = 620Da calculated, without(Na⁺)

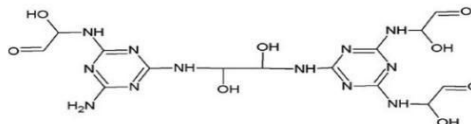
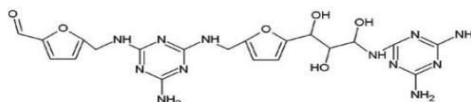
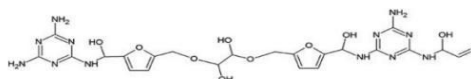
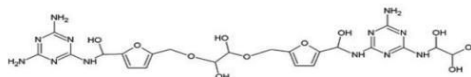
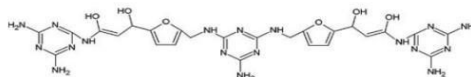
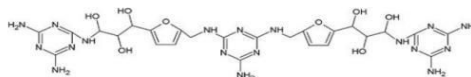


636.4Da = 638Da calculated, without(Na⁺)

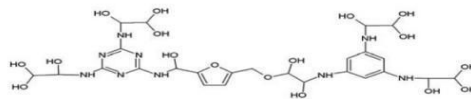
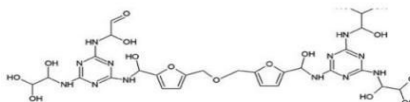


698.4Da = 699Da calculated, with23(Na⁺)

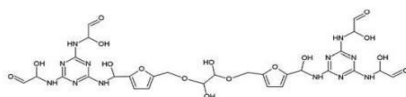
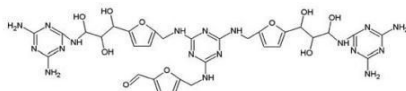
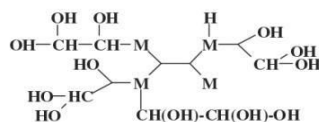
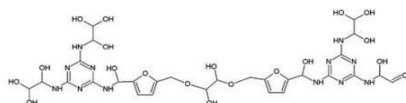
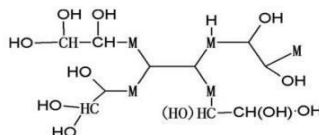
(Continued)

Table 4. (Continued).352.5Da = 351Da calculated, with 23Da (Na⁺)711.7Da = 712Da calculated, without(Na⁺)773Da = 750Da+23Da(Na⁺)792.6Da = 792Da calculated with23(Na⁺)Or = 794Da calculated, without Na⁺820.7Da = 820Da calculated without Na⁺

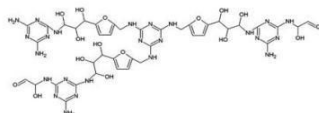
848.7Da = 850Da calculated

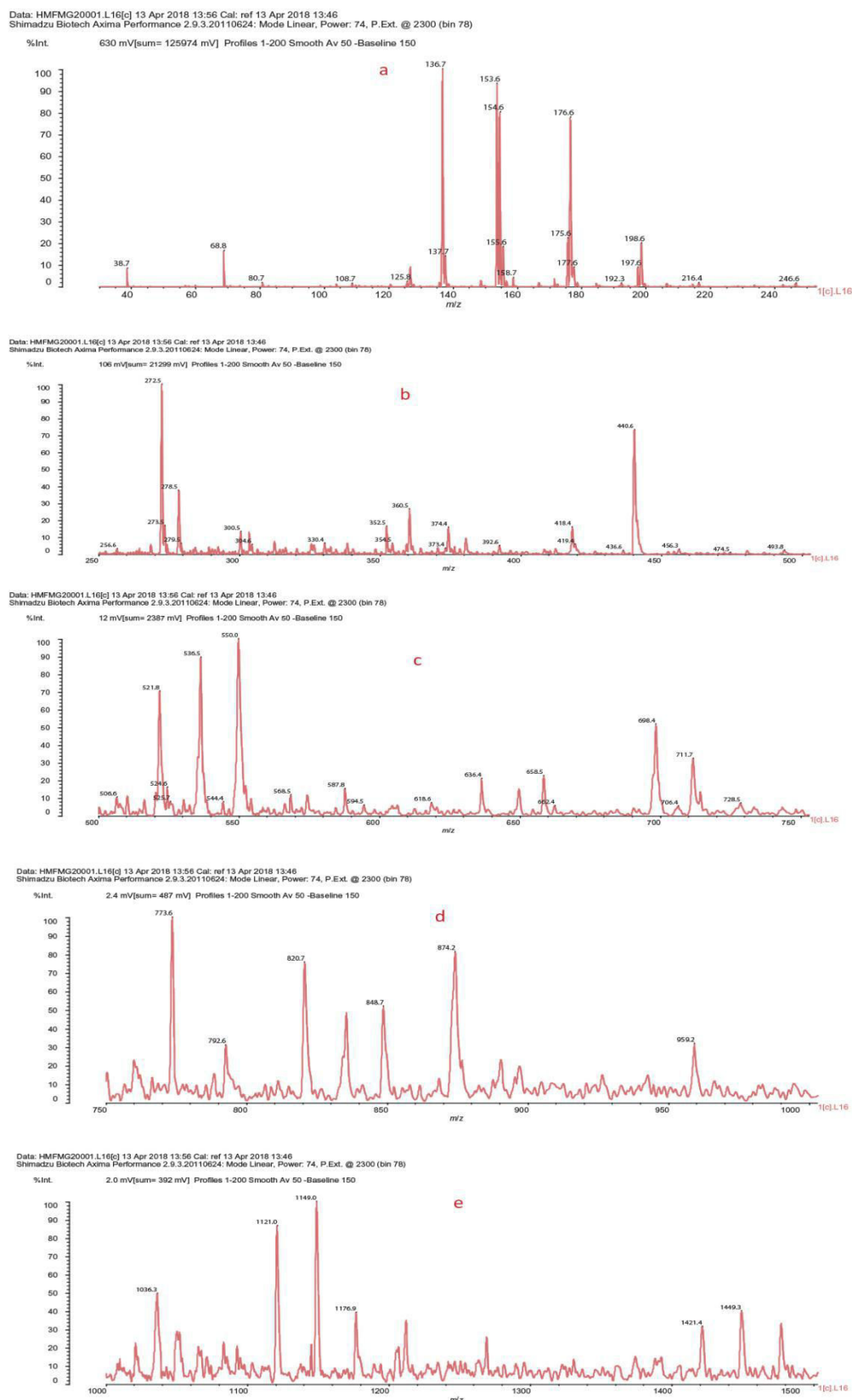
Or 848Da calculated without Na⁺959.2Da = 958Da calculated, without23(Na⁺)

(Continued)

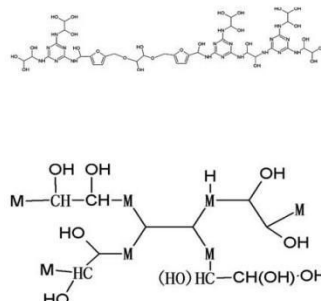
Table 4. (Continued).352.5Da = 351Da calculated, with 23Da (Na⁺)1036.3Da = 1036Da calculated, without 23(Na⁺)1121.0Da = 1121Da calculated, without 23(Na⁺)1149Da = 1126Da calculated + 23(Na⁺)1176.9Da = 1174 Da calculated, without 23(Na⁺)1449.3Da = 1450Da calculated, without 23(Na⁺)

Furthermore, also the MALDI ToF analysis showed for the modified HMFMDG resin that a great variety of oligomers, both linear and branched, have been formed (Table 4, Figure 8a-e), such as at 712Da:

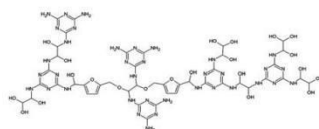


**Figure 8.** MALDI ToF spectrum of HMFMG resin: a–e.

This structure can also form C = C bonds by losing water and yielding the peak at 699Da:^[27] and a branched structure at 1450Da that can ensure the formation of a tridimensional network in the cured resin such as



Excess melamine after the first step of addition reaction can react with glyoxal at the second step, to form the structure like 850Da:



which has also been observed in the MG resin,^[14] a large amount of methylol being beneficial to the polycondensation reaction in the next steps of the curing process.

4. Conclusion

A hydroxymethyl furfural modified melamine glyoxal (HMFMG) resin can effectively overcome the poor bonding performances problems already observed for an MG resin alone, and improve its water resistance. Melamine, as a condensation product of urea, as well as hydroxymethyl furfural are both biosourced materials that coupled with the non-toxic glyoxal render the HMFMG adhesive particularly environment-friendly. There are two series of reaction between melamine and hydroxymethyl furfural observed by structural analysis by MALDI-TOF and FTIR. These are: (i) the addition reaction on the amino groups of melamine by the aldehyde group of 5-hydroxymethyl furfural, and the subsequent condensation engendered by the hydroxymethylene group so formed. (ii) The condensation reaction of the HMF hydroxymethyl group with the amino groups of melamine by elimination of one molecule of water. The modified HMFMG resin has been shown to have a higher reactivity and faster reaction rate during curing than the MG resin, hence showing a better performance in bonding plywood than the MG resin.

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3.3 Adhésif de contreplaqué résines alcool furfurylique-aldéhyde

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Résumé: L'alcool furfurylique, un matériau biosourcé, est largement utilisé dans l'industrie de la fonderie et également en tant qu'additif ou agent de modification dans le domaine des adhésifs. Toutefois, il n'a pas été signalé que les résines furaniques étaient utilisées seules comme adhésifs pour panneaux de bois. Dans le présent travail, des résines alcool furfurylique-aldéhyde ont été préparées en faisant réagir de l'alcool furfurylique avec trois aldéhydes différents, à savoir le formaldéhyde, le glyoxal et le glutaraldéhyde. L'acide p-toluènesulfonique et un système auto-neutralisant acide ont été utilisés comme durcisseurs de résine avec les différents types de résines préparés. Le MALDI-TOF, l'infrarouge à transformée de Fourier (FTIR), la résonance magnétique nucléaire (RMN 13C) et l'analyse thermomécanique (TMA) ont été utilisés pour analyser les propriétés thermomécaniques des résines et la structure des résines et des oligomères formés. Les résultats ont montré que le formaldéhyde et le glyoxal peuvent réagir avec l'alcool furfurly en donnant des résines d'excellentes performances. Cependant, la réaction du glutaraldéhyde avec l'alcool furfurylique s'est avérée difficile, l'autocondensation de l'alcool furfurylique prédominant. L'acidité de l'agent de durcissement a une grande influence sur les performances de collage de la résine. La résine furfurly alcool-glyoxal (FAG) a également montré une bonne force de liaison et une bonne résistance à l'eau, supérieures aux exigences standard ($\geq 0,7$ MPa), même en utilisant un système auto-neutralisant acide comme durcisseur. La résine FAG était particulièrement bonne étant donné qu'aucun formaldéhyde n'a été utilisé.

Mots clés: alcool furfurylique-aldéhyde; problèmes environnementaux; adhésifs pour le bois; acide auto-neutralisant; Les analyses thermiques; MALDI-TOF.



Furfuryl alcohol-aldehyde plywood adhesive resins

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ABSTRACT

Furfuryl alcohol, a biosourced material, is widely used in the foundry industry, and also as additive or modifier in the adhesives field. However, furanic resins have not been reported as being used alone as wood panel adhesives. In the present work furfuryl alcohol-aldehyde resins were prepared by reacting furfuryl alcohol with three different aldehydes, namely formaldehyde, glyoxal and glutaraldehyde. p-Toluene sulfonic acid and an acid self-neutralizing system were used as resin hardeners to prepare plywood and evaluate their bonding performances. Matrix assisted laser desorption ionization time of flight (MALDI-TOF), Fourier transform infrared (FTIR), nuclear magnetic resonance (¹³C-NMR) and thermomechanical analysis (TMA) were used to analyze the thermomechanical properties of the resins and the structure of the oligomers formed. The results showed that formaldehyde and glyoxal can react with furfuryl alcohol to obtain resins of excellent performance. However, the reaction of glutaraldehyde with furfuryl alcohol instead predominating. The acidity of the curing agent has a great influence on the bonding performance of the resin. The furfuryl alcohol-glyoxal (FAG) resin showed also a good bonding strength and water resistance, higher than the standard requirements (≥ 0.7 MPa), even when using an acid self-neutralizing system as hardener. The FAG resin was particularly good considering that no formaldehyde was used.

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adhesives for wood;
self-neutralizing acid;
thermal analysis; MALDI-TOF

1. Introduction

With the increasing interest in biosourced adhesives and resins due to a real or perceived future scarcity of oil-derived chemicals, as well as to the increasing public awareness of the need for protection of the environment, several different routes to biosourced wood panel adhesives have already been explored. Thus, resins and wood adhesives based on tannins^[1,2], lignin^[2,3], vegetable and waste animal proteins and other materials of natural origin have been abundantly reported in the literature.^[4,5]

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One of the biosourced materials that has been used in combination with phenol, tannins, lignin, proteins for a number of applications is furfuryl alcohol.^[1,6–9] Furfuryl alcohol is composed of a furanic nuclei and of a hydroxymethyl function, and is obtained by reduction of furfural. Furfural is obtained by acidification of waste vegetable materials such as sugar cane bagasse, softwoods and hardwoods waste as well as from cereals straw. Furanic resins and phenol-furanic resins are known and used commercially, for example to bind foundry cores sand.^[10,11] However, furanic resins alone have not been used as wood adhesives, probably among others for their dark colour, nonetheless that they tend to have excellent water and weather resistance. Their main drawback, in the case of furfuryl alcohol is the necessity to have a very acid pH for curing. While this is acceptable for certain applications it is not suitable for wood adhesives, where too low a pH and too high a residual acidity would hydrolyse the holocellulose of wood at the interface. This would cause, eventually, interfacial failure of the bonded wood joint or panel. However, recent work has also shown that reaction of furfuryl alcohol can occur under alkaline conditions.^[12]

The presence on furfuryl alcohol of only one reactive group, the hydroxymethyl one, causes its polycondensations with the only site reactive enough of the furan ring to lead exclusively to linear polymers. The absence of cross-linking has been eliminated in the past by addition of at least tri- or multi-functional coreactants such as a phenol-formaldehyde resin.^[13] However, a different approach could be taken to solve the same problem, namely reaction of the C5 site on the furan ring with an aldehyde. This would insert a second reactive hydroxymethyl group on the furan nuclei, leading, through a number of mechanisms, to cross-linking of the furanic resin so obtained.^[14,15] While this approach can be taken using formaldehyde, the problems linked to its toxicity, oncogenity and emission indicate that aldehydes less volatile and less or non-toxic should be used. It is for this reason that in the research work presented here furfuryl alcohol-formaldehyde (FAF), furfuryl alcohol-glyoxal (FAG) and furfuryl alcohol-glutaraldehyde (FAG') resins have been developed for use as wood panel adhesives.

2. Materials and methods

2.1. Materials

Furfuryl alcohol 98% by Acros organics(Geel, Belgium), formaldehyde 36% by VWR Chemicals(Briare, France), glyoxal 40% solution in water(Geel, Belgium), glutaraldehyde 50% solution in water (WGK Germany), morpholine 99% by Acros organics(Geel, Belgium), phosphoric acid 85% solution in water (Geel, Belgium), p-toluenesulfonic acid monohydrate 97.5% pure by Acros organics(Geel, Belgium).

2.2. Preparation of resins

FAG resin: The molar ratio of Furfuryl alcohol/Glyoxal was 1:1.3, Glyoxal and Furfuryl alcohol were placed in the three-neck flask and the pH was adjusted to 3.5–4, the mixture was heated to 70–75°C for 8 h. The reaction mixture was cooled to room temperature and adjusted PH was 6.5–7.0 ready for use.

Under the same conditions, the identical molar mass of Formaldehyde or Glutaraldehyde was replaced by Glyoxal to prepare the FAF and FAG' resins.

2.2.1. Preparation of morpholine complexes (1:1 molar equivalents)

According to a relevant reference^[16], 8.7g morpholine and 9.8g phosphoric acid(oily liquid) were mixed, while heating the components gently to between 50°C and 60°C. This results in an exothermic reaction, after which the mixture was cooled to room temperature.

2.2.2. Glue mix preparation

To the glue mixes were added 3% by weight p-toluenesulfonic acid (p-TSA) or 1%p-TSA+ 2% of the morpholine/phosphoric acid complex as hardener on furfuryl alcohol-aldehyde resin solids. The pH of the glue mixes were tested before bonding plywood panels.

2.3. Preparation and testing of three-layer plywood

Poplar (*Populus tremuloides*) veneers of 2mm thickness were used to prepare laboratory plywood panels of 450mm× 100mm× 5mm dimensions. The glue-mix spread was 250g/m² dgl (double glue line). Hot pressing time was 6 minutes at a temperature of 160°C and at 1.5MPa pressure. The plywood so prepared was stored at ambient temperature for 48h before being tested.

The dry shearing strength, 24h wet shear strength and 2h boiled water shear strength of the plywood panels were tested according to China National Standard GB/T 14074 (2006),^[17] China National Standard GB/T17657 (1999)^[18], and European Norm EN 636:2012 (2012).^[19] Both the final dry and the wet shear strengths were the mean results of 6 tests on independent specimens.

2.4. Thermomechanical analysis (TMA)

As for work published on other resins,^[20] the furfuryl alcohol-aldehydes resin adhesives were tested by thermomechanical analysis. The samples were prepared by applying each adhesive between two beech wood plies, to form a sandwich of 21mm x 6mm x 0.6mm dimensions. These specimens were tested in non-isothermal mode between 25°C and 250°C at a heating rate

of 10°C/minute with a Mettler Toledo 40 TMA equipment in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 seconds (6s/6s).

2.5. FTIR analysis

To confirm the presence of relevant structures, a Fourier Transform Infra-Red (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrophotometer. A blank sample tablet of potassium bromide, ACS reagent from ACROS Organics, was prepared for the reference spectrum. A similar tablet was prepared by spreading 5% w/w of the resin on the blank potassium bromide tablet, drying it very well before the analysis. The spectrum was obtained in transmission by combining 32 scans with a resolution of 2.0 cm⁻¹.

2.6. ¹³C-NMR analysis

A Nuclear Magnetic Resonance spectrometer (Brüker-AVANCE 600, Switzerland) was used to analyze the FF and FG resins. The resonance frequency used was 150 MHz. 300 µL of samples and 100 µL of dimethyl sulfoxide deuterium generation solvent (DMSO-d₆) were mixed to the sample to test. Test condition: relaxation delay time was 6 s; the number of transients was 800–1200 times; and temperature of 25 °C.

2.7. MALDI-TOF analysis

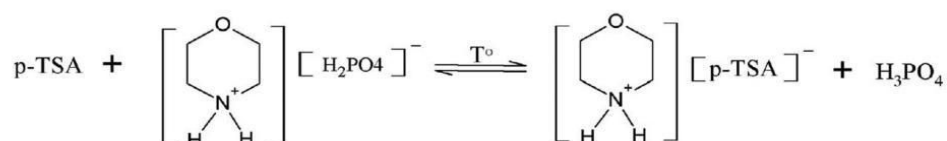
Samples for Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared first by dissolving 5mg of sample powder in 1mL of a 50:50 v/v acetone/water solution. Then 10 mg of this solution was added to 10µL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2µL of a NaCl solution 0.1M in 2:1 v/v methanol/water, and predried. Then 1µL of the sample solution was placed on its dedicated location and the plaque was dried again. The reference substance used for the equipment calibration was red phosphorus.

MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were carried out making 1000 profiles per sample with 2 shots accumulated per profile. The spectra precision is of ± 1Da.

3. Results and discussion

3.1. Influences of hardener on the pH value

The pH of the resin has a great influence on both the substrate and on furan resins hardening as excessive acidity may cause degradation of wood fibers, thus leading to irreversible damage to the adhesive/wood interface and either joint failure or decrease of the bonding strength and service life of the bonded products. Thus, the pH values of the resins with and without the two hardener combinations were tested (Table 1). When 3% of p-Toluenesulfonic acid (p-TSA) was used as hardener, the pH of the glue was almost as low as 2.5, too acid and damaging to the wood. When a self-neutralizing hardener (1%p-TSA+ 2% morpholine/phosphoric acid) was used a much less acid pH value of the resins was obtained, on par or even higher than the pHs 4.0–4.5 used for hardening UFs and MUFs adhesives.^[16] The self-neutralizing morpholine complex can effectively improve the bondline and interface residual resins acidity, its mechanism being already known as showed as follows:



3.2. Performance of plywood panels bonded with the furfuryl alcohol aldehyde resins

The performances of the resins and of the plywood panels bonded with the furfuryl alcohol formaldehyde (FAF), furfuryl alcohol glyoxal (FAG), and furfuryl alcohol glutaraldehyde (FAG') resins are shown in Table 2. When 3% of p-Toluenesulfonic acid was used as hardener, due to the different reactivities of the three aldehydes with furfuryl alcohol (formaldehyde > glyoxal > glutaraldehyde), the FAF resin showed the best dry strength, while the FAG' one just met the requirements of the Chinese national standard (GB/T9846.3–2004, ≥ 0.70 MPa). All of the resins showed good water resistance, compared to the dry strength. It is remarkable that the tensile strength increases after

Table 1. pH values of the resins with different hardener.

	Without hardener	3%p-TSA		1%p-TSA+ 2% morpholine/Phosphoric acid	
		Ambient	100°C, 2min	Ambient	100°C, 2min
FAF resin	6.70	2.66	2.40	5.30	4.91
FAG resin	6.58	2.47	2.34	4.97	4.75
FAG' resin	6.71	2.53	2.44	5.04	4.97

Table 2. Performances of resins and plywood panels.

resins	Solid content/%	Viscosity/mpa.s	Dry strength/MPa			24 wet strength/MPa			2h boiled strength/MPa		
			3%p-TSA	Mix		3%p-TSA	Mix		3%p-TSA	Mix	
FAF	33.1%	86	1.30 ± 0.05	0.89 ± 0.02		1.55 ± 0.05	0.90 ± 0.03		1.30 ± 0.07	0.93 ± 0.03	
FAG	49%	160	1.02 ± 0.04	0.75 ± 0.03		1.36 ± 0.06	0.74 ± 0.04		1.46 ± 0.10	0.88 ± 0.02	
FAG'	31.8%	223	0.76 ± 0.06	0.64 ± 0.05		1.04 ± 0.10	0.41 ± 0.07		0.90 ± 0.04	0.54 ± 0.05	

"3%p-TSA" means 3% p-Toluenesulfonic acid used as hardener

"Mix" means 1% p-Toluenesulfonic acid + 2% morpholine/phosphoric acid used as hardener



Figure 1. Fractures of the plywood samples in the tensile strength test. Please note the difference in percentages wood failure.

24 hours cold water soak and 2h boiled water treatment, in particular the plywood panels bonded with FAF and FAG. This is also shown by the different levels of percentage wood failure in [Figure 1](#).

The strength after the 2h boil test of the samples bonded with the FAF resin is lower than that after 24h in cold water for a number of reasons: first by the normal deterioration observed between the two tests in phenolic-type adhesives, this behavior indicating that the resin is well cured. Second, because there is a higher proportion of methylene ether bonds (C-O-C) formed in the reaction between furfuryl alcohol and formaldehyde (this being also confirmed by the ^{13}C -NMR analysis). Methylene ether bonds rearrange with ease to methylene bridges especially in hot water. Conversely, the FAG adhesive gives panels with a higher strength after 2 h boil than after 24h cold soak. The reason for this behavior is the curing to completion of the resin during the boil water test due to glue-line under-curing during hot pressing. This is the consequence of both the lower reactivity of glyoxal in relation to formaldehyde and because the FAG resin has a higher curing activation.

The combination of pH value and hardener type has a marked influence on plywood performance. Plywood prepared with lower acid value hardener has a better bonding performance. It's easily evaluated from the plywood test results during hot press in [Table 2](#), by comparing the bonding strength of plywood prepared by different hardener. Because of acid acts as a curing catalyst, stronger acidity means that the curing reaction can be more effectively promoted. Under the same hot pressing conditions, the resin curing reaction is more complete, so that the plywood has better performance.

3.2.1. Thermomechanical analysis (TMA)

The thermomechanical analysis (TMA) results of furfuryl alcohol-aldehyde resins without 3% p-Toluenesulfonic acid hardener and without hardener are shown in [Figure 2](#), resins with 3% p-Toluenesulfonic acid as hardener

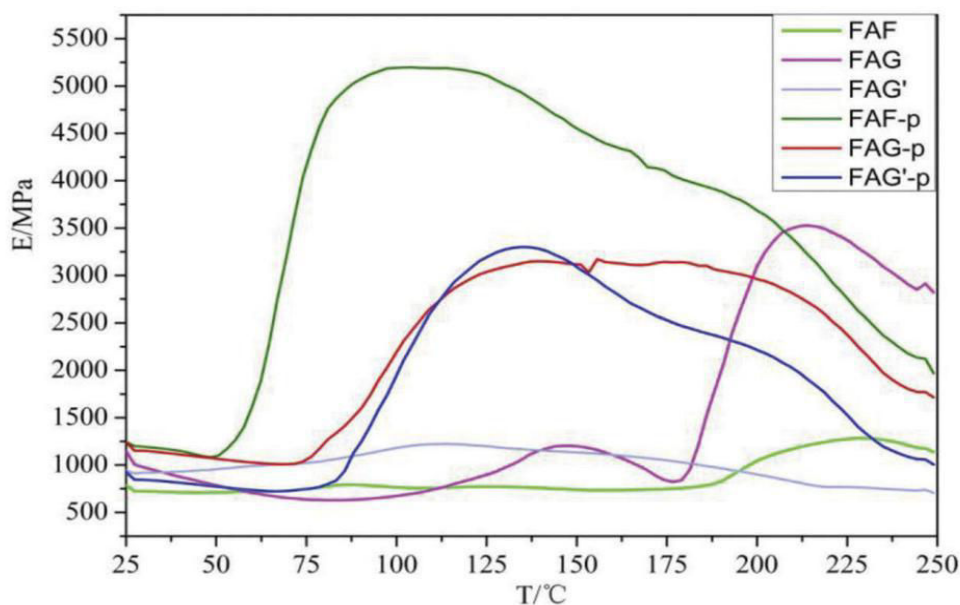


Figure 2. Thermomechanical analysis (TMA) spectra of resins with/without 3% p-TSA as hardener.

being named as FAF-p, FAG-p, FAG'-p. Resins with a mixed self-neutralizing hardener (1% p-Toluenesulfonic acid + 2% morpholine/phosphoric acid) were named as FAF-m, FAG-m, FAG'-m. From the graphs of these resins without any hardener it appears that the FAF starts to cure at 180°C, and FAG starts at almost 200°C, but FAG' shows no signs of hardening even at a temperature is 250°C. The FAF resin is thus more reactive and has lower curing activation energy than FAG and FAG', this is already confirmed by the thermomechanical analysis trace.^[21] When 3% p-Toluenesulfonic acid was used as hardener, the initial curing temperature of the furfuryl alcohol-aldehyde resins was much lower, in particular for the FAF. Moreover, FAG resin, FAG' resin have similar initial curing temperature, but the former has better heat resistance, the Young's Modulus of FAG dropped significantly at the temperature higher than 200°C, but the FAG' decreased at 135°C. In addition, the cured FAF resin has a highest Young's Modulus compared with other two resins, that's maybe also be the reason for the good shearing strength results of the plywood of FAF resin.

When the mixed self-neutralizing hardener (1% p-Toluenesulfonic acid + 2% morpholine/phosphoric acid) was applied to the resins, the TMA test results are shown in the Figure 3. It's indicated that spectra of the Young's Modulus of furfuryl alcohol-aldehyde resins start to increase at a higher temperature than 3% p-Toluenesulfonic acid as hardener (shown in the Figure 2), that means they are more difficult to cure with the mixture hardener, if under the same hot press conditions. It can explain why in

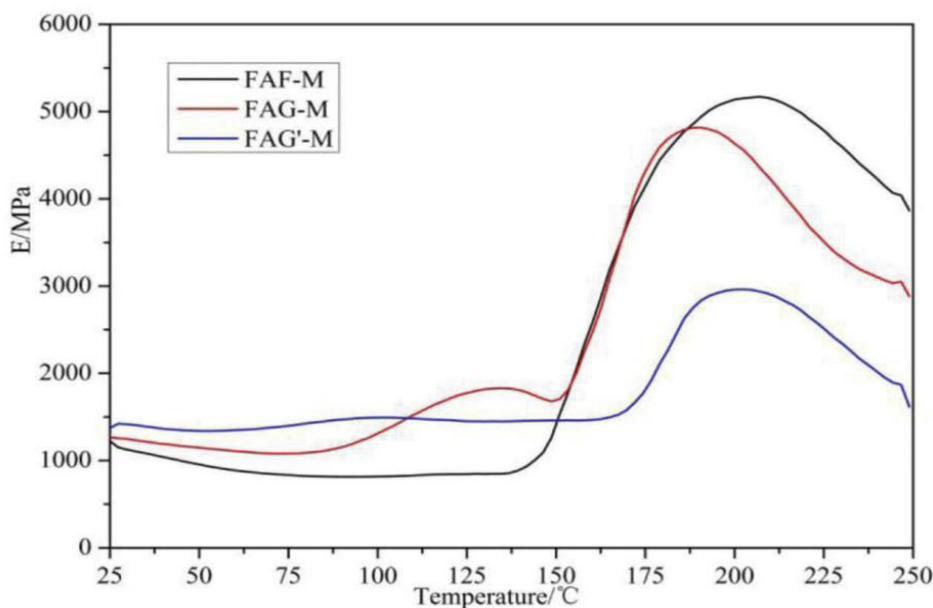


Figure 3. Thermomechanical analysis (TMA) spectra of resins with the mixed self-neutralizing hardener (1% p-Toluenesulfonic acid + 2% morpholine/phosphoric acid).

Table 2 the bonding strength of the resins with mixed self-neutralizing hardener are lower than those with the p-Toluenesulfonic acid as hardener. Conversely, FAF and FAG resins start to cure and their Young's Modulus increased at nearly 150°C, but for the FAG' resin it starts to increase at 175° C. As the temperature used for preparing the plywood was 160°C, this is also one reason for the bad bonding strength result of the FAG' resin.

3.2.2. FTIR analysis

The results of the FTIR analysis of the furfuryl alcohol-aldehyde resins are shown in Figure 4. A rather evident absorption peak is found at 1051 cm^{-1} , indicating that in the FAF resin there are more methylene ether bonds (C-O-C). The peak at 1120 cm^{-1} for the FAG resin is the asymmetrical ether bonds C-O-C stretching vibration of the furfuryl alcohol/glyoxal reaction product, it's proved that the furfuryl alcohol react with glyoxal.

The peak at 2918 cm^{-1} in the FAG' resin belongs to the C-H stretching vibration of the $-\text{CH}_2\text{OH}$ of furfuryl alcohol, and the peak at 892 cm^{-1} is the a-H in Furan ring, indicating that part of the furfuryl alcohol did not react with the glutaraldehyde. This confirms that the reaction of furfuryl alcohol with glutaraldehyde is more difficult under the same conditions than with formaldehyde and glyoxal.

Table 3 reports the main IR peak assignments.^[22–24]

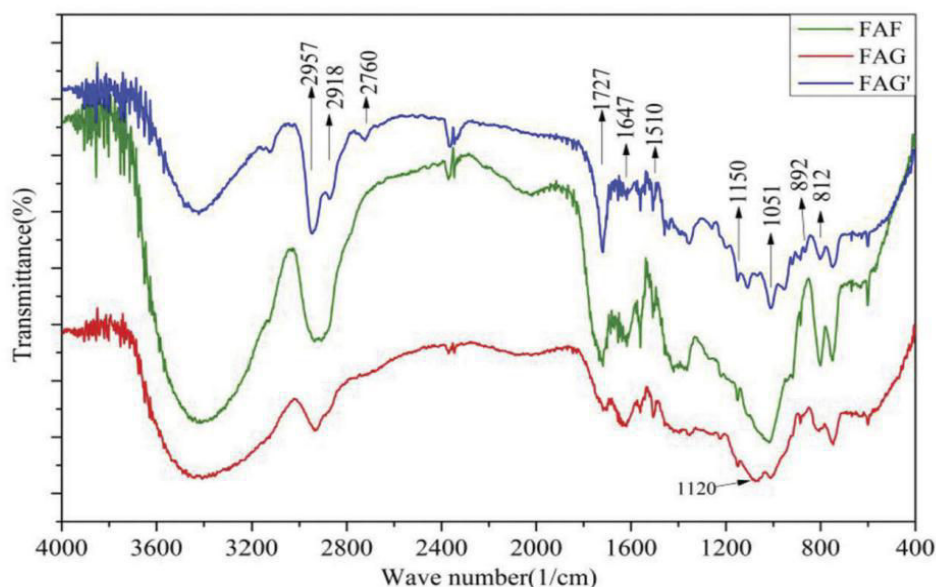


Figure 4. FTIR spectra of the furfuryl alcohol aldehyde resins.

Table 3. FTIR peak assignments.

Wavelength/cm ⁻¹	Group
812,917,1562	Furan ring characteristic peak
892	a-H in Furan ring
1051	C-O-C stretching vibration
1109	C-O stretching vibration of -COOC
1120	asymmetrical C-O-C stretching vibration
1151	C-O-C stretching vibration,
1267	CH ₂ bending vibration, C-O stretching vibration of -COOC
1396	CH ₃ Surface bending vibration
1460	CH ₂ deformation vibration
1508, 1562	C = C stretching vibration(aromatic furan ring)
1647	C = O(carbonyl) stretching vibration
1727	C = O (esterification)stretching vibration
2760	C-H absorption peak from O = C-H
2918	C-H stretching vibration from -CH ₂ OH of Furfuryl alcohol
2957	C-H stretching vibration
3100–3200	O-H stretching vibration

3.2.3. ¹³C-NMR analysis

¹³C-NMR spectrum of the FAF, FAG and FAG' resins (Figure 5) revealed the functional groups and help to surmise the reaction in the resin system. The 30ppm shift can be attributed to the -CH₂- of the self-condensation of the furfuryl alcohol, this can be find in the three resins. And it's also obviously that in the picture of FAG' resin there is more stronger peak than other two resins, that means more furfuryl alcohol has self-condensation rather than react with glutaraldehyde. The 56–57 ppm shift can be attributed to the hydroxymethyl group (-CH₂-OH) of furfuryl alcohol. The shift regions at

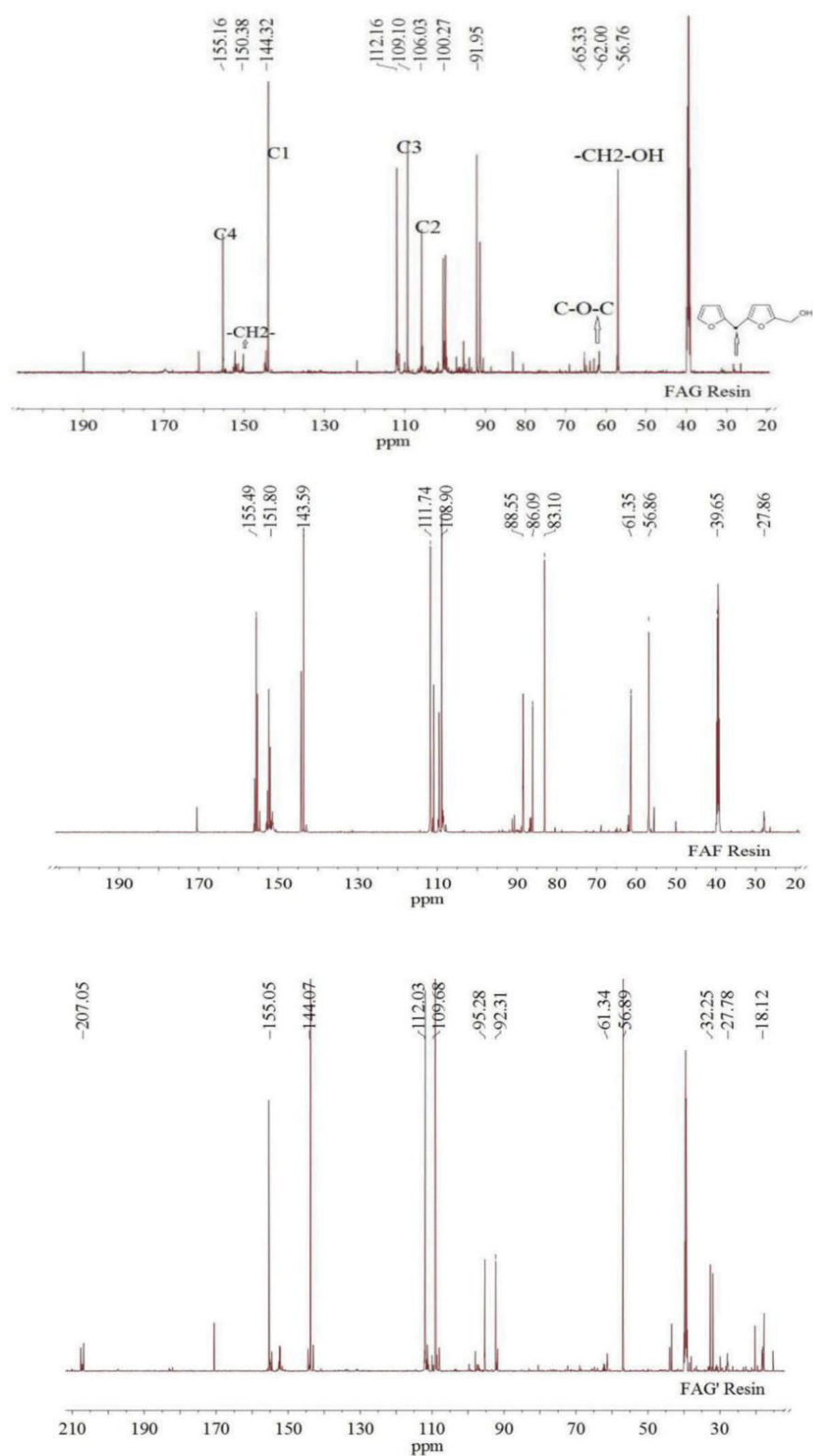
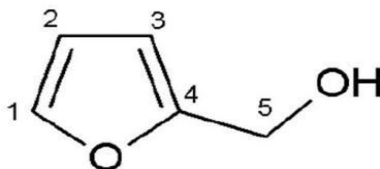


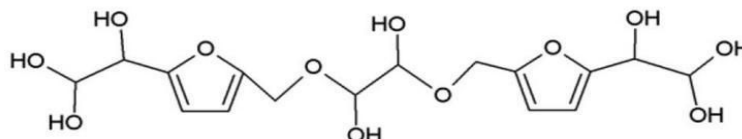
Figure 5. ^{13}C -NMR spectrum of the FAF, FAG and FAG' resins.

90 to 100 ppm are glyoxal self-condensation products. The shift region at 155 to 156 ppm belong to the C4 of the furanic nuclei of furfuryl alcohol, while the 142 to 143 ppm shifts belong to its C1, 106ppm belonging to its C2 and 110 to 112ppm belonging to its C3. [22,25,26]

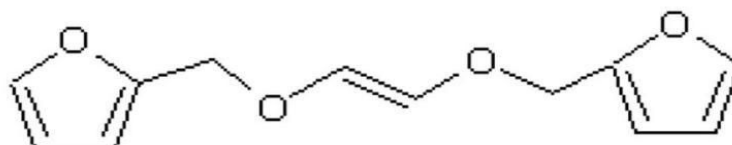


The 151 to 152 ppm and 60 to 61 ppm shifts are belong to bridge bonds and ether bonds, which can be attributed to the co-reaction between furfuryl alcohol and aldehyde. It's known from Figure 4 that the FAF resin has strongest peak in this places, followed by FAG, and finally was FAG', this confirmed also that the reactivities of the three aldehydes with furfuryl alcohol is formaldehyde > glyoxal > glutaraldehyde. The existence of a large number of bridges in the FAF resin is the main reason for good bonding strength and water resistance.

The 100.3 ppm shift in the picture of ^{13}C -NMR spectrum of the FAG resin belongs to $-\text{CH}(\text{OH})_2$, it can be unreacted glyoxal assumes in the water, or/and come from the structure of



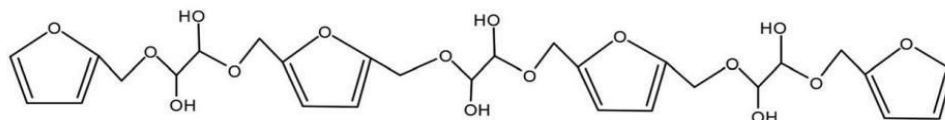
Or maybe also the two carbons in a $\text{C} = \text{C}$ double bond in structures [27], such as:



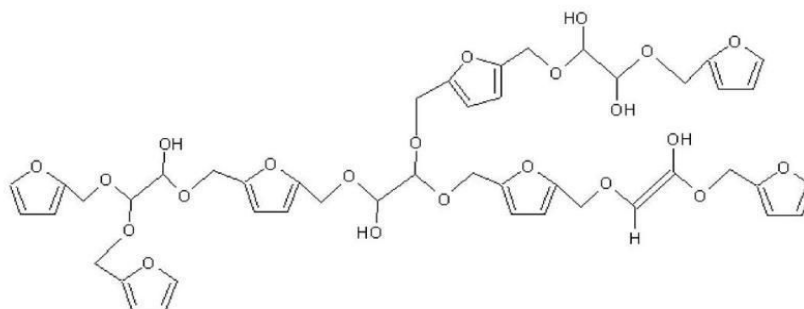
The presence of this structure reduces the hydrophilic group ($-\text{OH}$) in the resin, which is beneficial to improve the water resistance of the resin.

4. Maldi-tof

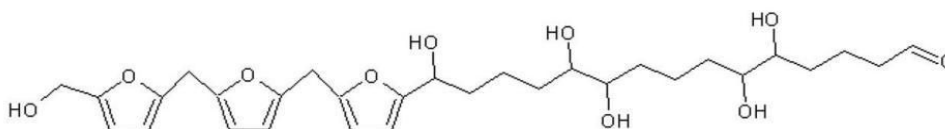
The MALDI ToF spectra of the FAF, FAG and FAG' resins revealed the formation of a great variety of oligomers. Concentrating on the FAG resin first to eliminate the use of the to-day unacceptable formaldehyde both linear as well as branched oligomers have been identified (Table 4 and Figure 6a-e), such as at 566 Da



and at 958 Da branched structures such as



In the case of the FAG' resin (Table 5, Figure. 7a-e) while similar oligomers to the FAG resin but in which glutaraldehyde residues are intercalated with furfuryl alcohol one do form, these are of lower molecular weight, in line with the lower reactivity of glutaraldehyde. However, for the FAG' resin the majority of the higher molecular weight oligomers appear to be formed by linear autocondensed furfuryl alcohol chains to which are linked some aldol-condensed glutaraldehyde residues,^[20,28] such as

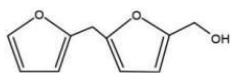


The formation of such oligomers appear to confirm the poorer performance of the FAG' resin and explain in part its poorer performance.

In the case of the FAF resin (Table 6, Figure 8a-e) a greater variety of oligomers appear to form with linear oligomers linked exclusively by either methylene ether bridges, or exclusively by methylene bridges and even mixed

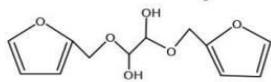
Table 4. Oligomers identified by MALDI-TOF mass spectrometry of the FAG resin.

176Da = FA+ FA without Na+

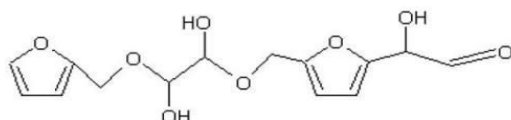


198Da = FA+ FA+ 23Da (Na+)

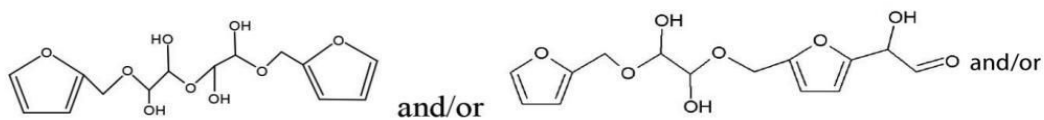
254Da = FA+ G+ FA by aldol condensation occurs



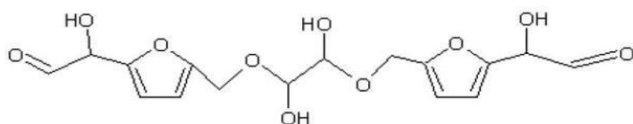
334.1Da = 335Da FA-G-FA -G with(Na+)



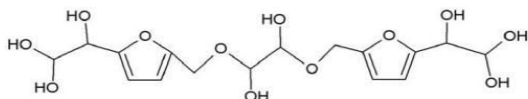
356Da = + 23Da (Na+)



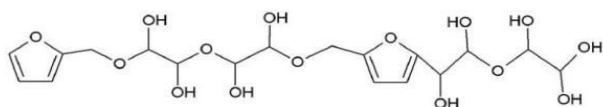
392Da = + 23Da (Na+)



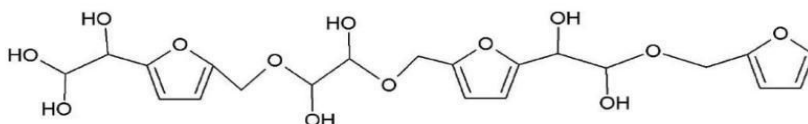
406Da =



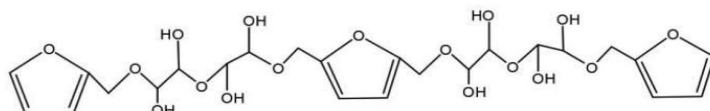
480Da =



486Da =



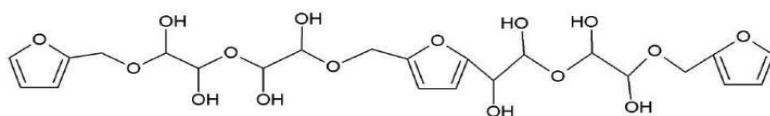
549Da = 526Da+ 23Da (Na+)



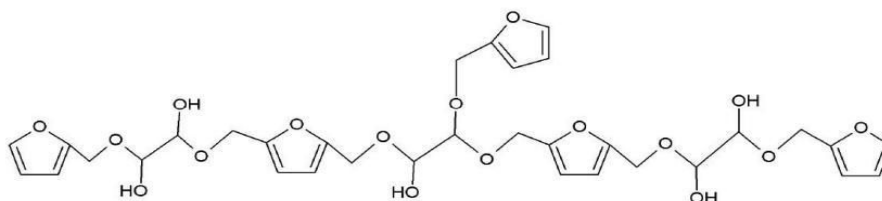
(Continued)

**Table 4. (Continued).**

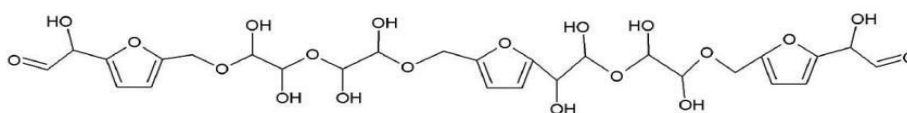
566Da =



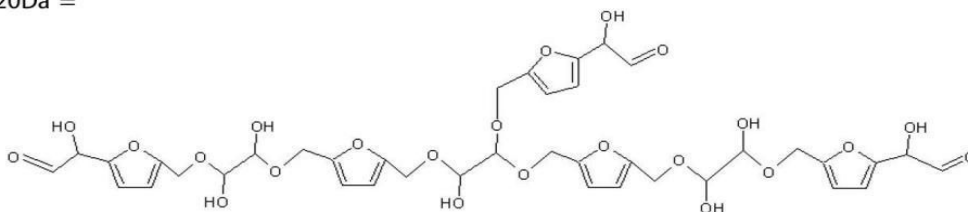
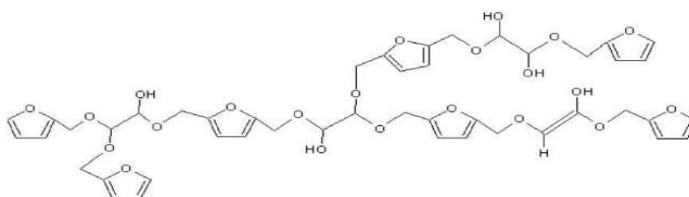
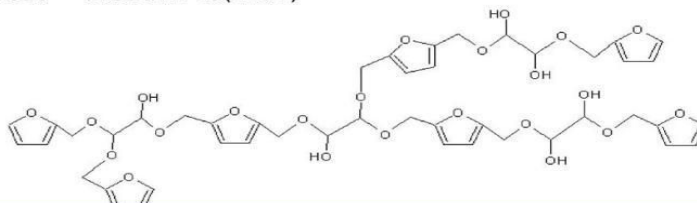
646Da =

681Da = 8 FA+ 23(Na⁺)

762Da =



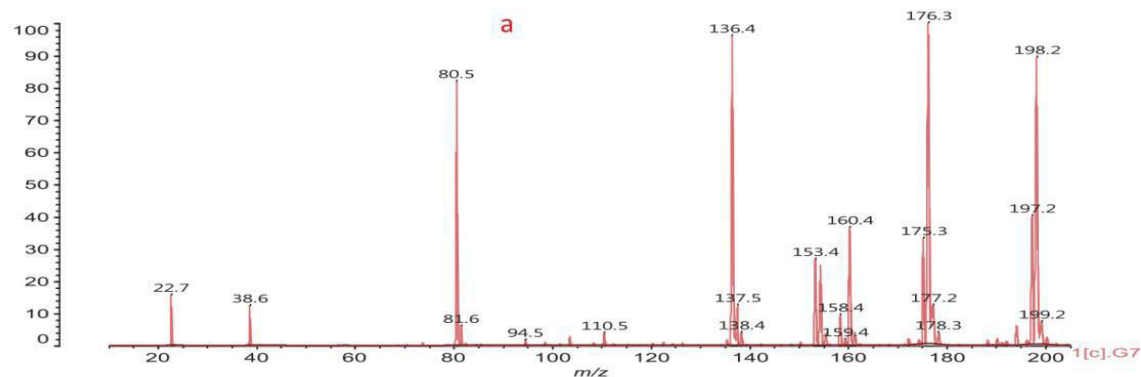
820Da =

841.9Da = 841Da(10*FA+ 23Na⁺)918Da = 895Da+ 23(Na⁺)958Da = 913Da+2*23(2Na⁺)

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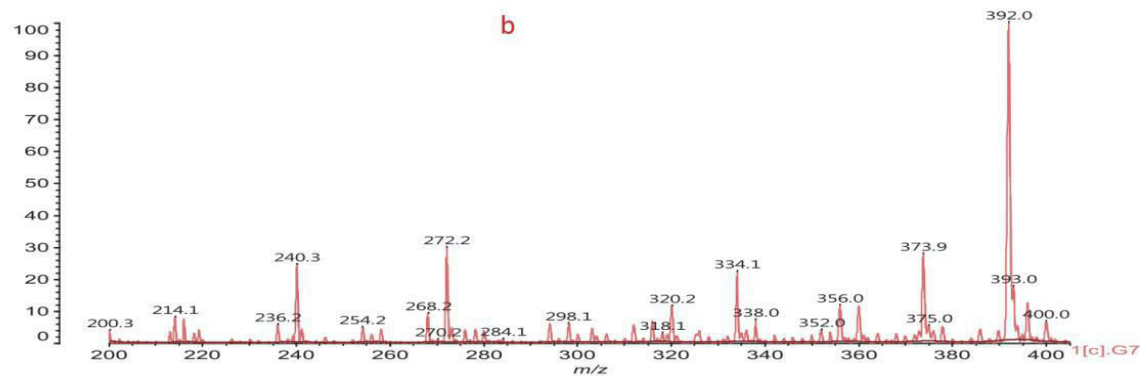
Data: Dry GFA0001.G7[c] 20 Dec 2017 16:59 Cal: ref 20 Dec 2017 16:04
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 77, P.Ext. @ 2300 (bin 78)

%Int. 307 mV[sum= 61439 mV] Profiles 1-200 Smooth Av 50 -Baseline 150



Data: Dry GFA0001.G7[c] 20 Dec 2017 16:59 Cal: ref 20 Dec 2017 16:04
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 77, P.Ext. @ 2300 (bin 78)

%Int. 216 mV[sum= 43103 mV] Profiles 1-200 Smooth Av 50 -Baseline 150



Data: Dry GFA0001.G7[c] 20 Dec 2017 16:59 Cal: ref 20 Dec 2017 16:04
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 77, P.Ext. @ 2300 (bin 78)

%Int. 47 mV[sum= 9419 mV] Profiles 1-200 Smooth Av 50 -Baseline 150

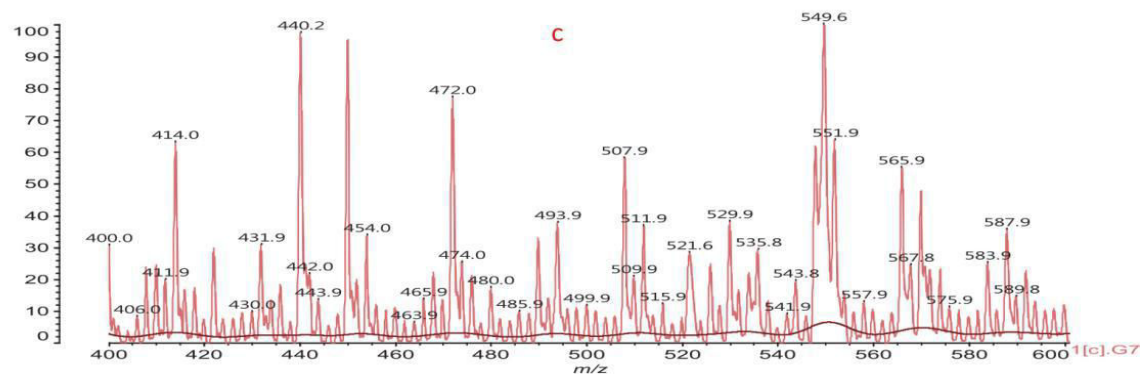
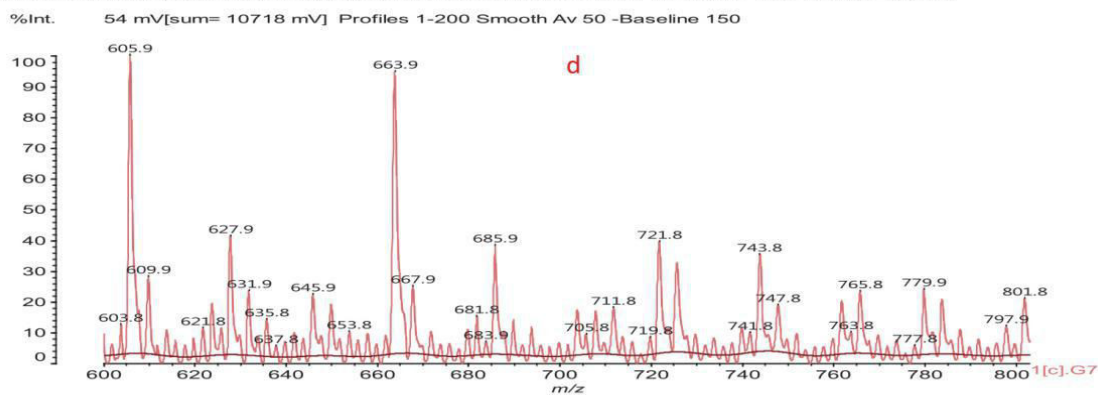


Figure 6. MALDI -TOF spectrum of the FAG resin: 200Da-1000Da range.

Data: Dry GFA0001.G7[c] 20 Dec 2017 16:59 Cal: ref 20 Dec 2017 16:04
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 77, P.Ext. @ 2300 (bin 78)



Data: Dry GFA0001.G7[c] 20 Dec 2017 16:59 Cal: ref 20 Dec 2017 16:04
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 77, P.Ext. @ 2300 (bin 78)

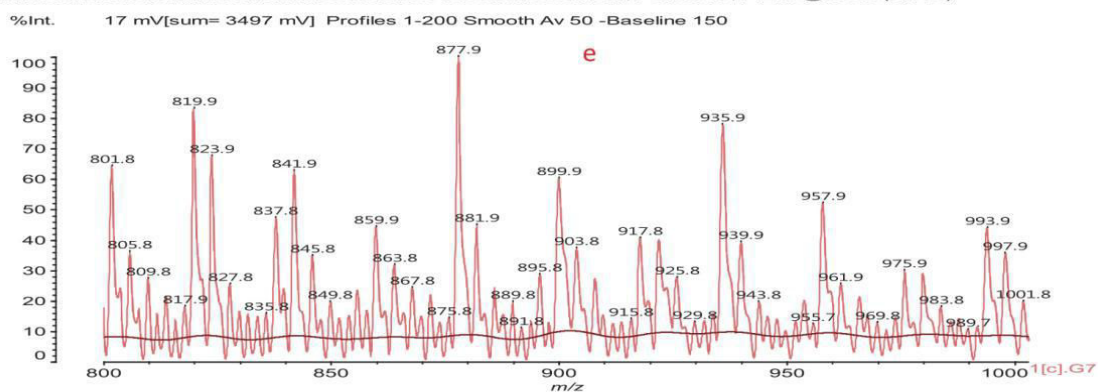
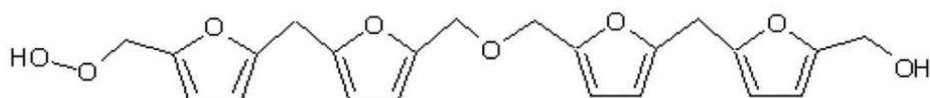
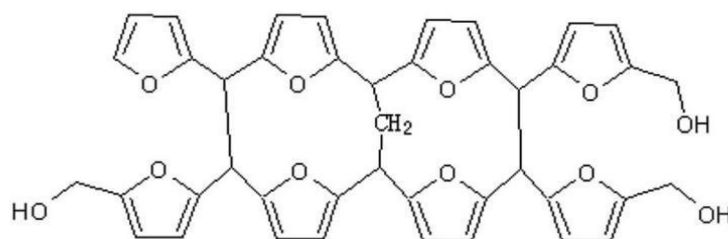


Figure 6. (Continued).

species presenting both types of bridges on the same structure occurs. An example of this latter is at 420 Da:

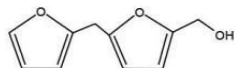


Equally, branched species, and even cross-linked residues can be observed by the MALDI ToF of the FAF resin such as ^[22,29,30]

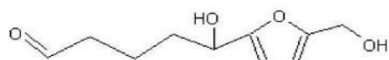


18  X. XI ET AL.**Table 5.** Oligomers identified by MALDI-TOF mass spectrometry of the FAG' resin.

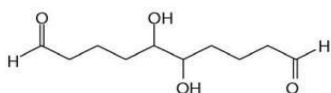
176Da = FA+ FA without Na+



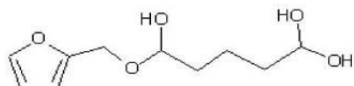
198Da = FA+ FA+ 23Da (Na+)/FA-G' without Na+



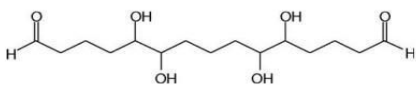
200 Da = G'-G'obtained by aldol condensation



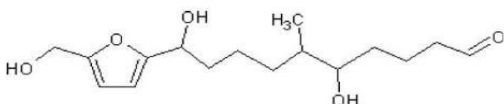
215Da = 214Da calculated,



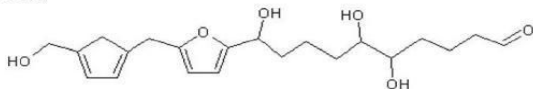
300Da =



298Da =



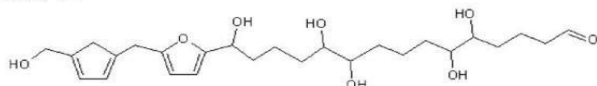
378Da =



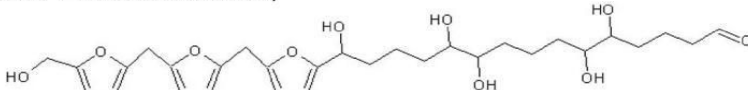
439Da = 438Da calculated,



478Da =



559Da = 558Da calculated,

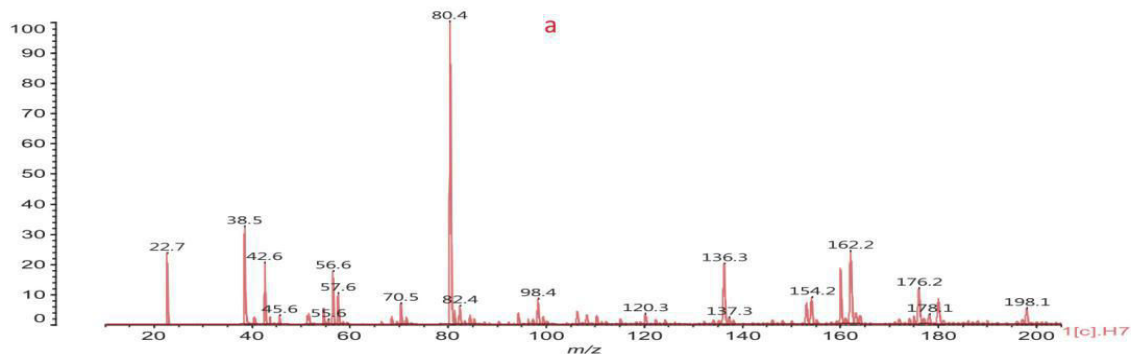


679Da = 678Da calculated, FA-FA-G'-G'-G'-G'-G'

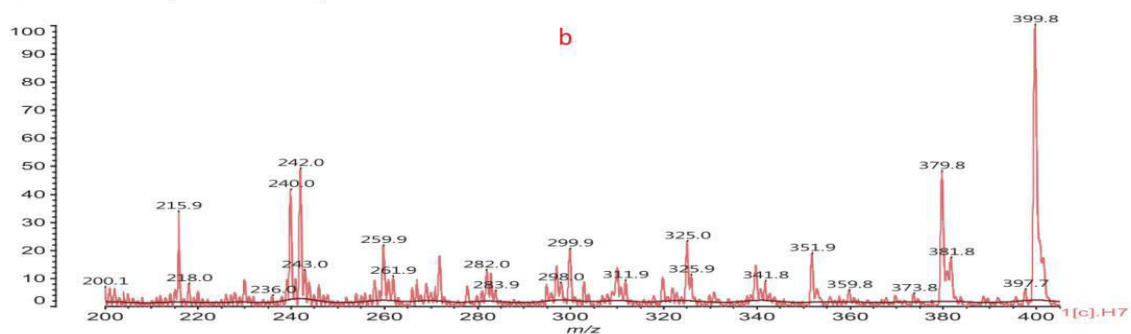
739Da = 738Da calculated, 9 FA self-condensing

759Da = 758Da calculated, FA-FA-G'-G'-G'-G'-G'-G'-G'

Data: Dry G'FA0001.H7[c] 20 Dec 2017 17:06 Cal: ref 20 Dec 2017 16:04
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 90, P.Ext. @ 2300 (bin 78)
%Int. 351 mV[sum= 70265 mV] Profiles 1-200 Smooth Av 50 -Baseline 150



Data: Dry G'FA0001.H7[c] 20 Dec 2017 17:06 Cal: ref 20 Dec 2017 16:04
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 90, P.Ext. @ 2300 (bin 78)
%Int. 49 mV[sum= 9888 mV] Profiles 1-200 Smooth Av 50 -Baseline 150



Data: Dry G'FA0001.H7[c] 20 Dec 2017 17:06 Cal: ref 20 Dec 2017 16:04
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 90, P.Ext. @ 2300 (bin 78)
%Int. 101 mV[sum= 20291 mV] Profiles 1-200 Smooth Av 50 -Baseline 150

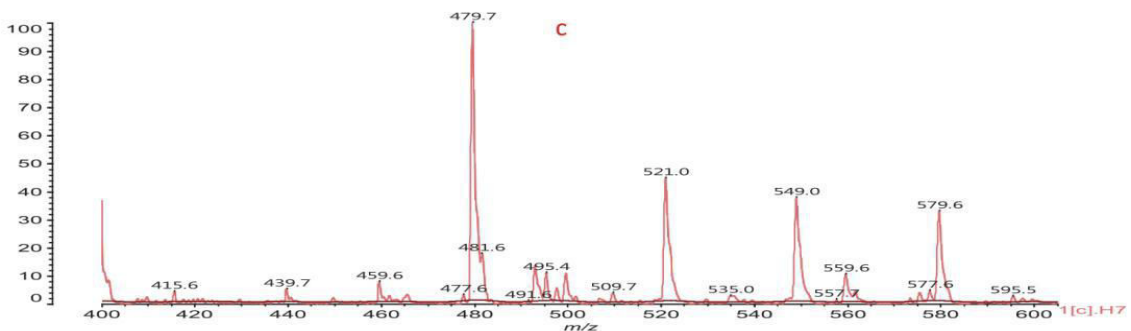


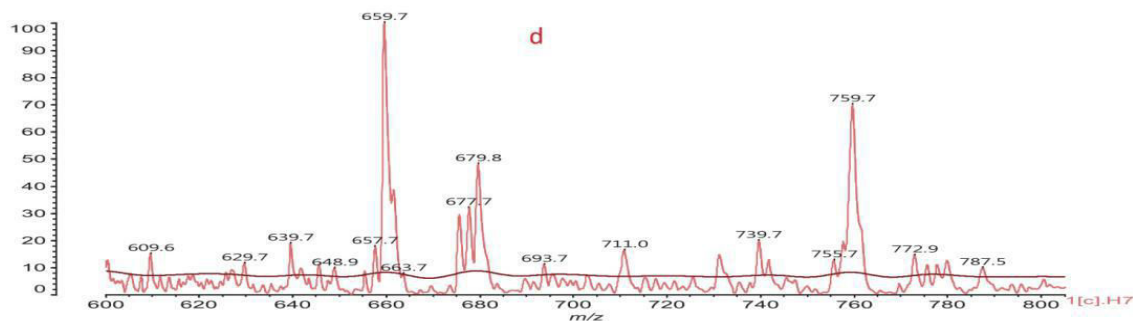
Figure 7. MALDI ToF spectrum of the FAG' resin: 20Da-1000Da range.

5. Conclusions

Furfuryl alcohol as a renewable biological resource, is widely used in the foundry industry, but hasn't been used alone as a wood adhesives. In this paper, furfuryl alcohol was reacted with formaldehyde, glyoxal, and glutaraldehyde to prepare the furfuryl alcohol-aldehyde resins as wood

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Data: Dry G'FA0001.H7[c] 20 Dec 2017 17:06 Cal: ref 20 Dec 2017 16:04
 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 90, P.Ext. @ 2300 (bin 78)
 %Int. 10.0 mV[sum= 1992 mV] Profiles 1-200 Smooth Av 50 -Baseline 150



Data: Dry G'FA0001.H7[c] 20 Dec 2017 17:06 Cal: ref 20 Dec 2017 16:04
 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 90, P.Ext. @ 2300 (bin 78)
 %Int. 1.8 mV[sum= 368 mV] Profiles 1-200 Smooth Av 50 -Baseline 150

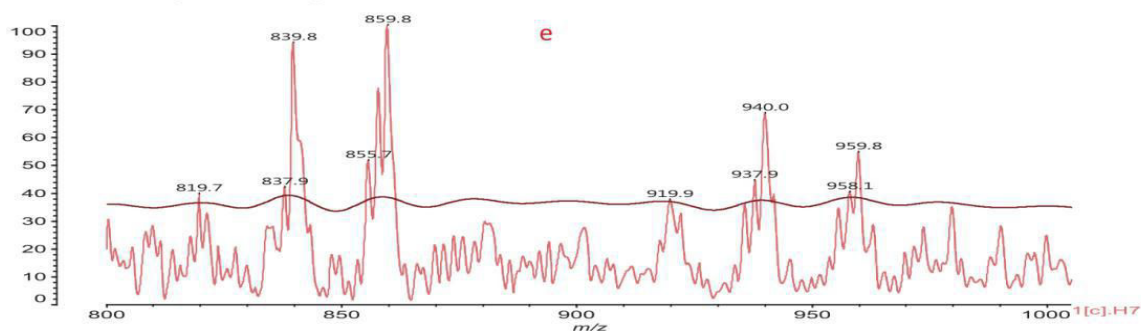
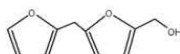


Figure 7. (Continued).

Table 6. Oligomers identified by MALDI-TOF mass spectrometry of the FAF resin.

176Da = FA+ FA without Na+

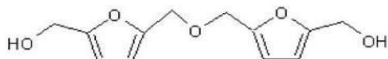


198Da = FA+ FA+ 23Da (Na+)

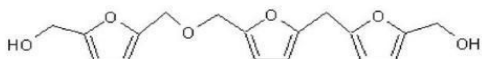
230Da = 231Da calculated, 208Da with Na+



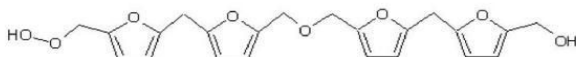
260Da = 261 calculated, 238Da with Na+



340Da = 341Da calculated



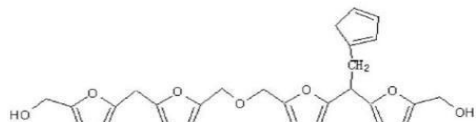
420Da =



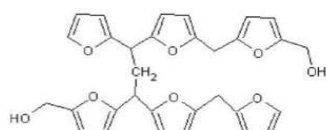
(Continued)

Table 6. (Continued).

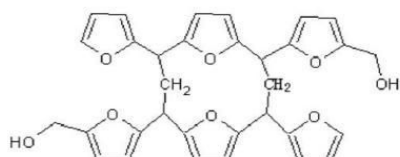
500Da =



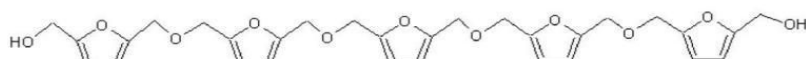
535Da = 512Da with Na+



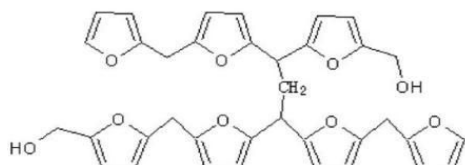
549Da = with Na+



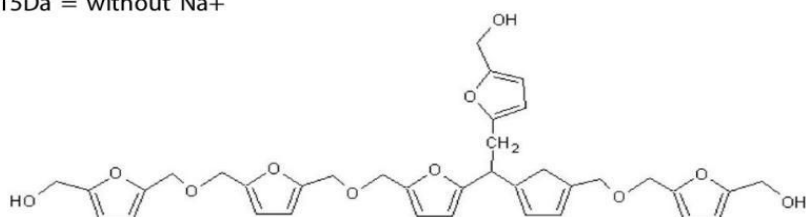
568Da =



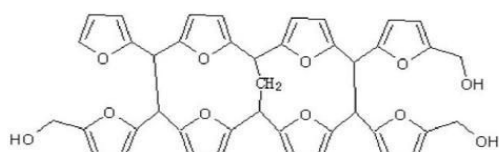
615Da = with Na+



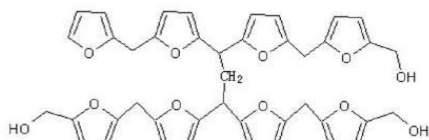
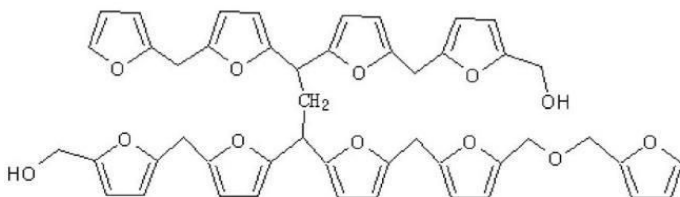
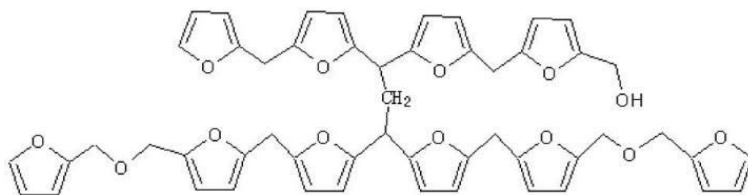
615Da = without Na+



721Da = with Na+



(Continued)

Table 6. (Continued).725Da = with Na⁺805Da = without Na⁺885Da = without Na⁺

panel adhesives. The furfuryl alcohol formaldehyde (FAF) resin has a good bonding performance and excellent resistance to water and hot water. However, due to the use of formaldehyde, it may present problems of formaldehyde emission. The furfuryl alcohol-glyoxal (FAG) resin also showed satisfactory results for plywood, the dry strength, 24 hours wet strength, and 2h boiled water wet strength being 1.02MPa, 1.36MPa, and 1.46MPa. These are significantly higher than the standard requirements ($\geq 0.7\text{MPa}$). Moreover, glyoxal is non-toxic and non-volatile^[31,32], so that the FAG resin can be considered a more environmentally friendly adhesive. Because of the lower reactivity between glutaraldehyde with furfuryl alcohol, FAG' resin exhibited the worst bonding performance compared to FAF and FAG, especially when the self-neutralizing hardener system (1%p-TSA+ 2% morpholine/phosphoric acid) was used, and the mechanical properties of plywood bonded with it could not meet the standard requirements.

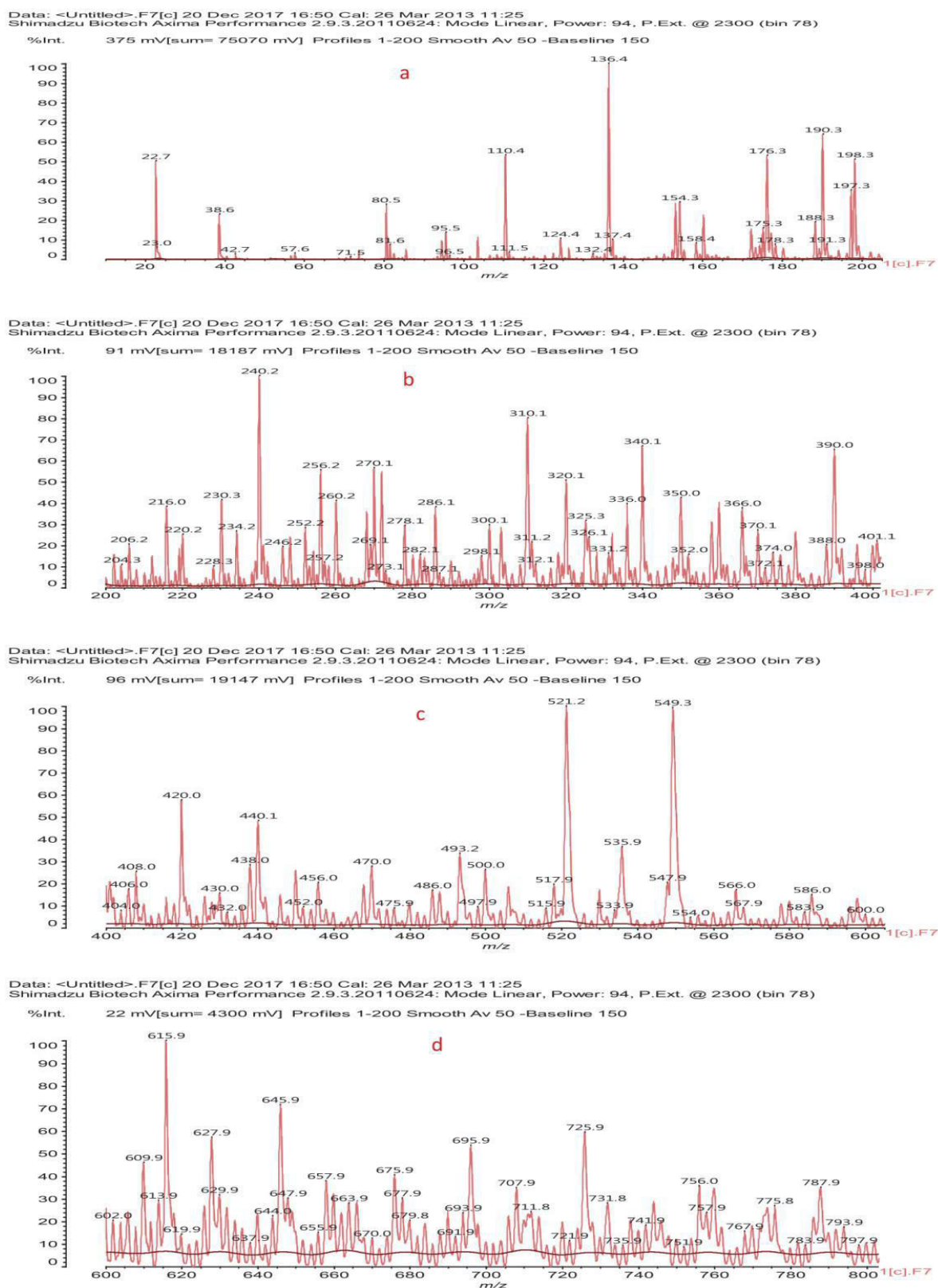


Figure 8. MALDI ToF spectrum of the FAG' resin: 20Da-1000Da range.

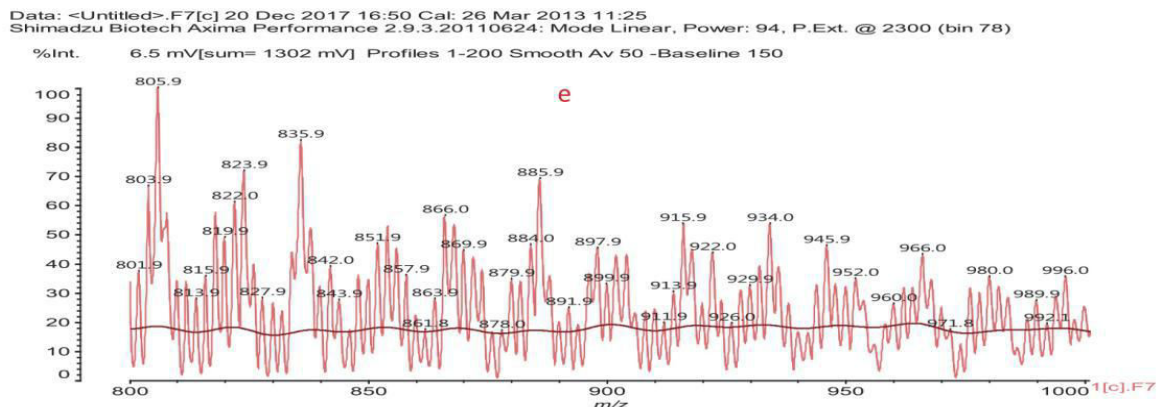


Figure 8. (Continued).

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3.4 Adhésif à base de tanin réticulé par les résines époxy, alcool furfurylique et glyoxal

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Résumé: Afin de préparer un adhésif naturel à base de tanin avec une bonne résistance à l'eau, une résine respectueuse de l'environnement, à base d'alcool furfurylique-glyoxal synthétisée en laboratoire, a été développée comme agent de réticulation pour les adhésifs à base de tanin. Les résultats de la résonance magnétique nucléaire (RMN) et MALDI-TOF ont indiqué que l'alcool furfurylique et le glyoxal réagissaient dans des conditions acides et que les groupes impliqués dans la réticulation de la colle tanin-furfuryl-glyoxal (TFG) sont -CH- (OH)-. Les résultats concernant la résistance au cisaillement humide du contreplaqué lié au TFG ont montré que le TFG a donné des résultats meilleurs que la résine tannin-alcool furfurylique (TF). De plus, l'adhésif TFG réticulé avec une résine époxy à 12% (EPR) présentait une bonne résistance à l'eau. Son module d'élasticité (MOE) était supérieur à celui des adhésifs tannin-alcool furfurylique-formaldéhyde (TFF), TF et phénol-formaldéhyde (PF).

Mots clés: alcool furfurylique-glyoxal; adhésif à base de tanin; agent de réticulation; résistance à l'eau.



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Tannin-based adhesive cross-linked by furfuryl alcohol-glyoxal and epoxy resins

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ABSTRACT

To prepare a natural tannin-based adhesive with good water resistance, an environment friendly furfuryl alcohol-glyoxal resin (FG) synthesized in the laboratory was developed as a cross-linker for tannin-based adhesives. ¹³C Nuclear Magnetic Resonance (NMR) and Matrix-Assisted Laser Desorption-Ionization Time-of-Flight (MALDI-TOF) mass spectroscopy results indicated that furfuryl alcohol and glyoxal reacted under acidic conditions and that the -CH-(OH)- groups could be shown to be the ones involved in the cross-linking of the tannin-furfuryl-glyoxal adhesive (TFG). The results for the wet shear strength of TFG-bonded plywood showed that the cured TFG was improved and better than that bonded with a tannin-furfuryl alcohol (TF) adhesive. Moreover, the TFG adhesive cross-linked with 12% epoxy resin (EPR) presented a good water resistance. It had a modulus of elasticity (MOE) higher than that of tannin-furfuryl alcohol-formaldehyde (TFF), TF and phenol-formaldehyde (PF) adhesives.

1. Introduction

During the last decades, PF wood adhesives have been widely used in the wood panel industry. However, the toxicity of free formaldehyde and phenol together with associated disposal problems have limited their further development [1,2]. Thus, with the gradually increasing needs for environment-friendly adhesives, considerable research has been conducted to develop bio-based resins coming from agricultural and forest resources such as tannin and furfuryl alcohol [3,4]. Natural condensed tannins extracted from tree bark has successfully been used to replace some petrochemical products owing to their similarity with the structure of phenol [5,6]. Furthermore, furfuryl alcohol obtained from the hydrolysis of wheat, corn and sugarcane waste has also been used to prepare polymers in industry due to the structure stability of the materials obtained and their good water resistance [7]. Nowadays biosourced materials based on tannin-furanic resins such as tannin-furanic foam [8,9], rigid plastics [10] and grinding wheels matrices [11,12] have been considerable interest to the research community. These materials present excellent mechanical properties when compared with oil-derived PF materials. However, for tannin-furanic (TF) wood panel adhesives, cross-linking is carried out under alkaline conditions to avoid wood substrate hydrolysis which would occur under acidic conditions and that the self-condensation of furfuryl alcohol predominates to such an extent to lead to little or no coreaction with

tannin thus showing poor water resistance. As hydroxymethyl groups (-CH₂OH) are present in furfuryl alcohol, formaldehyde has been used as a cross-linker between furfuryl alcohol and tannin for tannin-furanic-formaldehyde (TFF) adhesives [4]. However, TFF adhesives are not a desirable solution as an environment-friendly adhesive because of the potential toxicity of formaldehyde. Glyoxal is a non-toxic aldehyde although less reactive than formaldehyde [13]. Consequently, research on glyoxal, furfuryl alcohol and tannin has been conducted to ascertain the feasibility of tannin-furanic-glyoxal (TFG) adhesives presenting a good bonding strength and a better water resistance. In this paper, firstly tannin, furfuryl alcohol and glyoxal were used to cross-link bio-based TFG adhesives under acid conditions. Secondly, in order to improve the water resistance of TFG, hybrid cross-linkers were established between TFG resin and a commercial epoxy resin (EPR). This study is important for the development of environment-friendly wood adhesives to replace industrial PF wood adhesives.

2. Experimental

2.1. Materials

Mimosa(*Acacia mearnsii*, formerly *mollissima*, De Wildt) wood tannin extract powder was purchased from Wu Ning Tannin Extract Factory (Guanxi, China). Following water extraction from the bark, the

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tannin was extracted by ethanol to eliminate the majority of carbohydrates present.

Glyoxal (with a purity of 40%), furfuryl alcohol (with a purity of 98%) and formaldehyde (with a purity of 37%) were purchased from Acros Organics (Geel, Belgium).

Beech veneer (*Fagus sylvatica*) with a 1.5 mm thickness and 9–10% moisture content was supplied by Xin Fei Lin panel Company (Kunming, China).

Commercial EPR (E-44) was purchased from Sinopharm Chemical Reagent Company (Beijing, China).

PF control adhesive (molar ratio F/P = 2.2) was supplied by Xin Fei Lin panel Company (Kunming, China).

2.2. Preparation of TF, TFF and TFG adhesives

The TF adhesive was synthesized according to the method of Abdullah and Pizzi [3]: 70 g of tannin, 35 mL of furfuryl alcohol and 100 mL of distilled water were mixed in a beaker under stirring for 30 min at 60 °C under alkaline conditions to form the TF adhesive. During the process, the pH was adjusted by NaOH (40%) solution to pH 10.

The TFF adhesive was prepared by the following process: 28.9 mL of formaldehyde, 35 mL of furfuryl alcohol and 100 mL of distilled water were mixed in a flat-bottom flask with a thermometer and magnetic stirrer bar at 60 °C for 30 min to obtain the furfuryl alcohol-formaldehyde (FF) resin. During this process, 30% acetic acid was used to adjust the pH to 3. After that, 70 g of tannin was added at 60 °C for 30 min to obtain the TFF adhesive.

The TFG adhesive was synthesized as follows: first, 30 mL of furfuryl alcohol, 133 mL of glyoxal and 50 mL of distilled water were mixed in a flat-bottom flask with a thermometer and stirrer at room temperature for 1 h to obtain the furfuryl alcohol-glyoxal (FG) resin. During this process, 30% acetic acid was used to adjust the pH to 4. The process is important for the decrease of furfuryl alcohol self-condensation under strong acid conditions. Second, 60 g of tannin was added into FG resin under a pH of 4 at 70 °C for 30 min to form the TFG adhesive.

The gel times and viscosities of the TF, TFF, TFG and PF adhesives were determined according to GB/T14074.9 (2006). For the gel times test, 10 g of adhesive was put into a test tube, which was then immersed in a boiling water bath (100 °C) and gently, continuously, and rapidly stirred with a muddler using an upward-downward movement until gelation occurred. The gel time was measured from the start of immersion of adhesive in boiling water. A tu-4 viscosity cup was used to test the viscosities of these adhesives. The solids content of the various adhesives were measured by determining the weight of the adhesives before and after drying at 120 ± 1 °C in an oven for 2 h. The characteristics of the different adhesives are shown in Table 1.

2.3. Preparation of plywood

The Beech veneers were used for the preparation of three-layer plywood of dimensions 300 mm × 220 mm × 4 mm. Firstly, adhesive was brushed onto the veneer surfaces with an adhesive loading of 320 g/m². Then three veneers were combined and put into a press and bonded under a pressure of 1.5 MPa at 170 °C for 5 min. The TFG adhesives were mixed respectively with different amounts of EPR (weight

percentages of 3, 6, and 9) under stirring for 3 min before being brushed onto the surfaces of the veneers. After pressing, the plywood was conditioned in a laboratory at a constant temperature of 23 ± 0.1 °C and a relative humidity of 60% for 24 h.

2.4. Test of dry and wet shear strengths of plywood specimens

Each plywood specimen was cut into dimensions of 100 mm × 25 mm for shear strength testing. An Instron 4476 universal testing machine was used to measure the shear strength of the specimens with each specimen having a 25 mm × 25 mm bonded area. Wet and dry shear strengths were determined respectively according to the Chinese national standards GB/T17657-1999 and GB/T9846.7-2004. Before wet shear strength testing, the specimens were immersed in water at 63 ± 3 °C for 1 h or in boiling water (100 °C) for 3 h, the final wet shear strength has to equal 0.9 of the remaining strength. Eight replicates were tested to allow calculation of mean values and standard deviations.

2.5. ¹³C-NMR

A super conducting magnetic resonance imaging apparatus (Bruker-AVANCE 600, Switzerland) was used to detect the presence of FF and FG resins. The resonance frequency employed was 150 MHz. 300 µL of samples and 100 µL dimethyl sulfoxide (DMSO - d₆) solvent were mixed and assessed. Test conditions: relaxation delay time was 6 s; scanning accumulative number was 800–1200 times; and temperature of 25 °C.

2.6. MALDI-TOF-MS

The mass spectrometry detection of different cured tannin-based adhesives was implemented using a KRATOS Kompact MALDI 4 instrument (AXIMA Performance, Shimadzu). Firstly, different cured adhesives were dissolved in acetone (10 mg/mL). After that 2, 5-dihydroxy benzoic acid (C₇H₆O₄) as the matrix was mixed with NaCl (10 mg/mL) for the ion formation enhancement. The solutions of adhesive and matrix were mixed according to the proportions: 3 parts adhesive solution, 3 parts matrix solution and 1 part NaCl solution. 0.5–1 µL of the mixed solution was then placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer. The irradiation source was a pulsed nitrogen laser with a 337 nm wavelength and the duration of a single laser pulse was 3 ns. The measurement conditions were as follows: polarity-positive, flight path-linear, mass-high with 20 kV acceleration voltage and 100–150 pulses per spectrum. A delayed extraction technique was used by applying delay times of 200–800 ns [5].

2.7. Thermomechanical analysis (TMA)

The elasticity modulus (MOE) of different tannin based adhesives was obtained by a TMA instrument (Mettler-Toledo, SDTA840, New York, USA) with the STARE software (Mettler-Toledo, Version 14.0, New York, USA) for data treatment. Two beech veneers each 0.6 mm thick, bonded with each system, for a total samples dimension of 21 × 6 × 1.2 mm were tested. The heating rate was 20 °C/min and the temperature range was 25 °C–250 °C.

3. Results and discussion

3.1. Characteristics of laboratory plywood bonded with tannin-based adhesives

The results obtained from testing the plywood panels bonded with these tannin-based adhesives and PF adhesive are shown in Table 2. The dry shear strength values for all of the tannin-based plywood samples were sufficient to meet the requirements of the Chinese

Table 1
Characterization of laboratory tannin-based adhesives.

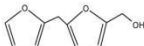
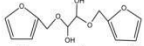
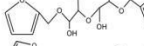
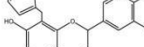
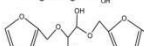
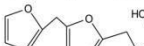
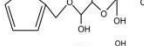
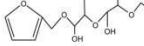
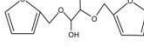
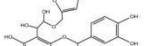
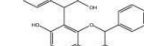
Adhesive type	Solid content/%	Viscosity/(mm ² /s)	Gel times/s
TF	35	215.25 ± 1.33	402 ± 3
TFF	48	309.41 ± 1.28	154 ± 4
TFG	47	291.48 ± 1.46	198 ± 4
PF	53	325.28 ± 1.51	126 ± 3

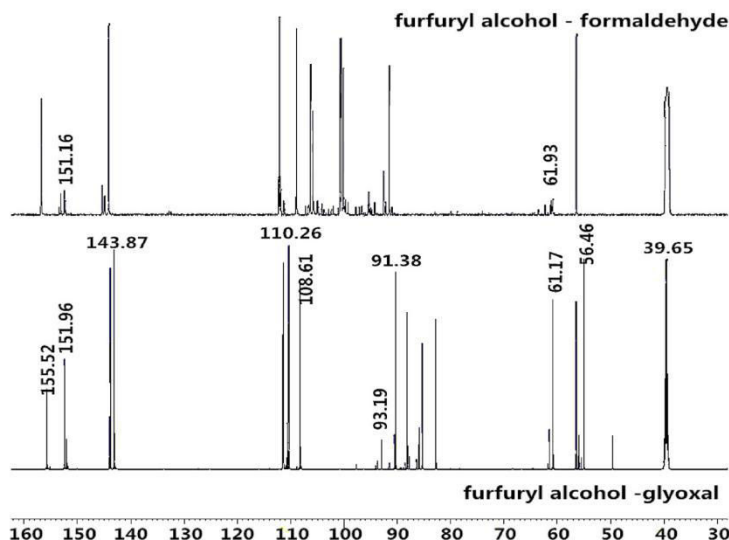
Table 2
Performance of tannin-based adhesives.

Adhesive Type	Dry shear strength/MPa	63 °C for 1 h	Boil test at 100 °C for 3 h
		Wet shear strength/MPa	Wet shear strength/MPa
TF	0.72 ± 0.09	0	0
TFF	1.65 ± 0.07	0.58 ± 0.09	0.51 ± 0.07
TFG	1.23 ± 0.08	0.55 ± 0.08	0
3%EPR + TFG	1.56 ± 0.08	0.63 ± 0.08	0.52 ± 0.09
6%EPR + TFG	1.61 ± 0.09	0.68 ± 0.09	0.55 ± 0.08
9%EPR + TFG	1.69 ± 0.07	0.65 ± 0.07	0.63 ± 0.08
12%EPR + TFG	1.82 ± 0.09	0.73 ± 0.07	0.72 ± 0.07
PF	1.67 ± 0.07	0.91 ± 0.08	0.93 ± 0.07

national standard (GB/T9846.3-2004, ≥ 0.70 MPa). For the TF adhesive, in order to avoid the self-condensation of furfuryl alcohol [3], its synthesis was conducted under alkaline conditions. However, the panel bonded using this adhesive presented poor water resistance. To decrease the self-condensation of furfuryl alcohol and improve the water resistance of TF adhesive, glyoxal as a coupling agent was then used to react with tannin and furfuryl alcohol under acid conditions for the preparation of the TFG adhesive. Meanwhile, the TFF adhesive prepared in the laboratory was compared with the TFG adhesive. As seen from Table 3, the dry shear strength of the panel bonded with the TFF adhesive was higher than that of the panel bonded with the TFG adhesive. Furthermore, compared to the TFF adhesive-bonded panel, the TFG adhesive-bonded one showed unacceptable water resistance when placed in boiling water (100 °C) for 1 h. However, the further addition of different proportions of EPR to the TFG improved markedly its water resistance. The panel bonded with the TFG adhesive cross-

Table 3
Oligomers identified by MALDI-TOF mass spectrometry in the reaction of furfuryl alcohol + glyoxal + mimosa tannin.

Experimental		Calculated		Chemical Species
[M + H] ⁺	[M + Na] ⁺	[M + H] ⁺	[M + Na] ⁺	
	200		201	
254		255		
	278		281	
312	334	313	335	
356		355		
410		411		
414.4		415		
468		469		
526	549	527	549	
566		567		
704		703		
760		761		
788		787		

Fig. 1. ^{13}C -NMR spectrum of the FF and FG resins.

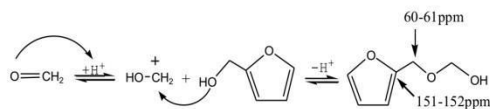
linked with 12% EPR showed good strength and its shear strength after 3 h in boiling water at 100 °C, tested wet, was as high as 0.72 MPa. In addition, the dry shear strength of the panel bonded with TFG + 12% adhesive was higher than that of the panel bonded with PF adhesive. On the contrary, compared with the TFG + 12% adhesive, the panel bonded with PF adhesive showed a good strength after soaking in water at 63 °C or in boiling water.

Further industrial optimization for a possible future industrial production is necessary but TFG + 12% EPR adhesive appears competitive with the TF and PF adhesives.

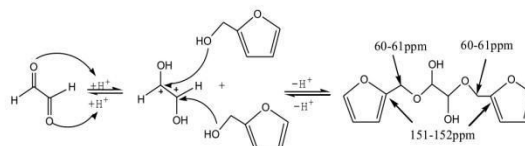
3.2. ^{13}C -NMR analysis

Glyoxal was used as a coupling reagent for cross-linking with furfuryl alcohol to decrease the self-condensation of furfuryl alcohol itself. To investigate the reaction of furfuryl alcohol and glyoxal, the FG resin was scanned by ^{13}C NMR. The FF resin was also scanned by NMR for comparison. Their NMR spectra are shown in Fig. 1. According to the literature [10,14,15], the methylene ($-\text{CH}_2-$) bridges due to furfuryl alcohol self-condensation are those corresponding to the peak region between 30 and 40 ppm. The spectrum of the FF resin, instead, does not present any peak in the 30–40 ppm region, while the self-condensation of furfuryl alcohol has appeared to have occurred by the presence of the signals at 151–152 ppm. Moreover, the 60–61 ppm shifts belong to methylene ether ($-\text{CH}_2-\text{O}-\text{CH}_2-$) bridges between furfuryl alcohol and formaldehyde (cf. Scheme 1).

For the spectrum of the FG resin, the peak at 56–57 ppm was attributed to the hydroxymethyl group ($-\text{CH}_2-\text{OH}$) of furfuryl alcohol, indicating that some residual resin reactivity is still present. The regions at 155–156 ppm, 142–143 ppm and 108–110 ppm belong to the structure of furfuryl alcohol. The 151–152 ppm and 60–61 ppm peaks can be attributed to the co-reaction between furfuryl alcohol and glyoxal (shown in Scheme 2), indeed similar to that of the FF resin. Conversely,



Scheme 1. The main reaction between formaldehyde and furfuryl alcohol.



Scheme 2. The main reaction between glyoxal and furfuryl alcohol.

no shifts between 30 and 40 ppm are observed in the spectrum of the TFG adhesive. These results indicate that cross-linking between glyoxal, or formaldehyde, and furfuryl alcohol do occur under acid conditions effectively avoiding self-condensation of furfuryl alcohol.

In all, the $-\text{CH}(\text{OH})$ -groups were established with the reaction of glyoxal with furfuryl alcohol. It could easily cross-link tannin under acid condition after curing process.

3.3. MALDI-ToF analysis

The results of the MALDI-TOF analysis of the different oligomers formed in the preparation of the FG and TFG resins generated by the copolymerization reaction of furfuryl alcohol, glyoxal and tannin are shown in Figs. 2 and 3. The main chemical structures of FG and TFG resins are shown in Table 3. All the peak values are based on the molecular weight (MW) of the species + 23 Da due to the Na^+ of the NaCl matrix enhancer used, or + 1 Da due to H^+ protonation [16,17]. Fig. 2 shows that the whole series of oligomers at 254 Da, 312/334 Da, 410 Da, 468 Da, 526/549 Da indicate that the co-reaction between furfuryl alcohol and glyoxal has indeed occurred. Meanwhile, the 200 Da and 278 Da peaks (shown in Fig. 3a) belong to the dimers and trimers formed by the bridge bonding of furfuryl alcohol monomers, indicating that simultaneously also the self-condensation of furfuryl alcohol has occurred. Fig. 3a and b also show some peaks at 254 Da, 312 Da, 410 Da and 526 Da, indicating that there is still some residual reactivity in the TFG resin due to the presence of still active hydroxymethyl groups ($-\text{CH}_2-\text{OH}$). The main flavonoid repeating units of mimos tannin are fisetinidin, robinetinidin, catechin and delphinidin [18]. The 356 Da (Fig. 3a) peak belongs to oligomers formed by furfuryl alcohol reacting with a fisetinidin monomer. Moreover, the peaks at 704 Da and 760 Da (Fig. 3c) can be attributed to products of the co-



In terms of plywood performance, the water resistance of TFG + 12% adhesive was better than that of the TFG adhesive, the establishment of a cross-link between FG resin and tannin contributed to the formation of oligomers (Table 3; 703 and 761 Da). These oligomers could easily cross-link EPR under acidic conditions during the curing process (Scheme 3). Numerous tertiary carbon hydroxylmethyls existed in the TFG + 12% EPR adhesive. The three-dimensional network structure of TFG + 12% EPR adhesive in the curing process was formed by the cross-linking of tertiary carbon hydroxylmethyls.

also starts to increase at a lower temperature, which means the energy of activation of hardening of the TFG + 12%EPR is apparently lower than TFF and TFG, this is confirmed by the thermomechanical analysis trace report previously [21]. Moreover, the MOE value of the TFG + 12%EPR adhesive was higher than that of the MOE value of the PF adhesive (1068 MPa).

In this paper, a renewable tannin-furfuryl alcohol-glyoxal wood adhesive is presented. Definite proportions of furfuryl alcohol and glyoxal in water were pre-condensed for 1 h at ambient temperature under acid conditions. This pre-polymer was then mixed with mimosa

Fig. 3. MALDI-TOF peaks of the TFG resin: a) 200–400; b) 400–600; c) 600–800.

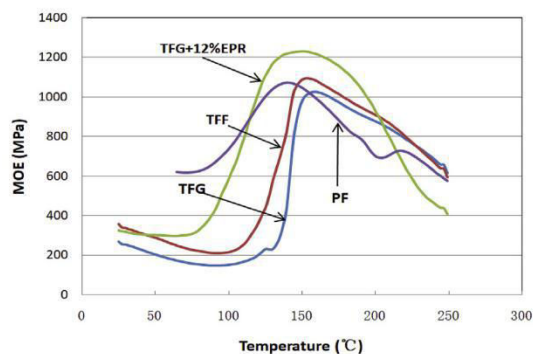


Fig. 4. Thermomechanical analysis (TMA) spectra of different tannin-based adhesives.

tannin at 70 °C for 30 min. The ^{13}C NMR and MALDI TOF results showed that there was a reaction between furfuryl alcohol and glyoxal. Moreover, the hydroxymethyl groups $-\text{CH}-\text{OH}-\text{R}-$ generated by this reaction appeared to be the reactive groups leading to the cross-linking of TFG adhesive. The wet shear strength of TFG plywood improved compared with that of TF plywood, although the wet shear strength obtained with the TFG adhesive was lower than that with the TFF wood adhesive. In order to prepare a tannin-based adhesive with good water resistance, 12% EPR was mixed with TFG adhesive, this yielding good water resistance of the plywood. Furthermore, the MOE value of plywood prepared with 12%EPR + TFG adhesive was higher than that of plywood prepared with TF and PF adhesives.

Acknowledgments

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3.5 Bioadhésifs de contreplaqué de tanin par génération d'aldéhydes non volatils par oxydation spécifique de mono- et disaccharides

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Résumé: Il a été montré que le periodate de sodium clive le glucose par oxydation spécifique pour donner un certain nombre d'aldéhydes non volatils qui peuvent réagir avec les composés phénoliques contenus dans l'extrait de tanin et conduire à une réticulation et un durcissement du tanin. Cette approche pour préparer une résine de tanin utilisable pour les adhésifs pour le bois peut être utilisée soit en traitant avec le periodate le mélange de tanin et de glucose, soit en traitant au préalable avec le periodate le glucose pour le scinder et générer les aldéhydes et ensuite pour le mélanger avec le tanin. Les résultats obtenus avec ces deux méthodes sont identiques, mais cette dernière méthode évite l'oxydation du tanin. Les aldéhydes ont été générés soit par scission directe de liaisons glucose C-C portant des hydroxyles orientés vicinaux, soit par recombinaison des aldéhydes ainsi formés par condensation d'aldol, soit par élimination d'eau entre deux groupes aldéhyde. L'analyse MALDI ToF a indiqué que les trois types d'aldéhydes semblaient réagir avec les polyphénols du tanin. Une analyse TMA sur un contreplaqué lié aux mélanges tanin + glucose + periodate a donné de bons résultats, avec une immersion dans une eau sèche et froide pendant 24 heures et une résistance au cisaillement de 3 heures à 63 ° C améliorant de manière concomitante la proportion de periodate utilisée pour l'étape d'oxydation.

Mots-clés: adhésifs pour bois, contreplaqué, oxydation spécifique du glucose, bio-génération de bioaldéhydes non volatils, clivage du glucose.

Tannin plywood bioadhesives by non-volatile aldehydes generation

by specific oxidation of mono- and disaccharides

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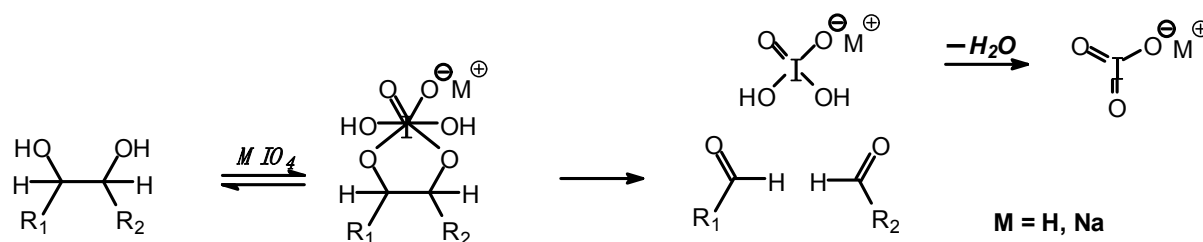
ABSTRACT

Sodium periodate has been shown to cleave glucose by specific oxidation to yield a number of non-volatile aldehydes which can react with the phenolic compounds in tannin extract and lead to tannin cross-linking and hardening. This approach to prepare a tannin resin usable for wood adhesives can be used by either treating with the periodate the mixture of tannin and glucose, or to treat beforehand with the periodate the glucose to cleave it and generate the aldehydes, and only afterwards to mix it with the tannin. The results obtained with these two methods are identical, but the latter method avoids oxidation of the tannin. The aldehydes were generated either by direct cleavage of glucose C-C bonds carrying vicinal oriented hydroxyls, or by recombination of the aldehydes so formed by aldol condensation or by water elimination between two aldehyde groups. MALDI ToF analysis indicated that all the three types of aldehydes appeared to react with the polyphenols in the tannin. TMA analysis an plywood bonded with the tannin+glucose+ periodate mixes gave good bonding results, with dry, 24 hours cold water soaking and 3 hours at 63°C shear strength improving concomitantly to the proportion of periodate used for the oxidation step.

Keywords: wood adhesives, plywood, glucose specific oxidation, biogeneration non-volatile bioaldehydes, glucose cleavage.

INTRODUCTION

Recently, to meet new environmental standard a number of different approaches to the use of natural materials have been taken to prepare wood adhesives without the use of formaldehyde. Among the more recent ones the use of specific oxidants of oligomeric carbohydrates in soy flour have shown particularly interesting results allowing not only the protein fraction but also the carbohydrate fraction to participate positively in the preparation of the adhesive. In this approach soy flour adhesives have been successfully prepared by treating soy flour with either potassium permanganate or sodium periodate [1]. Both potassium permanganate and sodium periodate are specific oxidants for carbohydrates reacting with adjacent vicinal hydroxyl groups to form dialdehydes [2] according to the reaction



The aldehydes so generated react with the active sites of the soy protein leading to cross-linking and yielding wood panels presenting very encouraging internal bond (IB) strengths, especially under wet testing conditions [1,2].

The oxidation with the periodate ion, resulting in 1,2-glycol scission, is one of the most widely used reactions in carbohydrate chemistry. The mild reaction and the aqueous solvent conditions for periodate oxidation are particularly apt to use with the water-soluble carbohydrates. The development and wide application of the reaction are due to its high degree of selectivity [1].

Such approach can be used to prepare adhesives also with other natural materials, such as condensed polyflavonoid tannins, even more reactive than proteins towards aldehydes, possibly even such carbohydrate-generated aldehydes. The chemical and physical characteristics of commercial condensed tannin extracts, such as those from mimosa, quebracho and pine bark, are influenced by the notable presence of simple carbohydrates (hexoses, pentoses and disaccharides) and complex glucuronates (hydrocolloid gums) as well as oligomers derived from hydrolysed hemicelluloses when these are present in sufficient quantity, that is often the case [3,4]. The percentage of these carbohydrates in commercial tannin extracts is, in general, between 5% and 10% of the total tannin extract weight [3].

The research presented here investigates the use of the specific oxidation approach outlined above to prepare plywood adhesives without formaldehyde from condensed tannin extracts additioned with glucose to further increase the proportion of aldehydes-yielding carbohydrates. It also investigates what types of aldehydes are formed by treating glucose with sodium periodate.

EXPERIMENTAL

Preparation of the resins

10g mimosa tannin was dissolved in water to prepare a 30% solution, the pH adjusted to 10, then 5g glucose was added and stirred well, after this, 5%, 8% and 10% of sodium periodate based on tannin and glucose total solids were added and mixed to obtain TG-5, TG-8 and TG-10 adhesives. For the MALDI analysis the 10g tannin+5g glucose+ 1.5g NaIO₄ mixture was placed in an oven at 120°C for 1 hour. For the plywood instead the reagents were mixed at ambient temperature for 20 minutes, then spread on the veneers and then hot pressed.

Plywood bonding

Wood veneers of 2 mm thickness of *Populus tremuloides* were cut into boards of dimensions 100 mm×180 mm× 6 mm. The glue spread used was of 260 g/m² double glue line, and the joints were hot-pressed at a pressure of 1.75 N/mm² and a temperature of 160°C for 3 minutes. Three-ply laboratory panels were prepared. Three bonded panels were prepared with each adhesive combination. Each bonded joint was cut into six samples with a bonded area of 2.5 cm×2.5 cm and tested according to GB/T17657-2013 [5]. For each adhesive combination 6 samples were tested dry, 6 samples were immersed in cold water for 24 hours then tested wet, and 6 specimen were immersed in 60±3°C water for 3 hours then cooled and tested wet. The tests were done in tension in an Instron 3300 dual column universal testing machine (Instron France, Elancourt, France) at a head rate of 2 mm/min.

Thermomechanical analysis (TMA)

The resins were tested by thermomechanical analysis according to a system already used and tested [6-11]. The samples were prepared by applying each adhesive between two beech wood plies, with dimensions of 21 mm × 6 mm × 1.1 mm. These beech resin-beech sandwich specimens were tested in non-isothermal mode between 25°C and 250°C at a heating rate of 10°C/minute with a Mettler Toledo 40 TMA equipment in three-point bending on a span of 18mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 s (6 s/6 s). The classical mechanics relationship between force and deflection

$$E = [L^3/(4bh^3)][F/(\Delta f_{\text{wood}} - \Delta f_{\text{adhesive}})]$$

allows the calculation of Young's modulus E for each case tested. Such a measuring system has been introduced and is used to follow the progressive hardening of the adhesive with the increase of temperature and to indicate comparatively if an adhesive system is faster or slower hardening and if it gives stronger joints than another one.

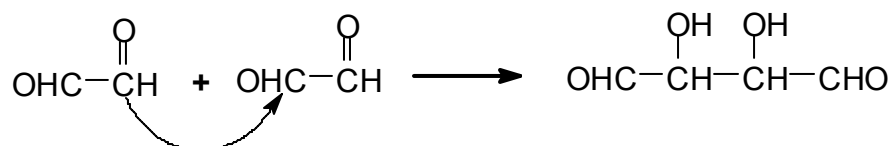
MALDI ToF.

Tannin structure and reactions have been extensively researched and determined by MALDI-ToF mass spectrometry [12-14]. Samples for Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared first dissolving 5mg of sample of NaIO₄ -treated glucose in 1mL of a 50:50 v/v acetone/water solution. Then 10 mg of this solution is added to 10μL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2μL of a NaCl solution 0.1M in 2:1 v/v methanol/water, and predried. Then 1μL of the sample solution was placed on its dedicated location and the plaque is dried again. MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were carried out making 1000 profiles per sample with 2 shots accumulated per profile. The spectrum precision is of +1Da

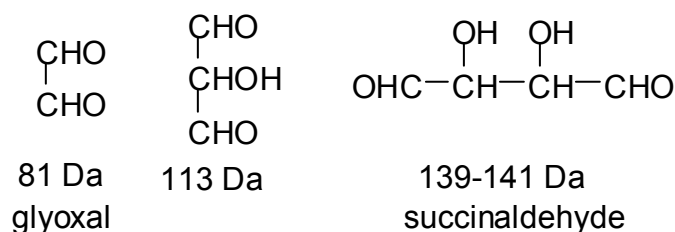
RESULTS AND DISCUSSION

Glucose oxidation reactions

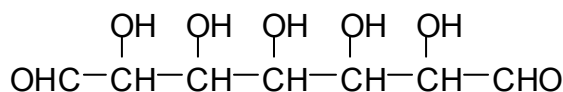
MALDI ToF has been shown to be an ideal technique to follow reactions of natural polymers for different reactions and under a set of different conditions, and particularly useful in identifying the oligomers formed [4,12-14]. The first three oligomers shown in the MALDI ToF spectra in Fig. 1 detailing the reaction products obtained by action of the periodate on glucose are given by the aldehyde formation by periodate (or permanganate) cleavage of C-C bonds with vicinal –OH groups of the glucose. The others are given by recombination of these species by dialdehydes aldol condensation. Aldol condensation can occur under both acid or alkaline conditions [15]. Thus, while glyoxal is formed by direct periodate cleavage of glucose (small peak at 81 Da in Fig. 1), due possibly to the acid environment induced by the periodate, the aldol condensation reaction starting from the glyoxal formed is for example:



Thus, from the 113 Da peak onward (to the 231 Da peak and further) the series that follows derives by the progressive addition of glyoxals by aldol condensation. The species that can be seen in the MALDI ToF spectra in Figure 1 a-e are discussed as follows. The 81 Da (with Na⁺) peak representing glyoxal is very small indicating that this species is likely to react further. Due to direct cleavage of glucose other dialdehydes are formed, thus the peaks with Na⁺



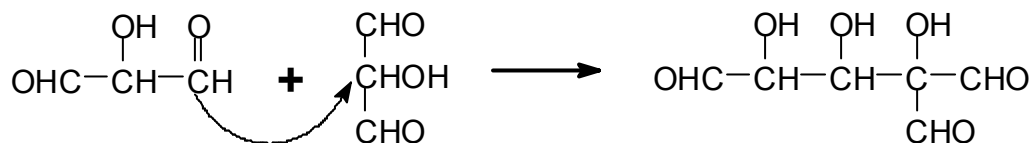
All of these peak taking in consideration the Na⁺ (23 Da) used as enhancer in the MALDI ToF analysis. The species at 139 Da can be formed by direct cleavage of glucose but equally by subsequent aldol condensation of the glyoxal formed by glucose cleavage. Also by aldol condensation is the species at 231 Da (with Na⁺)



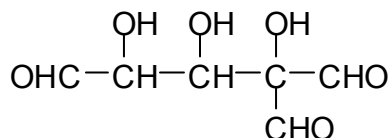
The species at 177 Da and 154 Da are due to the 2,3-dihydroxybenzoic acid (DHB) with and without Na⁺ used as the MALDI matrix, and should not be considered for evaluation. However there are indications late on the reaction with the tannins that these peaks could be a superimposition of compounds having a different origin. Thus, there are two other reactions occurring and giving a different combination of compounds by reaction with periodate (or with permanganate).

The first of these, causing also among others the peaks at 177 Da and 199 Da

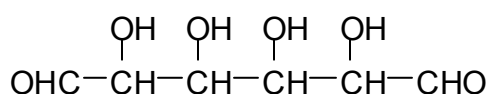
superimposed to the DHB signals, is again an aldol condensation of different aldehyde fragments obtained by periodate cleavage. This reaction is for instance



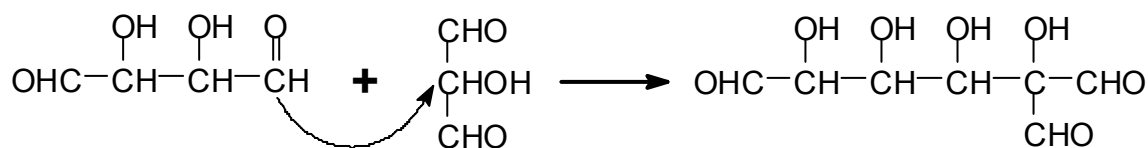
Where 176-177 Da without Na^+ and 199 Da with Na^+ ,



although these two peaks can also be attributed to the contribution of species obtained by direct cleavage to form a species such as

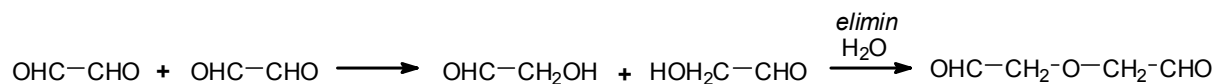


Such a reaction may increase the number of reactive groups on the molecule rendering it particularly apt to cross-linking and network formation. However such type of reaction can be confused with the signals of the DHB matrix (2,3-Dihydroxybenzoic acid) used to carry the sample for MALDI ToF analysis which has molecular weight of 154 Da +23 Da (Na^+) = 177 Da. For this reason such a reaction can be looked at from the second term of the series, thus

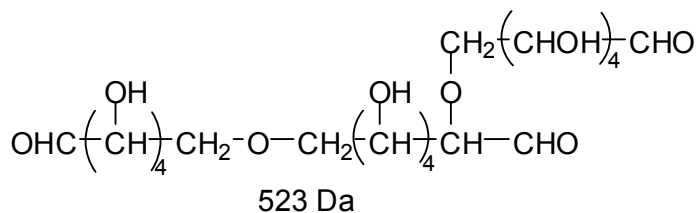
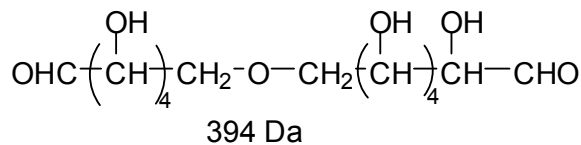
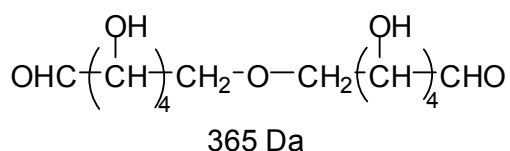


where the aldehyde produced has molecular weight of 206 Da +23 Da (Na^+) = 229 Da. Both peak at 206 Da and at 231 Da are present (Fig. 1a) indicating that the possibility of the existence of branched aldehyde is probable if not certain.

A third type of reaction appears also to occur due to water elimination between two aldehyde groups



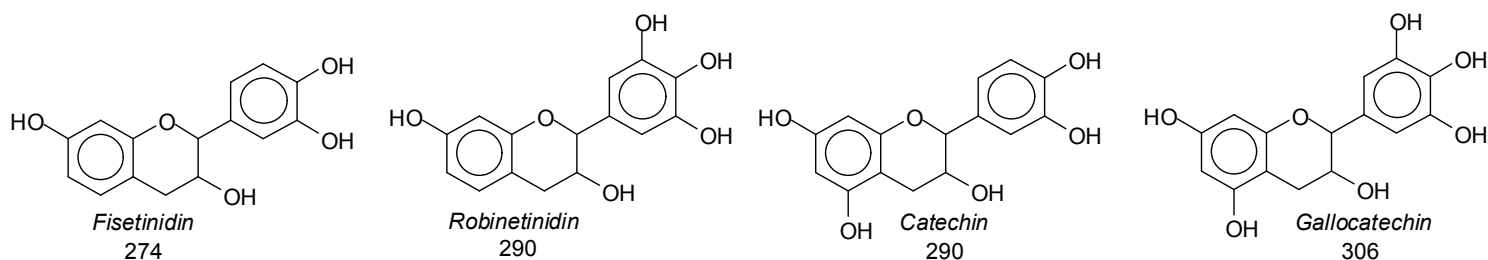
To this reaction of elimination are due the following peaks assigned to the corresponding compounds



Where in the 523 Da (calc. 527 Da) species branching can occur and again 3 aldehyde groups are present on the same oligomer, facilitating cross-linking. In the same category is the species represented by the peak at 402 Da (exp. 401 Da) without Na^+ . Compounds obtained by the combination of the three reactions outlined do occur, at higher molecular weights, but aldehyde groups are always present thus maintaining the reaction capacity of these compounds with the available reactive sites on the tannin. It must also be pointed out that the reactivity of the higher molecular weight aldehydes is likely to be relatively lower than that of more active, lower molecular weight aldehydes such as glyoxal and the one at 113 Da, namely OHC-CHOH-CHO . It must also be noted that all the aldehydes involved in the subsequent reactions with the tannin are also non-volatile, eliminating VOC emission.

Tannin reaction with glucose oxidation products

It also of interest to observe the products obtained by reaction of the tannin present when the glucose/tannin mixture is treated with sodium periodate. In Fig. 2 a,b,c are shown the MALDI spectra of the reaction product obtained and the peak assignments and compounds identified are listed in Table 1. The polyphenolic part of commercial mimosa tannin extract is 70% composed of robinetinidin with lesser but still noticeable amounts of fisetinidin (20%-25%) and of catechin (5%-10%). The polyphenolic part, included phenolic monomers and dimers, constitute approximately $\geq 85\%$ of the commercial tannin extract, with the rest being approximately 6% hydrocolloid gums, 3% various minor constituents and 5%-6% residual water [3].

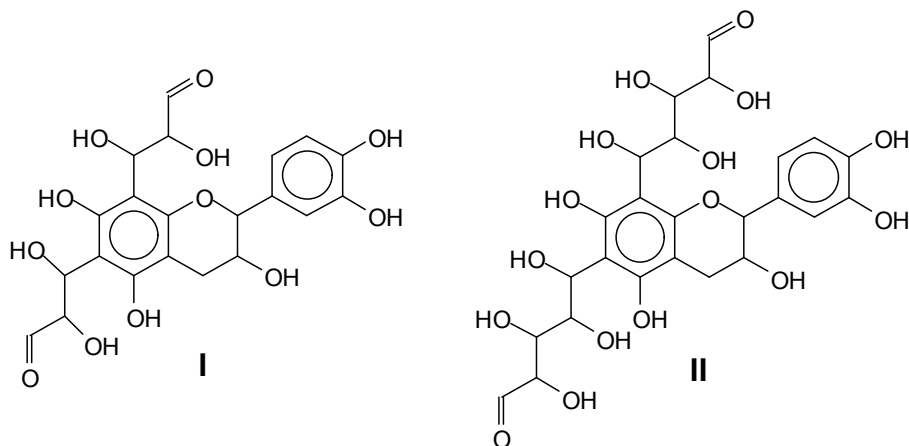


Minor amounts of gallocatechin (MW = 306) are also present. The molecular weight of robinetinidin and catechin are the same, rendering impossible which of the two

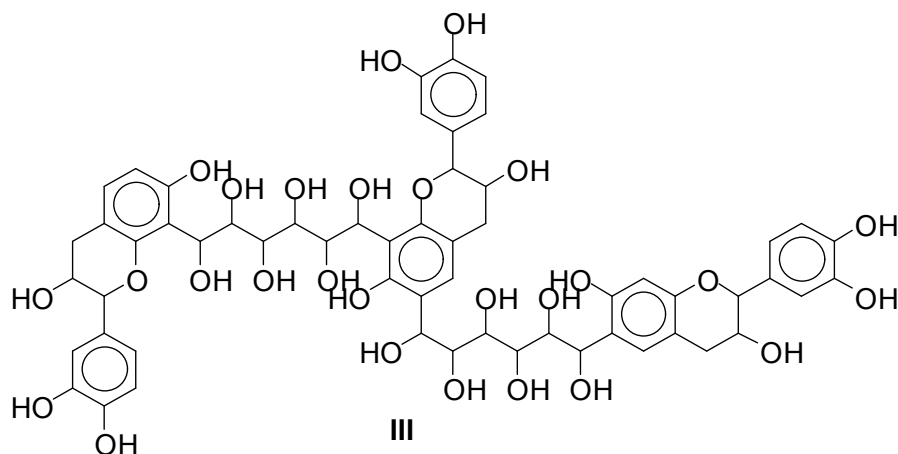
flavonoids enter into reaction just on the basis of the MALDI spectra. One can consider that the predominance of robinetinidin indicates that it is this unit the main one reacting and forming the compounds shown in Table 1. In Table 1 the three main units are indicated as Fis, Rob and Cat, with the Gallocatechin indicated as Gall.

It is interesting to note that the main aldehydes reacting with the flavonoids are glyoxal (OHC-CHO) and OHC-CHOH-CHO, with just some peaks in which the dialdehyde OHC-CHOH-CHOH-CHO may also have reacted, 699 Da and 394 Da, although for this latter an alternative interpretation also exists. Some aldehydes of higher molecular weight seem also to have reacted and formed bridges between two flavonoids such as for the peak at 761 Da., while others such as that at 177Da 199 Da, appear to have reacted less, and are still present in the MALDI spectra, while the corresponding 199 Da is much smaller indicating that the sodium salt of the same species has instead reacted. This does not mean that they do not react, but simply that the molecular weight of the compounds formed may be outside the range of the MALDI analysis, or that they are much slower reacting, or both. As a matter a fact the higher molecular weight chemical species formed indicate that also the aldehyde of higher molecular weight do react and do form bridges between flavonoid units, indicating that cross-linked network are formed on hardening.

A greatest number of species are formed by reaction of a flavonoid unit with one or two dialdehydes but with just one of the aldehyde groups of each dialdehyde, as for the 466/489 Da (I) and the 587/588 Da (II) ones.

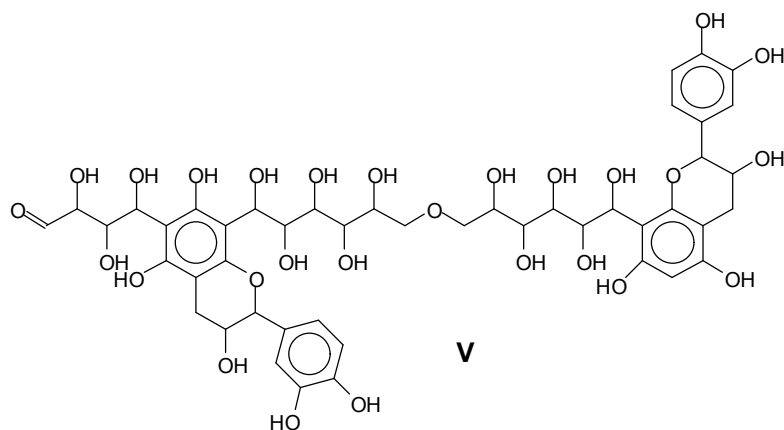
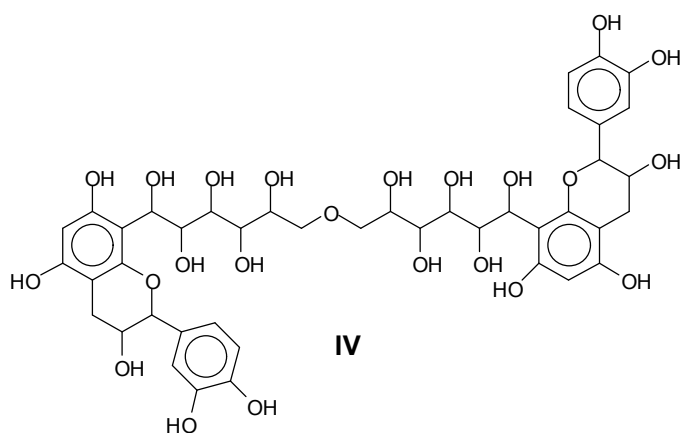


The aldehydes reacting with a flavonoid unit may be all of the same type as for (I) and (II), monomer species, or oligomer species such as (III) at 1178 Da,



or of different type as for all the species of the series 801 Da, 889 Da, 906 Da, 964 Da, 1063 Da, 1101 Da, 1149 Da and 1241 Da. All these species are moreover bridged species with the some of the dialdehydes involved having reacted and connecting with two flavonoid units. These species are most abundant in the higher molecular weights range, and give an idea of how the polymers are build and how this process leads to cross-linking.

In Table 1, several higher molecular weight oligomers are present in which low and high molecular weight dialdehydes have formed bridges between flavonoid units. In this respect is interesting to note that all the daldehydes identified in the oxidation of glucose can and do react with the flavonoid units and participate to the bridging of the tannins flavonoid units. This is the case for example of structures (I), (II) and (III) where the aldehyde comes from direct eaction periodate cleavage of glucose. But these same species can also be formed by reaction with aldehydes formed by aldol condensation such branched structures. A third category of oligomers are those formed by cross-linking with aldehydes having reacted with each other by water elimination, such as structures IV (923 Da) and V (1063 Da).



Where structure V is bridged by aldehyde of one origin but has also reacted with an aldehyde of different origin.

At the higher molecular weight the structures formed starting from 712 Da and continuing with 726 Da, 742 Da, 748 Da, 765 Da, 801 Da, 889 Da, 906 Da, 923 Da,

964 Da, 1063 Da and 1101 Da are all dimers formed by two flavonoid units linked by a dialdehyde, while the peaks at 1149 Da, 1178 Da (structure III) and 1241 Da are trimers where three flavonoid units linked by two dialdehydes. In Table 1 are given the simplified formulas of the species formed, while the corresponding structural formulas are given in the Supplementary Material. In Table 1 the each type of flavonoid unit within a reaction product is indicated as Fis (=Fisetinidin), Rob (=Robinetinidin), Cat (=Catechin) and Gall (=Gallocatechin). It must be noted that due to the identical molecular weights of robinetinidin and catechin, whenever one of Rob or Cat is mentioned in Table 1 the equal compound could be formed with the other molecule.

The tannin alone and the TG5, TG8 and TG10 resins were first tested by thermomechanical analysis (Fig. 3). The results show that TG5, TG8 and TG10 all give a higher Young's modulus than the control T, and this maximum value is reached faster than the tannin+glucose+periodate mix. The laboratory plywood results shown in Table 1 confirm the TMA analysis, with the average dry shear strength of the plywood panels progressively increasing as the proportion of NaIO₄ increases from 5% to 8% and 10% of total resin solids. As regards the cold water resistance of the plywood panels after 24 hours immersion in cold water the shear strength reaches a maximum for TG8. As regards instead the resistance to hot water, after 3 hours at 63°C [5], the wet shear strength increases progressively from TG5 up to TG10.

CONCLUSIONS

Treatment of glucose with sodium periodate yields a number of non-volatile aldehydes of low and higher molecular weight obtained from the cleavage of glucose by the periodate. These aldehydes are obtained either by glucose direct cleavage or by cleavage + recombination according to a few different mechanisms. Reaction of these various aldehydes so generated with tannin extract leads to tannin cross-linking and hardening. The combination of tannin extract + glucose + periodate has been shown to be useful in the bonding of plywood panels, satisfying the requirements of the GB/T17657-2013 standard [5]. The same effects have been shown to occur by just adding to the tannin in the same proportions as used in this paper the glucose pretreated beforehand by the periodate.

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Table 1 Assignments of oligomer structures formed in the tannin+glucose+sodium periodate reaction and determined by MALDI-ToF spectrometry

Peak	Chemical species
81 Da	= glyoxal, with Na ⁺
137-138 Da	= succinaldehyde
176-177 Da	= linear or branched aldehyde no Na ⁺ .
199 Da	= linear or branched aldehyde with Na ⁺
	OHC-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CHO and or/
	OHC-CH(OH)-CH(OH)-CH(OH)(CHO) ₂
231 Da	= OHC-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CHO with Na ⁺
365 Da	= OHC-[CH(OH)] ₄ -CH ₂ -O-CH ₂ -[CH(OH)] ₄ -CHO with Na ⁺
394 Da	= Fis -CH(OH)-CH(OH)-CH(OH)-CHO and/or Gall -CH(OH)-CH(OH)-CHO
	and/or OHC-[CH(OH)] ₄ -CH ₂ -O-CH ₂ -[CH(OH)] ₅ -CHO with Na ⁺
274 Da	= Fis monomer, no Na ⁺
290 Da	= Rob and/or Cat monomer, no Na ⁺
466 Da	= Cat -[CH(OH)-CH(OH)-CHO] ₂ no Na ⁺
489 Da	= Cat -[CH(OH)-CH(OH)-CHO] ₂ with Na ⁺
523 Da	= OHC-[CH(OH)] ₄ -CH ₂ -O-CH ₂ -[CH(OH)] ₄ -CH(-CHO)-OCH ₂ -(CHOH) ₄ -CHO
587-588 Da	= no Na ⁺
610-611 Da	= with Na ⁺
	Cat -[CH(OH)-CH(OH)-CHO] ₂ and/or
	Fis -[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₃ -CHO
616 Da	= Fis -[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₄ -CHO, no Na ⁺
638-640 Da	= OHC-[CH(-OH)] ₅ - Rob -[CH(-OH)] ₄ -CHO with Na ⁺
669-670 Da	= OHC-[CH(-OH)] ₅ - Rob -[CH(-OH)] ₅ -CHO with Na ⁺
	and/or Gall -Glyox- Gall , no Na ⁺
699-700 Da	= Gall -CH(-OH)-CH(-OH)-CH(-OH)- Gall
712-713 Da	= Fis -[CH(OH)] ₅ - Fis no Na ⁺
726 Da	= Fis -[CH(-OH)] ₅ - Fis no Na ⁺
742 Da	= Cat -[CH(-OH)] ₆ - Fis <u>or</u> Rob -[CH(-OH)] ₆ - Fis no Na ⁺
748-749 Da	= Fis -[CH(-OH)] ₅ - Fis with Na ⁺
765 Da	= Cat -[CH(-OH)] ₆ - Fis <u>or</u> Rob -[CH(-OH)] ₆ - Fis with Na ⁺
801 Da	= CHO-CH(-OH)- Cat -[CH(-OH)] ₆ - Fis no Na ⁺
889-890 Da	= CHO-[CH(-OH)] ₄ - Cat -[CH(-OH)] ₆ - Fis no Na ⁺
	<u>and/or</u> Fis -[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₅ - Fis
906 Da	= CHO-[CH(-OH)] ₄ - Cat -[CH(-OH)] ₆ - Cat
	<u>or</u> CHO-[CH(-OH)] ₄ - Rob -[CH(-OH)] ₆ - Rob no Na ⁺

923 Da = **Rob**-[CH(OH)]₅-CH₂-O-CH₂-[CH(OH)]₅-**Rob** no Na⁺
964 Da = CHO-[CH(-OH)]₄-**Rob**-[CH(-OH)]₅-**Rob**-CH(-OH)-CHO no Na⁺
1063 Da = **Rob**-[CH(OH)]₅-CH₂-O-CH₂-[CH(OH)]₅-**Rob**-[CH(-OH)]₃-CHO with Na⁺
1101 Da = **Rob**-[CH(OH)]₅-CH₂-O-CH₂-[CH(OH)]₅-**Rob**-[CH(-OH)]₅-CHO no Na⁺
1149 Da = **Fis**-[CH(-OH)]₅-**Fis**-[CH(-OH)]₆-**Fis** no Na⁺
1178 Da = **Fis**-[CH(-OH)]₆-**Fis**--[CH(-OH)]₆-**Fis** no Na⁺

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FIGURE LEGENDS

- Figure 1. MALDI-ToF spectra of glucose treated with 10% sodium periodate at 120°C for 1 hour. (a) 50 Da to 300 Da range. (b) 300 Da to 500 Da range. (c) 400 Da to 1000 Da range.
- Figure 2. MALDI-ToF spectra of the tannin/glucose 10/5 mixture treated with 10% sodium periodate at 120°C for 1 hour. (a) 50 Da to 300 Da range. (b) 300 Da to 600 Da range. (c) 600 Da to 900 Da range. (d) 900 Da to 1200 Da range.
- Figure 3. Thermomechanical analysis graphs of Young's modulus variation of joint bonded with T, TG5, TG8, TG10, as a function of time
- Figure 4. Shear strength results of plywood panels bonded with the T, TG5, TG8 and TG10 adhesive resins, dry, after 24 cold water soaking and after 3 hours on hot water at 63°C.

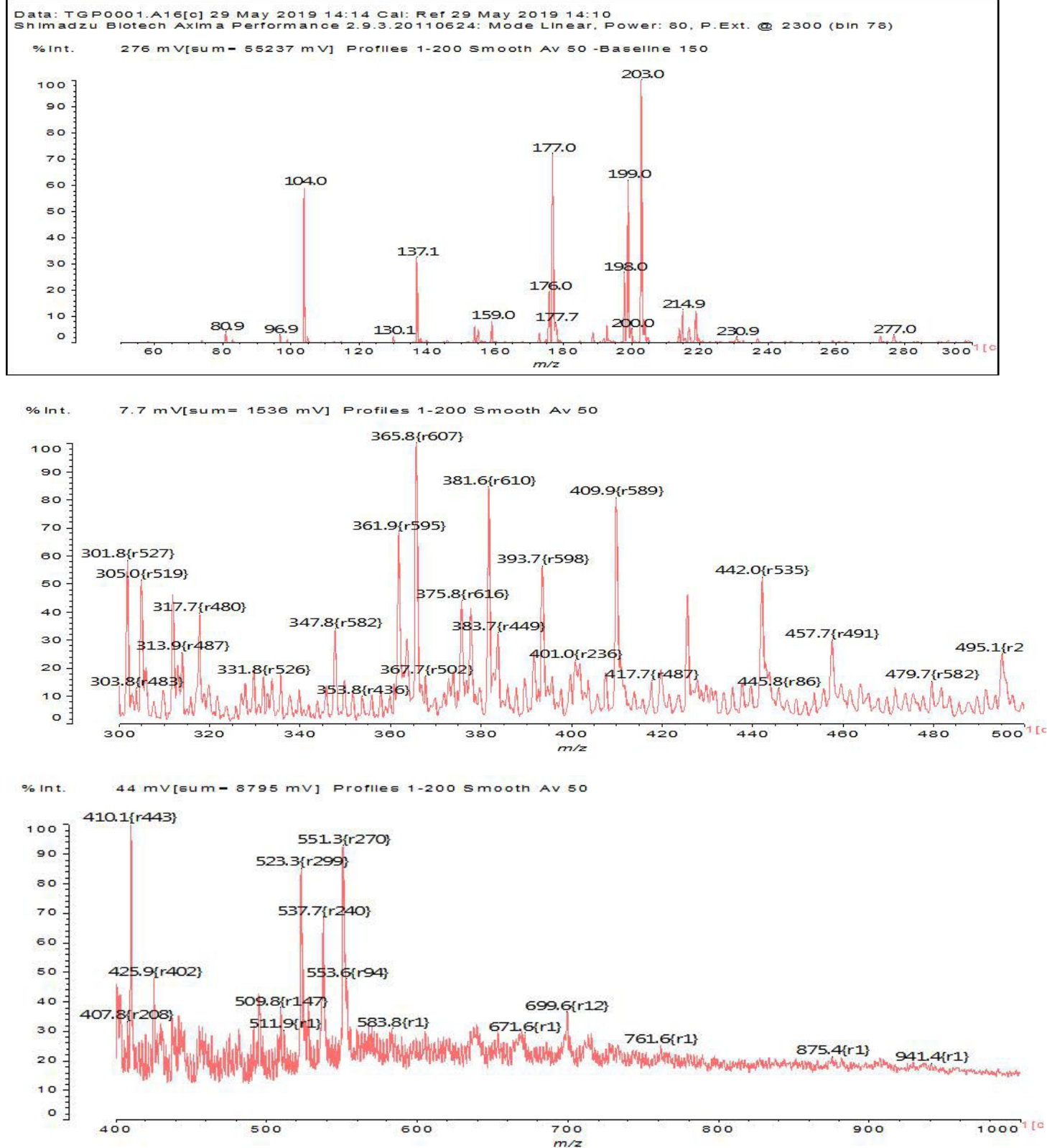


Fig. 1 a,b,c

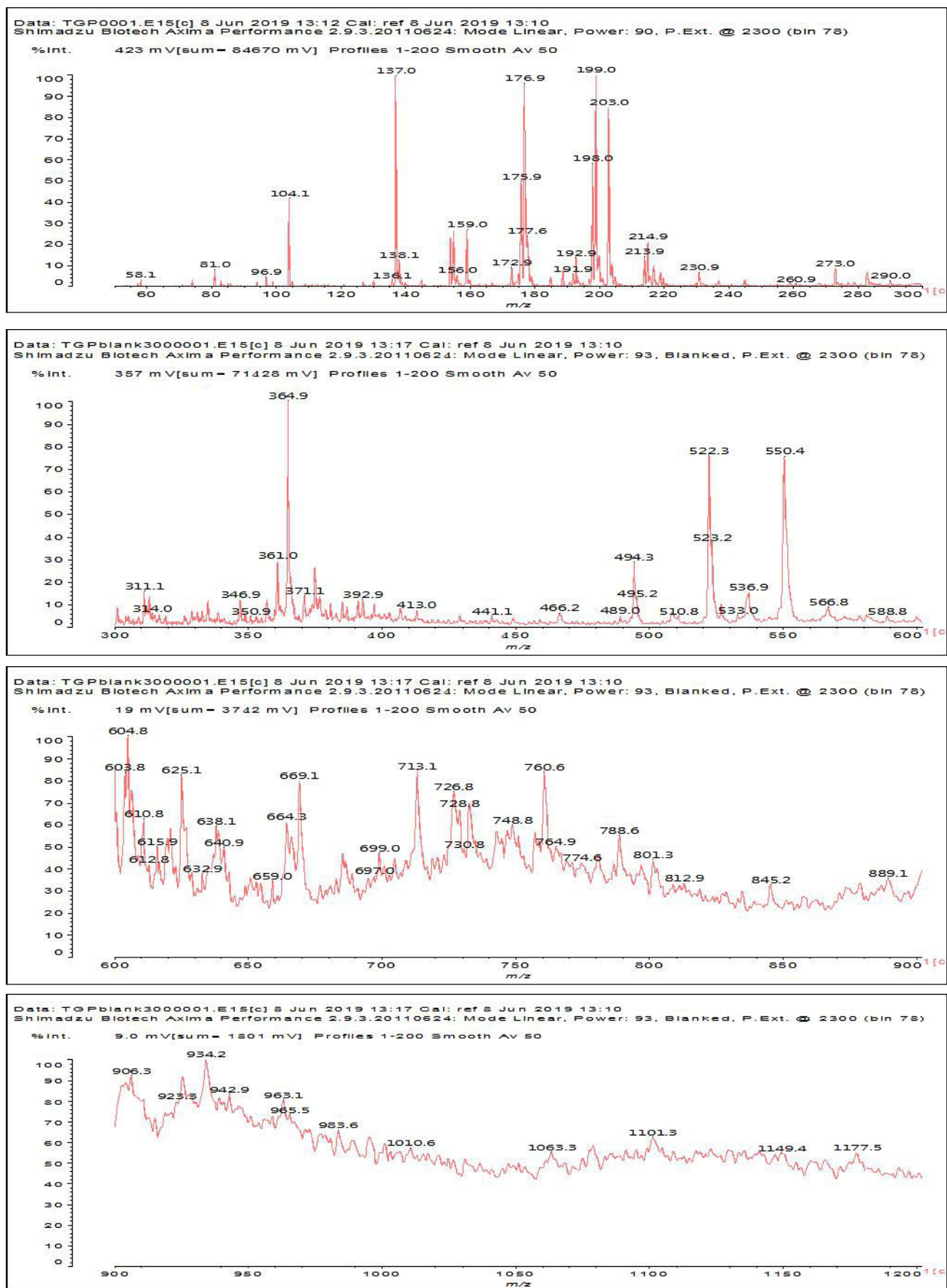


Fig. 2 a-d

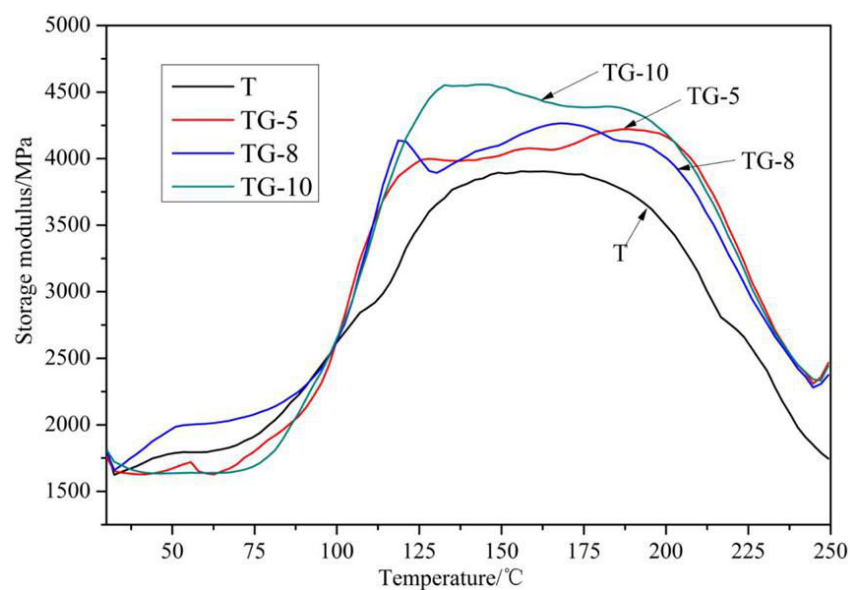
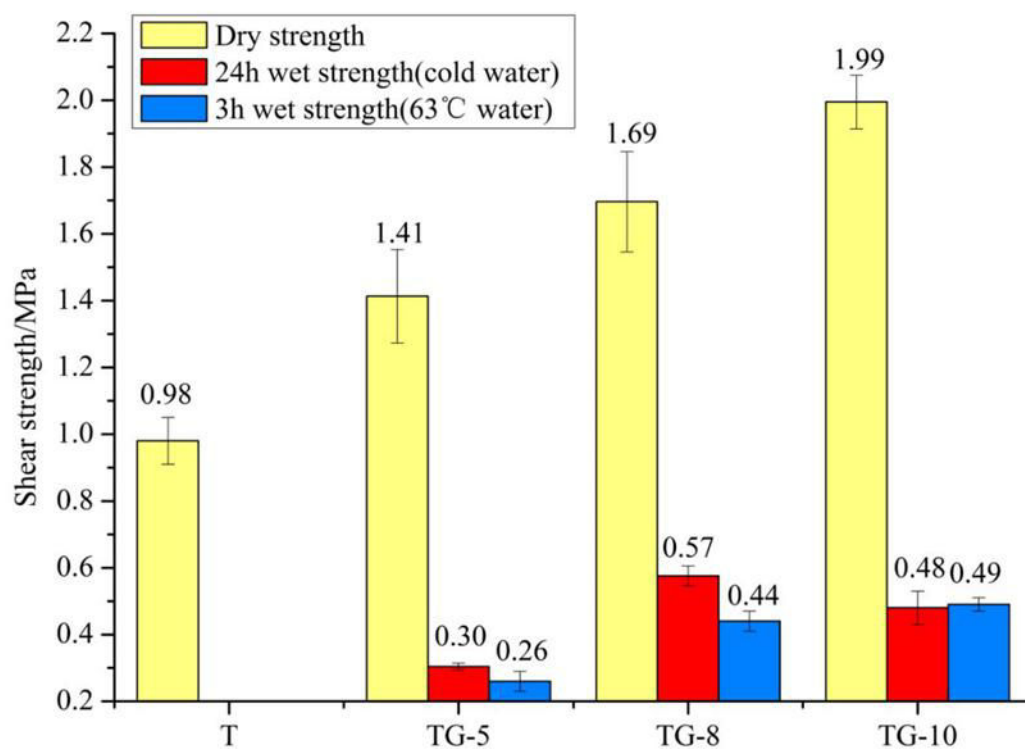


Fig. 3



T: Only tannin

TG-5: 5%NaIO₄+(10gtannin+5g glucose)TG-8: 8%NaIO₄+(10gtannin+5g glucose)TG-10: 10%NaIO₄+(10gtannin+5g glucose)

Fig. 4

3.6 Adhésifs à base de glutaraldéhyde-protéines de gluten de blé pour le collage du bois

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Résumé: L'hydrolysate de protéines de gluten de blé a été utilisé comme matière première pour la biomasse afin de préparer des adhésifs écologiques à base de protéines, la protéine de blé hydrolysée servant de témoin. Le glutaraldéhyde était utilisé pour le modifier afin d'obtenir un adhésif de glutaraldéhyde-protéine de blé (GP). La polyéthylénimine (PEI) a également été utilisée comme agent de réticulation. Le contreplaqué a été préparé et testé. Ses performances ont été utilisées pour mesurer les performances de collage de l'hydrolysate de protéines de gluten de blé. La calorimétrie à balayage différentiel (DSC) et l'analyse thermomécanique (TMA) ont été utilisées pour analyser les propriétés thermiques de l'adhésif et les microstructures des adhésifs durcis par microscopie électronique à balayage (MEB). Les résultats montrent que la modification par le glutaraldéhyde peut effectivement améliorer les performances de collage des adhésifs à base de protéines de blé, la résistance liée au contreplaqué ayant été améliorée par son addition. L'effet de la PEI en tant qu'agent de réticulation est devenu évident. Il peut grandement améliorer les propriétés de liaison des adhésifs à base de protéines de blé modifiés au glutaraldéhyde. L'analyse TMA indique que l'adhésif GP modifié au glutaraldéhyde a un module de stockage supérieur à celui qui n'a pas été modifié. Le module de l'adhésif a augmenté après l'ajout de l'agent de réticulation PEI.

Mots clés: protéine de blé; adhésif pour bois; performance de liaison; performance thermique

Glutaraldehyde-wheat gluten protein adhesives for wood bonding

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Abstract: Wheat gluten protein hydrolysate was used as a biomass feedstock to prepare environmentally friendly protein-based adhesives, with hydrolyzed wheat protein as control. Glutaraldehyde was used to modify it to obtain a glutaraldehyde-wheat protein (GP) adhesive. Polyethylenimine (PEI) was also used as a crosslinking agent. Plywood has been prepared and tested, the performances of it used to measure the wheat gluten protein hydrolysate adhesive bonding performance. Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were used to analyze the adhesive thermal properties and the microstructures of the cured adhesives by scanning electron microscopy (SEM). The results show that modification by glutaraldehyde can effectively improve the bonding performance of wheat protein adhesives, the plywood bonded strength having been improved by its addition. The effect of PEI as a crosslinking agent became evident. It can greatly improve the bonding properties of glutaraldehyde-modified wheat protein adhesives. TMA analysis indicates that the glutaraldehyde-modified GP adhesive has a higher storage modulus than the unmodified one. The modulus of the adhesive increased after adding the PEI cross-linking agent.

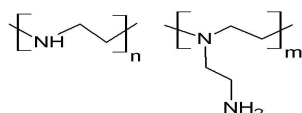
Key words: wheat protein; adhesive for wood; bonding performance; thermal performance

Introduction

Formaldehyde-based resins like urea-formaldehyde(UF) resin[1-4], melamine formaldehyde(MF) resin[5-6] and phenol-formaldehyde(PF) resin [7-9] are still the most widely used adhesives in wood industry. But due to the toxicity and carcinogenicity of formaldehyde, bio-sourced “natural” adhesives, such as tannin-based, lignin adhesive, carbohydrate adhesives, furanic resins, protein-based adhesive and

unsaturated oil adhesives have attracted the ever-increasing interest of researchers [10], and have now become a hot topic in the field of wood adhesives.

Protein based adhesives especially vegetable proteins, due to their low cost and ready availability, have been extensively studied. Among them, soy protein is the most studied of all. Its globular structure causes its reactive functional groups to be hidden within the structure, thus greatly limiting its application. It has been reported in the literature that by mean of certain treatment methods, more functional groups can be exposed and their reactivity improved [11-17]. However, due to the presence of a large number of hydrophilic groups in the protein such as amino groups, hydroxyl groups, carboxyl groups, etc., the water resistance of the protein adhesives is poor. To overcome this problem, considerable research work has been carried out. One approach has been to add a highly active substance that can react with these functional groups as a crosslinking agent [18-22].



Polyethylenimine(PEI) is a water-soluble polymer, which is very reactive. Moreover, it has been used to react with hydroxyl groups to crosslink cellulose for preparing paper with an improved wet strength. There are a large number of functional groups such as hydroxyl and carboxyl groups in the hydrolyzed protein adhesive, and they can combine with PEI with ease [23,24]. Thus, in the work presented here PEI was use as crosslinker for protein based adhesives to improve their bonding performances. To activate protein gelling and increase its reactivity, glutaraldehyde is used as a modifier to react with the hydrolyzed wheat protein. PEI is then used as crosslinker to obtain a good wheat protein adhesive.

2.1 Materials and methods

Glutaraldehyde(C₅H₈O₂, 50% water solution) used are of analytical grade (AR), obtained from Acros Organics, France; Soluble wheat protein obtained fromTereos-Syral(Mesnil-Saint-Nicaise, France; Hexamethylenetetramine obtained from Acros Organics(Geel, Belgium), Polyethylenimine(PEI) bought from Sigma Aldrich(St. Louis, USA).

2.2 Preparation of protein based adhesives

In order to expose more active groups of the protein, **soluble wheat protein was**

degraded under alkaline conditions [21]. 60g water, 0.2g CaO and 0.4g NaOH were added to the flask, the agitator switched on and then 20g of wheat protein was added slowly. The mixture was heated to 90°C and kept at this temperature under stirring for 1h, then 7.5g of glutaraldehyde was added, and the reaction mixture kept for another 1h under stirring at the same temperature.

2.3 Preparation of three-layer plywood

3mm thick *Populus tremuloides* veneers were used to prepare three-ply laboratory plywood panels of 450mm×100mm×5mm dimensions with a gluemix spread of 300g/m²(dgl, double glue line). The panels were pressed for 6 minutes at 180°C and 1.5MPa pressure. The plywood so prepared was stored at ambient temperature for 2 days before it was tested.

Dry shear strength, 24h wet shear strength and 2h boiling water shear strength of the plywood panels were tested according to China National Standard GB/T 14074 (2006) [25], China National Standard GB/T17657 (1999) [26], and European Norm EN 636:2012 (2012) [27].

Thermomechanical Analysis (TMA)

The protein based adhesives were tested by thermomechanical analysis as the reference [28]. The samples were prepared by applying each adhesive between two beech wood plies, with dimensions of 21mm x 6mm x 1.1mm. The specimens were tested in non-isothermal mode between 25°C and 250°C at a heating rate of 10°C/minute with a Mettler Toledo 40 TMA equipment in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 seconds (6s/6s). The classical mechanics relationship between force and deflection $E = [L^3/(4bh^3)][F/(\Delta f_{wood} - \Delta f_{adhesive})]$

allows the calculation of the Young's modulus E for each case tested.

FTIR

To confirm the presence of relevant structures, a Fourier Transform Infra-Red (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrophotometer. A blank sample tablet of potassium bromide, ACS reagent from ACROS Organics, was prepared for the reference spectrum. A similar tablet was prepared by mixing potassium bromide with 5% w/w of the sample powders to analyze. The spectrum was obtained in transmission measurement by combining 32 scans with a resolution of 2.0.

SEM

All the adhesives were cured at 103°C in the oven for a whole night, then cut to pieces of 5 mm×5 mm×3 mm dimension and covered with gold before scanning

electron microscopy (SEM) analysis. The analysis was performed with a Hitachi Tabletop Microscope TM3000 (Hitachi HighTechnologies, Velizy, France) under vacuum, at a working distance of 6.4 mm and 15 kV acceleratingvoltage.

3 Results and discussion

3.1 Results of plywood performance

Plywood panels bonded with wheat protein based adhesives were prepared and 5% amount of hexamethylenetetramine based on solid protein adhesives was used as a hardener. Dry shear strength and wet shear strength after 24 hours cold water soaking and after 2 hours in boiling water of the plywood panels bonded both with the wheat protein (P) adhesive and with the glutaraldehyde-modified wheat protein (GP) adhesive are shown in the Fig 1. This shows that glutaraldehyde modification of the protein can greatly improve the bonding performance of the adhesive. The bond strength of plywood panels prepared with GP adhesive is significantly better than that of panels bonded with the unmodified wheat protein adhesive. Dry shear strength increases from 0.76MPa to 1.14MPa, an improvement of 50%. Equally, the wet shear strength shows a marked improvement also. A known drawback of vegetable protein adhesives is poor water resistance [10,17]. The wet shear strength after 24 hours cold water soaking of the plywood bonded with the GP adhesive is as high as 0.91MPa, this solving satisfactorily the pure wheat protein adhesive drawback (at 0.44MPa). Furthermore, compared to the unmodified wheat protein adhesive, the modified GP adhesive presents good boiling water resistance, plywood shear strength after 2h in boiling water being 0.71MPa, which meet the China National Standard GB/T9846 requirements (≥ 0.7 MPa). Many potentially reactive groups, such as amino groups, become accessible in wheat proteins degraded by complex alkali, groups which can react with glutaradehyde to improve the bonding performance of the GP adhesive.

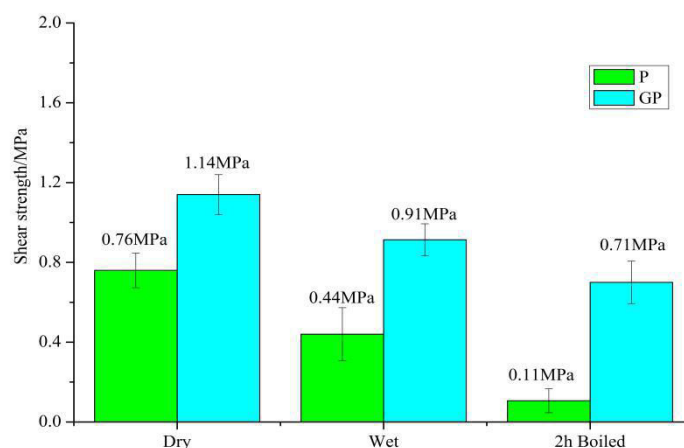


Fig.1 Performances of the plywood bonded with wheat protein adhesive and glutaraldehyde modified wheat protein adhesive

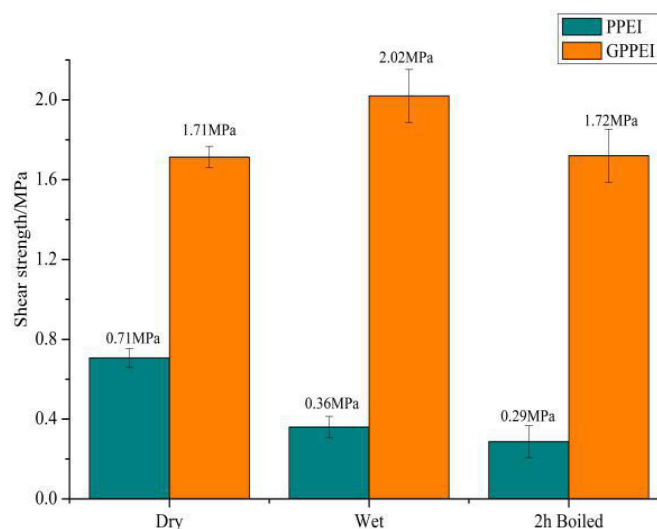


Fig.2 Performances of the plywood bonded with PPEI and GPPEI adhesives

To further improve the bonding properties of wheat protein adhesives, polyethyleneimine (PEI) has been added to the P and GP adhesives and used as a crosslinker. 3% by weight of PEI on liquid adhesive was thoroughly mixed with the P and GP adhesives before spreading on the plys. These mixed adhesives are called PPEI and GPPEI in this paper. Plywood panels were prepared and the dry shear strength, and both the wet strength after 24 hours cold water soaking and after 2 hours in boiling water were tested. The results are shown in Fig 2. Fig. 2 shows that the GPPEI adhesive by PEI addition to the GP adhesive, presents a marked improvement in bonding performance compared to the GP adhesive alone. The wet shear strength after 24 hours cold water soaking and after 2 hours in boiling water are as high as

2.02MPa and 1.71MPa. Thus, they are higher than double that of the GP adhesive. There is no positive effect of the addition of PEI on the protein adhesive alone as the performance of the plywood bonded with the PPEI adhesive (Fig 2), the wet strength being lower. The reason may be that due to the higher reactivity of PEI, the viscosity of the adhesive increases sharply after its addition, hence that the ductility and permeability of the adhesive on the surface of the wood are lower.

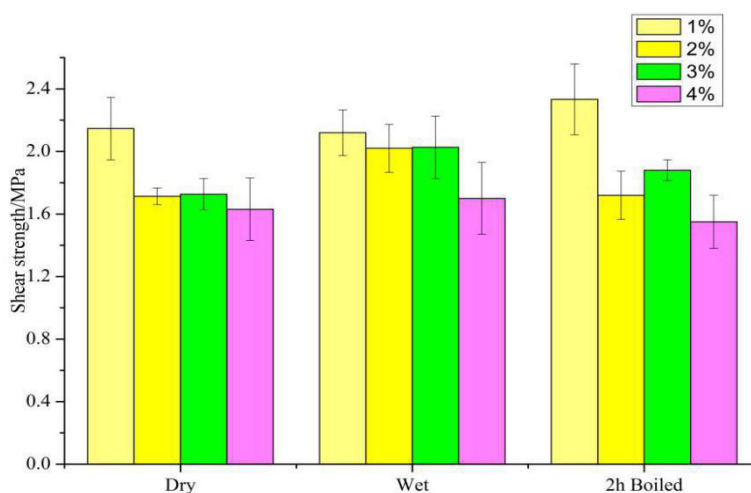


Fig.3 Performances of the plywood prepared by GPPEI adhesives with different addition amount of the PEI

The effect of the level of PEI addition on the performance of the GPPEI adhesives was investigated by adding 1%, 2%, 3%, and 4% of PEI on weight of the liquid GP adhesive. The results of the plywood bonded with them were tested and are showed in Fig 3. As can be seen from the results the bonding performance decreased with increasing additions of PEI, even if the decrease is not large. In reality, the viscosity of the adhesive progressively increases with increasing proportions of PEI being added. Such an excessively high viscosity is not conducive to an easy spreading of the adhesive, thus resulting in a reduced plywood performance.

Thermal performance analysis

The thermomechanical analysis (TMA) results of the unmodified wheat protein adhesive, the GP adhesive and of GP with 3% PEI are show in Fig. 4. The results shows that the storage modulus of the GP adhesive (3554MPa) is markedly higher than that of the unmodified wheat protein adhesive (2211MPa). This means that the GP adhesive gives a higher strength than the P adhesive [29,30]. This is also

consistent with the plywood test results that shows that the GP adhesive has a better bonding performance than the wheat protein adhesive alone. After mixing with PEI the maximum peak of the storage modulus for both the PPEI and GPPEI adhesives are improved, as shown by the curves in Fig 4. This proves that PEI can enhance the performance of protein adhesives [23,24]. In addition, all these adhesives reach the highest modulus at a similar temperatures (around 130°C), but the growth rate of the modulus curve of the GP adhesive is significantly higher than that of the unmodified protein adhesive. This indicates that GP is more reactive, and that protein adhesive can be activated by treatment with glutaraldehyde.

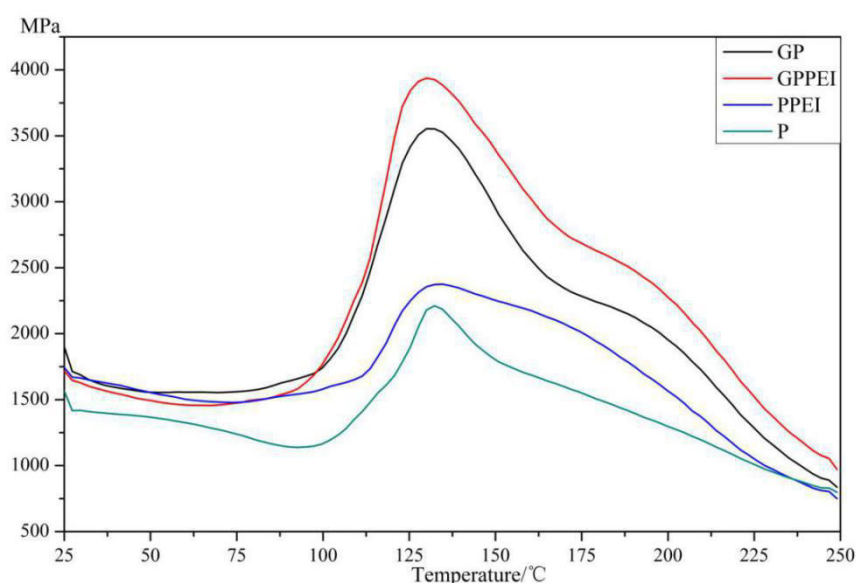


Fig.4 Thermomechanical analysis (TMA) spectra of wheat protein based adhesives

Differential Scanning calorimetry (DSC) was used to analysis the curing behavior of all protein adhesives, and shown in Fig 5. The results show that there is little difference in the curing peak temperature for all these adhesives. This means that the activation energy of curing is relatively close for them. It is also confirmed by the TMA analysis. The integrated area of the adhesive curing peak represents the extent of the exotherm during curing, thus denoting the degree of curing of the adhesive[31,32]. A larger peak area indicates a higher degree of cure. Therefore, as GPPEI is the adhesive with the largest peak (Fig.5), this means that it achieves the most complete cure during the hot press process as the curing temperature is 180 ° C. This is also one of the reasons for the excellent bonding performance of the GPPEI adhesive for plywood.

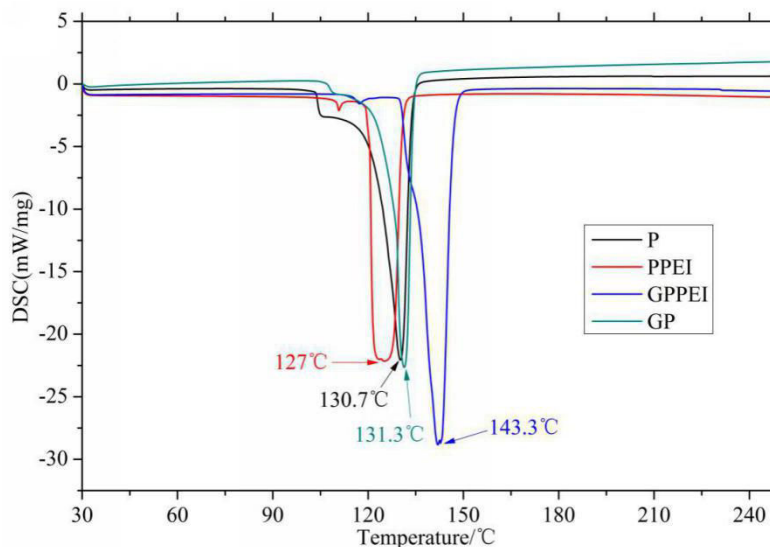


Fig.5 Differential Scanning calorimeter(DSC) spectra of wheat protein based adhesives

Analysis of *FTIR*

The FTIR spectra of the protein-based adhesives are shown in Fig.6. The wide peak nearby the 3300 cm^{-1} region in the curves of P and GP was characteristic of the O–H and N–H groups, which were then able to react with polyethyleneimine and formed C–O and C–N bonds. A peak at about 2930 cm^{-1} was attributed to the $-\text{CH}_2$ group. The main absorption peaks at 1655 , 1560 , and 1242 cm^{-1} are characteristic of the amide I (C=O stretching), amide II (N–H bending or C–N stretching), and amide III (C–N and N–H stretching)[33,34]. By comparing the curves of the adhesives P and GP after modification, their peaks shapes appear to be similar, which means that the glutaraldehyde modified wheat protein adhesive does not form new functional groups.

The absorption peak at 1112 cm^{-1} belongs to the C–O stretching vibration from $-\text{COO}-$ group, which weakens or even disappears in the PPEI and GPPEI spectra. This proves that reactions do occur between the PEI and protein adhesive or glutaraldehyde protein adhesive. Highly reactive amine groups can react with the C=O group to form a hydroxyl group. The absorption band of the disulfide bond or primary alcohol group were observed at 1055 cm^{-1} , which means that in the PPEI and GPPEI spectra more hydroxyl groups are produced compared to the P and GP adhesives. This confirms the reactions between the PEI crosslinker and the P or GP adhesive also, and that the hydroxyl group that forms is also the reactant for the subsequent curing reaction.

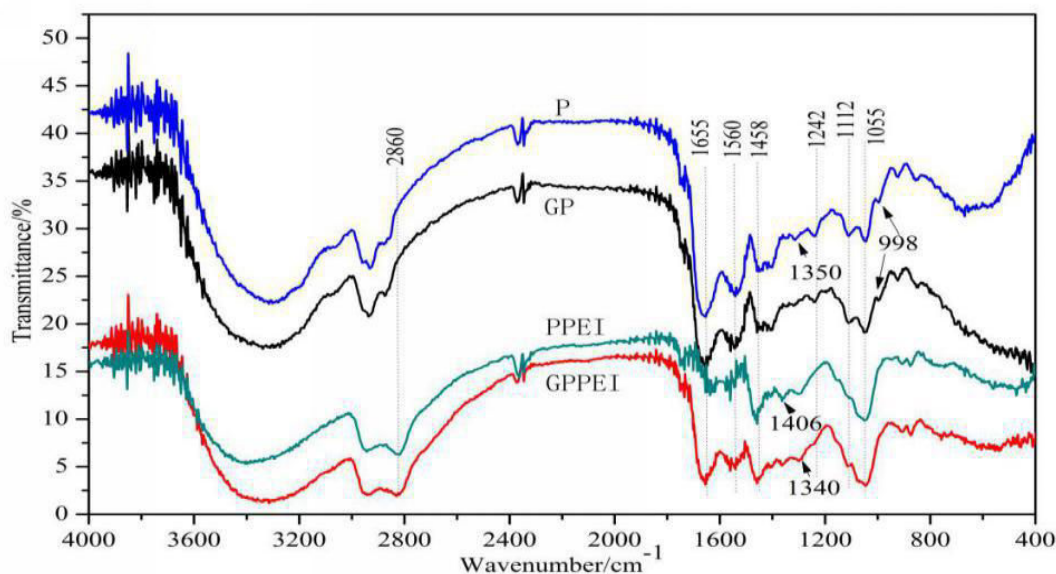


Fig.6 FTIR spectra of the wheat protein based adhesives

Analysis of SEM

Scanning electron microscopy (SEM) of all the protein-based adhesives were tested by scanning electron microscopy (SEM) and the results as shown in Fig 7. Under the electron microscope, the surface morphology of the cured adhesive was observed at a magnification of 250X. Many large and deep cracks can be found in the cured wheat protein only adhesive (Fig.7, a). However, they become smaller, shallower and shorter in the glutaraldehyde modified GP adhesive (Fig.7,b). This means that the GP adhesive has better toughness or is more elastic and better distributed the stresses than the wheat protein only adhesive. This is also one reason why the GP has a better bonding performance than the P adhesive. With the addition of PEI as a crosslinking agent, cracks (Fig.7,c) on the surface of the cured unmodified protein based PPEI adhesive significantly reduced compared with P adhesive (in the Fig.7,a), but there were still long cracks. However, it is shown in (Fig.7,d) that there are no cracks in the cured glutaraldehyde modified protein adhesive mixed with polyethylenimine (GPPEI), and it is perfect. This indicates that polyethylenimine can effectively improve the toughness or elastic of wheat protein-based adhesives, thereby improve bonding properties of its. This proves also the results of plywood performance in Figure 2.

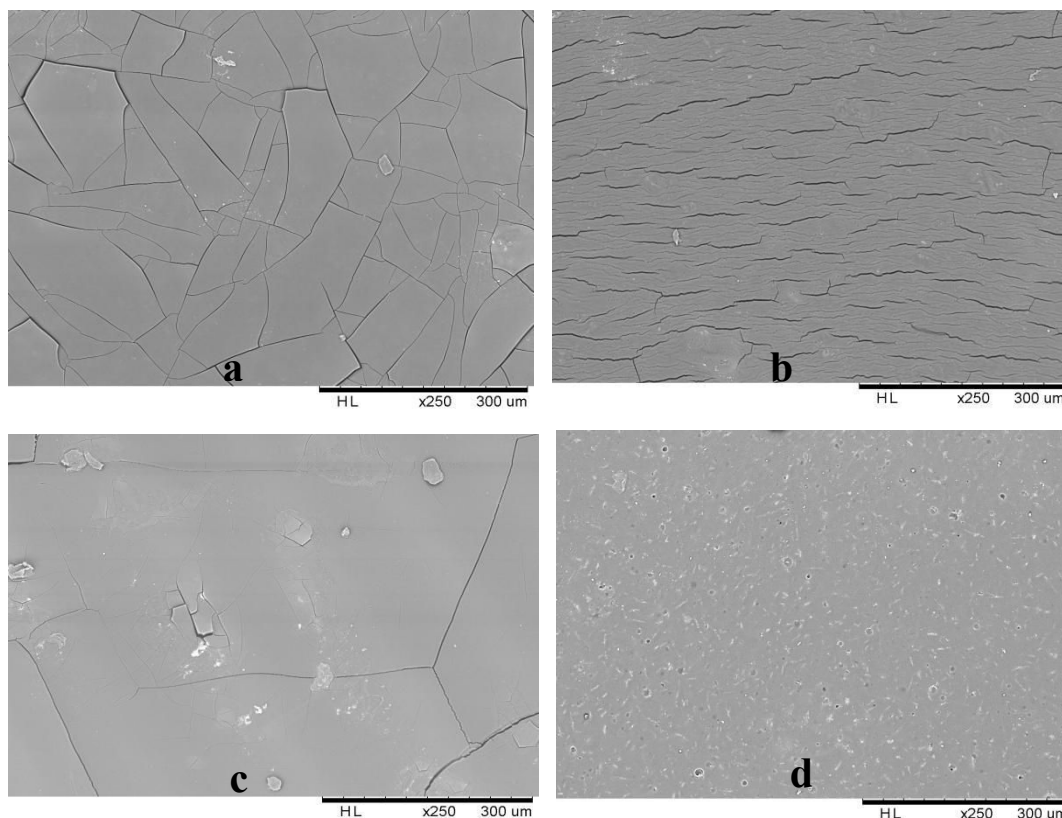


Fig.7 pictures of SEM results of the wheat protein based adhesives(a: wheat protein adhesive; b:Glutaraldehyde modified protein adhesive(GP); c: wheat protein mixed with PEI adhesive(PPEI); d: GP adhesive mixed with PEI(GPPEI))

4 Conclusion

Glutaraldehyde has a good modification effect on wheat protein adhesives. Compared with the unmodified protein adhesive (P), the dry shear strength of glutaraldehyde modified protein(GP) adhesives increased by 50%, in 24h cold water strength improving by more than 100% to arrive 0.91MPa. The effect of PEI as a cross-linking agent is obvious, which can greatly improve the bonding properties of GP adhesive. This is due to the modification of glutaraldehyde to make the reactive groups like -COOH and -OH increased, and these functional groups to react with the amine group in PEI, thus to improve bonding performance. TMA analysis showed that the glutaraldehyde-modified protein gel had a higher storage modulus than the unmodified one. The modulus of the adhesive increased after adding the PEI cross-linking agent, which confirmed the shear strength of the plywood test results. SEM can observe that the modified GP adhesive seems has better toughness than unmodified, however, this is not enough. When PEI is added, the toughness of the adhesive is better improved, and there is no crack on the surface of the cured adhesive

GPPE1.

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3.7 Polyamides à base d'isolats de protéines de soja utilisés comme adhésifs pour le bois

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Résumé: L'isolat de protéine de soja (SPI) a d'abord été mis à réagir avec de l'anhydride maléique, puis de l'hexaméthylènediamine pour synthétiser des polyamides à base d'isolat de protéine de soja (SPIPA). Ses propriétés de liaison ont été mesurées en préparant du contreplaqué à trois couches de laboratoire. En outre, un agent de couplage au silane (KH560), de l'acide citrique et de l'anhydride maléique ont été ajoutés en tant qu'agents de réticulation au mélange de colle SIPA avant le pressage à chaud des panneaux. ATR FT-MIR et MALDI-ToF ont été utilisés pour déterminer les structures de la SPIPA, et une analyse thermomécanique (TMA) a été utilisée pour analyser ses propriétés thermomécaniques. Les résultats montrent que l'anhydride maléique réagit avec les acides aminés de la molécule de protéine de soja, puis avec l'hexaméthylènediamine pour former un polyamide à structure carbamate. Ceci est confirmé par les résultats ATR FT-MIR et MALDI-ToF. De plus, l'analyse structurale indique qu'un grand nombre de structures ramifiées sont formées et se produisent dans la SPIPA, rendant possible la formation d'un réseau pendant le durcissement, garantissant les performances de collage de l'adhésif. L'adhésif SPIPA présentait une bonne force de liaison et une bonne résistance à l'eau par rapport aux exigences standard de la norme nationale GB / T 9846-2015 en Chine. En particulier lorsque de l'anhydride maléique a été ajouté en tant qu'agent de réticulation, notamment dans l'adhésif SPIPA-MA, les panneaux ont été améliorés pour leur résistance au cisaillement à sec et à l'état humide, de sorte qu'il puisse être considéré comme un adhésif pour bois à base de protéine de soja approprié.

Mots-clés: SPI; Les polyamides; Adhésif de bois; Contre-plaqué; MALDI-ToF

Soy Protein Isolate based Polyamides as Wood Adhesives

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Abstract: Soy protein isolate(SPI) was reacted first with maleic anhydride and then hexamethylenediamine to synthesis soy protein isolate based polyamides (SPIPA). Its bonding properties were measured by preparing laboratory three-layer plywood. Furthermore, a silane coupling agent (KH560), citric acid and maleic anhydride were added as crosslinkers to the SIPA glue mix before hot-pressing the panels. ATR FT-MIR and MALDI-ToF were used to determine the structures of the SPIPA, and thermomechanical analysis (TMA) was used to analyze its thermomechanical properties. The results shows that maleic anhydride reacts with amino acids in the soy protein molecule and then reacts with hexamethylenediamine to form a carbamate-structured polyamides. This is confirmed by the ATR FT-MIR and MALDI-ToF results. Moreover, structural analysis indicates that a large number of branched structures are formed and occur in the SPIPA, rendering possible the formation of a network during curing, ensuring the bonding performance of the adhesive. The SPIPA adhesive presented good bonding strength and water resistance over the standard requirements of China National Standard GB/T 9846-2015. Especially when maleic anhydride was added as a crosslinking agent, namely in the SPIPA-MA adhesive, the panels dry and wet shear strength were improved so that it can be considered as a suitable soy protein based wood adhesive.

Key words: SPI; Polyamides; Wood adhesive; Plywood; MALDI-ToF

1 Introduction

The increasing consumer interest in healthy and sustainable products has recently caused bio-based adhesives to become a hot topic of research. In this respect considerable research work has focused on tannins, lignins, proteins and carbohydrates (Pizzi 2006, Pizzi 2016, Hemmilä et al. 2017). Among the protein based adhesive, soy protein has been the first choice because of its abundant yield and low price resulting from the preparation of by-products of soybean oil(Vnučec et al. 2017). There are two main aspects of the application of soy protein adhesives in the wood industry. One is to use soy protein or degraded soy protein as an addition to traditional synthetic wood adhesives, thus to reduce the synthesis cost and formaldehyde emission. Conversely, soy protein has been used as a wood adhesives after partial hydrolysis and modifications(Pizzi 2016). However, the main limiting factor of the latter is its poor water resistance, most research work focusing now on how to improve it. The most common method is by chemical modification by adding a modifier or crosslinking agent after the soy protein hydrolysis to achieve good bonding performance and water resistance (Zhong et al.2003, Liu and Li 2002, Sun and Bian 1999, Hettiarachchy et al.1995).

Polyurethanes are used as wood adhesives in structural glulam and fingerjointing, and their most common isocyanate precursor, namely polymeric diphenylmethane diisocyanate (pMDI) is also used as a modifier/crosslinker to improve the performance of the protein adhesives(Lei et

al.2010, Stephanou and Pizzi 1993). However, pMDI is toxic, and thus potentially harmful, especially during its synthesis. Another interesting modifier for protein adhesives is polyamides(PA). Polyamides have been used for improving performance of the soy protein based adhesives, and have shown a better water resistance than modifications with polyisocyanate and epoxy (Gao et al 2015, Gui et al 2013). Modified polyamides such as polyamidoamine-epichlorohydrin (PAE) were also reported as wet strength modifier for soy bean protein adhesives, the wood composite bonded with it having shear strengths comparable to or higher than those bonded with commercial phenol formaldehyde resins (Li 2004). All these modification methods need to mix the protein adhesive with the modifier before use. This makes it rather complicated when they are used for wood bonding. The work described here was thus aimed at preparing a new polyamide-based wood adhesive based on soy protein isolate itself by a convenient process but also presenting good bonding characteristics.

2 Experimental

2.1 Materials

Soy protein isolate by Yuxin Soybean Protein Co., Ltd(Qingdao, China), citric acid by Acros organics(Geel, Belgium), Hexamethylenediamine 98% by Sigma-Aldrich (Saint Louis, France), maleic anhydride by Sigma-Aldrich (Saint Louis, France), 98% silane coupling agent KH560 from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2 Preparation of SPIPA adhesive

The SPIPA adhesive was prepared as follows: 80 g SPI was dissolved in 400 g of deionized water under magnetic stirring, then 53.5 g maleic anhydride was added and the mixture was heated to 60 °C for 120 min, 105 g hexamethylenediamine were then added and heated to 90 °C for another 2 h, then cooled to room temperature. The mixture was roto-evaporated at 60°C for 1 hour to eliminate the excess of water to obtain a final solids content of 45-50%, with a viscosity of around 1.2 pa.s.

2.3 Thermomechanical Analysis (TMA)

The resins were tested by thermomechanical analysis. The samples were prepared by applying each adhesive between two beech wood plies, with dimensions of 21 mm × 6 mm × 1.1 mm. These beech-resin-beech sandwiches were tested in non-isothermal mode between 25°C and 250 °C at a heating rate of 10 °C/minute with a Mettler Toledo 40 TMA equipment (Mettler Toledo, Zurich, Switzerland). They were tested in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 seconds (6s/6s). The classical mechanics relationship between force and deflection

$$E = [L^3/(4bh^3)][F/(f_{\text{wood}} - f_{\text{adhesive}})]$$

allows the calculation of the Young's modulus E for each case tested. Such a measuring system has been introduced and is used to follow the progressive hardening of the adhesive with the increase of temperature and to indicate comparatively if an adhesive system is faster or slower hardening and if it gives stronger joints than another one.

2.4 ATR FT-MIR analyses

All of the sample extracts were analyzed with a PerkinElmer Frontier ATR-FT-MIR provided by an ATR Miracle diamond crystal. The powder and liqueid samples were laid on the diamondeye(1.8 mm) of the ATR equipment and the contact for the sample was ensured by tightly

screwing the clamp device. Each extract was scanned registering the spectrum with 32 scans with a resolution of 4 cm^{-1} in the wave number range between 600 and 4000 cm^{-1} .

2.5 MALDI-TOF analysis

Sample for matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared by first dissolving 7.5 mg of sample powder in 1mL of a 50:50 v/v acetone/water solution. Then 10 mg of this solution was added to 10 μL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 μL of a NaCl solution 0.1 M in 2:1 v/v methanol/water, and predried. Then 1.5 μL of the sample solution was placed on its dedicated location and the plaque was dried again. Red phosphorous was to standardize the MALDI equipment. MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were carried out making 1000 profiles.

2.6 Three-layer plywood preparation and testing

The performance of the SPIPA adhesive was tested by preparing laboratory plywood panels and evaluating their shear strength dry, after 24 hours cold water soaking, and after 2 hours in boiling water. The plywood panels of 400 mmx200 mmx5 mm were prepared for each adhesive and 2 mm poplar (*Populus tremuloides*) veneers. The glue spread used was of 260 g/m^2 double glue line, and hot pressing time was of 6 minutes at 1.5 MPa pressure, and temperature was 200 °C based on the consequence of the TMA traces. After hot pressing the plywood was stored under ambient conditions for 48 hours then it was cut and tested for shear strength dry, after 24h cold water soaking and after 2h in boiling water according to China National Standard GB/T 14074 (2006), China National Standard GB/T17657 (1999), and European Norm EN 636:2012 (2012).

The boards bonded with the SPIPA glue mixes with 7%(based on SPIPA solid adhesive) citric acid (CA), maleic anhydride(MA) and silane coupling agent KH560(KH) as crosslinkers to strengthen it were also prepared and tested, and named SPIPA-CA, SPIPA-KH and SPIPA-MA.

3 Results and discussion

3.1 Plywood performance

The results of the laboratory three layer plywood bonded with the SPIPA adhesives are shown in Table 1. The board prepared with the SPIPA adhesives show encouraging results for both dry shear strength and the wet strength, the dry shear strength is 1.09MPa, this being above the standard requirement ($\geq 0.7\text{MPa}$)(GB/T 4897.5-2003, EN312.2003). Of even greater interest is that SPIPA adhesives show a good water resistance. Thus, the 24-hour cold water soak shear strength of the plywood bonded with it is 0.85MPa, and the 2-hour boiled water strength is 0.78, both values being over the standard requirements for use under wet conditions. Citric acid has already been shown to be a bond enhancer in panels adhesives (Del Menezzi et al.2018, Umemura et al.2013, Umemura et al.2012a,Umemura et al.2012b,) and silane KH560 has also been shown to be an enhancer of non-isocyanate polyurethanes wood adhesives for particleboard (Xi et al.2018). The performance of boards called SPIPA-CA, SPIPA-KH and SPIPA-MA, which bonded with the SPIPA glue mixes with 7%(based on SP-NIPU solid adhesive) citric acid (CA), maleic anhydride(MA) and silane coupling agent KH560(KH) as crosslinkers are shown in Table 1. The dry strength of all the plywood panels prepared with these adhesives are improved, and this is greatest when MA is used as the crosslinker (an improvement of 53%). MA as a crosslinking agent

appears also to effectively improve the water resistance of a SPIPA adhesive, especially after the 2h boiled water test, the strength reaching 0.9MPa. The mainly reason for this is that maleic anhydride reacts with the hydrophilic functional $-NH_2$ and $-OH$ groups in soy protein, hence reducing the hydrophilic groups in the adhesive system. This is confirmed by the ATR FT-MIR and MALDI ToF analysis. At the same time, the proportion of functional groups such as esters ($-COO-$) and amide bonds ($-CON-$) increase, contributing to the improvement in bonding performance.

However, when KH560 was selected as the crosslinker, the water resistance of the plywood panels prepared with it is decreased, which may be caused by the $-Si-O-$ bond present in the silane coupling agent. This group is more easily hydrolyzed in the presence of water, possibly resulting in a reduced water resistance of the adhesive (Xie et al.2010, Salon et al.2005, Bel et al.2008). The hydrolytic degradation is more rapid under hot water conditions, this being the reason for the SPIPA-KH exhibiting a lower boiling water strength.

In the case of citric acid being used as a gluemix additive the improvement in dry strength is mainly due to the improved adhesion effect already reported by a number of authors(s(Del et al.2018, Umemura et al.2013, Umemura et al.2012a).

Table 1. Performance of plywood shear strength bonded with SPIPA adhesives

Adhesives	Dry strength/MPa	Wood failure	24h wet strength/MPa	Wood failure	2h boiled water strength/MPa	Wood failure
SPIPA	1.09±0.09	100%	0.85±0.03	85%	0.78±0.03	65%
SPIPA-KH	1.23±0.07	90%	0.66±0.10	70%	0.55±0.07	20%
SPIPA-CA	1.23±0.10	95%	0.75±0.04	70%	0.77±0.05	55%
SPIPA-MA	1.67±0.12	100%	0.96±0.07	75%	0.92±0.01	85%

3.2 Thermomechanical Analysis(TMA)

The thermomechanical analysis traces of SPIPA adhesive alone and mixed with different crosslinkers are shown in Fig. 1. The curves of the increase of Young's modulus as a function of temperature show an upsurge starting at around 210°C. This means that curing of the SPIPA resin occurs at a high temperature as sugar based non-isocyanate polyurethanes already reported in previous literature(Xi et al.2018, Xi et al.2019). The increase of Young's modulus has been shown to correlate with the bonding strength of the adhesive(Pizzi 1998, Kamoun and Pizzi 2000, Lecourt et al.2003). Comparing the TMA curves of the four adhesives in Figure 1, it appears that SP-NIPU-MA has the highest modulus value (2600 MPa), followed by SPIPA-CA, SPIPA-KH, and the lowest being SPIPA alone, consistent with the shear test results of the plywood panels. In addition, when KH560 or MA was used as the crosslinker, the corresponding curves SPIPA-KH, SPIPA-MA start to show an increase in the Young's modulus showing a small peak at lower temperature (about 70 °C). This is mainly due to the epoxy group in the silane KH560 cross-linking agent or the maleic anhydride reacted with the $-NH_2$ group in the SPIPA structure at a lower temperature. Since only a small amount of cross-linking agent was added, accounting for just 7% of the mass of the SPIPA solids, only a small peak is present.

Before that the TMA curves show a significant increase around 230°C in the modulus value, the overall trend of the modulus values in the TMA curves of the four adhesives decreases. This is mainly due to the decrease in viscosity of the adhesive as the temperature increases, resulting in

adhesive penetration into the wood, causing softening or degradation during heating thus reducing strength. It is evident from the TMA curves that the curing temperature to be used for such adhesives is relatively higher than what common to-day for equivalent panels bonded with traditional adhesives (Lei and Frazier 2015, Simon et al. 2002).

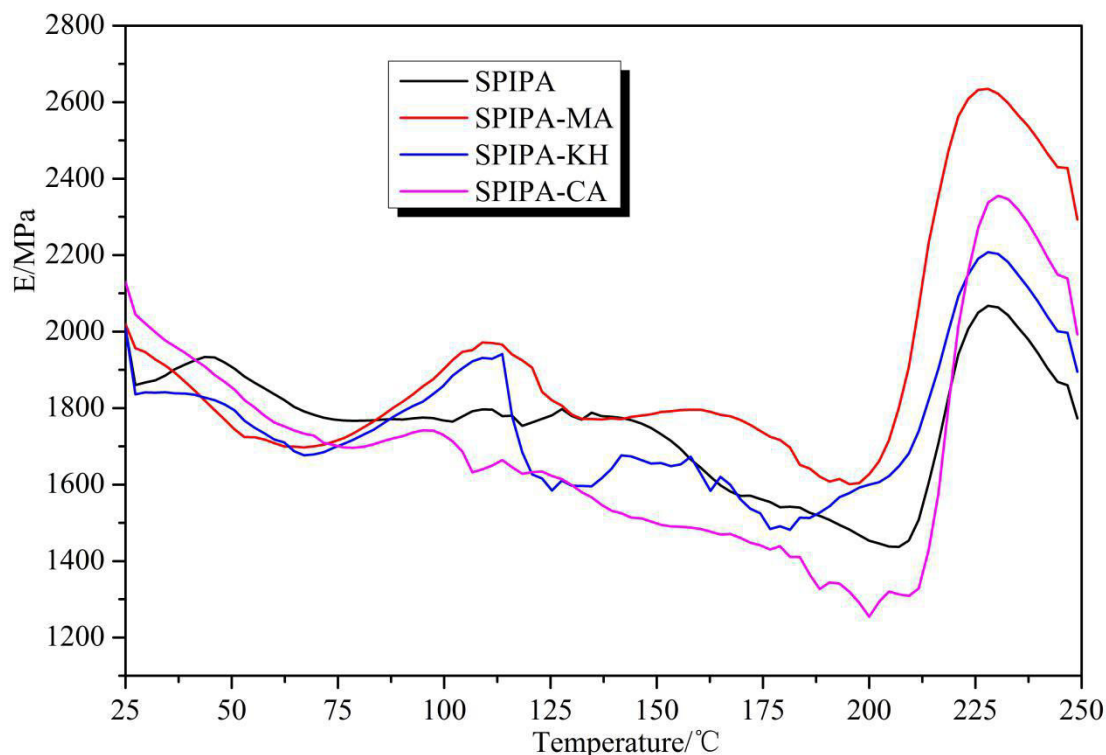


Figure1 . TMA curves of curing of SPIPA adhesives on wood.

3.3 ATR FT-MIR analyses

The FTIR spectra of the soy protein isolate (SPI), of the reaction product of the soy protein isolate with maleic anhydride (SPIMA) and of the SPIPA adhesive alone are shown in Fig.2. The wide peak at 3274cm^{-1} is characteristic of the O–H and N–H groups (Lei et al.2014), which were decreased in SPIMA when compared with SPI. This is because maleic anhydride reacts with the hydroxyl and amine groups in SPI. Furthermore, comparing the SPI and SPIMA curves in Fig1, it is apparent that the strong absorption peak of primary alcohol group observed at 1074cm^{-1} is weakened and nearly disappears, which means that the -OHs in soy protein reacts with maleic anhydride to form a COO-bond. This is also further put in evidence by the appearance of a new peak at 1703 cm^{-1} , which is assigned to the an ester group (Liu et al.2008, Eslah et al.2016).

The peak at about 2930 cm^{-1} is attributed to the $-\text{CH}_2$ group, which obviously is enhanced in the SPIPA sample. This is due to the addition of hexamethylenediamine increasing the proportion of $-\text{CH}_2-$ groups. The main absorption peaks at 1627 , 1532 , and 1236 cm^{-1} are characteristic of the amide I ($\text{C}=\text{O}$ stretching), amide II ($\text{N}-\text{H}$ bending or $\text{C}-\text{N}$ stretching), and amide III ($\text{C}-\text{N}$ and $\text{N}-\text{H}$ stretching) (Lin et al.2012, Schmidt et al.2005). By comparing the curves of SPIMA and SPIPA, the peak of $-\text{COOH}$ group at 1703cm^{-1} disappears, as it reacts with hexamethylene diamine.

Fig.3 shows the FTIR spectra of the cured SPIPA adhesives with the addition of crosslinkers. First of all, the absorption peak of the OH and NH groups at 3295cm^{-1} has disappeared when comparing SPIPA with SPIPA-MA, SPIPA-KH and SPIPA-CA. This means that the crosslinker

reacts with the -OH and -NH groups, thereby increasing the bonding strength. Peaks of C-N stretching vibration at 1556, and 1372 cm^{-1} are greatly enhanced by the addition of the crosslinking agent (Fig.3). The reason is mainly because the -COOH or epoxy groups in the crosslinking agent react with the amino group of SPIPA to form a large amount of C-N bonds. This indicates that reactions between the SPIPA adhesive and the crosslinkers do occur.

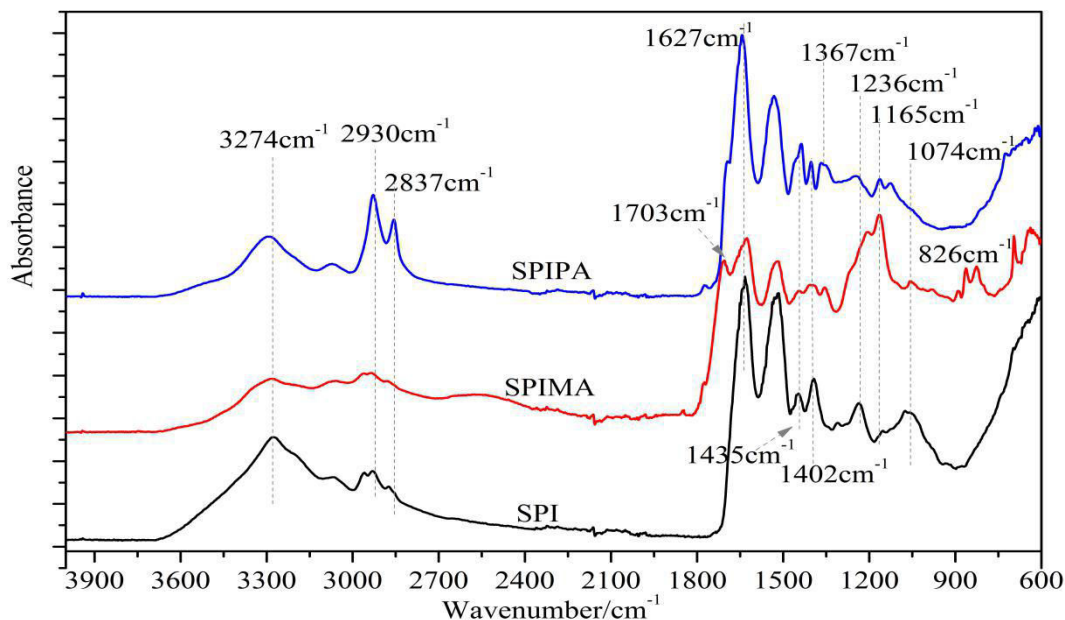


Figure 2. FTIR spectra of SPI, product of maleic anhydride react with SPI(SPIMA) and SPIPA adhesive.

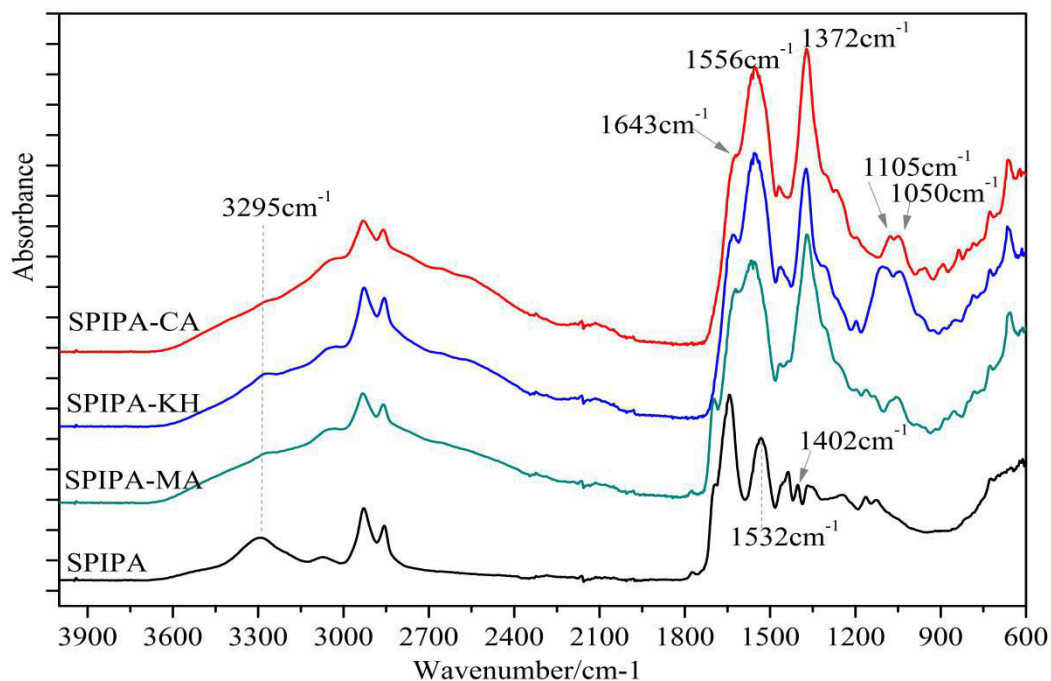
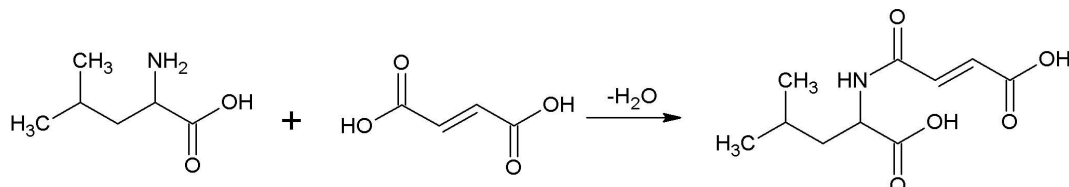


Figure3. FTIR spectra of SPIPA and different crosslinker mixed with it.

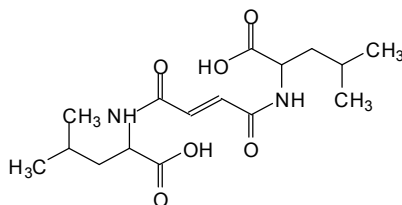
3.4 MALDI ToF analysis

Table 2 and Figs.4-7 report the MALDI-ToF results obtained for the SPIPA adhesive. It is always rather complex to determine with MALDI what occurs with proteins, due to their complex

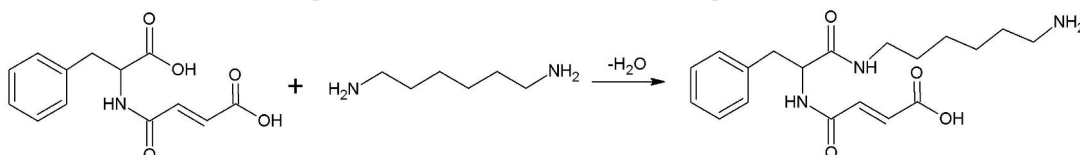
structures consisting of many different amino acids and their sequencing (Creighton 1996, Vnučec 2017). However, the presence of some single aminoacids or of fragments of sequences of aminoacids can still be observed, as well as some reaction products between the maleic anhydride and hexamethylenediamine with them. The product of one molecule of aminoacid reacted with one maleic anhydride are observed, for example, at 251Da, this being a reaction product of leucine with maleic acid that hydrolyzed from maleic anhydride, such as



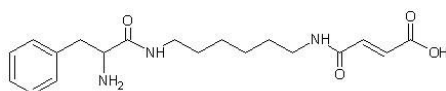
This is also verified by the SPIMA curve results in the FTIR analysis. Obviously, here should be also considered the possibility of further reaction with amino acid that would demonstrate the possibility of maleic acid as a cross-linking agent between two amino acid molecules. Thus the species at 340 Da (calculated as 342 Da without Na^+) could well be a maleic acid bridge between two leucines. Such as



Due to the presence of carboxyl ($-COOH$) groups in the structure, such a type of species from amino acid react with maleic acid can also further react with hexamethylene diamine (HMD) to form an amide link, such as the species at 361Da, which can be interpreted as:

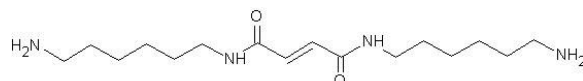


A possible branched isomer structure at this molecular weight can be also considered, namely:



Despite this, both structures prove that the reaction of amino acids with maleic acid and hexamethylenediamine to obtain small molecular weight substances with amide bonds do occur.

Linear oligomers with amide linkages formed from maleic anhydride reacting with hexamethylenediamine can be also found, as for example the species at 311Da, as:

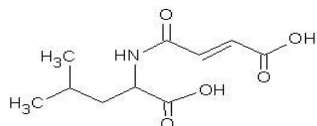


Aminoacid's dimers, trimers, and even higher oligomers reacted with maleic anhydride and hexamethylenediamine can also be observed, such as 537Da, 699Da in Table 2. And larger-structure aminoacids react with maleic anhydride or/and hexamethylenediamine giving the

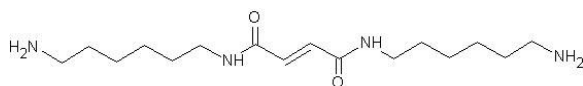
species at 965.4Da, 1036Da, 1550Da and 1765Da as shown in Table.2. The formation of these larger molecular structures means that polymers with many amide bonds are synthesized, this being the case of the SPI polyamides presented in this work. The existence of all these branched species shows that the reaction between soy protein with maleic anhydride and hexamethylenediamine does occur, and also produces a number of complex branched structures. Thus, hardened tridimensional networks are formed on curing, yielding good bonding results (Xi et al.2018b).

Table 2. Proposed oligomer structures for the MALDI ToF spectra peaks in Figs 4-7 for the SPIPA

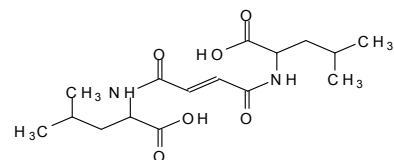
251Da(calc. 252)= Reaction of Leucine with maleic anhydride, with Na⁺



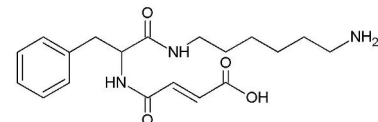
311.7Da(calc. 312)=Maleic anhydride react with Hexamethylenediamine without Na⁺



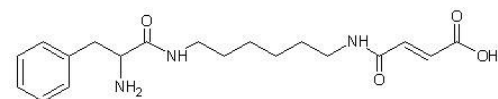
340Da(calc. 342)=Maleic anhydride react with two leucines without Na⁺



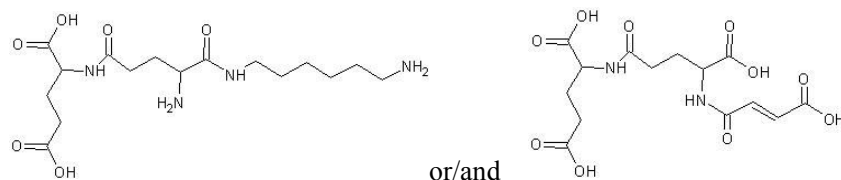
361.5Da(calc. 361) =Phenylalanine-maleic anhydride-diamine without Na⁺



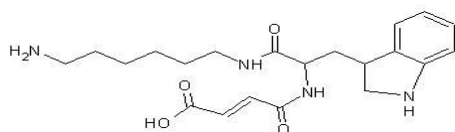
Or/and



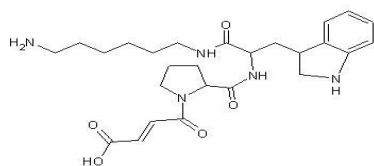
375Da (calc. 374) =Dimer glutamate-maleic anhydride or diamine



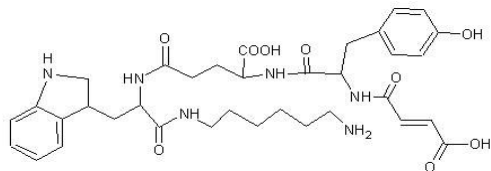
401Da (calc. 400) =Tryptophan-maleic anhydride-diamine without Na⁺



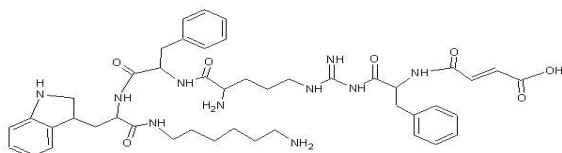
537.3Da (calc.537) =Tryptophan- Proline-maleic anhydride-diamine+ 23 (Na⁺)



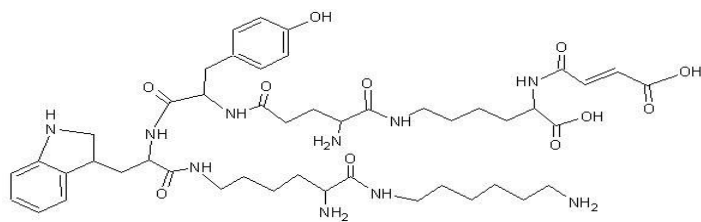
699.2Da (calc. 699) = Tryptophan-glutamate-tyrosine-maleic anhydride-diamine, without Na⁺



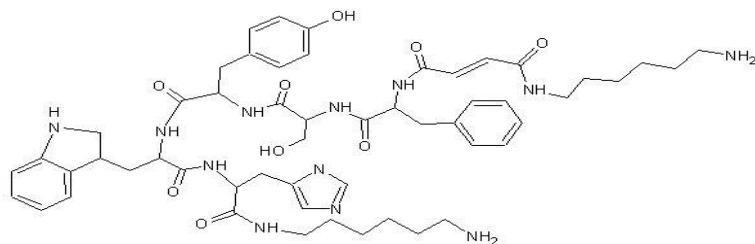
874Da (calc. 873) = Tryptophan-phenylalanine-arginine-phenylalanine-maleic anhydride-diamine with Na⁺



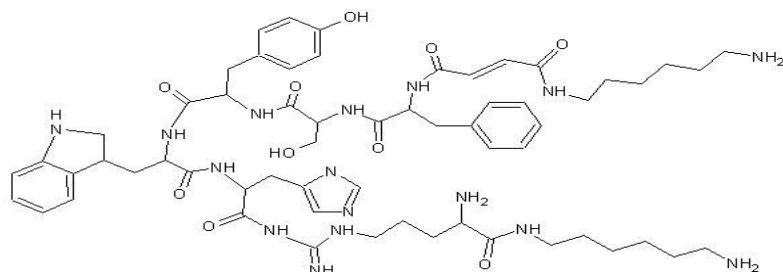
965.4Da (calc. 966) = Tryptophan-tyrosine-glutamate-[lysine]₂-maleic anhydride-diamine without Na⁺



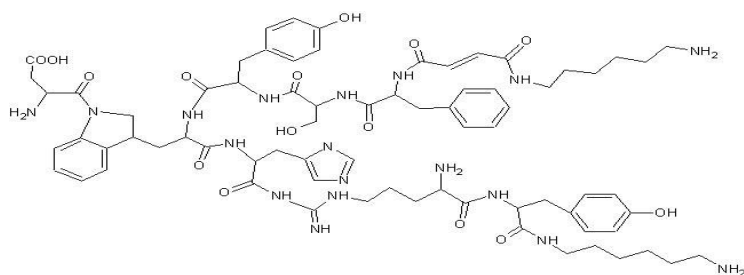
1036.6Da (calc. 1038) = Tryptophan-tyrosine-histidine-phenylalanine-serine-lysine-maleic anhydride-diamine without Na⁺



1212.1Da (calc. 1212) = 1038 + 1x Arginine without Na⁺



1550.1Da (calc. 1550) = 1212 + 1x Tyrosine + 1x Aspartic acid (with Na⁺)



1765.8Da (calc. 1765) = 1550 + 1x Proline + 1x Hexamethylenediamine (with Na⁺)

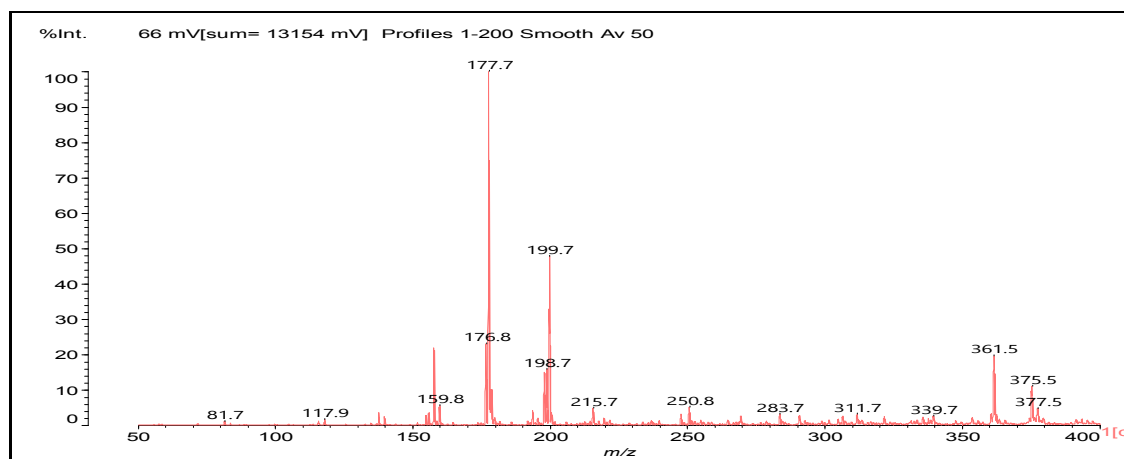
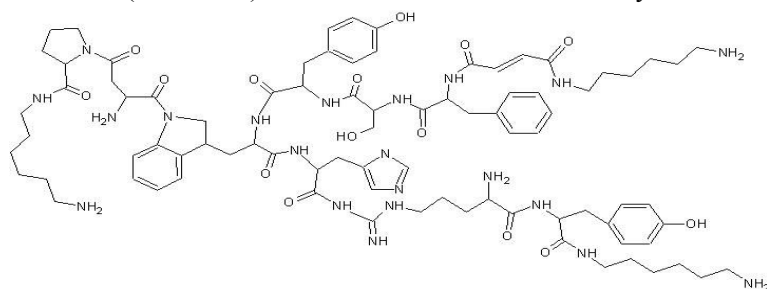


Figure 4. MALDI ToF spectrum of the SPIPA resin: 50Da-400Da range.

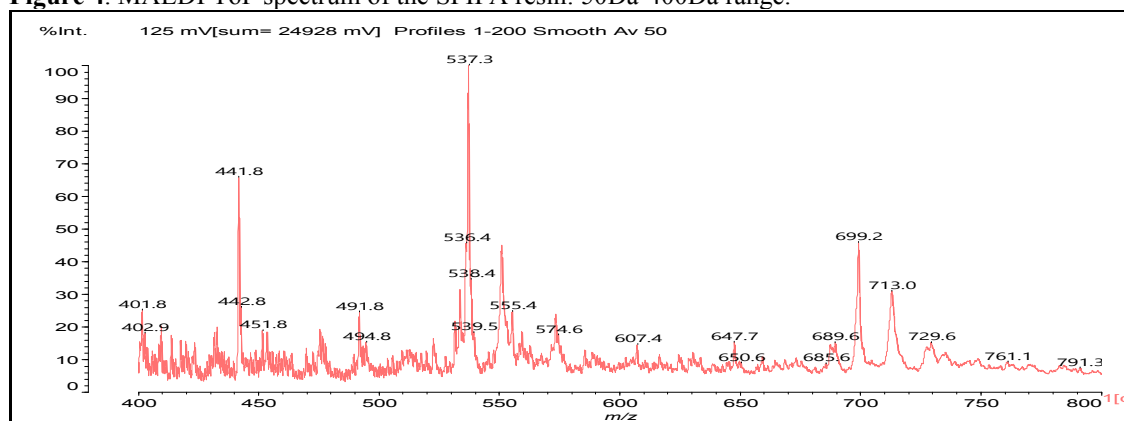


Figure 5. MALDI ToF spectrum of the SPIPA resin: 400Da-800Da range.

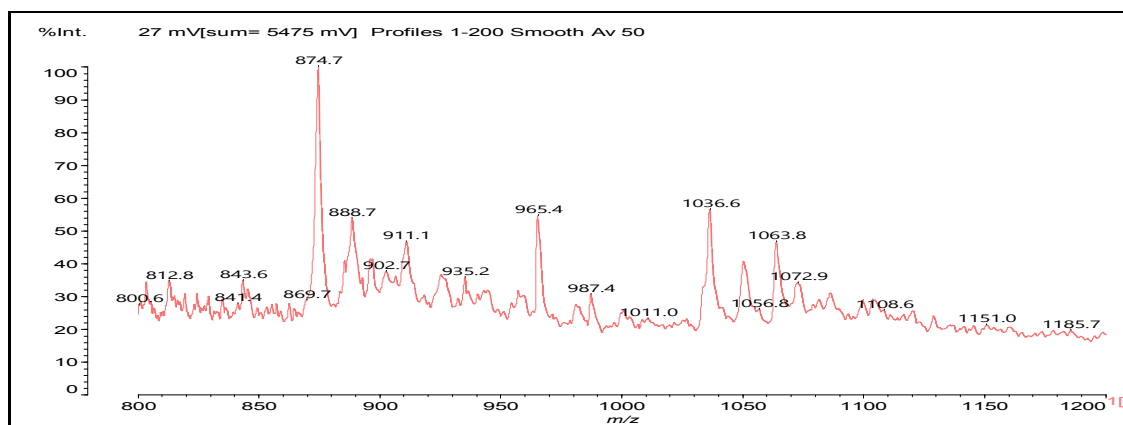


Figure 6. MALDI ToF spectrum of the SPIPA resin: 800Da-1200Da range.

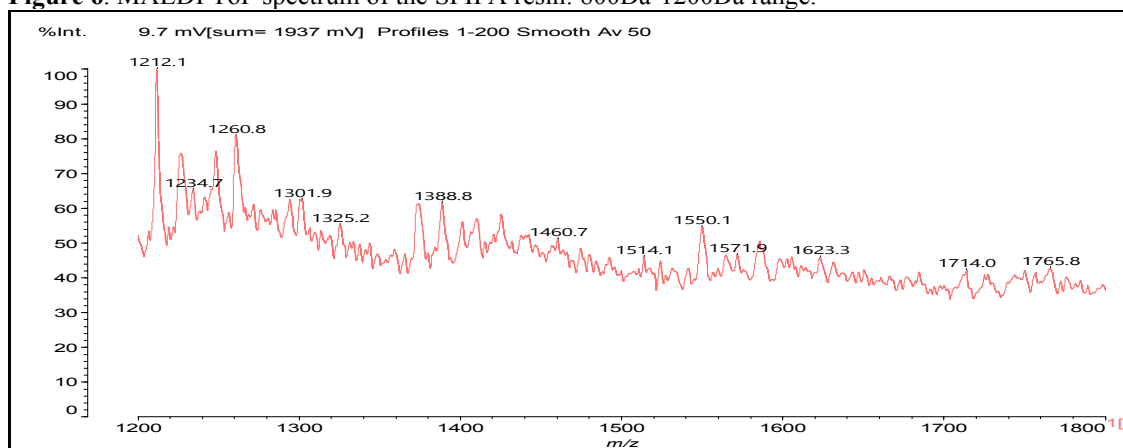


Figure 7. MALDI ToF spectrum of the SPIPA resin: 1200Da-1800Da range.

4 Conclusions

Soy protein as a biomass material to prepare environmental friendly wood adhesives is a hot topic, but most of the research works are based on isolates obtained after acid or alkali hydrolysis of it, by adding cross-linking agent or modifiers to enhance bonding performances. The SPIPA resin adhesives presenting a amide structure obtained by reacting SPI with maleic anhydride and hexamethylenediamine was successfully prepared in this work. ATR FT-MIR and MALDI-ToF analysis also confirmed the occurrence of their reactions. This SPIPA presented both a good bonding performance and a good water resistance well over the relevant standard requirements of GB/T 9846-2015(≥ 0.7 MPa), while a higher curing temperatures was required, as proved by the TMA test results. The crosslinkers used can increase the dry bonding strength of SPIPA, while the silane KH560 one reduces its water resistance. Only SPIPA-MA with maleic anhydride as crosslinker had satisfactory cold and boiling water resistance, which is improved when compared to SPIPA. These resins can then be potentially used as suitable soy protein based wood adhesives.

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protein-derived plywood bioadhesives via soy protein isolate fiber self-reinforced soybean meal composites. *Ind. Crop. Prod.* 133, 10-17.

3.8 Revêtements et adhésifs polyuréthane sans isocyanates à partir de mono- et di-saccharides

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Résumé: Des polyuréthanes non isocyanates biosourcés (NIPU) ont été préparés à partir de mono- et disaccharides, à savoir glucose et saccharose, en réaction avec le diméthyle carbonate et l'hexaméthylène diamine. Les oligomères obtenus ont été détectés par spectrométrie MALDI-ToF, CP-MAS ¹³C RMN et FTIR. Il a été démontré que le NIPU, dérivé du glucose, durcissait à une température nettement plus basse que ceux dérivés du saccharose. Les NIPU obtenus ont été appliqués comme revêtements de surface pour le bois et l'acier. Les revêtement ont été testé avec le test de coupe croisée (sur acier) et les résultats étaient encourageantes. La NIPU à base de glucose a donné des bons résultats de revêtement de surface à 103 ° C, tandis que la NIPU à base de sucrose n'a pas donné des bons résultats qu'à des températures de durcissement nettement plus élevées. Les résines saccharidiques NIPU ont également été testées en tant qu'adhésifs à joints de bois thermosensibles, la NIPU de glucose a donné des résultats très encourageants.

Mots clés: Polyurethanes, non-isocyanates, NIPU, Adhésifs, Revêtements, Urethanes, Carbonates, MALDI-TOF, RMN-¹³C, FTIR

Article

Isocyanate-Free Polyurethane Coatings and Adhesives from Mono- and Di-Saccharides

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Abstract: Mostly biosourced non-isocyanate polyurethanes (NIPU) were prepared from mono- and disaccharides, namely glucose and sucrose, reacted with dimethyl carbonate and hexamethylene diamine. The main aim of this research was to show that NIPU can be prepared from mono- and disaccharides, this just being an initial exploratory work and its sole main aim. The oligomers obtained were detected by MALDI-ToF, CP-MAS ¹³C NMR, and FTIR spectrometries. The glucose-derived NIPU were shown to harden at a markedly lower temperature than the sucrose-derived ones and to be easier to handle and spread. The NIPU obtained were applied as wood and steel surface coatings and tested by the sessile drop test (on wood) and cross-cut test (on steel) with encouraging results. The glucose NIPU gave good surface coating results already at 103 °C, while the sucrose NIPU yielded good results only at a markedly higher temperature of hardening. The NIPU saccharide resins were also tested as thermosetting wood joint adhesives with the glucose NIPU yielding very encouraging results.

Keywords: polyurethanes; non-isocyanates; NIPU; adhesives; coatings; urethanes; carbonates; MALDI-TOF; ¹³C NMR; FTIR

1. Introduction

Polyurethanes can and have already been prepared for a number of possible applications by using biosourced polyols from renewable materials [1–8]. However, polymeric isocyanates need always to be used in industry to prepare polyurethanes even if in conjunction with biosourced polyols. This has already been the case with many biosourced polyols.

Studies on alternate reaction routes to prepare non-isocyanate based polyurethanes (NIPU) do already exist. In general, oligomers terminated with five-membered cyclic carbonate groups [9] are reacted with diamines to form polyhydroxyurethanes [10]. Several studies on this type of approach do exist in the literature [11–26]. The technological barrier to the synthesis of biobased cyclic carbonates could be overcome by the chemical transformation of epoxidized vegetable oils or by the use of glycerine carbonate-based intermediates. Polyamines could also be produced from fatty diacids [27].

Dimethyl carbonate is also a good reagent and solvent that can be used for the first step of carbonation [28,29]. Indeed, it is classified as a flammable liquid with an odor similar to methanol, which has no irritating or mutagenic effects, either by contact or inhalation (indexing from Merck) [29].

Carboxymethylation of hydroxyl groups by dimethyl carbonate group is generally observed at temperatures around 90 °C. This is close to the boiling point of dimethyl carbonate, by bimolecular nucleophilic substitution, acyl-cleaving, in basic catalysis [29].

More recently, a few works on preparing polyurethanes without isocyanates based on tannins showed some interesting performance [30–32], especially for wood coating. What was more remarkable in two of them was that the small fractions of monomeric carbohydrates, mainly glucose, within the tannin extracts used for reaction, also appeared to somewhat participate to the formation of urethanes [30,32]. This was the case even when including aminated tannin as a biosourced polyamine [32].

This paper then deals with the initial development of the preparation of non-isocyanate-mediated urethanes starting from monosaccharides (glucose) and disaccharides (sucrose). It deals with their analysis and checking their applicability and initial potential performance as both wood surface coatings and simple thermosetting wood adhesives. Thus, the main aim of this research was to show that NIPU can be prepared from mono- and disaccharides. The present research is just an initial exploratory work, with this being its sole main aim.

2. Materials and Methods

2.1. Preparation of Isocyanate-Free Polyurethanes

The synthesis proceeded in two steps: first the glucose and the sucrose were carbonated. The carbonated glucose is called sample A1 and the carbonated sucrose sample B1. The second step consisted in reacting A1 and B1 with hexamethylene diamine to give samples A2 and B2.

Synthesis of A1 and A2: 20 g of glucose were mixed with 13.5 g of dimethyl carbonate and 16.67 g of water, and heated to 50 °C for 40 min, and cooled to room temperature. A part of this mixture was dried at 103 °C overnight, and this was sample A1. Then, 3.88 g of hexamethylenediamine was added to 5 g of the remaining mixture in a test tube, mixed well, and then dried overnight at 103 °C. This sample was sample A2.

Synthesis of B1 and B2: Sucrose was used to instead glucose to prepare the B1, B2 under the same set of reaction conditions as A1 and A2.

The method and procedure employed are the same use for the preparation of urethanes from hydrolysable [30] and condensed tannins [31].

For the thermomechanical analysis (TMA) the samples of A1, A2, B1, and B2 were prepared as follows: glucose mixed with dimethyl carbonate and water was heated to 50 °C for 40 min and cooled at the room temperature (named A1). Hexamethylene diamine was then added to the mixture and heated to 90 °C for 30 min, then cooled to room temperature (named A2).

The sucrose mixed with dimethyl carbonate and water, heated to 50 °C for 40 min, and cooled at the room temperature, was named B1. Hexamethylene diamine was then added to the mixture and heated to 90 °C for 120 min (because the reaction was slower a longer reaction time was used), then cooled to room temperature (named B2).

It must be clearly pointed out that A1 and B1 are just intermediate products of the two-step reaction process. It is for this reason that they have not been tested either for bonding or for coatings.

2.2. MALDI-TOF Analysis

Samples for matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared first by dissolving 5 mg of sample powder in 10 mL of a 50:50 *v/v* acetone/water solution. Then 10 mg of this solution was added to 10 µL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 µL of a NaCl solution 0.1 M in 2:1 *v/v* methanol/water, and predried. Then, 1 µL of the sample solution was placed on its dedicated location and the plaque was dried again. The reference substance used for the equipment calibration was red phosphorus.

MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-

positive tuning mode. The measurements were carried out making 1000 profiles per sample with two shots accumulated per profile. The spectra precision is of +1 Da.

2.3. FTIR

Fourier Transform Infra-Red (FTIR) analysis were carried out using a Shimadzu IR Affinity-1 (Shimadzu Europe Ltd., Manchester, UK) spectrophotometer. A blank sample tablet of potassium bromide, ACS reagent from ACROS Organics (Geel, Belgium), was prepared for the reference spectra. Similar tablets were prepared by mixing potassium bromide with 5% weight on weight of the sample powders to analyze. The spectra were obtained in transmittance by combining 32 scans with a resolution of 2.0 cm^{-1} in the $400\text{--}4000\text{ cm}^{-1}$ range.

2.4. Cross-Polarisation Magic Angle Spinning Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR) Spectra

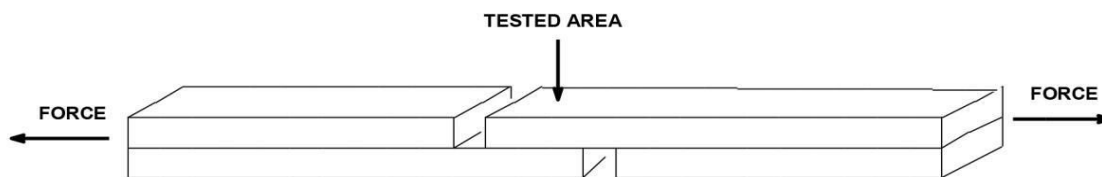
The reaction mixtures of glucose and sucrose with dimethyl carbonate and of the reaction of the product obtained with hexamethylene diamine were analyzed by solid state CP MAS ^{13}C NMR. Spectra were obtained on a Brüker AVANCE 400 MHz (Brüker, Billerica, MA, USA) spectrometer with a 4 mm probe at a frequency of 12 kHz. The pulse duration at 90° was $4.1\text{ }\mu\text{s}$, with a contact time of 2 ms and a recycling delay of 4 s. Chemical shifts were determined relative to tetramethyl silane (TMS) used as a control. The spectra were accurate to 1 ppm. The spectra were run with the suppression of the spinning side bands.

2.5. Thermomechanical Analysis (TMA)

Resin A2 and B2 were tested by TMA on a Mettler 40 (Viroflay, France) thermomechanical analysis apparatus. Triplicate samples of two beech wood plies each 0.6 mm thick bonded with either A2 or B2 for a total sample dimensions of $21\text{ mm} \times 6\text{ mm} \times 1.15\text{ mm}$ were tested in non-isothermal mode between 40 and $220\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in three points bending on a span of 18 mm exercising a force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][\Delta F/\Delta f]$ allows the calculation of the Young's modulus E for each case tested [30,33].

2.6. Wood Joints Bonding

Pine (*Pinus sylvestris*) wood veneers of 3 mm thickness were cut into boards of dimensions $7.5\text{ cm} \times 18\text{ cm}$. The adhesive-coated area for each veneer board was $2.5\text{ cm} \times 18\text{ cm}$. The glue spread used was of a $260\text{ g}/\text{m}^2$ double glue line, applied by a manual roller spreader, and after an open assembly time of 12 min and a closed assembly time of 10 min the joints were hot-pressed at a pressure of $2.75\text{ N}/\text{mm}^2$ and a temperature of $220\text{ }^\circ\text{C}$ for 6 min to form a two-ply wood composite board. Three bonded joints were prepared with each adhesive combination. The joints were conditioned at ambient temperature and an equilibrium moisture content of 12%. Each bonded joint was cut into six samples with a bonded area of $2.5\text{ cm} \times 2.5\text{ cm}$. For each adhesive combination six samples were tested dry, six samples were immersed in cold water for 24 h then tested wet, and six specimen were immersed in boiling water for 2 h then cooled and tested wet, according to British Standard BS 1204 (1993) [34]. The tests were done in tension in an Instron 3300 dual-column universal testing machine (Instron France, Elancourt, France) at a head rate of $2\text{ mm}/\text{min}$. The specimens were tested in tension, as shown in Scheme 1.



Scheme 1. An exemplificative sketch of the bonded wood joint test.

2.7. Surface Coatings Applications

Duplicate samples of both A2 and B2 were spread at a load of 150 g/m² onto pine wood block surfaces 7.5 cm × 18 cm and were cured at 130 °C overnight (14 h) and at 300 °C for 5 min. The contact angles of a drop of water on the four coatings so prepared were monitored every one minute for 10 min and compared to the same for an untreated surface of wood. The contact angle of the treated and untreated wood surfaces was obtained from the water drop being placed on the surface with a syringe and measured with an EasyDrop contact angle apparatus, using drop shape analysis software (KrüsGmbH, Hamburg, Germany).

Equally, A2 and B2 were spread by knife on two stainless steel plates at a load of 50 g/m², and then cured in an oven at 300 °C for 3 min. After cooling they were subjected to an adhesion test by the cross-cut test according to French (European) standard NF EN ISO 2409 [35]. For this, the coating was cut through to the metallic substrate with a razor blade in order to produce edges from which the coating may then be lifted. The cutting pattern consisted of a 10 × 10 grid of vertical and horizontal cuts spaced at 1 mm × 1 mm. A strong adhesive tape was then applied over the cut area and tightly pressed. The tape was then rapidly pulled off. This operation was repeated three times. Finally the coating was examined to determine the number of blocks removed, this constituting an evaluation of the coating adhesion.

3. Results and Discussion

Table 1 and Figures 1–12 report the MALDI-ToF results obtained for the A2 NIPU resin based on glucose. There are examples of glucose molecules just reacted with the dimethyl carbonate (which are present in abundance in the A1 spectra, not reported here) such as the species at 263.8 Da.

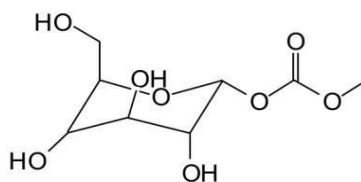


Figure 1. Moncarbonated glucose, peak at 263.8 Da.

The subsequent initial reaction of the hexamethylene diamine with this type of species forms a urethane link, such as the species at 322.8 Da.

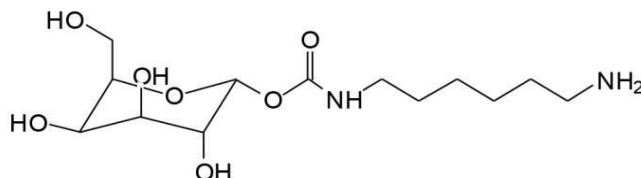


Figure 2. Urethane formed by reaction of moncarbonated glucose with hexamethylene diamine; 322 Da peak.

Many species of this type appear to be formed (Table 1) where the glucose has formed two or more urethanes on the same glucose moiety, as well as species presenting both dimethyl carbonate-linked and urethanes formed, such as the species at 378.8 Da

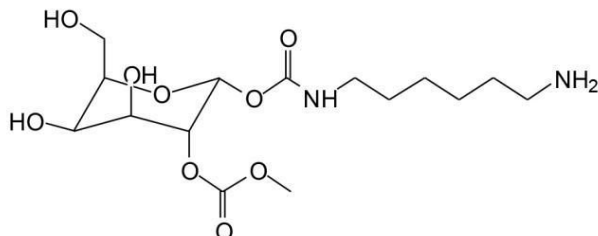


Figure 3. Example of a dicarbonated glucose having formed a urethane with hexamethylene diamine. 378.8 Da peak.

It must be clearly pointed out that for all the species indicated in Table 1, as shown in Figure 4:

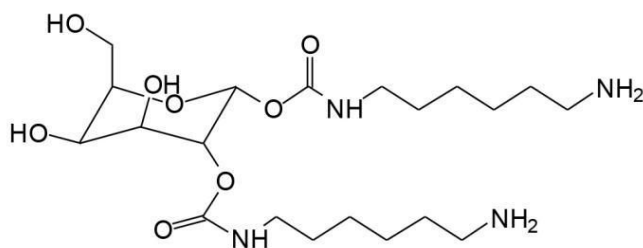


Figure 4. Example of one of the possible glucose diurethane structures.

The species can correspond also species of the same molecular weight but of structure as shown in Figure 5:

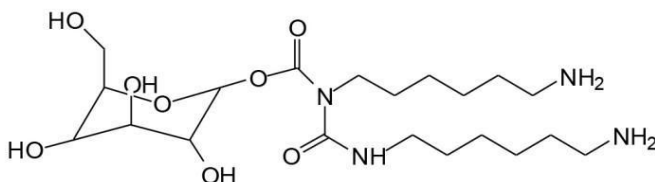


Figure 5. Example of alternative, possible glucose diurethane structures.

More interesting for the potential application of these NIPU resins are the oligomers formed, such as the trimer at 1225.6 Da, in which up to six urethane linkages are present, in its linear configuration.

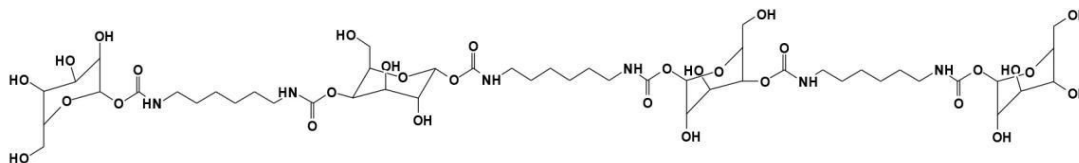


Figure 6. Example of the linear structure, one of the possible structures of the trimer at 1225.6 Da.

Additionally, a multitude of possible branched configurations exist, such as:

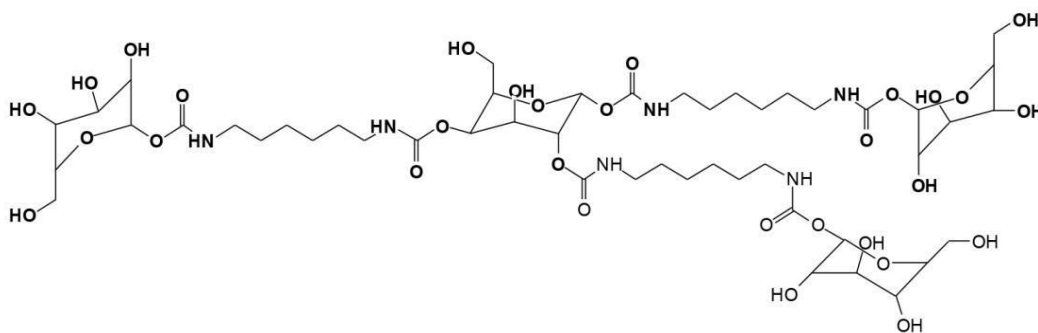


Figure 7. An example of one of the possible branched structures of the trimer at 1225.6 Da.

The existence of branched species indicates that these resins do cross-link, as the results found, and are discussed later for both bonding and coating.

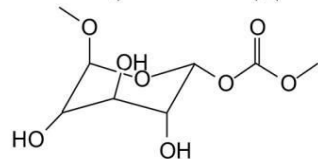
Table 1. Proposed oligomer structures for the MALDI ToF spectra peaks in Figures 1–4 for the reaction of carbonated glucose with a diamine.

116.9 Da = dimethyl carbonate + Na⁺

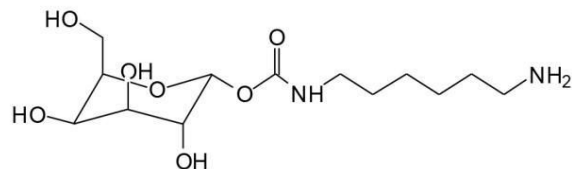
176.7 Da = glucose (calc. 180) deprotonated × 2

200 Da = glucose deprotonated + 23 Da (Na⁺)

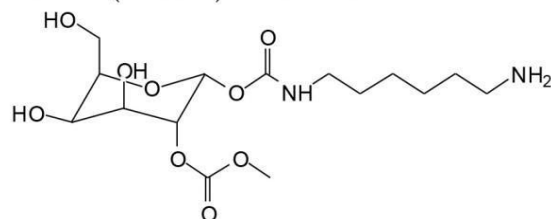
263.8 Da (calc. 261 Da) (with Na⁺) protonated



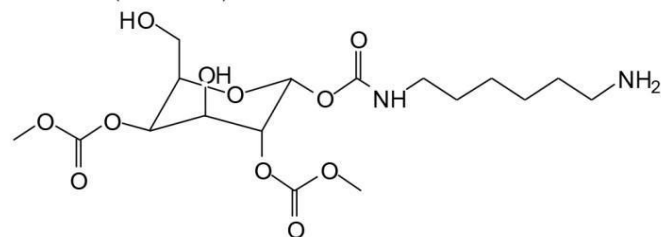
322.8 Da without Na⁺



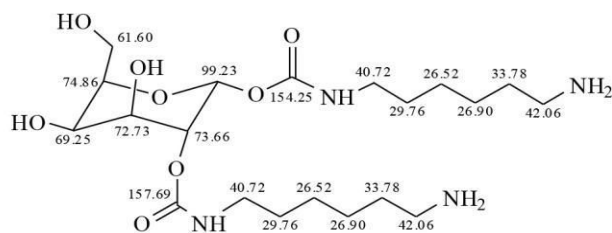
378.8 Da (calc. 380) without Na⁺



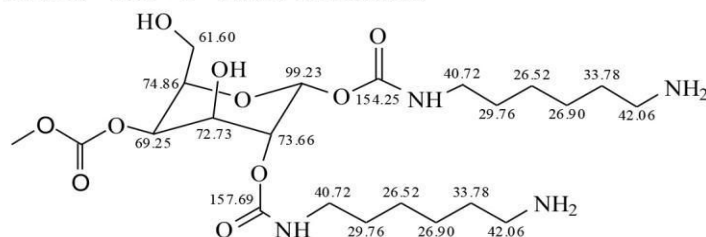
440.9 Da (Calc. 439) without Na⁺



464 Da = without Na⁺

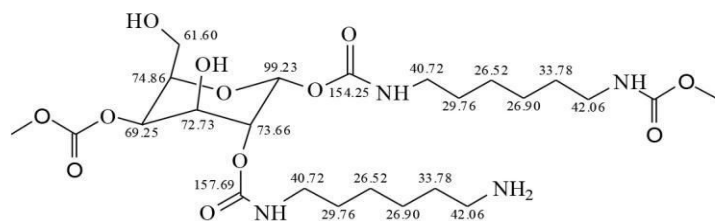


522 Da = 464 + 1 × DMC without Na⁺

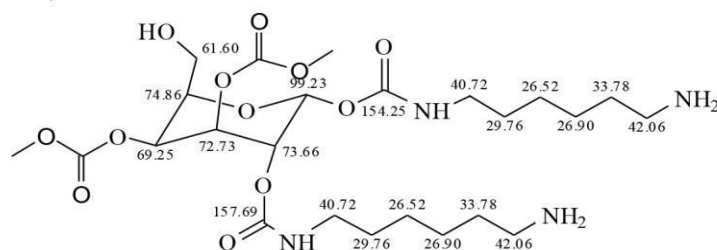


546 Da = 522 + 23 (Na⁺)

580 Da = without Na⁺

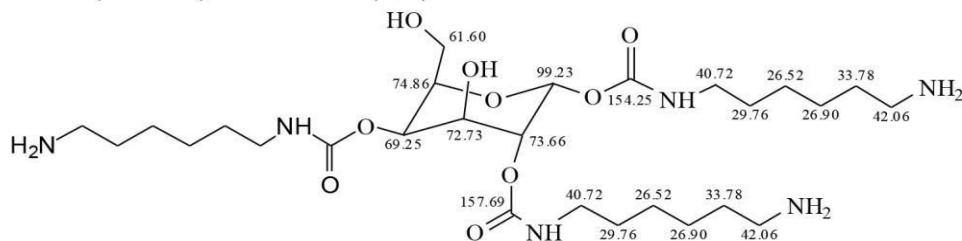


and/or

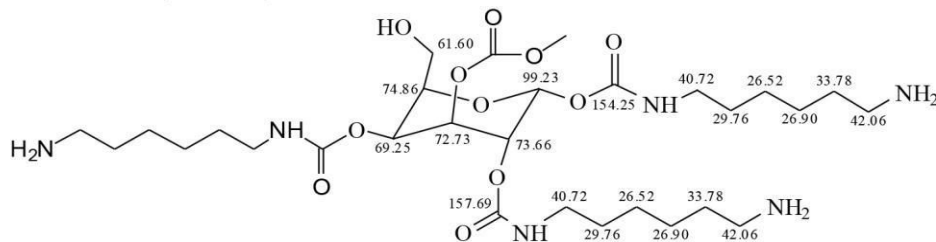


601 Da = 580 + 23 (Na⁺) deprotonated = (603 Da calculated)

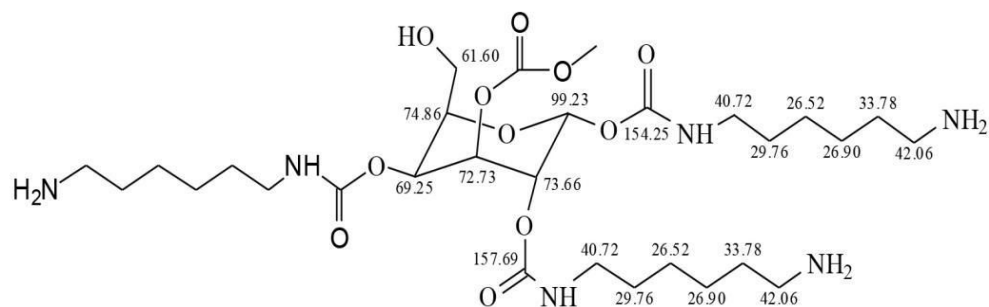
632 Da (calc. 629) with + 23 Da (Na⁺)



and/or 632.9 (calc. 635) without Na⁺

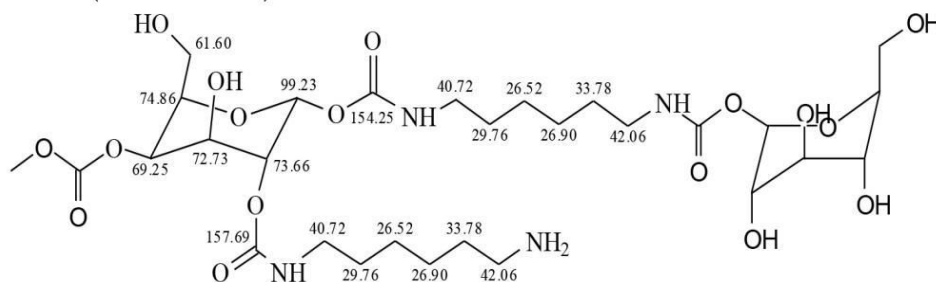


667 Da (calc. 675) with + 23 Da (Na⁺)

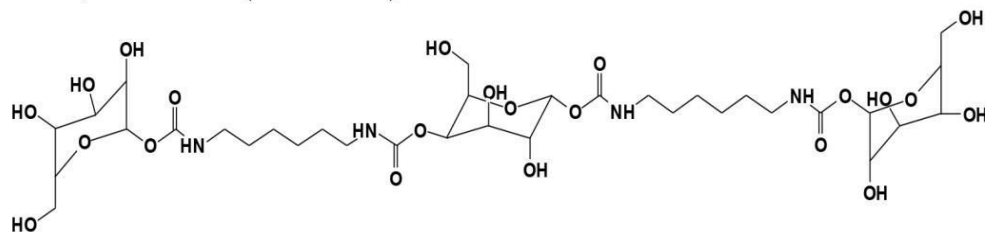


689 Da = 667 + Na⁺. Thus a case of a structure with 2 × Na⁺

733 Da (730 calculated) without Na⁺



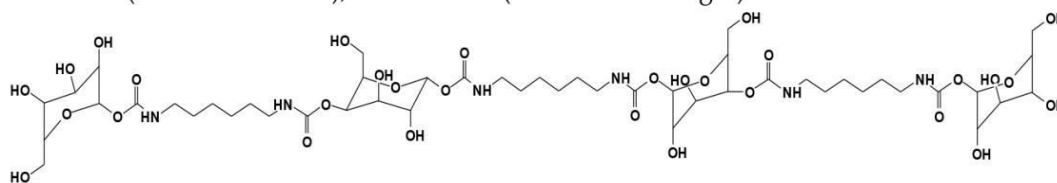
879 Da, without Na⁺ (calc. 878 Da) a PUR tetramer



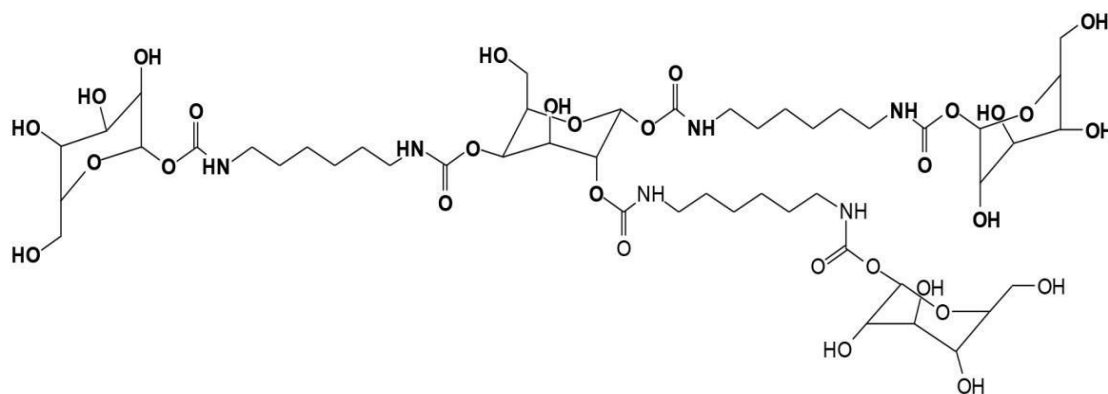
903 Da = 879 Da + Na⁺ (+23 Da) (Calculated 902 Da) a PUR tetramer

925 Da = 879 Da + 2 × Na⁺ (calculated 926 Da) a PUR tetramer

1225.6 Da (1225.2 calculated), without Na⁺ (6 urethane linkages) PUR tetramer



And



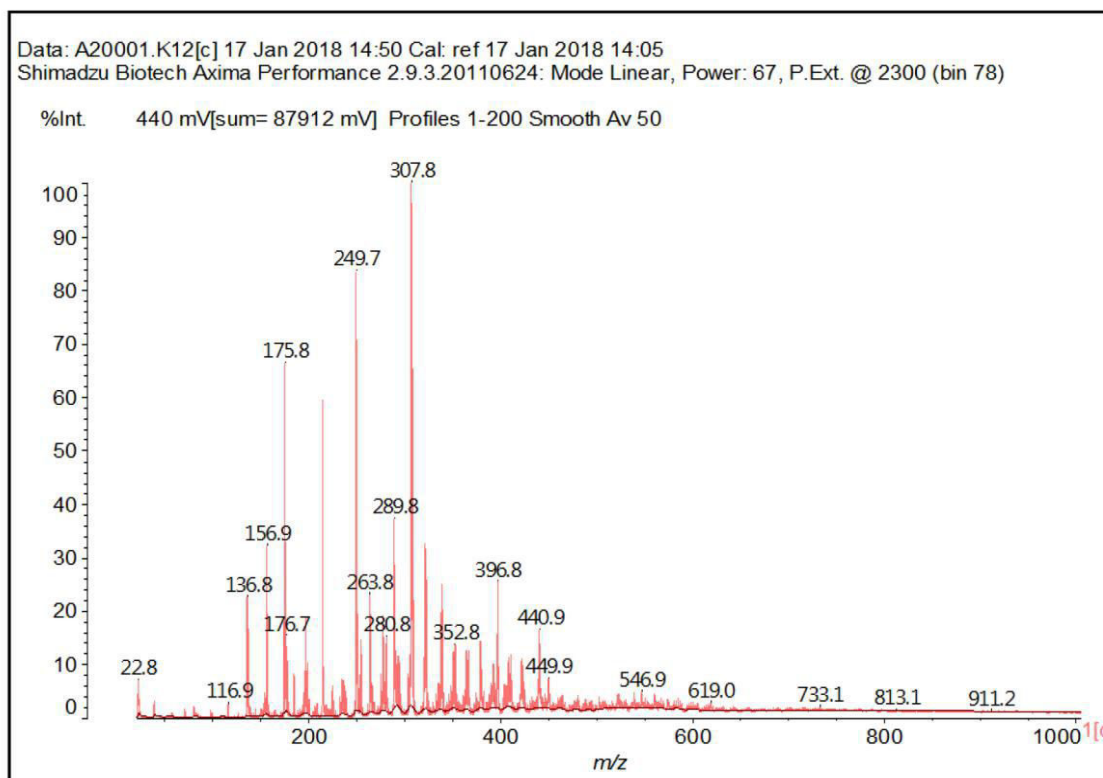


Figure 8. MALDI ToF spectrum of the A2 NIPU resin: 20–1000 Da range.

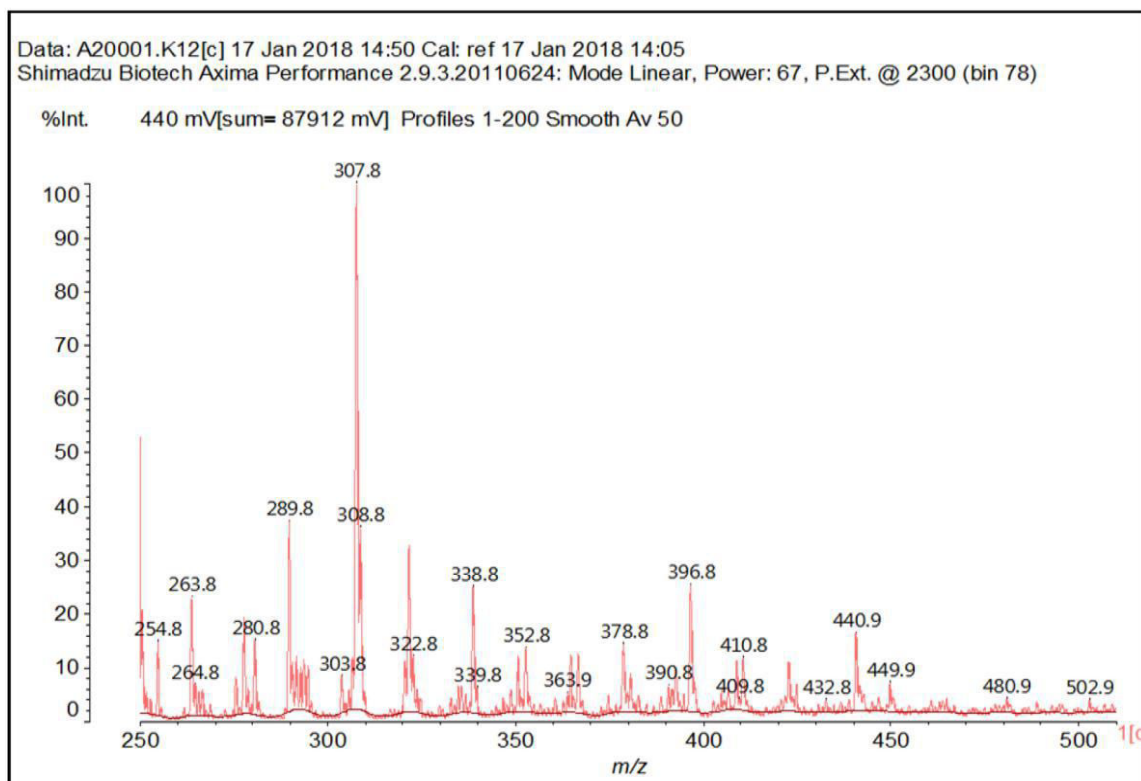


Figure 9. MALDI ToF spectrum of the A2 NIPU. Detail of the 250–500 Da range.

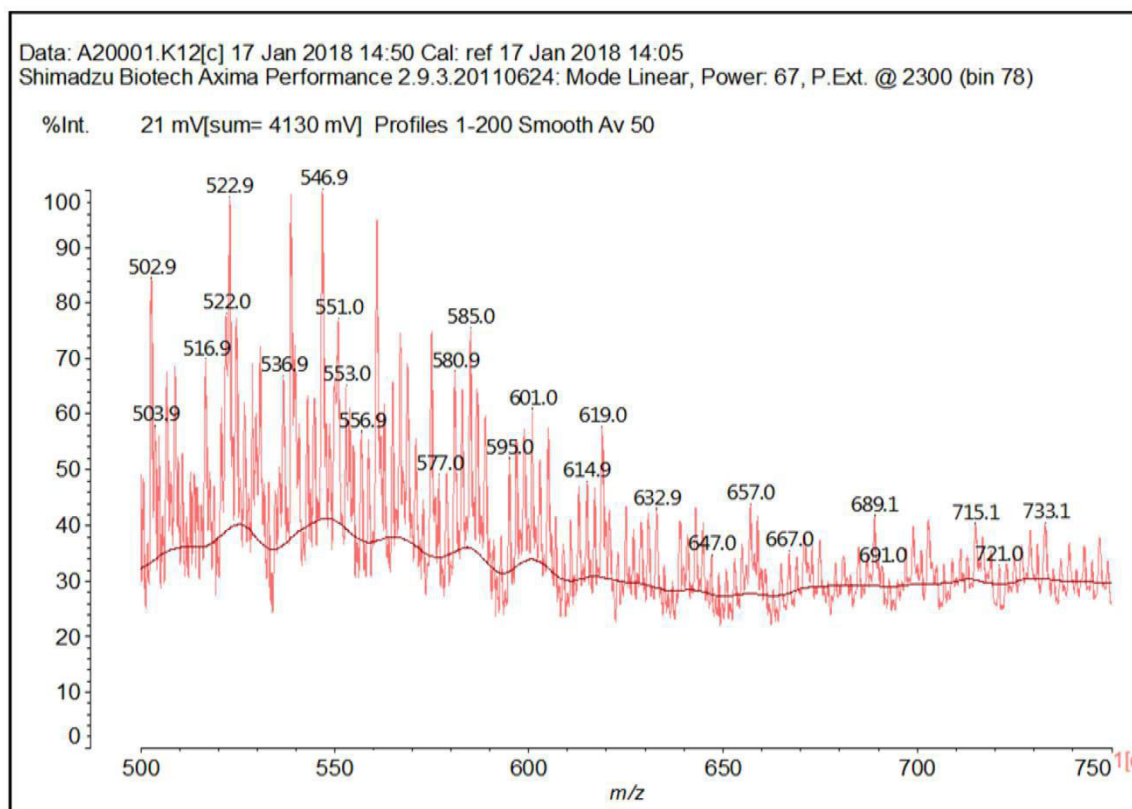


Figure 10. MALDI ToF spectrum of the A2 NIPU resin. Detail of the 500–7500 Da range.

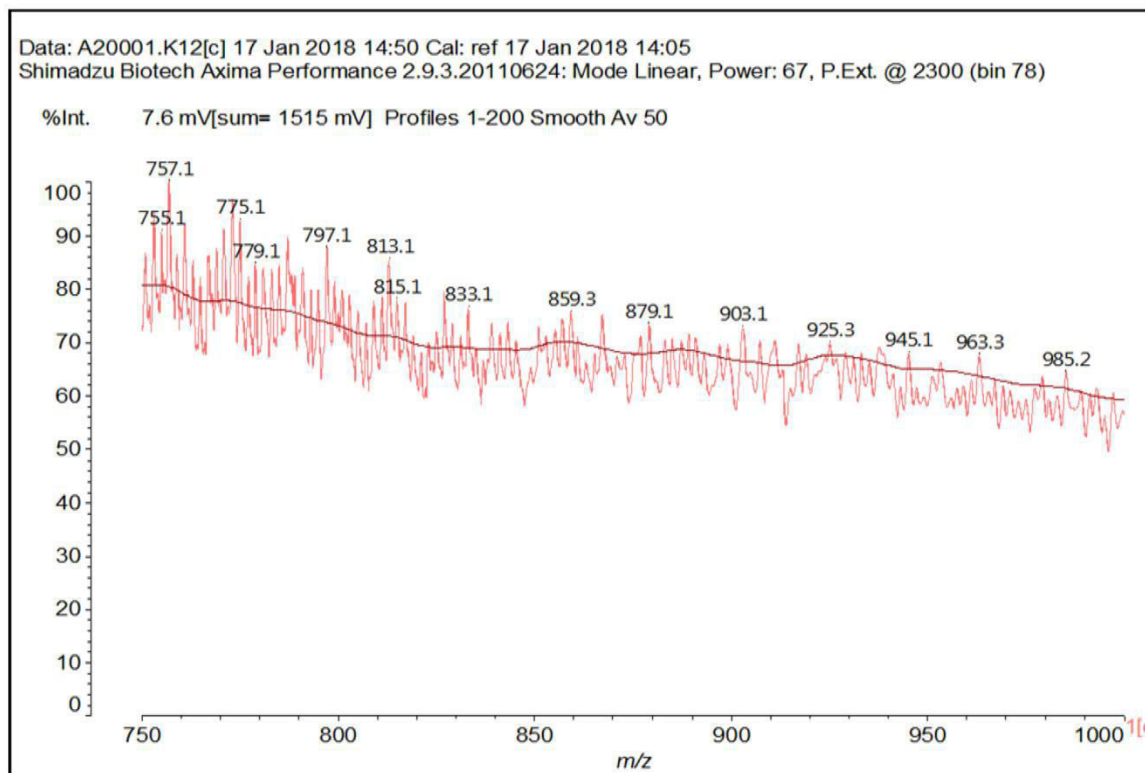


Figure 11. MALDI ToF spectrum of the A2 NIPU resin. Detail of the 750–1000 Da range.

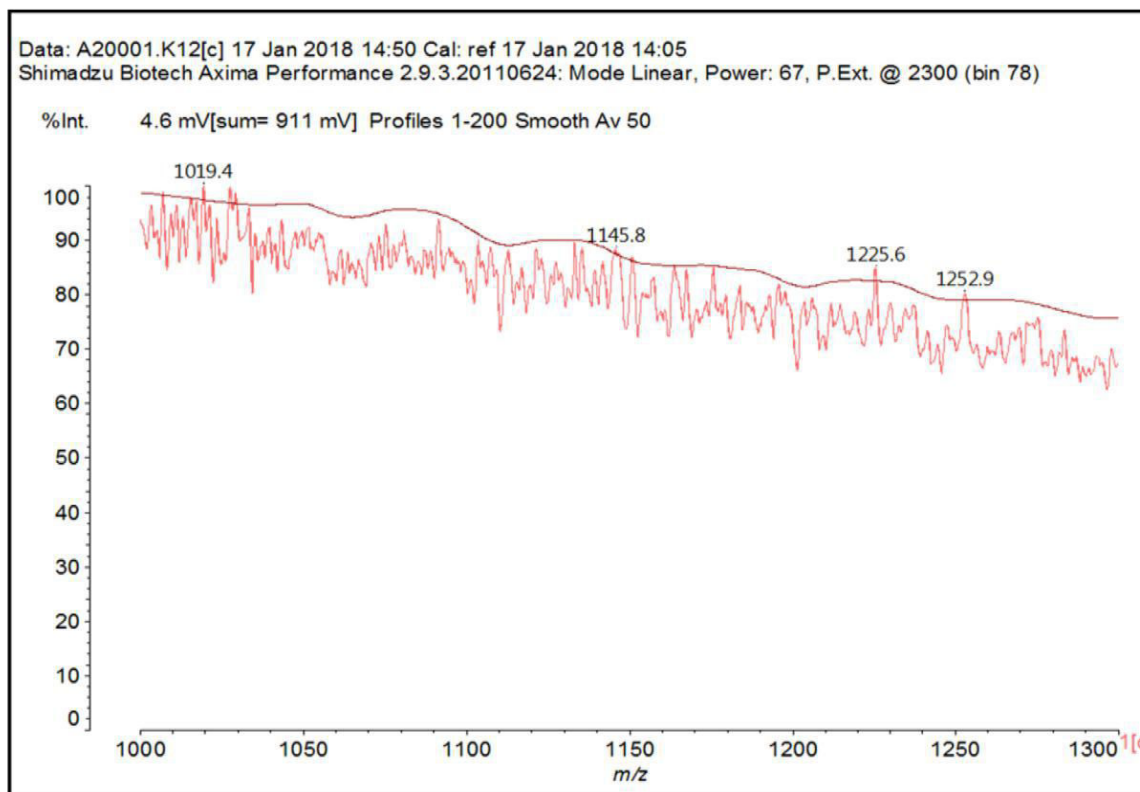


Figure 12. MALDI ToF spectrum of the A2 NIPU resin. Detail of the 1000–1300 Da range.

Of further interest are the results of CP MAS ^{13}C NMR analysis of A1 carbonated glucose and of the A2 glucose-based non-isocyanate polyurethane resin shown in Figures 13 and 14. These indicate that species other than those identified by MALDI ToF also occur in the reaction mixture.

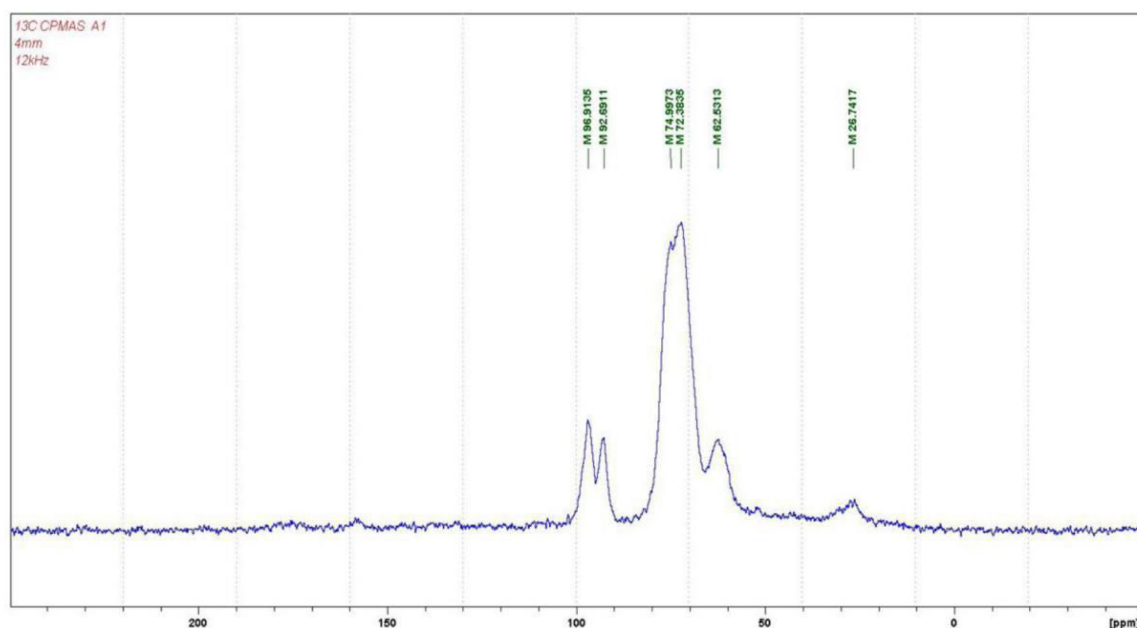


Figure 13. CP-MAS ^{13}C NMR spectrum of the carbonated glucose A1.

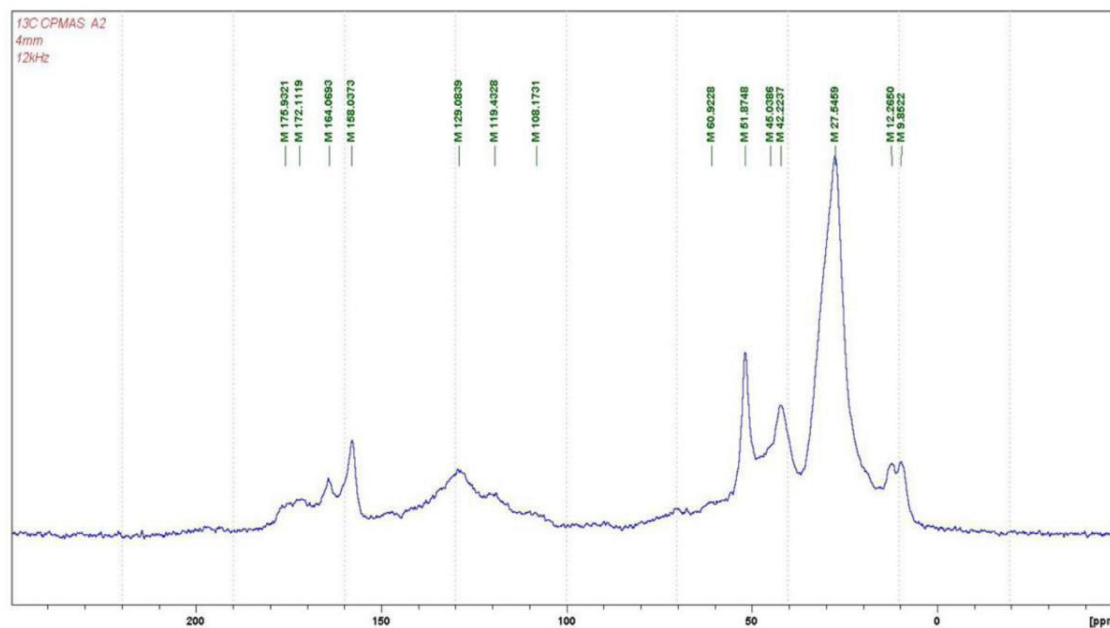


Figure 14. CP-MAS ^{13}C NMR spectrum of the A2 NIPU resin.

The peak at 92.7 ppm in Figure 13 also attests that a number of species in which a glucosidic bond between two glucoses has been formed have also been formed such as the structure shown in Figure 15:

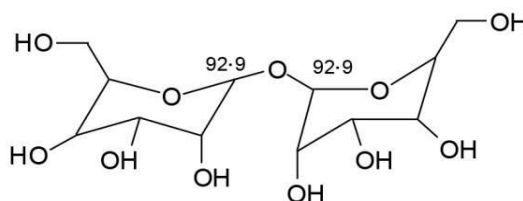


Figure 15. Example of two glucoses linked by a glucosidic bond formed by the elimination of CO_2 from two glucoses linked by a dimethyl carbonate. The peak is shown in Figure 13.

The peaks at 96.9 and 62.5 ppm belong to the glucose, the latter to the $-\text{CH}_2\text{OH}$ side chain of its pyranose ring. Of interest is the presence of the two peaks at 74.9–75 and 72.3 ppm. The former can be attributed to carbons of the glucose pyranose ring in both glucose moieties reacted and not reacted with DMC. The latter only appears for carbons belonging to carbonated glucose. A small peak at 26.7 ppm indicates that a very small proportion of glucose also appears to be present in its open form [36,37].

More complex, but more interesting, is the CP MAS ^{13}C NMR of the final A2 resin shown in Figure 7. The interpretation of the peaks has been carried out according to literature references [31,32,36–41]. The peak at 61 ppm is the one belonging to the $-\text{CH}_2\text{OH}$ side chain of the pyranose ring. The peak is very small, but its presence indicates that a very small proportion of this glucose site has not reacted. The peak at 52 ppm is attributed to the methyl of the $-\text{COO}-\text{CH}_3$ of carbonated glucose not reacted with the diamine, confirming the existence of species already identified by MALDI ToF. The peaks at 42 and 27.5–28 ppm belong to the methylene groups ($-\text{CH}_2-$) of the diamine chain, respectively, directly linked and not linked to urethane groups. The 42 ppm thus confirms the reaction of the diamine and formation of urethane groups. The peak at 158 ppm is the peak belonging to the $\text{C}=\text{O}$ of the $-\text{NH}-\text{COO}-$ of the urethane bridges. The peak is quite marked indicating that the

proportion of urethane formed is relatively high, in line with that indicated by the intensity of the 42 ppm peak. Up to here the signals remarked were expected, but even more interesting are the rest of the peaks. The very small peaks at 176 and 172 ppm could either belong to the formation of -COOH groups derived either from oxidation of the aldehyde group of the open form of glucose, or by a rearrangement of the dimethyl carbonate, although this latter appears unlikely. The peak at 164 ppm is due to an internal rearrangement giving the group. The most likely rearrangement is the one corresponding to a group of the type (Figure 16):

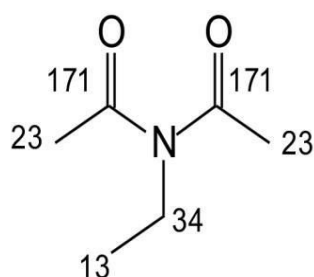


Figure 16. Example of rearranged group corresponding to the 164 ppm peak.

This indicates the possibility of very small amounts of oligomers formed by just the reaction of DMC and diamine. The very small peaks at 164, 129, and 108 ppm are indicative of internal rearrangements of the amine and of the amine-DMC adducts, rearrangements of the type shown in Figure 17.

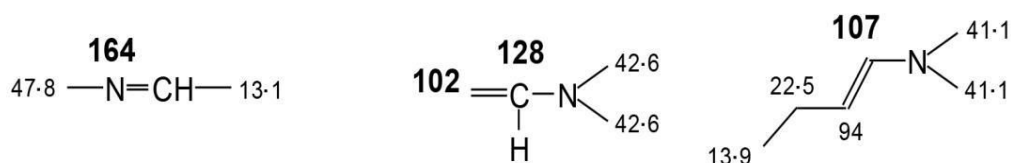


Figure 17. Internal rearrangement of the amine and the amine-DMC adducts corresponding to the 164, 129, 108 ppm peaks.

These indicate perhaps some form of degradation of some products, although its extent is rather small. Finally, the peaks at 12.3 and 9.9 ppm are attributed to -CH_3 groups in a sterically-hindered configuration. This latter probably belongs to the $\text{CH}_3\text{CH}_2\text{COOH}$ or, even more probably, $\text{CH}_3\text{CH}_2\text{CONH}_2$ formed by internal rearrangement of DMC or of the carbonated amine to an amide. These rearrangements are, however, small and do not appear to interfere with the performance of the material in both bonding and coatings applications.

The results of the FTIR analysis of the A2 and B2 resins are shown in Figures 18 and 19. The peaks for urethane linkages are seen at 1711, 1547, 1475, and 1251 cm^{-1} [39–41]. These are small and not so clearly seen. On the A1 FTIR in Figure 8 the 1744 cm^{-1} of the C=O of the carbonate and a peak at 1621 cm^{-1} , that can possibly be attributed to the aldehyde group of the open form of the glucose, are very clearly visible. Table 2 reports the main IR peak assignments.

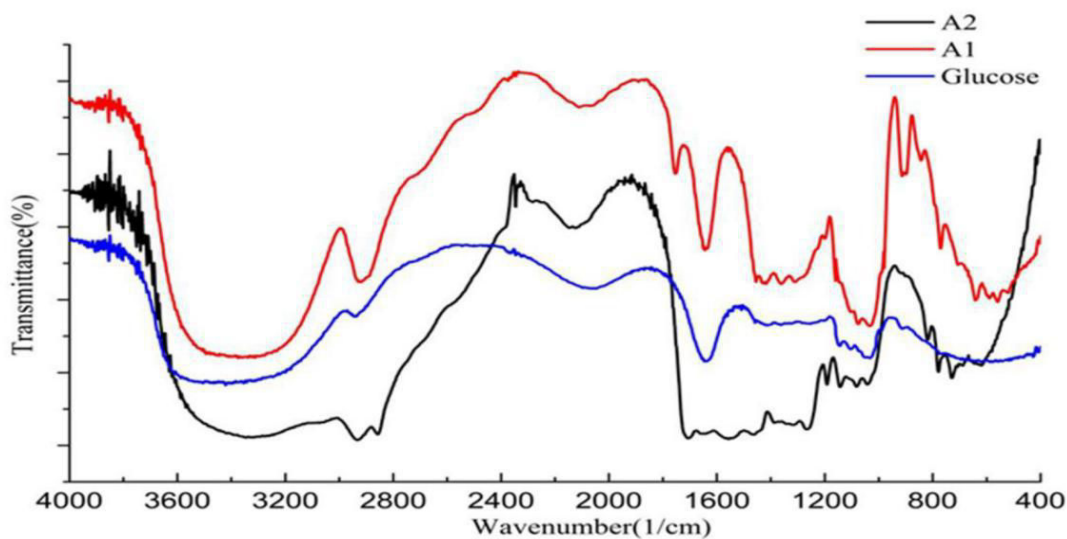


Figure 18. FTIR spectra of glucose, carbonated glucose A1, and glucose-based A2 NIPU resin.

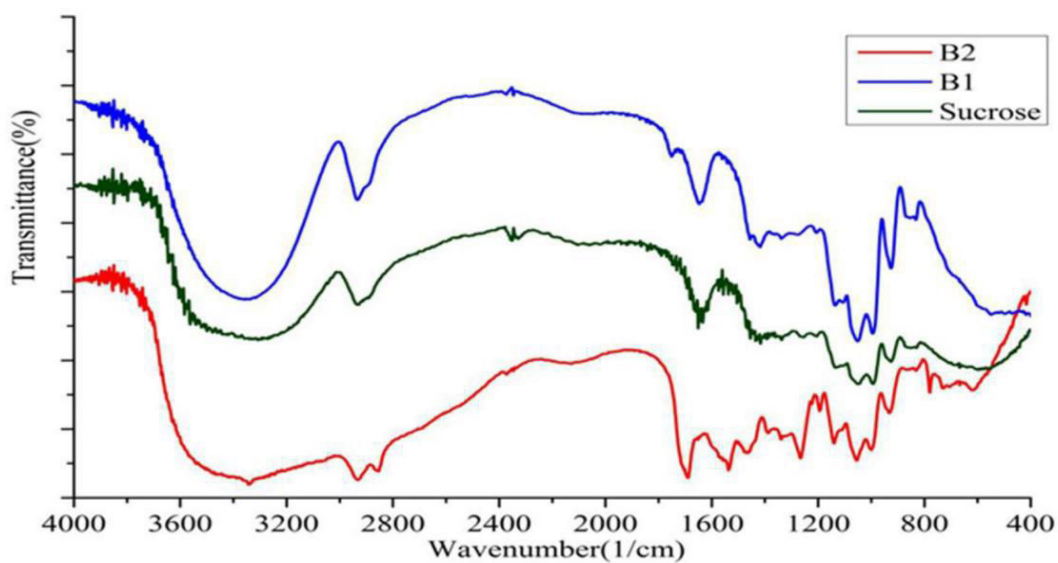


Figure 19. FTIR spectra of sucrose, carbonated sucrose B1, and sucrose-based B2 NIPU resin.

Table 2. FTIR peak assignments.

Peaks (cm ⁻¹)	Assignment
1051, 1087, 1150	C–O–C stretching vibration
1193	C–O stretching vibration
1325	–C–N stretching vibration
1394.5	–CH ₃ Surface bending vibration
1573	N–H bending vibration, urethane bridge
1642	C=O (carbonyl) stretching vibration
1718	C=O stretching vibration of urethane bridge
1744	C=O stretching of carbonate
2857, 2932	C–H stretching vibration
3100–3200	N–H, O–H stretching vibration

The specimens as shown in Scheme 1 were tested in tension. The results of bonded wood joints in Table 3 indicated that bonding did occur with the non-isocyanate glucose and sucrose polyurethane (NIPU) resins prepared. Those obtained from glucose appeared to be somewhat better and also easier to handle and to spread. These are, indeed, only initial exploratory results and the formulation and both ratios of reagents and the reaction process can be improved much further. However, it can be noted that, in the case of the A2-bonded joints, very interesting results are obtained after cold water soaking for 24 and 2 h in boiling water. These results are comparable to those obtained dry. Considering the liophilicity of glucose towards water this is remarkable and again confirms the formation of water repellent cross-linked polyurethane resins. One problem encountered is that the classical hardeners/accelerators used to form and harden polyurethanes are of no use in NIPU systems due to the absence of isocyanates. This means that these systems can harden exclusively by heat. Thus, cross-linking accelerators based on alternative reactions need to be found for this type of polyurethane obtained by such an alternative route. It must be clearly pointed out that A1 and B1 are just intermediate products of the two-step reaction process, and it is for this reason that they have not been tested either for bonding or for coatings.

Table 3. Strength results of wood joints bonded with glucose (A2) and sucrose (B2) NIPU resins.

Resin	Dry strength (MPa)	24 h Cold Water Soak Strength (MPa)	2 h Boiled Strength (MPa)
A2	3.15 ± 0.05	3.62 ± 0.02	3.38 ± 0.04
B2	2.76 ± 0.09	1.32 ± 0.08	1.24 ± 0.04

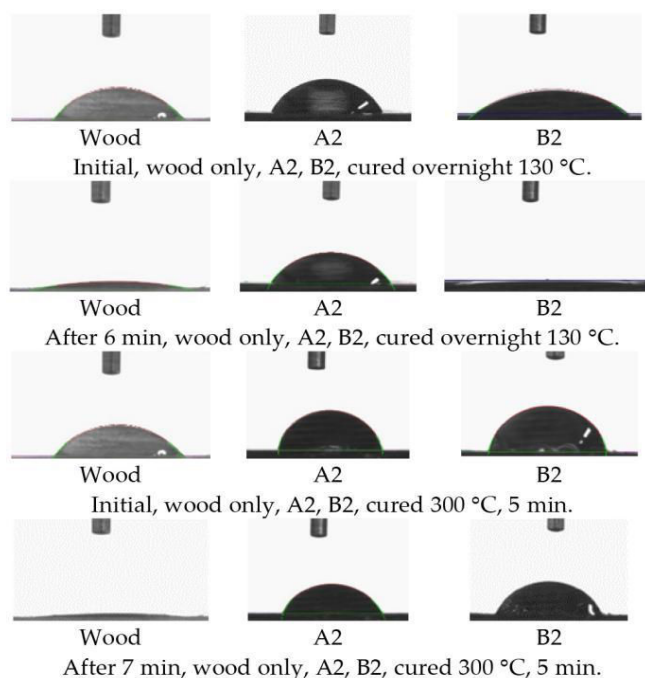
Of considerable interest are the results obtained by coating wood surfaces with A2 and B2 NIPU resins. Thus, the contact angles of A2 coatings are always higher than those of both untreated wood and of B2 coated wood (Tables 4 and 5; Figure 20). The contact angle for un-coated and coated wood are affected by the roughness of the contact surface and, thus, the results cannot surpass 90°.

Table 4. Water contact angle theta on glucose (A2) and sucrose (B2) NIPU resins cured at 130 °C overnight.

	Wood	A2	B2
Time (Minutes)	Theta (Degrees)	Theta (Degrees)	Theta (Degrees)
0	49.1 ± 1.24	64.4 ± 1.41	40.0 ± 2.17
1	36.1 ± 0.43	63.2 ± 1.30	20.6 ± 3.22
2	31.0 ± 1.68	61.6 ± 1.64	11.2 ± 0.10
3	28.2 ± 2.06	61.0 ± 1.19	8.8 ± 0.0
4	22.6 ± 1.66	59.9 ± 1.36	5.3 ± 0.39
5	19.5 ± 3.24	58.3 ± 1.35	3.6 ± 0.0
6	13.6 ± 0.81	57.2 ± 1.34	-
7	-	56.9 ± 0.97	-
8	-	54.7 ± 1.95	-
9	-	50.6 ± 1.02	-
10	-	49.2 ± 0.97	-

Table 5. Water contact angle on glucose (A2) and sucrose (B2) NIPU resins cured at 300 °C for 3 min.

	A2	B2
Time (Minutes)	Theta (Degrees)	Theta (Degrees)
0	80.6 ± 1.82	80.3 ± 0.65
1	76.3 ± 2.56	79.0 ± 1.40
2	74.5 ± 2.18	77.2 ± 2.15
3	73.4 ± 2.54	75.4 ± 2.04
4	72.1 ± 2.05	73.4 ± 0.38
5	69.0 ± 2.31	73.5 ± 0.78
6	67.7 ± 2.04	71.4 ± 1.70
7	65.9 ± 1.44	68.8 ± 1.70
8	64.8 ± 2.22	67.9 ± 2.81
9	62.9 ± 1.19	66.3 ± 2.69
10	62.3 ± 1.37	64.7 ± 1.70

**Figure 20.** Comparative sessile water drop contact angles on an untreated wood surface, on a wood surface treated with a glucose-based A2 coating, and on a wood surface treated with a sucrose-based B2 coating. The initial angle when cured overnight at 130 °C (**top**). The angle after 6 min wetting when cured overnight at 130 °C (**second from Top**). The initial angle when cured at 300 °C for 5 min (**second from Bottom**). The angle after 7 min wetting when cured at 300 °C for 5 min (**bottom**).

The contact angles of water sessile drops on any wood surfaces tend to decrease with contact time. This is true since the tendency for a given mass of liquid to spread on a solid surface increases as the contact angle decreases [42–47].

TMA was used to prove that the curing temperature for A2 is lower than for B2. TMA is now frequently used in this manner to determine the differences in wood adhesives, and there are many references on this [33,43]. The TMA curves indicate the reason why A2 showed better bonding strength and better performance as a wood coating than B2. This infers that A2 coatings have the added advantage on B2 coatings that their energy of activation of hardening is apparently lower. This appears to be the case as at 130 °C A2 coatings are capable of cross-linking and hardening while B2 coatings are patently not able to (Table 4). This is confirmed by the thermomechanical analysis trace [42] shown in Figure 21 where A2 NIPU resin curing and cross-linking appears to start at a much

lower temperature than for the B2 NIPU resin. The A2 resin curing appears to start at around 100 °C and it reaches its max cure at around 200 °C, while the B2 NIPU resin only appears to start curing at 205 °C. These TMA results appear to indicate that for sucrose the problem may be due either to diffusion problems or to a higher energy of activation of hardening, or to both. The TMA is used here to monitor the progress of cross-linking and hardening of the resins [33,42]. As condensation and cross-linking proceeds the reaction slows down when one progressively approaches $T_g(\infty)$ due to difficulties in molecular diffusion in the medium [48,49]. This is possibly due to the higher viscosity of the sucrose based resin. A temperature of 300 °C, albeit for a short period of five minutes, is sufficient to cross-link, harden, and render water-repellent B2 coatings, also further improving the performance of A2 coatings, to the point that their level of water repellence is comparable (Table 5). It is in the field of wood surface coatings that mono- and di-saccharide based NIPU show the initial best promise.

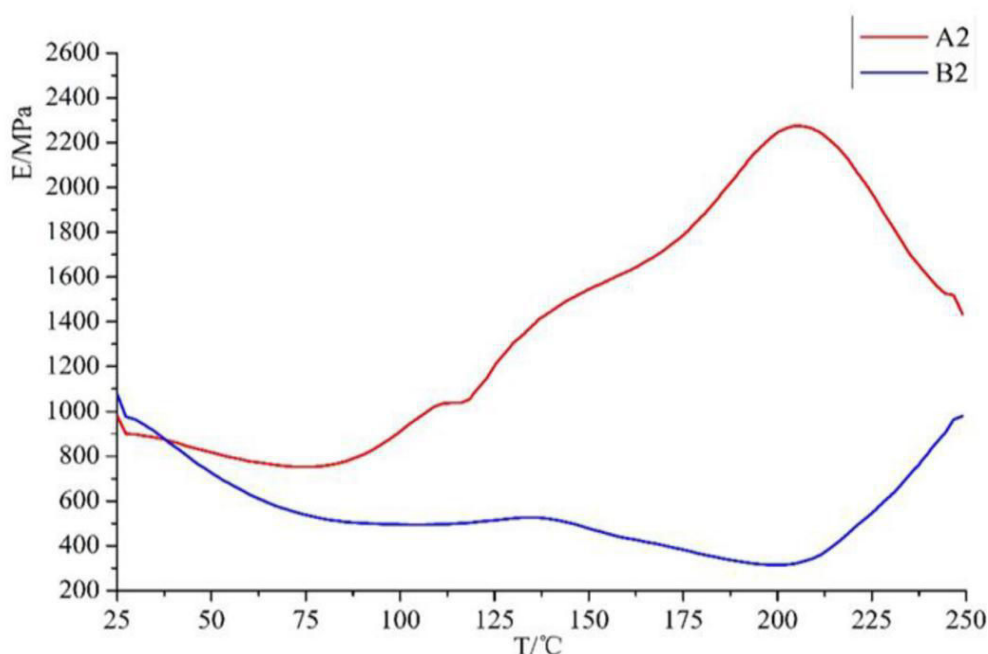


Figure 21. Comparative thermomechanical analysis (TMA) traces of curing of A2 and B2 NIPU resins on wood.

However, the potential of this type of NIPU resin is also shown by its capability of coating a steel surface. Figure 22 shows two steel plates coated with, respectively, B2 and A2. The figure shows clearly the better ease of spreading and good film appearance obtained with A2 coating on steel in relation to the poor performance of B2 coatings on steel. Of particular interest is the cross-cut adhesion test [34], the results of which are shown in Figure 23. This figure shows the aspect of the coated metal surfaces after the cross-cut test. None of the squares of the lattice are detached and the edges of the cut lines are smooth. Accordingly, adhesion to the metal plates of these coatings can be evaluated as being excellent. This is particularly true for coating A2 based on glucose, which presents an impressive performance.

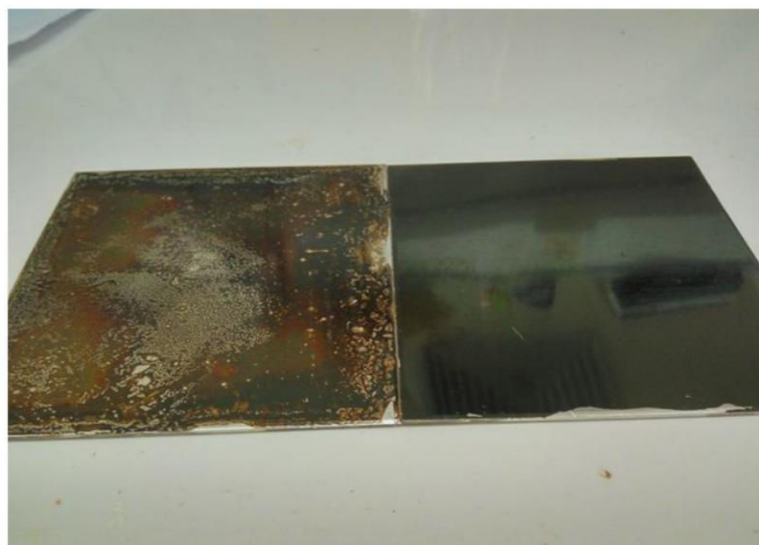


Figure 22. B2 (left) and A2 (right) NIPU resin surface coatings on stainless steel plates after curing at 300 °C for 3 min.

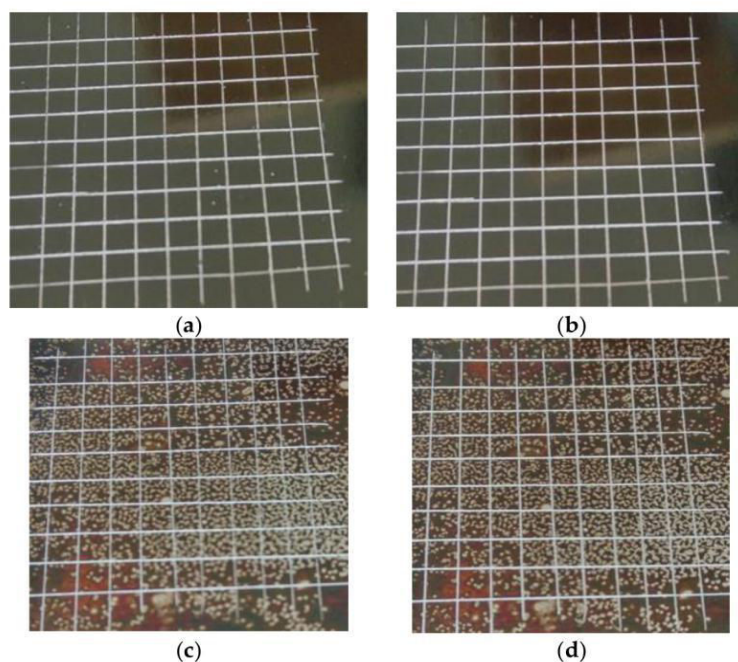


Figure 23. Cross-cut test according to NF EN ISO 2409 of glucose-based and sucrose-based surface coatings on stainless steel cured for 3 min at 300 °C. (a) A2 before washing in hot water; (b) A2 after washing in hot water; (c) B2 before washing in hot water; and (d) B2 after washing in hot water.

4. Conclusions

Mono- and disaccharides appeared to yield workable non-isocyanate polyurethanes having a definite potential for application as both wood and steel surface thermosetting coatings and for thermosetting wood adhesives. Several type of oligomer species were observed by using different analytical techniques, namely by MALDI-ToF, ^{13}C NMR, and FTIR. The products obtained were tested as surface coatings on both wood and steel, as well as to prepare bonded wood joints. The results obtained for bonded wood joints yielded encouraging results, although these will have to be further evaluated on the light of existing standards. The more interesting results were obtained for

the application of glucose-based NIPU as wood surface coatings. These yielded high water wetting angles and with the wetting angle maintaining a high value as a function of time even at the lower temperature of curing used. In this respect glucose-based NIPU wood surface coatings appeared to perform better than sucrose-based NIPU. This is most likely based on a number of different reasons such as better ease of spreading and lower temperature of curing. At a higher curing temperature instead, the contact angles obtained for glucose- and sucrose-based wood coatings were comparable. This indicates that, for sucrose, the problem may be due either to diffusional problems or to a higher energy of activation of hardening, or to both. Again, for steel surface coatings, glucose-based NIPU performed much better than sucrose-based ones as regards their uniformity of surface spread. The cross-cut test indicated excellent resistance of these surfaces to mechanical wear.

The main aim of this research was to show that NIPU can be prepared from mono- and disaccharides, this just being an initial exploratory work and its sole main aim. Mono- and disaccharides constitute a considerable reservoir of reasonably low-cost biosourced material easily available everywhere in the world rendering their use for such applications an interesting industrial alternative to existing routes of NIPU resins.

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Author Contributions: Xuedong Xi prepared the resins and did the experiments. Luc Delmotte conducted the CP-MAS ^{13}C NMR spectra. Antonio Pizzi coordinated the project, analyzed and interpreted all the MALDI ToF and CP-MAS ^{13}C NMR spectra, deduced from the data all the reactions occurring, and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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3.9 Adhésif polyuréthane non isocyanate à base de saccharose utilisé pour les panneaux de particules

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Résumé: Des polyuréthannes non isocyanates à base de saccharose (S-NIPU) ont été synthétisés par la réaction déjà codifiée du saccharose, le diméthyle carbonate et l'hexaméthylène diamine et elles sont utilisés pour la première fois comme adhésifs pour la liaison de panneaux de particules. Pour diminuer la température de durcissement de l'adhésif NIPU, un agent de couplage au silane a été utilisé comme promoteur de réticulation. Les performances des panneaux de particules préparés à des températures de pressage de 230, 200 and 180 °C et à des temps de pressage de 8, 10 et 12 min ont été testées. La structure des oligomères obtenus est détectée par spectrométrie MALDI-ToF. L'analyse thermomécanique (TMA) et l'analyse calorimétrique différentielle (DSC) ont également été utilisées pour analyser leur comportement. Les panneaux de particules collés avec l'adhésif S-NIPU à 230 ° C a donné d'excellentes propriétés qui diminuaient toutefois avec la réduction du temps de pressage. L'agent de couplage au silane utilisé comme agent de réticulation a considérablement réduit la température de durcissement de l'adhésif et a permis d'obtenir une bonne liaison à une température de presse inférieure. Les résultats obtenus confirment que le couplage de l'adhésif S-NIPU avec un silane utilisé comme agent de réticulation peut donner des résultats suffisamment améliorés pour servir d'adhésif approprié pour les panneaux de particules, les panneaux de fibres de densité moyenne et d'autres types de panneaux de bois en particules. C'était également la première fois qu'un adhésif NIPU est utilisé pour le collage du bois.

Mots clés: polyuréthanes non isocyanates; saccharose; colle à bois; panneaux de particules; MALDI-ToF

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ORIGINAL



Non-isocyanate polyurethane adhesive from sucrose used for particleboard

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Abstract

Sucrose-based non-isocyanate polyurethanes (S-NIPU) were synthesized by the already codified reaction of sucrose, dimethyl carbonate and hexamethylene diamine and used for the first time as adhesives for bonding particleboard. To decrease the NIPU adhesive curing temperature, a silane coupling agent was used as a crosslinking promoter. The performance of particleboards prepared at a press temperature of 230 °C, 200 °C and 180 °C and a press time of 8 min, 10 min and 12 min was tested and evaluated. The structure of the oligomers obtained was detected by matrix-assisted laser desorption ionization time-of-flight mass spectrometry. Thermomechanical analysis and differential scanning calorimetry were also used to analyze their behavior. The particleboards bonded with the S-NIPU adhesive at 230 °C showed excellent properties, which, however, decreased as the press time was reduced. The silane coupling agent used as a crosslinking promoter significantly reduced the curing temperature of the adhesive and allowed to obtain good bonding at a lower press temperature. The results obtained confirmed that coupling the S-NIPU adhesive with a silane used as a crosslinking promoter can yield sufficiently improved results to function as a suitable adhesive for particleboard, medium density fiberboard and other types of particulate wood panels. It was also the first time that a NIPU adhesive was used for wood bonding.

Xuedong Xi and Zhigang Wu have contributed equally to this work.

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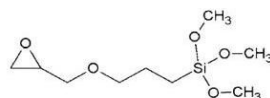
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Introduction

Polyurethanes (PU) are widely used in many fields, because of their excellent durability, impact resistance, bond performance, corrosion resistance and so on. PUs are also used as high-performance adhesives in the wood industry (Stoeckel et al. 2013; Pizzi and Mittal 2011; Cornille et al. 2017), for example, in the production of oriented strand board (OSB) (Ayrilmis et al. 2009), straw particle board (Zhang and Hu 2014; Mo et al. 2003; Fiorelli et al. 2012) and laminated timber/glulam (Properzi et al. 2003; George et al. 2003). The traditional synthesis route of PU is based on the reaction of polyols with polyisocyanates. Because polyisocyanates (such as TDI and HDI) have strong volatility and toxicity, thus being both harmful and not environment friendly, non-isocyanate polyurethanes (NIPU) have been synthesized and the research on them is now in full swing. Studies on reaction routes to prepare NIPU do already exist. In general, a five-membered cyclic carbonate is reacted with diamines to form polyhydroxyurethanes. Numerous research works on this topic do exist in the literature (Rokicki and Piotrowska 2002; Tomita et al. 2001a, b; Kihara and Endo 1993; Kihara et al. 1996; Figovsky and Shapovalov 2002; Birukov et al. 2009; Boyer et al. 2010; Kathalewar et al. 2013a, b; Camara et al. 2014; Cornille et al. 2016).

Some research works report the preparation of NIPU based on biomass materials, such as by chemical transformation of epoxidized vegetable oils, by the synthesis of biobased cyclic carbonates then reacted with diamines (Haniffa et al. 2017; Kathalewar et al. 2013a, b; Poussard et al. 2016). Recently, research on the use of biomass to prepare NIPUs has intensified with works on their preparation based on tannins or lignin, which showed some interesting performance as wood or steel surface coatings (Thébault et al. 2014, 2015; Santiago-Medina et al. 2018). Furthermore, non-isocyanate polyurethanes from monosaccharides (glucose) and disaccharides (sucrose) were prepared, and their suitability was proved as both wood and steel surface coatings, as simple thermosetting wood adhesives (Xi et al. 2018a), and even with the initial encouraging results as NIPU foams (Xi et al. 2018b). These NIPU resins, however, needed a relatively high temperature to cure to ensure a decent performance. To overcome such a problem and to be able to use NIPUs as wood panel adhesives at the usual temperatures for this application, a silane coupling agent (HK560) having the following structure:



was used as a crosslinking promoter in this paper. Particleboards were prepared and tested to check the adhesive performance.

Experimental

Materials

Sucrose by Acros Organics (Geel, Belgium), dimethyl carbonate by Sigma-Aldrich (Saint Louis, France), hexamethylenediamine 98% by Sigma-Aldrich (Saint Louis, France) and 98% silane coupling agent KH560 from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) were used.

Preparation of S-NIPU resin

The S-NIPU resin was prepared according to the procedure defined in a previous work (Xi et al. 2018a), namely: 20 g of sucrose were mixed with 13.5 g of dimethyl carbonate and 16.67 g of water, heated to 50 °C for 40 min and then cooled to room temperature. A total of 27.16 g hexamethylenediamine was then added to the mixture and heated to 90 °C for 120 min and then cooled to room temperature. A part of this mixture was dried at 103 °C overnight for the MALDI-TOF analysis.

Thermomechanical analysis (TMA)

The resins were tested by thermomechanical analysis. The samples were prepared by applying each adhesive between two beech wood plies, with dimensions of 21 mm × 6 mm × 1.1 mm. These beech–resin–beech sandwiches were tested in non-isothermal mode between 25 and 250 °C at a heating rate of 10 °C/minute with a Mettler Toledo 40 TMA equipment (Mettler Toledo, Zurich, Switzerland). They were tested in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 s (6 s/6 s). The classical mechanics relationship between force and deflection

$$E = [L^3/(4bh^3)][F/(f_{\text{wood}} - f_{\text{adhesive}})]$$

allows the calculation of the Young's modulus E for each case tested. Such a measuring system has been introduced and is used to follow the progressive hardening of the adhesive with the increase in temperature and to indicate comparatively if an adhesive system is faster or slower hardening and if it gives stronger joints than another one.

Differential scanning calorimetry (DSC)

The test was performed on a Perkin–Elmer DSC calorimeter type DSC 204F1 (Perkin–Elmer, Rodgau, Germany). The freeze-dried specimens were heated from 35 to 240 °C at a heating rate of 15 K/min, and the thermal changes were recorded. The software used for data analysis was PYRISTM Version 4.0.

MALDI-TOF analysis

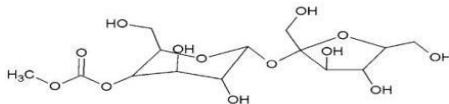
Samples for matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared by first dissolving 5 mg of sample powder in 1 mL of a 50:50 v/v acetone/water solution. Then, 10 mg of this solution was added to 10 μ L of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 μ L of NaCl solution 0.1 M in 2:1 v/v methanol/water and pre-dried. Then, 1 μ L of the sample solution was placed on its dedicated location, and the plaque was dried again. Red phosphorous was used to standardize the MALDI equipment. MALDI-TOF spectra were obtained by means of an Axima Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were taken by making 1000 profiles per sample with two shots accumulated per profile. The spectrum precision is of +1 Da.

Particleboard preparation and testing

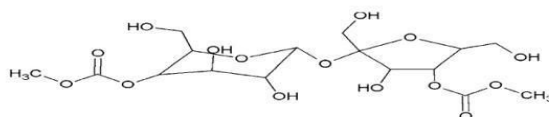
Three identical monolayer particleboards of $350 \times 310 \times 10$ mm³ size were prepared. The adhesive solids load was 10% on bone-dry wood. The panels were pressed with a three-stage hot pressing cycle, with a pressure cycle of 33 kg/cm², 15 kg/cm² and 5 kg/cm² for 8 min (2 min–4 min–2 min), 10 min (3 min–4 min–3 min) and 12 min (4 min–5 min–3 min). Three different hot pressing temperatures were used: 180 °C, 200 °C and 230 °C. After cooling and sanding the panel surface, the boards were cut to 50 mm $\times$ 50 mm for the tests of dry internal bond (IB) strength, elastic modulus and water absorption thickness expansion ratio and a size of 250 mm $\times$ 50 mm for bending strength test. At least three samples were tested for each test according to China National Standard GB/T 17657-1999. The density profile of the boards was also tested by their thickness scan at a rate of 0.4 mm/s using a DAX 6000 profile densitometer (GreCon, Alfeld, Germany).

Results and discussion

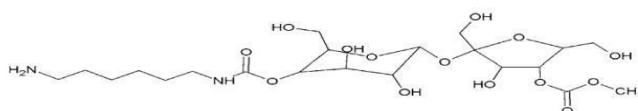
Table S1 and Figs. S1–S7 in Supplementary Material report the MALDI-ToF results obtained for the S-NIPU resin adhesive. The reaction product of sucrose and dimethyl carbonate (DMC) is found as the species at 422.5 Da.



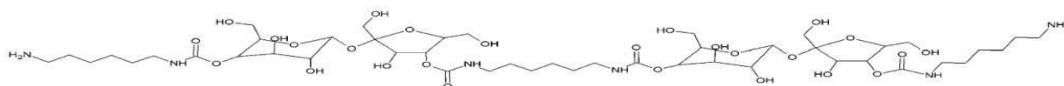
In addition, the reaction of one molecule of sucrose with two or more molecules of dimethyl carbonates was observed, for instance at 480 Da.



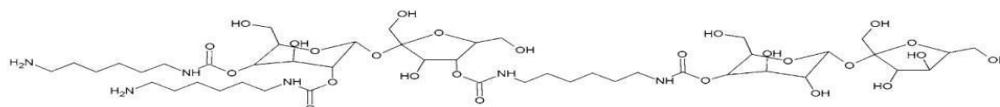
This type of species reacted with the hexamethylenediamine (HMD) to form a urethane link, such as the species at 568 Da are also found.



Oligomers with multiple urethane links formed as a linear molecule were also found, as for instance at 1137 Da

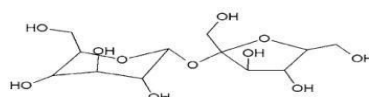


It is worth to clearly point out that a multitude of possible branched structures at the same molecular weight can occur, such as for example as follows:

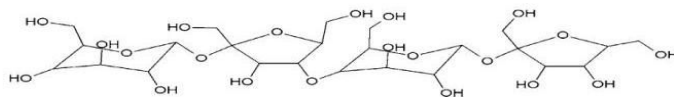


The existence of branched species indicates that these resins do crosslink and do form tridimensional polymer networks during the curing process, which allows to obtain a good bonding performance as shown by the results found and discussed later for particleboard.

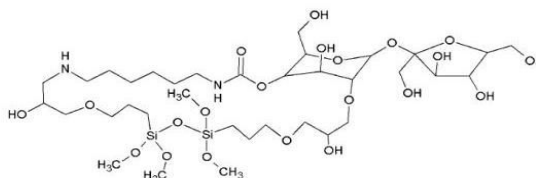
An unreacted sucrose unreacted with dimethyl carbonate is also observed in the reaction mixture as 365 Da (Table S1, Supplementary Material):



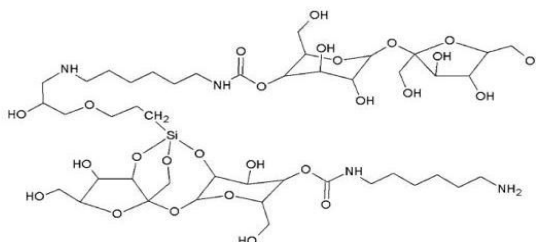
Oligomers obtained by reaction between two sucroses by elimination of a water molecule to form an ether bond have also been observed, such as the species at 690 Da:



The cured S-NIPU with KH560 adhesive was also tested by MALDI-ToF (Fig. S7, Supplementary Material), but the cured adhesive was practically insoluble in the acetone/water solution, so that the MALDI-ToF results obtained were rather limited. Only two small peaks of the initial reaction of the silane coupling agent with a low molecular weight NIPU could be identified, one of which at 933.5 Da (Fig. S7, Supplementary Material) having the following structure:



and one at 1108.8 Da (Fig. S7, Supplementary Material) with the following structure:



This is reported as indication that the reaction between the S-NIPU and the silane coupling agent does indeed occur (Fotea and D'Silva 2004; Serier et al. 1991).

Performance of the S-NIPU resin and of the particleboard bonded with it

The performance of the laboratory monolayer particleboards bonded with the S-NIPU resin pressed at 230 °C for 12 min is shown in Table 1. The boards show encouraging results for internal bond (IB) strength, being as high as 1.02 MPa, thus far above the standard requirement (≥ 0.35 MPa) (China National Standard GB/T 4897.5-2003; EN 312 2003). The 24-h water thickness swelling is only 12%, without any water repellent like emulsified paraffin being added, showing that the board appears to have good water resistance. In particular, the boards presented a residual internal bond strength of 0.32 MPa even after immersion in boiling water for 1 h. These effects are due to the urethane link in the cured S-NIPU adhesive, the structure of which gives good stability and hydrolysis resistance. However, the wood

Table 1 Performance of the S-NIPU resin and the particleboard bonded with it

Viscosity of the resin/mPa s	63.75
Solid content/ %	47.5
Density of the particleboard g/cm ³	0.71
Dry internal bond strength/MPa	
Maximum	1.38
Minimum	0.93
Average	1.02 ± 0.12
2-h water absorption thickness expansion ratio/ %	7.57
24-h water absorption thickness expansion ratio/ %	12.22
Bending strength/MPa	19.09
Elastic modulus/MPa	3185.52
Internal bond strength after 1-h boiling water/MPa	0.32

degraded when kept at high temperature for an excessively long time, and then, the board color became brown, which is a disadvantage, and will reduce the performance and service life of the board. Thus, reducing the curing temperature of the adhesive or shortening the hot pressing time becomes a necessity when using the S-NIPU resin. The density profile characteristic of the particleboard prepared in Table 1 is shown in Fig. 1.

Effect of hot press time on particleboard properties

The test results for particleboards prepared at 230 °C at different pressing times are shown in Table 2. The hot press time has clearly a great influence on the performance of the boards (Table 2). When the curing time is 8 min, the particleboard internal bond strength is only 0.38 MPa. Although this is higher than the standard requirements of 0.35 MPa, it is still the lowest IB strength result when compared with the other two boards. All the panel properties improve as the press time increases. This is mainly due to the high curing activation energy of the S-NIPU adhesive (Xi et al. 2018a, b), as it is not completely cured at short press

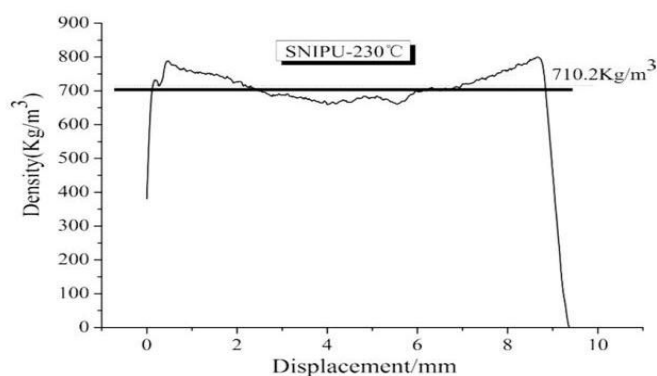
Fig. 1 Density profile of particleboard prepared at 230 °C

Table 2 Performance of particleboard prepared at different hot pressing time

Hot press time of the board	12 min	10 min	8 min
Density of the particleboard g/cm ³	0.71	0.71	0.70
Dry internal bond strength/MPa			
Maximum	1.38	0.60	0.42
Minimum	0.93	0.54	0.36
Average	1.02	0.58	0.38
2-h water absorption thickness expansion ratio/ %	7.57	14.4	22.6
24-h water absorption thickness expansion ratio/ %	12.22	23.0	30.1
Bending strength/MPa	19.09	14.35	11.65
Elastic modulus/MPa	3185.52	2219.3	2092.61

times. Consequently, this indicated that a reduction in the curing temperature of the adhesive is needed, possibly by adding a crosslinking promoter.

Differential scanning calorimetry (DSC)

To reduce the curing temperature of the S-NIPU resin, 15% of a silane coupling agent (KH560) based on the resin's solid content was used as crosslinking promoter. DSC was used to monitor the curing behavior of the S-NIPU adhesive and of the S-NIPU mixed with the crosslinker (called "S-NIPU + KH560"). The results are shown in Fig. 2. First of all, the DSC curves of both the two samples increase rapidly at the beginning of the test, this being due to the endothermic dissolution of the samples. Secondly, while the curing temperature peak of the S-NIPU is at 138.5 °C, the "NIPU+KH560" adhesive has this peak at just 126 °C, indicating that "NIPU+KH560" is more reactive and has a lower curing activation energy than S-NIPU. Thus, the silane coupling agent (KH560) can reduce the curing temperature of the S-NIPU resin to achieve more complete curing and a better bonding performance under the same pressing conditions.

Fig. 2 DSC curves of S-NIPU resin and adhesive of S-NIPU mixed with KH560

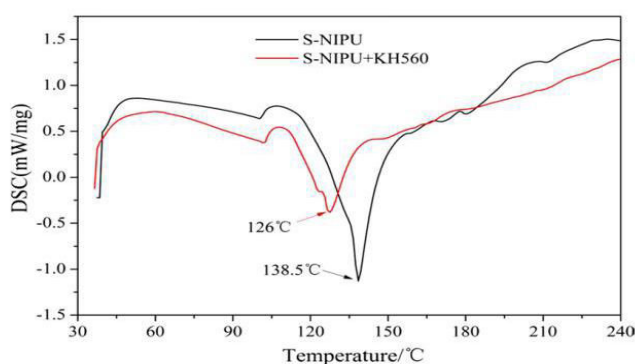


Fig. 3 TMA curing traces of S-NIPU adhesive and of S-NIPU + KH560 on wood

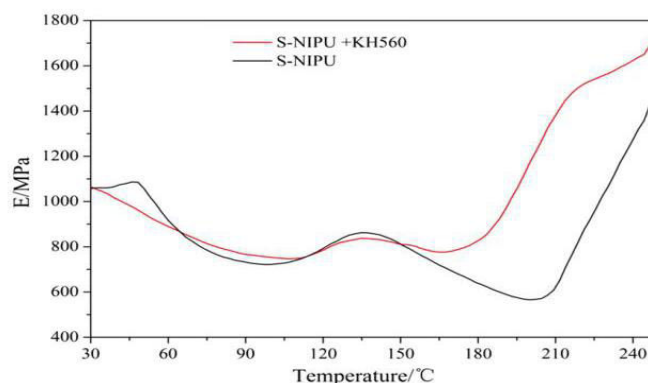


Table 3 Performance of the S-NIPU resin and the particleboard bonded with it

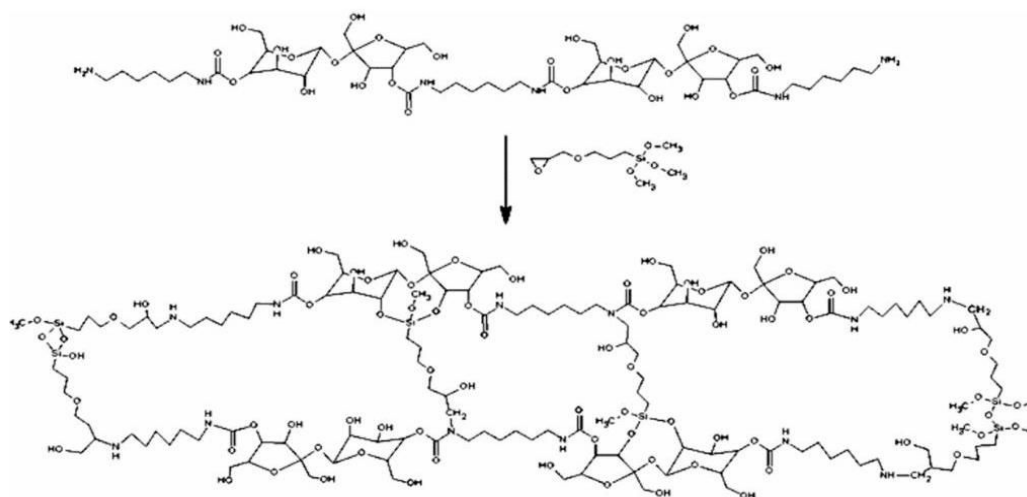
Adhesive	S-NIPU only		S-NIPU + KH560	
	180 °C	200 °C	180 °C	200 °C
Hot pressing temperature				
Density of the particleboard g/cm ³	0.68	0.70	0.71	0.70
Dry internal bond strength/MPa				
Maximum	0.29	1.01	0.48	1.53
Minimum	0.13	0.75	0.36	0.73
Average	0.23	0.87	0.44	1.06
2-h water absorption thickness expansion ratio/ %	29.52	11.08	31.6	12.99
24-h water absorption thickness expansion ratio/ %	83.15	19.95	57.5	17.73
Bending strength/MPa	5.67	15.21	7.69	19.69
Elastic modulus/MPa	884.37	2905.55	1321.79	3738.15

TMA

The thermomechanical analysis trace of S-NIPU + KH560 shown in Fig. 3 indicates that curing and crosslinking appear to start at a much lower temperature, namely at around 180 °C. Conversely, the S-NIPU resin alone appears to start curing at the much higher temperature of 205 °C. These results then lead to the same conclusion arrived at by DSC analysis. Thus, the silane coupling agent (KH560) can reduce the curing temperature of the S-NIPU resin by lowering its activation energy of curing. Furthermore, after curing, the Young's modulus of the S-NIPU + KH560 adhesive is always higher than that of the S-NIPU alone. This means that the S-NIPU + KH560 adhesive performs better than the S-NIPU resin when cured under the same conditions, which is confirmed by the particleboard results shown in Table 3.

Influences of the KH560 silane on the performance of particleboards

The results for particleboards bonded with S-NIPU and S-NIPU + KH560 at 180 °C and 200 °C are shown in Table 3. The KH560 silane clearly appears to have a positive effect on the S-NIPU resin. By comparing the performance of two boards produced at 180 °C, KH560 improved the IB strength of the particleboard from 0.23 MPa of S-NIPU alone to 0.44 MPa of the S-NIPU + KH560. The other properties such as water resistance and bending strength are also improved. The same occurred at the 200 °C press temperature, where the effect of the KH560 on S-NIPU is even more evident. It is especially notable that at 200 °C, the performance of the board bonded with S-NIPU + KH560 is even better than for the board pressed at 230 °C with S-NIPU alone. This confirms that KH560 can decrease the curing temperature of S-NIPU and improve its performance. The schematic reaction between KH560 and S-NIPU is as follows:



Epoxy functional groups react with amino groups to form C-N linkages, and this reaction easily occurs even at lower temperature as has been reported by Rozenberg (1986), Riccardi et al. (1984) and Serier et al. (1991). This is why KH560 can reduce the curing temperature of the S-NIPU resin. Furthermore, based on this reaction, the tridimensional network structure is better, enough to improve the bonding performance of the S-NIPU adhesive.

The surface color of the particleboards prepared at 180 °C and 200 °C is closer to that of wood and not dark brown as the boards prepared at 230 °C, thus without wood degradation under these hot press conditions. The results of the S-NIPU + KH560 shown in Table 3 indicate that a satisfactory particleboard can be prepared at a hot press temperature between 180 and 200 °C. The density profiles characteristic of the particleboard prepared at 180 °C and 200 °C (Table 3) is shown in Fig. 4 and shows a fairly regular shape for all of them.

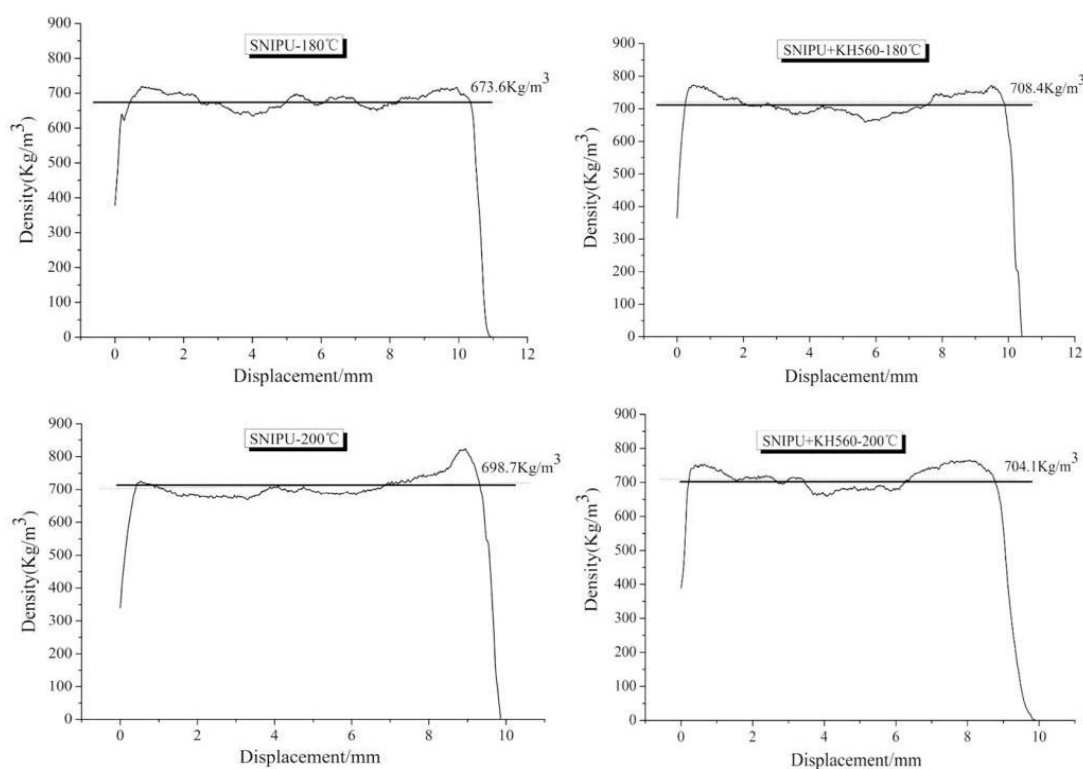


Fig. 4 Density profile of particleboards prepared at 180 °C and 200 °C

Conclusion

Sucrose as a bio-sourced material can yield a non-isocyanate polyurethanes (S-NIPU) resin that can be used to bond particleboards. The boards' testing performance confirms that the S-NIPU resin has a definite potential for application as a wood adhesive. It has excellent bonding properties, water resistance and heat resistance. The silane coupling agent (KH560) can significantly reduce the curing temperature of the S-NIPU resin, so as to achieve a more complete cure at a lower temperature. Incidentally, the IB strength of the particleboard prepared at 200 °C is as high as 1.06 MPa. This makes the S-NIPU resin an interesting possibility as a high-performance and environmentally friendly adhesive for wood panels.

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3.10 Mousses rigides de polyuréthane non isocyanate à base de glucose biomatériau

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Abstract: Des polyuréthanes non isocyanates à base de glucose (NIPU) ont été préparés par réaction de glucose avec le diméthyle carbonate et l'hexaméthylène diamine. Ceux-ci ont été utilisés pour préparer des mousses de polyuréthane partiellement biosourcées par réaction avec du NaHCO₃ en tant qu'agent gonflant et le silane comme agent de couplage. Les mousses sont moussées et durcies par application de chaleur. Les mousses présentaient une résistance au feu très limitée, ce qui indique que, comme pour les mousses synthétiques en polyuréthane, l'utilisation éventuelle d'un ignifuge semble nécessaire. L'absorption d'eau pendant 2 heures a été utilisée pour voir si des cellules fermées ou ouvertes apparaissent. La caractéristique de son comportement de stress de stress a été effectuée. Même si la compression aplatit effectivement les parois cellulaires, la structure cellulaire est maintenue et les parois cellulaires n'ont pas été détruites. Cela indique un certain niveau d'élasticité dans les parois cellulaires des formulations contenant du NaHCO₃. En effet, la macro-apparence de cette mousse confirme cette explication, car la mousse est densifiée et colle.

Mots-clés: biofoams de polyuréthane, polyuréthanes non isocyanates, NIPU, biofoams, glucose,

Glucose-Biobased Non-Isocyanate Polyurethane Rigid Foams

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Abstract: Glucose-based non-isocyanate polyurethanes (NIPU) were prepared by reaction of glucose with dimethyl carbonate and hexamethylene diamine. These were used to prepare partially biobased polyurethane foams by reaction with NaHCO_3 as a blowing agent and addition of a silane coupling agent having different functions such as coreactant and adjuvant to obtain more uniform and smaller cells. The foams were foamed and hardened by applying heat. The foams presented very limited fire resistance indicating that as for synthetic polyurethane foams the eventual use of a fire retardant appears to be necessary. The 2 hours water absorption was used to indicate if close cells or open cells occur. More characteristic is their stress strain behaviour. While compression does indeed flatten the cell walls nonetheless the cellular structure is maintained and the cell walls have not been destroyed. This indicates a certain level of elasticity in the cell walls of formulations containing NaHCO_3 . In effect the macro-appearance of this foams, confirms this explanation as the foam is densified and holds together.

Keywords: Polyurethane biofoams; non-isocyanate polyurethanes; NIPU; biofoams; glucose

1 Introduction

Polyurethanes are the ubiquitous material used for numerous applications and which are prepared by the reaction of a polyol with di-or poly-isocyanates. While several synthetic and natural polyols have been developed and used over the years to produce these important polymers, isocyanates are still the only reagents used industrially to produce them. To-day, the inherent toxicity of isocyanates during use has spawned a considerable research effort to try to develop alternative routes to the preparation of polyurethanes. The route to prepare polyurethanes without the use of isocyanates has been opened by some seminal work in the 1990's and early 2000's [1-3]. Since then, numerous research works have explored a considerable number of variations on the same theme of the original synthesis route [4-17]. The main approach of most of this research work has been aimed at the preparation of polyhydroxyurethanes by reacting compounds presenting hydroxyl groups with a cyclic carbonate and with a diamine, all these being of synthetic origin. The large majority of these works used synthesised cyclic or dicyclic carbonates and aliphatic diamines to react with other synthetic materials. To eliminate the additional step to prepare dicyclic carbonates in these synthesis, a different approach has been to use the simpler, non-cyclic dimethyl carbonate for the first step of carbonation [18,19] as it has neither irritating nor mutagenic effects [19]. Hydroxy groups are then carboxymethylated by nucleophilic substitution [19]. Only a few of these works linked carbonates and diamines with a biosourced material [3,14,15,17,20-23]. The technological barrier to the synthesis of biobased cyclic carbonates could be overcome either by the more simple route of using a non-cyclic dicarbonate [20-23] or by transforming epoxidized vegetable oils or using glycerine carbonate intermediates [17]. Biobased polyamines could also be produced from fatty diacids [17] or from aminated tannins [22,24].

More recently, non-isocyanate polyurethanes (NIPU) were prepared from hydrolysable and condensed tannins [20-22] for use as wood surface finishes [21]. These latter works were remarkable first as they used the non-cyclic dimethyl carbonate; second as partially (approximately 50%) biobased NIPU were prepared; and third as, by using an aminated tannin in the place of synthetic di- and poly-amine, reached a biobased content of more than 70% [22]. In these works, it was found that the small proportion of carbohydrates always present in commercial tannin extracts also participated to the formation of urethane linkages [20,22]. As a consequence of this finding, biosourced non-isocyanate polyurethanes (NIPU) were also prepared from carbohydrates, namely glucose and sucrose, by reacting them with the non-cyclic dimethyl carbonate and hexamethylene diamine [23]. These carbohydrate-based NIPUs, in particular the glucose-based NIPUs, were used as wood and steel surface finishes and also tested as wood adhesives, in all these cases with rather encouraging results.

One of the main uses of polyurethanes is for the manufacture of foams. As NIPUs behave differently from isocyanate containing polyurethanes it was of interest to use glucose-based NIPUs to prepare rigid foams. The main challenge to achieve this is that, differently from self-blowing isocyanate-based polyurethanes, the reactions for the formation of NIPUs are not markedly exothermic. Second, catalysts for isocyanate-based polyurethanes, which help the foaming and hardening reactions to occur, do exist and are well-known. This is not really the case now for NIPUs. Thus, NIPUs can only rely on, and need application of external heat to foam and harden.

This paper then deals with initial attempts to prepare glucose-based NIPU foams through a number of different formulation approaches and thus to study what are the limitations, characteristics and foreseeable problems for the application of biobased NIPUs to rigid foams.

2 Experimental

Synthesis of the glucose based Non-Isocyanate Polyurethane (g-NIPU)

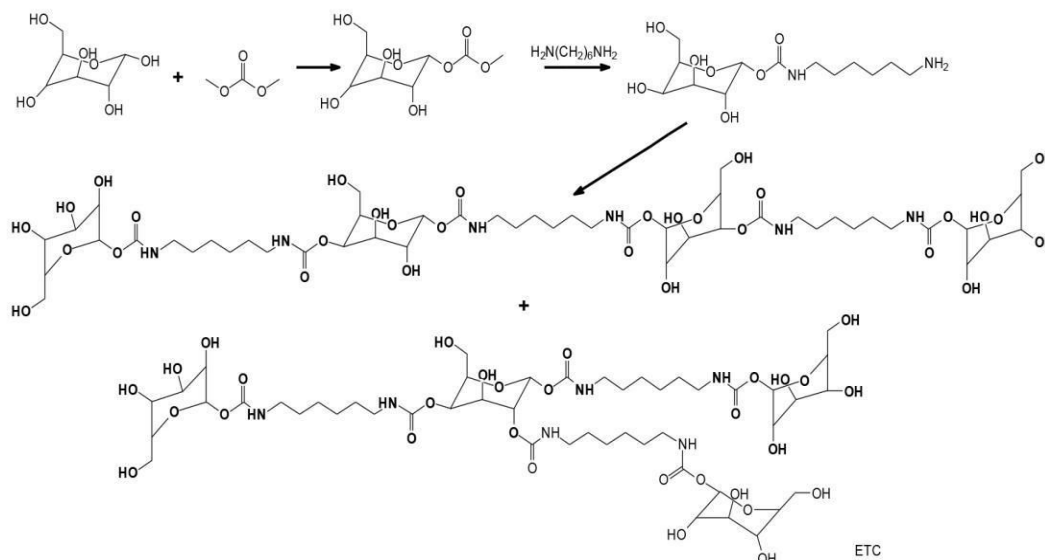
The glucose NIPUs were prepared according to a procedure already reported [23]: 160 g of glucose were mixed with 106.7 g of dimethyl carbonate and 133.36 g of water, and heated to 50°C for 40 min. Then 310.4 g hexamethylene diamine (70% solution) were added to the mixture and heated to 90°C for 30 min, then cooled to room temperature.

The reaction has been documented in reference [23] and occurs according to the following sequence of reactions: Preparation of NIPU foams: The glucose-NIPU was rotary evaporated at 60°C for 2 h, and then cooled down to room temperature ready for use. A certain amount of silane coupling agent (KH560) was mixed very well with the glucose-NIPU, and NaHCO_3 added as blowing agent, then the mixture was allowed to rest for a period of time (cf. Tab. 1). It was then placed in an oven at 200°C for 30 min foaming time. The foam was removed from the foaming beaker after 1 h and placed at ambient temperature (25°C and 12% relative humidity) for 2 days before its characterisation. When g-NIPU was mixed with the silane coupling agent (KH560), the mixture did start gelling. The silane coupling agent used as a compatibilizer it was also added as its addition has been found to lead to foams with smaller cells [25] as well as starting to slowly react already at ambient temperature with the NIPU polyurethane. The foams prepared were tested for their absorption by keeping them immersed in water at ambient temperature for two hours.

24 h Water absorption: In order to investigate the water absorption of glucose-NIPU foams and the effect of their densities on water absorption, 4 samples were tested for their 24 h water absorption.

Compression: The foams obtained were compression tested. Different addition amount of KH560 were added. Thus, "1" indicates only the glucose-NIPU alone, "2" is a foam formed by 20 g glucose-NIPU+2 g KH560, while "a" is a foam formed by 20 g NIPU+1.5 g KH560.

Ignition test:

**Table 1:** Formulations of non-isocyanate polyurethanes (NIPU) foams and their physical characteristics

No.	Foam formulations	Rest time (min)	Density (g/cm ³)	2h water absorption (%)	Fire resistance (s)
1	20 g NIPU	--	0.059	362	67
2	20 g NIPU + 2 g KH560	150	0.306	72	135
3	20 g NIPU + 1.5 g KH560 + 0.2 g NaHCO ₃	150	0.127	172	91
a	20 g NIPU + 1.5 g KH560	90	0.075	259	83
b	20 g NIPU + 1.5 g KH560 + 0.2 g NaHCO ₃	90	0.090	320	85
c	20g NIPU + 1.5g KH560 + 0.5 g NaHCO ₃	90	0.088	281	85

A foam sample of $2.5 \times 2.5 \times 2.5$ cm cut from the prepared foams is placed in a porcelain crucible preheated on a Bunsen burner and with the crucible at 600°C. Heating with the burner is maintained at the same temperature until the sample chars and does not burn anymore and the time to reach this state is measured. The test is done in duplicate for each type of foam to be tested.

3 Results and Discussion

The non-isocyanate polyurethane formulations used to prepare foams are shown in Table 1. The lack of an isocyanate in the formulation precludes, at least at this stage, the preparation of self-blowing foams. As non-isocyanate polyurethanes (NIPU) cannot use catalysts the problem is to produce expansion/foaming of the mixture while simultaneous hardening occurs. Application of heat has shown to be the answer for hardening NIPU polyurethanes, at least for their applications as adhesives and surface coatings [23]. In the case of NIPU foams the further difficulty is then to cause foaming coordinated with hardening by application of heat. While the use of a blowing agent such as pentane did yield NIPU foams, unfortunately when the mixtures were heated the much lower boiling point of pentane in relation to the temperature of curing, while yielding very rigid foams, also gave foams unacceptable due to their big, disorderly and rather uneven cells. The approach was then taken to add together sodium bicarbonate as a blowing agent with a silane coupling

agent as a compatibilizer, the combination of the two known to lead to controlled more even foaming [25]. This approach appeared to work and the different formulations tried are shown in Tab. 1.

The results in Tab. 1 show that the addition of sodium bicarbonate under the conditions of hardening used does yield open cells foams as indicated by the values of density and percentage water absorption after 2 h immersion in water. The absence of sodium bicarbonate and silane does yield a foam having rather short fire resistance, arriving at the formation of char in only 67 seconds, but of rather low density. The low density obtained is possibly consequence of evaporation of some hexamethylene diamine liberated from the urethane bond during the high temperature hardening and possibly of some lack of controlled even foaming due to the absence of both silane compatibiliser and bicarbonate foaming agent. The presence of a silane alone (formulation 2), without sodium bicarbonate, on the contrary depresses this effect yielding foams of much higher density, reflected in the lower percentage water absorption probably due to a certain percentage of close cells in the foams. However, comparing formulation b with the identical formulation 3 (Tab. 1) only different in the resting time used, yields a foam of much lower density and much higher water absorption. This indicates that (i) the resting time is an important parameter influencing the properties of these foams, and (ii) that the resting influences the percentage of open cells in the foam, this being high for formulation b.

Starting with formulation 3 (Tab. 1) the density starts to decrease and the influence of the resting time, although still present, is much less marked than for cases in which the sodium bicarbonate is absent. This is shown by comparing the difference between formulation 3 using 150 s resting time and similar formulations b and c for which only 90 s resting time was used. Equally, as the density decreases the water absorption increases. This indicates that the percentage of open cells appears to increase considerably. Figure 1 shows that water absorption levels after about 3 h water immersion appearing to be in direct relation to foam density for formulations a, b and c. However, this is not exactly true, as the only other conclusion that can be deduced is that the absorption of the formulations containing the NaHCO_3 have, as expected, slightly higher water absorptions due to the presence of the bicarbonate. The smaller size of the cells of foam “b” helps to absorb and retain water, so that the water absorption of b is higher than for other foams. The case of “20 g NIPU+1.5 g KH560 for 150 min rest time” was also tried but the results were not encouraging thus it has not been shown in Table 1, as the foam was of higher density and fire resistance than sample a and presenting a lower water absorption rendering its results very similar to those of foam 3.

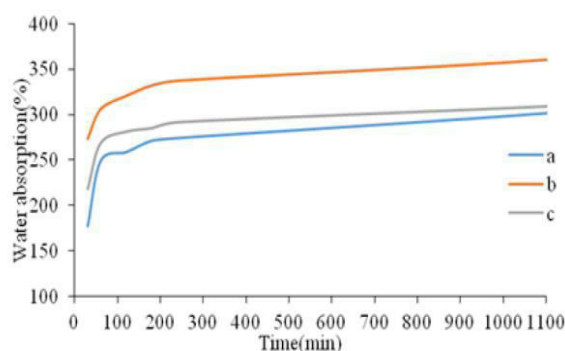


Figure 1: Water absorption curves as a function of time

The fire resistance of these foams does not appear to be very different (Tab. 1, Fig. 2). The only correlation that exists is between foam density and time taken by the foam to reach the flame-absent charred state. The higher the density the longer is the time to reach the charred terminal state. The results in Tab. 1 also clearly indicates that these foams are not fire resistants and that as for isocyanate-based polyurethane foams fire retardants would need to be added [26].

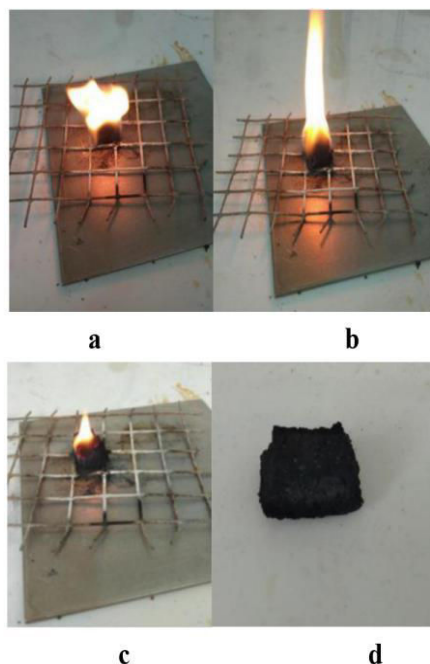


Figure 2: Ignition tests of sample 2 that formed by 20 g glucose-NIPU + 2 g KH560, (a) at ignition (b) after 90 s, (c) after 120 s, and (d) after 150 s

Fig. 3(a) reports the stress vs. strain curves in compression for foam 1, 2 and a (Tab. 1). This shows that the mechanical resistance of foam 2 is better than for the others this being exclusively due to the much higher density of this foam. Fig. 3(b) shows for foams a, b and c that their stress vs. strain curves are comparable due to the fact that their densities are very similar, again demonstrating as for other foams that compression resistance is directly proportional to foams density [27]. Last, Fig. 4 compares the stress vs strain curves in compression of two identical formulations, namely b and 3, the main difference of which is the resting time. It appears that the longer is the resting time the higher is the stress at a given strain. The reason for using silaneKH560 is as NIPU needs a higher temperature to further the reaction and cure. KH560 does easily start to react with NIPU at lower temperature (even at room temperature) to start forming a network. This is also the reason why a resting time is used, because during the resting time, KH560 can react with NIPU and start to solidify and cure. This is the reason why the foam density is higher the longer is the resting time. Lastly, the use of KH560 coupled with resting time yields foams with more uniform and smaller cells than without.

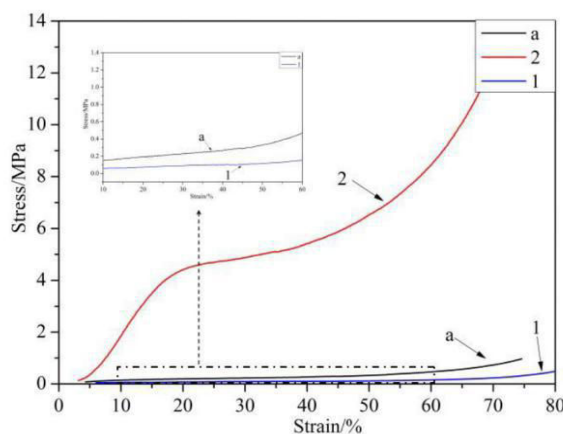


Figure 3a: Stress vs. strain curves where (1) indicates only the glucose-NIPU alone, (2) is a foam formed by 20 g glucose-NIPU+2 g KH560, while (a) is a foam formed by 20 g NIPU+1.5 g KH560

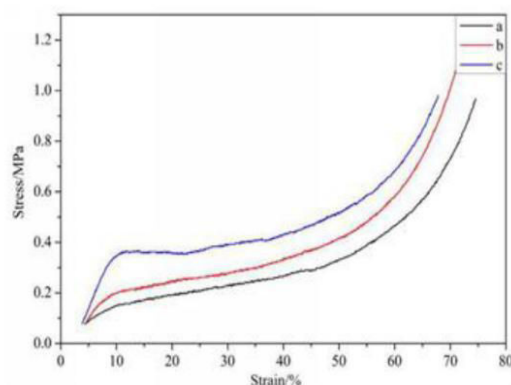


Figure 3b: Stress vs. strain curves where different amounts of NaHCO_3 were added: (a) is a 20 g NIPU + 1.5 g KH560 foam, (b) is a 20 g NIPU + 1.5 g KH560 + 0.2 g NaHCO_3 foam, and (c) is a 20 g NIPU + 1.5 g KH560 + 0.5 g NaHCO_3 foam

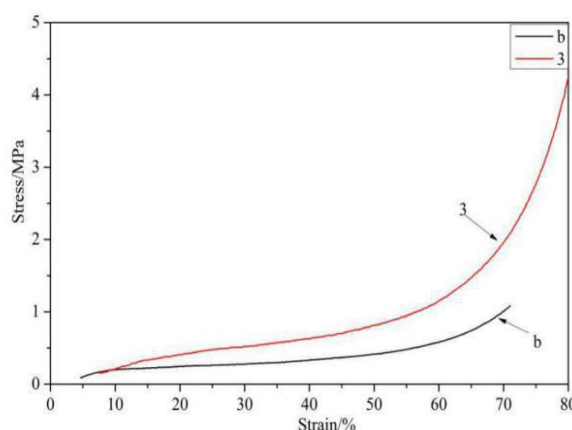
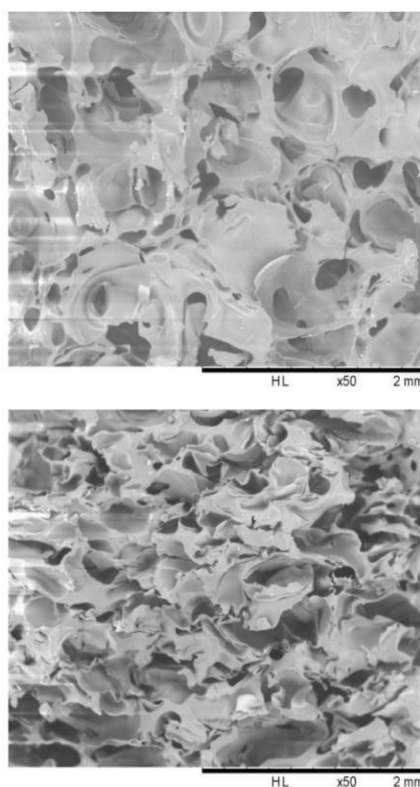


Figure 3c: Influence of the rest time to the compression performance; (b) rest time of 90 min; (3) rest time of 150 min

In particular the foams without silane KH560 are more rigid, brittle and have a cell distribution uneven and irregular. Thus, to add a small amount of a non-ionic surfactant such as a silicone coupling agent in general tends to decrease the density of the foam [25]. Furthermore, at the macroscopic level, the aspect of these foams is more homogeneous, with finer and smaller cells than foams which do not contain any surfactant. Such differences can be explained by the triple function of the surfactant: (i) to improve the compatibility of the reactants, mainly of the blowing agent with the resin and catalyst; (ii) to lower the surface tension of the system, thereby forming finer bubbles, hence smaller cells and (iii) to prevent the cell wall from becoming thin and unstable during foaming i.e., to prevent the developing foam from collapsing or rupturing [28-30]. Thus, the inclusion of a surfactant in the foam composition allows to modify the cells size independently of the density of the material, contrary to what found from previous work on other biosourced foams [31-33]. As a consequence, the capacity of thus achieving independence from the other foaming parameters greatly increases formulation possibilities and the range of materials that can be developed, hence their greater diversity of properties and applications.

Compression of the different foams in Tab. 1 yielded some information of interest. They were observed before and after by scanning electron microscopy (SEM). Figs. 4(a), 4(b) show that, after compression, foam 2 cell walls are crushed and destroyed and the cellular structure is completely lost (Fig. 4(a), right). This indicates perhaps that due to this foam higher density the cell walls are more rigid and brittle and consequently what occurs is what shown in Fig. 3(b), the cellular walls being crushed and broken. The case is different in Figs. 5(a), 5(b) for foam 3. While compression has flattened the cells

structure (Fig. 5(a), right), nonetheless the cellular structure is maintained and the cell walls have not been destroyed. This indicates a certain level of elasticity in the cell walls of formulations containing NaHCO_3 . In effect the macro-appearance of this foam in Fig. 5(b), confirms this explanation as the foam is densified and sticks together. The same is apparent from Figs. 6(a), 6(b), 6(c) for formulations a, b and c for which some of the compressed foams also do not show cellular collapse, although to different extents, but only flattening while still maintaining their cellular structure. This indicates too that while there is clearly an effect of the foam density on the residual elasticity of the cell walls there are also other effects to consider. Thus, foam c, which has a higher proportion of bicarbonate, shows much more damage after compression (Fig. 6 right) than foam b, the higher level of bicarbonate having rigidified somewhat more the cell walls. This is an indication that NaHCO_3 does not only play a role as blowing agent of the foam by liberating CO_2 , the role for which it was added, but that it does also appear that some reaction occurs between the bicarbonate and the glucose-NIPU to rigidify the cell walls. Compression of glucose-NIPU foams gives a product which behaves differently than other rigid biobased foams, such as tannin-furanic rigid foams [27], as when compressed they are not crushed but just compacted and stronger and harder than before compression. This behaviour confirms what observed by SEM, namely that there is a certain elasticity inherent to the cell walls and these do not collapse during compression. Such a behaviour is characteristic of networks cross-linked by urethane bridges in contrast to rigid foams, synthetic or biobased, cross-linked by other types of bridges [27]. Furthermore, this residual elasticity could depend from the temperature, hence the internal pressure generated during foaming, decreasing when a surfactant/coupling agent is included in the formulation [25]. Thus, the foam with the added silane is more elastic and less brittle. Conversely, inclusion of other types of surfactants/coupling agents must be evaluated for each specific case [25] as for example addition of anionic surfactants, leads to collapse and destruction of the cellular structure. Such types of additives, if needed, must anyhow be combined with non-ionic surfactants which ease the emulsion of all the components of the formulation.

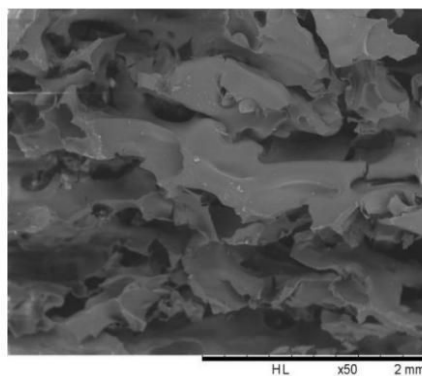
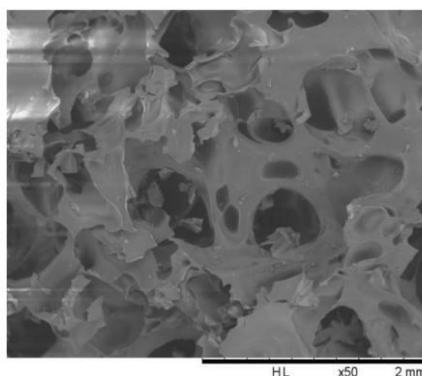


(a)



(b)

Figure 4: (a) Scanning electron microscope image of formulation 2 foam before compression (left) and after compression (right). (b) Photograph of section of foam 2 before compression (left) and after compression (right)



(a)



(b)

Figure 5: (a) Scanning electron microscope image of formulation 3 foam before compression (left) and after compression (right). (b) Photograph of section of foam 2 before compression (left) and after compression (right)

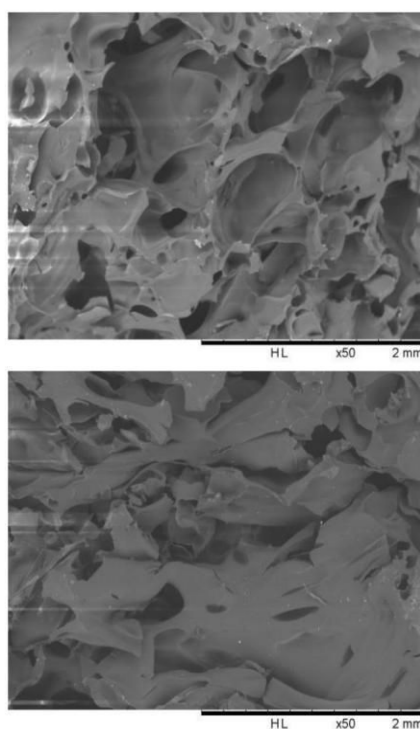


Figure 6a: Scanning electron microscope image of sample “a” before compression (left) and after compression (right)

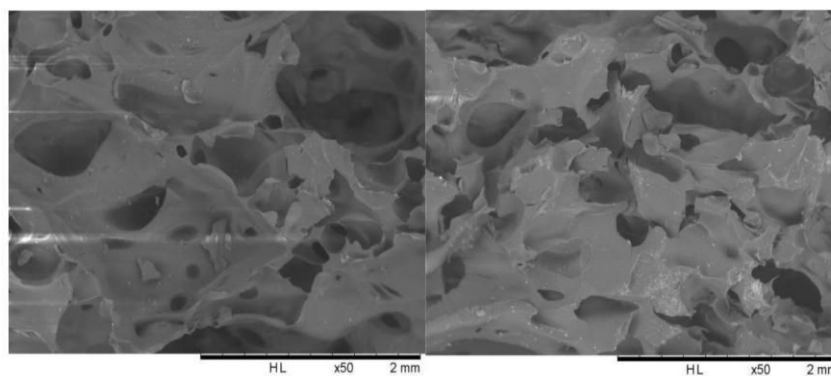
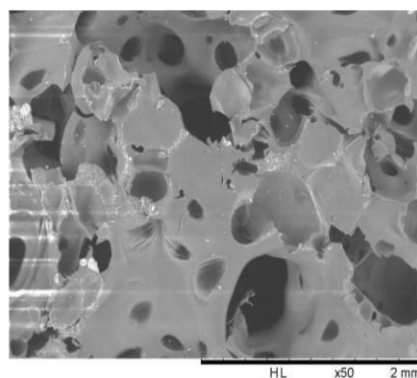


Figure 6b: Scanning electron microscope image of sample “b” before compression (left) and after compression (right)



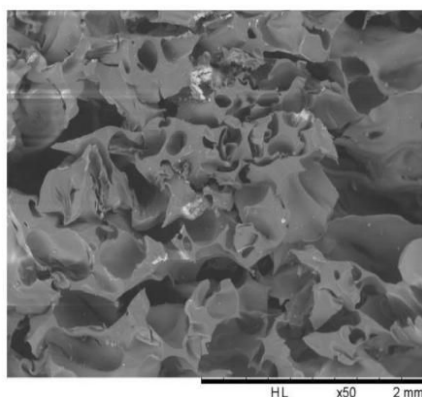


Figure 6c: Scanning electron microscope image of sample “c” before compression (left) and after compression (right)

5 Conclusions

In conclusion, glucose-based non-isocyanate polyurethanes (NIPU) have been shown to be able to be used to prepare partially biobased foams, although what presented is only an early beginning. They present two of the same characteristics of isocyanate based polyurethanes, thus (a) the flexibility of the urethane bridges cross-linked network which does constitute the foams cell walls, and (b) the limited resistance to fire that has to be addressed in the future, as for synthetic PUR, by the need to add fire retardants. The stress/strain curves and the SEM of the foams before and after compression have shown that, in the main, while the cells are flattened, the original cellular structure is not lost. This has indicated that there is a certain elasticity inherent to the cell walls and that these do not collapse during compression. This may render NIPU foams more adapt for use as a core material for sandwich composite laminates and for other broader applications.

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4. CONCLUSIONS

Les objectifs de cette étude est préparation et modification de résine de mélamine glyoxal sans formaldéhyde utilisé, et préparer des bio-adhésifs écologiques et des polyuréthanes non isocyanates(NIPU) à base de biomasse à partir de matériaux de biomasse. Réaliser leur application sur le contreplaqué et les panneaux de particules. Nous avons testé différents types d'assemblages avec additifs et avons obtenu les résultats suivants:

I -Pour les résines à base de mélamine- glyoxal

Les résines mélamine-glyoxal-glutaraldéhyde (MGG) en l'absence totale de formaldéhyde se sont révélées capables de lier du contreplaqué de qualité intérieure et extérieure dans des conditions de presse importantes sur le plan industriel lorsqu'un liquide ionique est utilisé comme durcisseur. De petites proportions de glutaraldéhyde ont amélioré la résistance à l'eau des liaisons de panneaux obtenues. Ces résines ont montré un durcissement en deux étapes en raison de la réactivité différente des deux aldéhydes utilisés. Le rôle du liquide ionique a été capital dans la performance obtenue, son rôle ne se limitant pas à une fonction de durcisseur, mais : (i) en diminuant nettement l'énergie d'activation de la trempe des résines MGG'. (ii) En favorisant une certaine condensation aldolique limitée des aldéhydes lors du durcissement des résines MGG', même sur des sites aldéhyde pré-réagis avec de la mélamine. (iii) en provoquant la déméthylation de la lignine et en rendant ainsi le substrat en bois plus susceptible d'adhérer, et (iv) en favorisant éventuellement la réaction des groupes aldéhyde de la résine avec la lignine du substrat.

Une résine mélamine-glyoxal modifiée par l'hydroxyméthylefurfural (HMFMG) peut efficacement surmonter les problèmes de performances observés avec la résine MG seule et améliorer sa résistance à l'eau. La mélamine, en tant que produit de condensation de l'urée, ainsi que l'hydroxyméthyle furfural sont deux matériaux biosourcés qui, sont associés au glyoxal non toxique, rendent l'adhésif HMFMG particulièrement écologique. Il y a deux séries de réactions entre la mélamine et l'hydroxyméthyle furfuryle observées par analyse structurale par MALDI-TOF et FTIR. Ce sont: (i) la réaction d'addition sur les groupes amino de la mélamine par le groupe aldéhyde du 5-hydroxyméthyle furfural et la condensation ultérieure

engendrée par le groupe hydroxyméthylène ainsi formé. (ii) La réaction de condensation du groupe hydroxyméthyle de l'HMF avec les groupes amino de la mélamine par élimination d'une molécule d'eau. Il a été démontré que la résine HMFMG modifiée avait une réactivité supérieure et une vitesse de réaction plus rapide pendant le durcissement que la résine MG, montrant ainsi une meilleure performance de liaison du contreplaqué que la résine MG.

II - Pour les résines à base de furannique

L'alcool furfurylique, ressource biologique renouvelable, est largement utilisé dans l'industrie de la fonderie, mais n'a pas été utilisé seul comme adhésif pour le bois. Dans cet article, l'alcool furfurylique a été mis à réagir avec du formaldéhyde, du glyoxal et du glutaraldéhyde pour préparer les résines d'alcool furfurylique-aldéhyde en tant qu'adhésifs pour panneaux de bois. La résine d'alcool furfurylique formaldéhyde (FAF) présente une bonne performance de liaison et une excellente résistance à l'eau et à l'eau chaude. Cependant, en raison de son utilisation, le formaldéhyde peut poser des problèmes d'émission de formaldéhyde. La résine d'alcool furfurylique-glyoxal (FAG) a également montré des résultats satisfaisants pour le contreplaqué : la résistance à sec, la résistance à l'état humide pendant 24 heures et la résistance à l'eau bouillie pendant 2h étaient de 1,02 MPa, 1,36 MPa et 1,46 MPa. Celles-ci sont nettement supérieures aux exigences standard ($\geq 0,7$ MPa). De plus, le glyoxal est non toxique et non volatile [31,32], de sorte que la résine FAG peut être considérée comme un adhésif plus écologique. En raison de la réactivité plus faible entre le glutaraldéhyde et l'alcool furfurylique, la résine FAG présente les performances de liaison les plus médiocres par rapport aux FAF et FAG, en particulier lorsque le système de durcisseur auto-neutralisant (1% p-TSA + 2% morpholine / acide phosphorique) est utilisé, et les propriétés mécaniques du contreplaqué collé sur celui-ci ne pouvaient pas satisfaire aux exigences standard.

III- Pour les adhésifs écologiques à base de matériaux de biomasse

L'adhésif renouvelable 'tannin-alcool furfurylique-glyoxal' pour bois est synthétisé. Des proportions définies d'alcool furfurylique et de glyoxal dans l'eau ont été pré-condensées pendant 1 heure à la température ambiante dans des conditions acides. Ce pré-polymère a été ensuite mélangé avec du tanin de mimosa à 70 ° C pendant 30 minutes. Les résultats de RMN ^{13}C et MALDI TOF ont montré qu'il y a

une réaction entre l'alcool furfurylique et le glyoxal. De plus, les groupes hydroxyméthyle $-CH-OH-R-$ générés par cette réaction semblaient être les groupes réactifs conduisant à la réticulation de l'adhésif TFG. La résistance au cisaillement à l'état humide du contreplaqué TFG s'est améliorée par rapport à celle du contreplaqué TF, bien que la résistance au cisaillement à l'état humide obtenue avec l'adhésif TFG soit inférieure à celle avec l'adhésif à bois TFF. Afin de préparer un adhésif à base de tanin présentant une bonne résistance à l'eau, un EPR à 12% a été mélangé à un adhésif à base de TFG, ce qui a permis d'obtenir une bonne résistance à l'eau du contreplaqué. De plus, la valeur de MOE du contreplaqué préparé avec 12% d'adhésif EPR + TFG était supérieure à celle du contreplaqué préparé avec des adhésifs TF et PF.

Le traitement du glucose avec du periodate de sodium donne un certain nombre d'aldéhydes non volatils de poids moléculaire faible et supérieur obtenus à partir du clivage du glucose par le periodate. Ces aldéhydes sont obtenus soit par clivage direct au glucose, soit par clivage + recombinaison selon quelques mécanismes différents. La réaction de ces divers aldéhydes ainsi générés avec l'extrait de tanin conduit à une réticulation et à un durcissement du tanin. La combinaison extrait de tanin + glucose + periodate s'est révélée utile pour le collage de panneaux de contreplaqué.

Le glutaraldéhyde utilisé pour modifier la résine à base de protéines de blé appelé GP et montre des bonnes performances par rapport à la résine non modifiée (P). La résistance au cisaillement à sec des adhésifs à base de protéines modifiés au glutaraldéhyde (GP) a augmenté de 50%, la résistance à l'eau froide augmentant de plus de 100% en 24h pour atteindre 0,91 MPa. L'effet de la Polyéthylène imine(PEI) en tant qu'agent de réticulation est évident, ce qui peut grandement améliorer les propriétés de liaison de l'adhésif GP. Cela est dû à la modification du glutaraldéhyde pour faire augmenter les groupes réactifs tels que $-COOH$ et $-OH$, et pour que ces groupes fonctionnels réagissent avec le groupe amine dans le PEI, améliorant ainsi les performances de liaison. L'analyse TMA a montré que la résine de protéines modifiée au glutaraldéhyde avait un module d'élasticité supérieur à celui de la résine non modifiée. Le module d'élasticité de l'adhésif a augmenté en plus après l'ajout de l'agent de réticulation PEI, ce qui a confirmé la résistance au cisaillement des résultats des tests de contreplaqué. SEM peut observer que l'adhésif GP modifié semble avoir

une meilleure ténacité que non modifié, mais cela ne suffit pas. Lorsque du PEI est ajouté, la ténacité de l'adhésif est améliorée, et il n'y a pas de fissure à la surface de l'adhésif durci GPPEI.

La protéine de soja en tant que matière de biomasse servant à préparer des adhésifs pour bois écologiques est un sujet brûlant, mais la plupart des travaux de recherche reposent sur des isolats obtenus après hydrolyse acide ou alcaline de celle-ci, en ajoutant un agent de réticulation ou des modificateurs pour améliorer les performances de collage. Les adhésifs à base de résine SPIPA présentant une structure amide obtenue en faisant réagir de l'IPS avec de l'anhydride maléique et de l'hexaméthylènediamine ont été préparés avec succès dans ce travail. Les analyses ATR FT-MIR et MALDI-ToF ont également confirmé la survenue de leurs réactions. Cette SPIPA présentait à la fois une bonne performance de liaison et une bonne résistance à l'eau bien supérieure aux exigences standard pertinentes du GB / T 9846-2015 ($\geq 0,7$ MPa), tandis qu'une température de durcissement plus élevée était nécessaire, comme le prouvent les résultats des tests TMA. Les agents de réticulation utilisés peuvent augmenter la force de liaison à sec de SPIPA, tandis que le silane KH560 réduit sa résistance à l'eau. Seul SPIPA-MA avec l'agent de réticulation l'anhydride maléique présentait une résistance satisfaisante à l'eau froide et à l'eau bouillante, ce qui est amélioré par rapport à SPIPA. Ces résines peuvent ensuite être potentiellement utilisées en tant qu'adhésifs de bois à base de protéines de soja appropriés.

IV- Pour les résines des non-isocyanates polyuréthanes(NIPU) à base matériaux de biomasse

Les mono- et les disaccharides peuvent être utilisé pour synthétisé des non isocyanates polyuréthanes (NIPU), avec un potentiel certain pour une application en tant que revêtements thermodurcissables à la fois pour le bois et l'acier et aussi comme adhésifs thermodurcissables pour bois. Les mono- et les disaccharides constituent un réservoir considérable de matière biosourcée d'un coût raisonnable et facilement disponible partout dans le monde, ce qui rend leur utilisation pour de telles applications une alternative industrielle intéressante.

Le saccharose en tant que matériau biosourcé peut donner une résine polyuréthanes non isocyanate (S-NIPU) utilisable pour élaborer des panneaux de

particules. Les performances mécaniques confirment que la résine S-NIPU a un potentiel certain pour une application en tant qu'adhésif pour bois. Elle possède d'excellentes propriétés de liaison, de résistance à l'eau et de résistance à la chaleur. L'agent de couplage au silane (KH560) peut réduire considérablement la température de durcissement de la résine S-NIPU, de manière à obtenir un durcissement plus complet à une température inférieure. De cette manière, la force IB du panneau de particules préparé à 200 ° C peut atteindre 1,06 MPa. Cela fait de la résine S-NIPU une possibilité intéressante en tant qu'adhésif de haute performance et respectueux de l'environnement pour les panneaux en bois.

Il a été démontré que les polyuréthanes non isocyanates à base de glucose (NIPU) pouvaient être utilisés pour préparer des mousses partiellement biosourcées, bien que ce qui est présenté n'est qu'un début. Ils présentent deux caractéristiques identiques à celles des polyuréthanes à base d'isocyanate : a) la flexibilité du réseau réticulé des ponts d'uréthane qui constitue la paroi cellulaire de la mousse, et b) la résistance limitée au feu à prendre en compte, pour les PURS synthétiques, par la nécessité d'ajouter des retardateurs de feu. Les courbes contrainte / déformation et le SEM des mousses avant et après compression ont montré que, dans l'ensemble, lorsque les cellules sont aplaties, la structure cellulaire initiale n'est pas perdue. Ceci a indiqué qu'il existe une certaine élasticité inhérente aux parois des cellules et que celles-ci ne s'effondrent pas pendant la compression.