南京林業大學 Nanjing Forestry University

Nancy-Université Université Henri Poincaré

enstib

lermab

NANJING FORESTRY UNIVERSITY

Discipline : Wood science

THESIS in cosupervision China - France

To obtain the degree of

DOCTOR of the UNIVERSITY HENRI POINCARE – NANCY 1

Presented and defended publicly in 2009 by

UNIVERSITÉ HENRI POINCARÉ – NANCY 1

Ecole Nationale Supérieure des Technologies et Industries du Bois

Laboratoire d'Études et de Recherche sur le Matériau Bois – L'équipe d'accueil UHP

École Doctorale RP2E

Discipline : Sciences du bois

THÈSE en co-tutelle France - Chine

pour obtenir le grade de

DOCTEUR de l'UNIVERSITÉ HENRI POINCARÉ – NANCY 1

et soutenue publiquement en 2009 par

Hong LEI

Title / Titre

Synthetic and Natural Materials for Wood Adhesive Resins

Résines à base de Matériaux Naturels et Synthétiques Destinées aux Adhésifs pour le Bois

***Thesis supervisors* / Directeurs de thèse**

***Pr Antonio PIZZI** : Professeur, Université Henri Poincaré – Nancy 1 – ENSTIB,France*

***Pr Guanben DU** : Professor, Université Nanjing Foresty- Nanjing, Chine*

Président / President :

Rapporteurs / Reporters :	M. Delmas	Professeur ENSIACET, Toulouse
	B. Charrier	MdC IUT Mont de Marsan, Université de Pau et du Pays de l'Adour
Examinateurs / Inspectors :	P. Triboulot	Professeur ENSTIB, Université Henri Poincaré
	G. Du	Professor Southwest Forestry College, Kunming
	A. Pizzi	Professeur ENSTIB, Université Henri Poincaré

ACKNOWLEDGEMENT

On the occasion of the completion of the thesis, please allow me to convey my appreciation firstly to my supervisors Prof. Antonio PIZZI and Prof. Guanben DU. Every detail of this thesis, such as the writing, experiment and so on, is bound up with their patient supervisition. I am grateful for their care and help not only in my study but also on my work and life in the period of application for a Ph.D degree. It is under their encouragement and support that I have overcome the difficulty ecountered and rapidly accommodate to the working environment abroad. I have learnt a lot from their active minds, serious work attitude, diligent work style and generous heart. From them, I have learned what is required to be an excellent researcher. Please accept my heartiest thanks and best wishes to you two.

Thank Prof. Dingguo ZHOU of Wood Industry College, Nanjing Forestry University and Prof. Pascal TRIBOULOT of ENSTIB, Nancy 1 University for their support to my study.

Thank Madam Marie-Laure ANTOINE of ENSTIB, Nancy Université for her help on instrument operation on Thermomechanical Analysis and Fourier Transform Infrared Spectroscopy. Thanks to Prof. Alain CEZARLD for the help on Wide Angle X-ray Analysis. He gave me some important advice on the influence of nanoclay on urea-formaldehyde resin.

Thank Dr. Gianluca TONDI, Dr. Hamid MANSOURI, Dr. Pantea OMRANI, Dr. Aurelien DESPRES, Dr. Ludovic RESCH, Mrs Gisele AMARAL-LABAT. I will never forget the help they have given to me. And I appreciate our friendship.

Thank Mr. Haisheng YU for the understanding and support. His selfishless dedication and encouragement help me to the end of the thesis.

Thanks to my parents!

Thanks to all of the teachers, classmates, and friends who have given me some help!

SUMMARY

There are two main cases natural material to be used as wood adhesives: in one case, a natural material is used as the main components of wood adhesives on the basis of adhesion capability of the natural material or similarity of structure characteristic between natural material and synthetic ones. In another case, a natural material is used for the modification of wood adhesives, that is to say, to be as an auxiliary of the wood adhesive.

Therefore, some work has been done on natural material from the two cases. Natural adhesives used in this work include tannin, lignin, and soy-based adhesives, which can be used as the main components to bond wood after being modified or cross-linked. A mineral material such as montmorillonite, which has been widely-used in nano-composites, is used, too. It is possible to improve the performance of commonly-used wood adhesives, such as urea-formaldehdye and phenol-formaldehyde resins by adding it.

Environment-friendly tannin/lignin and soy protein-based wood adhesive were studied. The feasibility and mechanism to use non-toxic, non-volatile glyoxal to substitute toxic, volatile formaldehyde in relevant formulations was analyzed. The suitable addition percentage was determined. The lab-prepared particleboard procedure was optimized too. The main objectives on natural wood adhesive then are to completely eliminate formaldehyde from the adhesive and to increase the proportion of natural, envinronmentally friendly materials in these adhesive formulations.

The results shown in this work confirmed few aspects of these formulations, namely:

(1) The performance of these formulations is determined to a great degree by the amount or proportion of the pMDI used. Although the addition of the very reactive tannin allowed a marked decrease in the proportion of pMDI in the lignin-based adhesive, it does not appear that pMDI could be eliminated completely. The strength of glyoxalated soy resin by itself is weak. CP-MAS ^{13}C-NMR results showed that the reaction between glyoxal and soy protein

occurred indeed. But the hydroxy groups that resulted couldn't condense to a cross-linked structure. Therefore, pMDI is a necessary cross-linker to glyoxalated soy protein adhesive. Its addition amount determines the performance of the final resin.

(2) Lignin-based adhesives and glyoxalated soy-based wood adhesives mixed with pMDI and mimosa tannin satisfying the requirements of relevant international standards for the manufacture of wood particleboard were obtained. These lignin-based or soy-based wood adhesives did not use any formaldehyde in their formulation, this having been substituted by a non-volatile non-toxic aldehyde, namely glyoxal. In these formulations, 70%-80% the total resin solid was natural material. Lignin-based adhesive with weight ratio glyoxalated lignin:pMDI:tannin=75:25:20 gave a better result. While for soy-based adhesive, the best formulation of all the ones tried was the glyoxalated soy/tannin/pMDI 54/16/30 by weight. This resin can be used in a much lower proportion on wood chips and can afford pressing times fast enough to be significant under industrial panel pressing conditions.

(3) The IB strength results of boards bonded with the heat-treated (under pressure, for further depolymerization) lignin(GLAF) are worse than when using the original lignin itself; this result was confirmed by both FTIR and TMA. Thus, the heat treatment under pressure that is so beneficial when applied to reduce the degree of polymerization of high-molecular-weight kraft lignins does not appear to work when applied to already low-molecular-mass lignins.

(4) The particleboard strength with formulations based on glyoxalated soy was better than that with glyoxalated lignin. When both of them were used in the same formulation, to increase the proportion of glyoxalated soy was helpful to the improvement of panel performance. The results of CP-MAS ^{13}C-NMR proved that the reaction between lignin and glyoxal occured.

Some work has been done on the study of the influence of nano-montmorillonite (MMT) on urea-formaldehyde resin and phenolic resin adhesives to see if this could also be extended to resins. The level of exfoliation of the MMT being mixed with these resins was determined by X-ray powder analysis. The thermal and mechanical characteristics of the mixed system were studied. The main objective of studying the influence of MMT on wood adhesive is to estimate

the feasibility of using MMT as fillers in wood adhesive, to study the modification mechanism of MMT on the wood adhesive, and to optimize the modification procedure. Some conclusions can be drawn.

(1) X-ray diffraction (XRD) characterization indicates that Na montmorillonite (Na-MMT) is completely exfoliated when mixed with UF resins, while it only has some degree of intercalation when added to PF and PUF resins. It means that it is difficult for resole-type phenolic resins with three-dimensional structure to be effectively mixed with nano clay at molecular level.
(2) The addition of Na-MMT could accelerate the curing of UF resin and was helpful to the formation of regular cross-linked structures. Na-MMT has the same accelerating effect on PF and PUF resins, too.
(3) The results of the thermomechanical analysis (TMA) showed that the modulus of elastic, MOE, of a UF resin/Na-MMT system without hardener increased with the increasing the addition of Na-MMT up to 4% on solid resin load. However, for the UF system with hardener, Na-MMT had no obvious effects on the final dry strength performance of the resins.
(4) The addition of small percentages of Na-MMT does not appear to improve much the resins dry performance, while it seems to increase the water resistance of the UF-bonded and phenolic-bond panels. Na-MMT could decrease the formaldehyde emission of particleboard, too. Both dry strength and wet strength performance with Na-MMT as fillers were better than those with wheat flour. The modification mechanisms for Na-MMT and wheat flour on UF resins are probably different.
(5) When organic montmorillonite (O-MMT) with larger interlayer distance is used by adding proportions of up to 5% on PF resin solids, an improvement in both dry and after boiling tensile strength could be noticed. MMT with a limit increase of interlayer distance had effects on PF and PUF.

Key words: Natural material, tannin, lignin, soy protein-based adhesive, MMT

RESUME

On dénombre deux sortes principales de matériaux naturels utilisés comme colles à bois : d'un côté le matériau naturel constitue le composant principal de la colle et le mécanisme est fondé sur le pouvoir d'adhésion sur un matériau naturel ou sur l'affinité entre matériaux naturels et synthétiques. De l'autre, le matériau naturel est à l'origine d'une modification de la colle, en d'autres termes, il constitue un composant auxiliaire à cette colle.

Des travaux de recherche recouvrant les deux cas précédemment cités ont d'ores et déjà été réalisés. Les colles naturelles utilisées comprennent tanins, lignine et soja, éléments principaux entrant dans la constitution après avoir été modifiés ou réticulés. Un minéral naturel, la montmorillonite, abondamment utilisé dans le domaine des nano-composites, a également été utilisé. Il est ainsi possible d'améliorer les performances des colles à bois couramment employées telles les colles urée-formaldéhydes ou phénol-formaldéhyde.

Des résines « vertes » à base de lignine, tanins et protéines de soja ont été étudiées. La faisabilité et le mécanisme de l'utilisation du glyoxal à différents taux (non toxique et non volatile) en substitution de la formaldéhyde (toxique et volatile) ont été analysés. Une optimisation dans la préparation des panneaux de particules conçus en laboratoire à été réalisée. Les objectifs principaux pour les colles naturelles à bois sont l'élimination totale de la formaldéhyde et l'augmentation de la proportion de matériaux naturels et non nocifs dans les formulations.

Les résultats issus de ces travaux confirment les quelques aspects suivants concernant ces formulations :

(1) La performance de celles-ci a été déterminée en majeure partie en fonction de la proportion de pMDI ajoutée. Bien que l'ajout de tanins réactifs aient permis une diminution notables de pMDI dans les colles à base de lignine, il apparaît que la pMDI ne peut en aucun cas être

totalement proscrite. La réticulation de la résine de soja elle-même est relativement faible. Les résultats des études par CP-MAS et ^{13}C-NMR ont montré que des réactions existent entre le glyoxal et les protéines de soja. Mais les groupes hydroxyles qui en résultent n'ont pas pu réticuler. La pMDI est donc un réticulant nécessaire pour les colles à base de protéines de soja. Le taux d'addition de celle-ci a des répercussions sur la performance de la résine finale.

(2) Des colles à base de lignine et à base de soja glyoxalé mélangé à la pMDI et au tanin de mimosa satisfaisantes les exigences données par les normes internationales pour la fabrication des panneaux de particules ont été obtenues. Aucune formaldéhyde n'a été utilisée dans les formulation. Elle a été substituée par une aldéhyde non toxique et non volatile : le glyoxal. Dans ces formulations, de 70 à 80% de la résine définitive sont des constituants naturels. Les colles à base de lignine avec un ratio lignine : pMDI : tanin de 75 :25 :20 ont montrées les meilleures performances. Pour les colles à base de protéine de soja, les résultats les plus concluants ont été obtenus pour un ratio soja : tanin : pMDI de 54 :16 :30.

(3) La cohésion au sein des panneaux de particules avec la lignine ayant subi un traitement thermique (compression puis dépolymérisation) est inférieure à celle des panneaux avec de la lignine classique. Ces résultats ont été obtenus par FTIR et TMA. Le traitement thermique nécessaire à l'abaissement du degré de polymérisation des lignines Kraft de hauts poids moléculaires n'est pas utile pour des lignines Kraft de plus faibles poids moléculaires.

(4) La cohésion des panneaux à partir de colle de soja glyoxalé est meilleure que celle des panneaux avec des colles à base de lignine glyoxalée. En cas d'utilisation simultanée des deux, il est nécessaire d'augmenter la proportion de soja glyoxalé pour obtenir de meilleures performances. Les résultats obtenus par CP-MAS et ^{13}C-NMR prouvent l'existence de réactions entre lignine et glyoxal.

Des études ont été effectuées sur l'influence de la nano-montimorillonite (MMT) sur des résines à base d'urée et de phénol-formaldéhyde. Le taux d'exfoliation de la MMT mélangée avec ces résines était déterminé par analyse aux rayons X de poudre. Des études thermiques et mécaniques de ces systèmes ont été réalisées. L'objectif principal de l'étude de l'influence de la MMT dans les colles à bois est d'étudier le mécanisme de modification qui apparait afin d'optimiser le procédé. Les conclusions obtenues sont les suivantes :

(1) L'étude par diffraction de rayon X a montré que la Na-MMT est intégralement exfoliée quand elle est mélangée avec des résines UF, alors qu'elle n'a que quelques degrés d'intercalation lorsqu'elle est ajoutée à des résines PF ou PUF. Il est donc difficile d'obtenir un bon mélange avec des résines phénoliques à structure tridimensionnelle.

(2) L'ajout de Na-MMT accélère la solidification de la résine UF et aide à la formation de la structure régulièrement réticulée. Les mêmes effets ont été observés sur des résines PF et PUF.

(3) Les résultats des analyses thermo-mécaniques (TMA) montrent que le module d'élasticité d'une résine UF/Na-MMT sans durcisseur augmente en fonction de l'ajout de Na-MMT au-delà de 4% en masse de résine solide. Cependant, pour les résines UF avec durcisseur, Na-MMT n'a aucun effet sur les performances finales de celles-ci.

(4) L'ajout d'un faible pourcentage de Na-MMT ne semble pas modifier significativement la performance des résines sèches mais la résistance à l'eau des panneaux contenant des résines UF ou phénolique s'est vue augmenter. La présence de Na-MMT permet également de diminuer les émissions de formaldéhyde. Les panneaux contenant du Na-MMT (contraintes sèche et humide) sont meilleurs que ceux avec de la farine de blé. La modification des mécanismes pour Na-MMT et la farine sur les résines UF sont probablement différentes.

(5) Une utilisation de MMT organique avec de grandes distances entre les couches à plus de 5% en masse en résine PF entraîne une augmentation des contraintes sèche et humide. La MMT avec de faibles distances entre les couches a des effets sur la PF et la PUF.

Mots clés : matériau naturel, tanin, lignine, colle à base de protéine de soja, MMT.

LISTE OF PAPERS IN THE PERIOD OF APPLICATION OF Ph.D DEGREE

1. **Hong Lei**, A. Pizzi, A. Despres, H. Pasch, Guanben Du. Esters acceleration mechanisms in phenol-formaldehyde resin adhesives. Journal of Applied Polymer Science. 2006,100:3075-3093.

2. **Hong Lei**, A. Pizzi, Guanben Du, *et al.* Variation of MUF and PMUF resins mass fractions during preparation. Journal of Applied Polymer. 2006,100:4842-4855.

3. **Hong Lei**, A. Pizzi, Guanben Du. Coreacting PMUF/ Isocyanate resins for wood panel adhesives. Holz als Roh-und Werkstoff. 2006,64:117-120.

4. **Hong Lei**, A. Pizzi, Guanben Du. Environmentally friendly mixed tannin/lignin wood resins. Journal of Applied Polymer Science. 2008, 107:203-209.

5. **Hong Lei**, Guanben Du, A. Pizzi, Alain Celzard. Influence of nanoclay on urea-formaldehyde resins for wood adhesives and its model. Journal of Applied Polymer Science. 2008, 109:2442-2451.

6. Guanben Du, **Hong Lei**, A. Pizzi, H. Pasch. Synthesis-structure-performance relationship of cocondensed phenol-urea-formaldehyde resins by MALDI-ToF and ^{13}C-NMR. Journal of Applied Polymer Science. 2008, 110:1182-1194.

7. **Hong Lei**, Guanben Du, A. Pizzi. Review of tannin-based wood adhesive. China Forest Products Industry (China). 2008(06):15-19.

8. **Hong Lei**, Guanben Du, A. Pizzi, *et al*. Comparative structure development of phenol-urea-formaldehdye resin. Chemistry and Industry of Forest Products (China). 2009,29(2):73-78.

9. Guanben Du, **Hong Lei**, A. Pizzi. Influence of urea addition on phenol-urea-formaldehyde resin. Journal of Beijing Forestry University. 2009,31(2):121-127.

10. Guanben Du, **Hong Lei**, A. Pizzi, *et al*. Structure progressing of phenol-urea-formaldehyde resin under alkaline condition. Chemistry and Industry of Forest Products (China). 2009.

11. Guanben Du, **Hong Lei**, A. Pizzi. Study on curing reaction of urea-formaldehyde resin by thermal mechanical analysis. Journal of Beijing Forestry University. Accepted.

12. **Hong Lei**, A. Pizzi, Guanben Du. Environment-friendly gluten-based mixed resins for particleboard. Journal of Applied Polymer Science. Submitted.

TABLE OF CONTENTS

CHAPTER I

LITERATURE SURVEY AND MAIN OBJECTIVES

I.1. INTRODUCTION

Wood adhesive play an important role in the wood panels industry. The performance of final panels depends on that of adhesive in a great degree. The development of wood adhesives could be divided into two stages. For the first stage the predominant adhesive is based on the natural or green polymer. The commonly-used natural adhesives include gums adhesives, protein adhesives, resin adhesives, etc. The main characteristics of this kind of wood adhesives are environment-friendly and ease of handling. But most of these adhesives have no enough strength and no water resistance. At the second stage, natural adhesives have been replaced by synthetic thermosetting resins for wood panels, such as urea-formaldehyde (UF) resins, phenol-formaldehyde (PF) resins, melamine-formaldehyde (MF) resins, whose performances, especially the strength and water resistance, are usually better. Panels of higher quality can be prepared with synthetic resins as adhesives. However, the development of synthetic resins is restricted by the non-renewability and toxicity of the materials being based on petroleum products. Lately, there has been a considerable industrial interest in the development of natural, or green, wood adhesives to substitute synthetic thermosetting resins as adhesives for wood panels because of an undue increase in the cost of petroleum and the mounting environmental pressure worldwide. A number of different approaches have been investigated, namely, the use of soy protein adhesives, the upgrading of vegetable tannin adhesives to formulations without aldehydes or even without hardeners and lignin-based wood adhesives.

Some natural materials can be modified or cross-linked with other materials to be used as adhesives, such as condensed tannins, proteins, and so on. There are also some other natural materials, which can be used as extenders or fillers of the adhesives to improve in the performance.

I.2. TANNIN-BASED WOOD ADHESIVES

Tannins are natural compounds that have been employed since antiquity for the conversion into leather of hides and skins. Their phenolic nature makes them to be used as adhesives and

substitute part or all of the phenol used in adhesives.

There are two main classes of natural tannins which can be used for adhesives: hydrolizable tannins and condensed polyflavonoid tannins. The former, including chestnut, myrabolans and dividivi extracts, are mixtures of simple phenols, such as pyrogallol and ellagic acid, and of esters of a sugar, mainly glucose, with gallic and digallic acids.

Condensed polyflovonoid tannins, instead, constitute more than 90% of the total world production of commercial tannins and they can be used in wood adhesives. Condensed tannins are known for their wide distribution in nature and particularly for their substantial concentration in the wood and bark of trees. These include various species of Acacia (watter or mimosa bark extract; cube gambier extract from Acacia catechu, etc.), Quebracho (quebracho wood-extract), Helmlock (Tsuga heterophylla from North America), Sumach (rush species from Mediterranean countries) and mangrove extracts, from which commercial tannin extracts for leather manufacture are or have been commercially prepared. The production of tannins for leather manufacture reached its peak immediately after World War II and has since progressively declined. Thus, this progressive decline of their traditional market coupled with the increased price and decreased availability of synthetic phenolic materials due to the first oil crisis in the early 1970's stimulated fundamental and applied research on the use of such tannins as a source of pre-condensed phenolics for wood adhesives.

Successful commercialization of tannin adhesives was first introduced in South Africa in the early 1970's. Today synthetic phenolic adhesives for particleboard and plywood are not used anymore in the country and only mimosa tannin adhesives are used for exterior and marine applications.

I.2.1. Tannin structure and composition[1-3]

Condensed tannin consists of flavonoid units which have undergone various degrees of condensation. Typical flavonoid units or monoflavonoids are those of black wattle bark extract

(Acacia mearnsii):

The main polyphenolic pattern is represented by flavonoid analogs based on resorcinol A-rings and pyrogallol B-rings (I) and constitutes the 70% of the tannins. 25% of the total bark tannin fraction consists of resorcinol A-rings and catechol B-rings (II) and the remaining 5% is a mixture of phloroglucinol-pyrogallol (III) and phloroglucinol-catechol (IV) flavonoids.

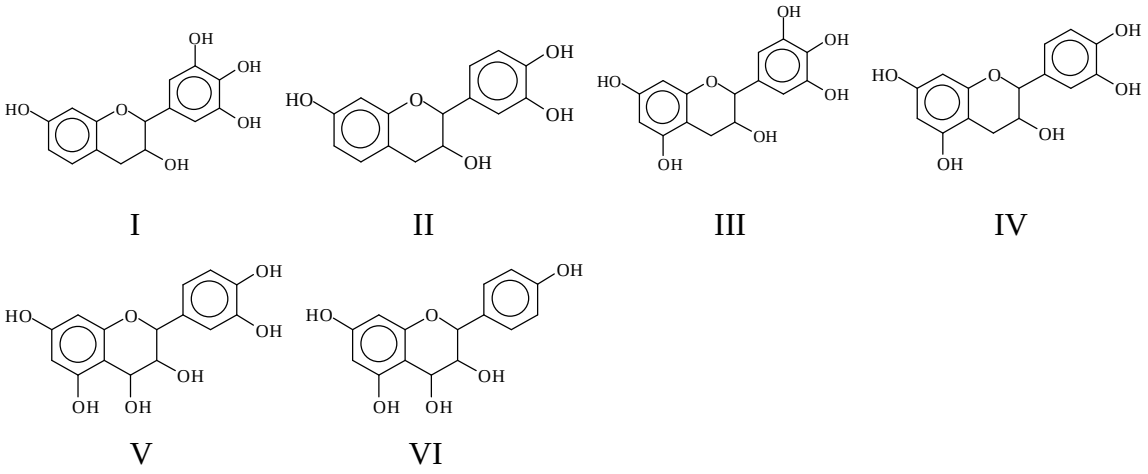


Figure I.1. Main flavonoid units of condensed tannin

These four patterns constitute 65% to 80% of mimosa bark extract. The remaining parts are the "nontannins" which are simple carbohydrates, hydrocolloid gums and nitrogen compounds (amino and imino acids). The most important of these are the gums which contribute significantly to the viscosity of the extract in spite of their low concentration (3 to 6%). Composition similar to that of mimosa bark extract described above, though slightly different and less surely determined, is found in the quebracho wood extract.

Most of the main pine species present only two patterns. The main pattern is represented by phloroglucinol A rings and catechol B rings structures (V). The other pattern, present in much lower proportion, is represented by phloroglucinol A rings and phenol B rings (VI).

Flavonoid units can be bound through 4,6- and/or 4,8- linkages to form polyflavonoids. The average tannin unit of wattle extract consists of four to five flavonoid units joined together mainly through 4,6-linkages and exhibit an average mass number of 1250. The average mass

number of quebracho tannin is 1784 and that of pine is about 4300. Pine tannin is phloroglucinolic in nature and the flavonoid units are joined together through 4,8-interflavonoid linkages. The presence of only 4,6-(V) or 4,8-linkages (VI) result in linear polymeric tannins. However, the simultaneous occurrence of 4,6- and 4,8- linkages is also possible where both resorcinolic and phloroglucinolic A-rings occur, thus resulting in angular rather than linear polymeric tannins (VII). Comparing mimosa and quebracho tannins by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-ToF), it appears that mimosa tannin is heavily branched due to the presence of considerable proportions of angular units in its structure while quebracho tannin is almost completely linear. These structural differences also contribute to the considerable differences in viscosity of water solutions of the two tannins[4].

I.2.2. Tannin reaction with aldehydes

Tannins, being phenolic in nature, undergo the same well-known reaction of phenols with formaldehyde either base- or acid-catalyzed, weakly basic base-catalyzed reactions being predominantly used in industrial applications. The nucleophilic centers on the A-rings of any flavonoid unit tend to be more reactive than those found on the B-rings. Formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages to reactive positions of the flavonoid molecules, mainly the A-rings. In condensed tannin molecules the A rings of the constituent flavonoid units retain only one highly reactive nucleophilic center, the remainder accommodating the interflavonoid bonds. Resorcinolic A rings (wattle) show reactivity toward formaldehyde comparable, though slightly lower, to that of resorcinol. Phloroglucinolic A rings (pine) behave instead as phloroglucinol. Pyrogallol or catechol B rings are by comparison unreactive, and may only be activated by anion formation at relatively high pH[5]. Hence, the B rings do not participate in the reaction except at high pH values (pH10) where the reactivity toward formaldehyde of the A rings is so high that the tannin-formaldehyde adhesives prepared have unacceptably short pot lives. In general, tannin adhesives practive only the A rings are used to cross-link the network. However, because of their size and shape, the tannin molecules become immobile at a low level of condensation with formaldehyde, so that

the available reactive sites are too far apart for further methylene bridge formation. The result is incomplete polymerization that leads to the weakness and brittleness that are characteristic of many tannin formaldehyde adhesives.

Bridging agents with longer molecules such as phenolic and aminoplastic resins[6-8], have been used to solve this problem by helping to bridge distances too large for interflavonoid methylene bridges. It has been shown that while catecholl and the catecholic B-rings do not react with formaldehyde at pH lower than 10, the addition of zinc acetate as the reaction mixture induces the B-rings to react with formaldehyde at lower pH values, the optimum being in the pH range 4.5-5.5, as shown by the higher amount of formaldehyde consumed[9]. This finding implies that in the presence of zinc acetate further cross-linking of the tannin-formaldehyde network could be achieved through B-ring participation to the reaction. However, although an improvement in strength can be achieved by the addition of zinc acetate at economically acceptable levels (5-10% on resin solids), the improvement is not enough to give the same performance of fortified tannin resins. MDI with high reactivity can be used to let B-ring participate reaction of crosslinking. And at the same time, the reaction between pMDI and carbohydrates or hydrocolloid gums will do some help to the increase of the bonding strength, too.

The reaction rate of wattle tannins with formaldehyde is slowest in the pH-range 4.0-4.5 whereas for pine tannins between 3.3 and 3.9.

Formaldehyde is generally the aldehyde used in the preparation, setting and curing of tannin adhesives. It is normally used as liquid formalin solution or as its polymeric form of paraformaldehdye, which is capable of fairly rapid depolymerization under alkaline conditions. The reaction of formaldehyde with tannins may be controlled by addition of alcohols to the system. Under these circumstances some of the formaldehyde is stabilized by the formation of hemiacetals (e.g., $CH_2(OH)(OCH_3)$ if methanol is used). When the adhesive is cured at an elevated temperature, the alcohol is driven off and formaldehyde is progressively released from the hemiacetal. This ensures that less formaldehyde is volatilized when the reactants reach curing temperature, and also that the pot life of the adhesive is extended.

Hexamethylenetetramine (hexamine) may also be added to resins due to its formaldehyde-releasing action under heat. Although unstable in acid environment, under alkaline conditions hexamine liberates formaldehyde only when heated, thus providing indefinite pot life at room temperature. However, recent results showed that in most cases in presence of chemical species with very reactive nucleophilic sites, such as melamine, resorcinol and condensed flavonoid tannins, hexamine does not decompose to formaldehyde and ammonia. Instead, the very reactive but unstable intermediate fragments react with the very reactive nucleophilic sites, such as tannin, melamine, etc. to form aminomethylene bridges before yielding formaldehyde. Any species with a strong negative charge under alkaline conditions is capable of reacting with the intermediate species formed by decomposition of hexamine far more readily than formaldehyde. This explains the capability of wood adhesives formulations based on hexamine to render bonded panels of extremely low formaldehyde emission[10]. If no highly reactive species with strong negative charge is present then decomposition of hexamine proceeds rapidly to formaldehyde formation as reported previously. Formaldehyde emissions from wood particleboards bonded with pine and wattle tannin-based adhesives, using hardeners paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxyl)nitromethan), were measured by the perforator method (DIN EN 120- European Committee For Standardization 1991). All particleboards made using the wattle tannin systems with the three different hardeners were satisfied grade E1, while in the case of pine tannin only the use of the hexamine hardener led to grade E1 being satisfied. This tendency was attributed to the curing mechanism of the hardener, the reactivity of the tannin molecule toward formaldehyde and the fast reactivity toward formaldehyde of pine tannin[11].

In view of the fact that the methylene linkages may be too short for optimum cross-linking, other aldehydes which also have bifunctional characters have been substituted for formaldehyde. Of these, one of the most frequently used is furfuraldehyde (furfural). This has been found to be unsuitable because of its slow reaction with phenols, but Pizzi and Scharfetter[12] have shown that furfuraldehyde is an efficient cross-linking agent and excellent plasticizer for tannin adhesives when coupled with formaldehyde. Total replacement of

formaldehyde by other aldehydes proved non feasible because of their slow reactivity towards tannins. To all practical effects, mainly two aldehydes, formaldehyde and furfural, have been used to date in the preparation of tannin adhesives. Other aldehydes are sometimes used in a supportive role of formaldehyde, when particular effects or physical characteristics of the adhesive are needed. For example, substitution of 10-30% formaldehyde, on an aldehyde group molar basis, with n-butyraldehyde, which due to its saturated hydrocarbon chain is somewhat water repellant, can improve the water resistance of cured tannin-formaldehyde networks by a structural modification rather than "cosmetic" addition of water repellents such as waxes. Tannin adhesives prepared and/or set and/or cured with other adhesives only, or with mixtures of formaldehyde and high proportions of other aldehydes, can give cured bonds weaker than those obtained with formaldehyde alone or its mixtures with furfural.

The metal ions effect on phenol-formaldehdye reactions can be applied to condensed tannins of the flavonoid type with some degree of success. The metal ion accelerating effect is the following:

$$Pb^{II}, Zn^{II}, Cd^{II}, Ni^{II} > Mn^{II}, Mg^{II}, Cu^{II}, Co^{II} > Mn^{III}, Fe^{III} >> Be^{II}, Al^{III} > Cr^{III}, Co^{III}$$

I.2.3. Acid and alkaline hydrolysis and autocondensation

When heated in the presence of strong mineral acids, tannins are subject to two competing reactions. One is degradative leading to anthocyanidins and catechin formation whereas the second one is condensative as a result of hydrolysis of heterocyclic rings (p-hydroxybenzylether links). The p-hydroxybenzylcarbonium ions created condense randomly with nucleophilic centrs on other tannin units to form "phlobaphenes" or "tanner's red". Other modes of condensation (e.g., free radical coupling of B-ring catechol units) cannot be excluded in the presence of atmospheric oxygen[13].

The interflavonoid bonds of the condensed tannins with phloroglucinolic A-rings are susceptible to cleavage under even mild alkaline conditions. This could lead to increased reactivity with aldehydes. Increased reactivity can be introduced through heterocyclic ring

opening which can also lead to autocondensation; reactivity is increased due to A-ring liberation to a more reactive phloroglucinolic species.

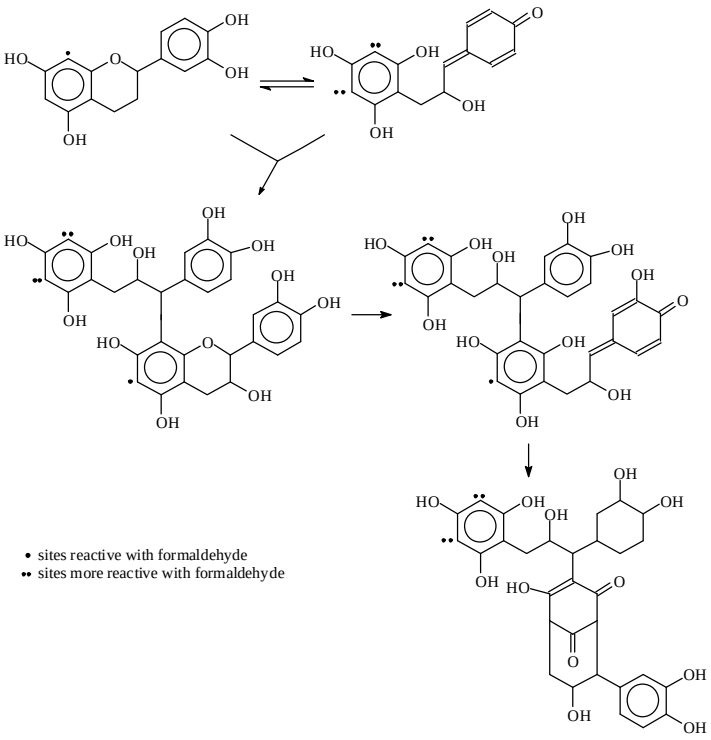


Figure 1.2. Autocondensation reactions of tannins

The liberated phloroglucinolic species of the intermediate products can account for a significant increase in reactivity. If the rearrangement goes extensively to completion, however, the number of potential cross-linking is decreased. An increase in tannin reactivity due to base-catalysed rearrangements has also been demonstrated by other research groups. The formation of activated species referred to above, was in all cases done by using model compounds. However, one must bear in mind that the scenario is quite different with real tannin extracts which constitute a complex system as a result of which different activation conditions may have to be applied in order to bring about the desirable changes. Nevertheless, the work with model compounds has demonstrated that tannin structural rearrangements are possible and that, depending on the conditions applied, such rearrangements can increase or decrease reactivity towards aldehydes.

The autocondensation reactions characteristic of polyflavonoid tannins have only recently been utilized to prepare adhesive polycondensates, i.e., hardening in absence of aldehyde. This

autocondensation reaction is based on opening under alkaline or acid conditions of the O1-C2 bond of the flavonoid repeat unit and subsequent condensation of the reactive centre formed at C2 with the free C6 or C8 sites of a flavonoid unit on another tannin chain. Although this reaction may lead to considerable increase in viscosity, gelling does not generally occur. However, gelling takes place when the reaction occurs (1) in presence of small amount of dissolved silica (silicic acid or silicates) catalyst or some other catalysts and (2) on a lignocellulosic surface. In the case of the more reactive pine tannin, cellulose catalysis is more than enough to cause hardening and to produce boards of strength satisfying the relevant standards for interior grade panels. In the case of the less reactive tannins, such as mimosa and quebracho, however, the presence of dissolved silica or silicate catalyst is the best approach to achieve panel strength as required by the relevant standards. The amount of silicic acid or silicates has some effects on the gelling. Gelling speed become faster with the increase of addition amount of silicates, while once a certain amount of silicates has been reached, the speed becomes stable. Though dry strength of panels by autocondensation increases obviously, the resulted crosslinking is not strong enough for exterior-graded panels[14]. For preparing exterior-graded panels, aldehyde curing agents should be added. The mechanism of autocondensation of polyflavonoid has been examined by ^{13}C-NMR, ESR and so on[15-17].

Zinc acetate also appears to cause a similar type of autocondensation, but this is much slower, occurs mostly at higher curing temperatures, and not at ambient temperatures as for the other materials already examined, and leads to a much softer gel. As a consequence, zinc acetate does not appear to produce an effect strong enough to invert the relative ease of interflavonoid bond cleavage and pyran ring opening in procyanidins. Thus, in the presence of zinc acetate, autocondensation will occur of prodelphinidins to prodelphinidins and prodelphinidins to procyanidins, but never or rarely of procyanidins to pocyanidins[18].

Polyflavonoid tannin autocondensation was found to be facilitated by the reaction occurring on cellulose and lignocellulosic substrates. Although the mechanism of polyflavonoid autocondensation induced by cellulose differs from that induced by the action of Lewis acids, the subsequent reaction of autocondensation appears to be similar[19].

I.2.4. Sulfonation

Sulfonation of tannins is one of the most useful reactions in flavonoid chemistry and can be particularly useful in the preparation of tannin-based adhesives. Sulfonation is a classic example of the errors that can be introduced in extending the reactions of flavan-3-ols as model compounds to the behaviour of the condensed tannin polymers without due consideration of the reactions at the interflavonoid bond. The literature prior to 1983 suggested that sulfonated of condensed tannins proceeds by opening of the pyran ring with the formation of the sulfonic acid function on the carbon α to the B-ring.

However, it is now known that reaction of 5,7-dihydroxy proanthocyanidins with sulfite ion under the usual pH conditions proceeds by cleavage of the interflavonoid bond with the formation of flavan-4- or proanthocyanidin-4-sulfonates as indicated by the scheme below.

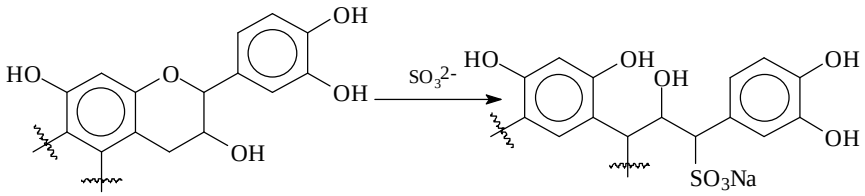


Figure 1.3. Sulfonation of tannins

Sulfited products without opening of the etherocyclic ring are also possible in the case of the phloroglucinolic tannins due to the relative ease with which the interflavonoid bond is cleaved. Flavan-2,4-disulfonates are also formed quite readily.

The fact that sulfonation of phloroglucinolic condensed tannins involves interflavonoid bond cleavage has important implications for the utilization of this class of tannins as the molecular weight can be tailored to suit their use in applications such as wood adhesives. In addition, sulfonation affords tannins of lower viscosity and increased solubility due to:

(1) Elimination of the etherocyclic ether group which is water repellent.

(2) The introduction of the sulfonate group and another hydroxyl group, both hydrophilic.

(3) The decrease in polymer rigidity, steric hindrance, and intermolecular hydrogen bonding

obtained by the opening of the etherocyclic ring.

(4) Acid hydrolysis of the hydrocolloid gums and of the interflavonoid bond.

However, sulfonation may present a distinct disadvantage in that sulfonate groups promote sensitivity to moisture with adhesive deterioration. Nevertheless, this problem could, at least to a certain extent, be solved by desulfonation. Desulfonation of 2,4,6-trihydroxybenzyl sulfonic acid and sodium epicatechin-(4 β)-sulfonate is a very facile reaction under mild alkaline conditions (i.e., pH>8.0 and ambient temperature) whereas hydroxybenzylsulfonic acids with resorcinol or phenol functionality resist desulfonation even at pH12 and 90°C. Therefore, not only is it possible to reduce the molecular weight with improvements in the viscosity and solubility of the product, it is also possible to remove the sulfonic acid function and obtain aldehyde condensation products that are insoluble in water.

I.2.5. Chemistry and technology of industrial tannin adhesive formulations

Tannin extract always contain a nontannin fraction, consisting mainly of sugars and hydrocolloid gums. The nontannin fraction which varies in different extracts does not participate in resin formation. Commercial wattle bark extract and quebracho extract normally contain 70-80% active phenolic ingredients, while pine bark yields an extract containing only 50-60%. While the sugar effect is a mere dilution effect of the adhesive resin solids which consequently worsens the adhesive properties, the hydrocolloid gums have a much more marked effect on both original strength and water resistance of the adhesive.

Because of the negative contribution of the nontannin components in the extracts, unmodified tannin adhesives are unsuitable for wood products where high performance is demanded, with further refining of tannin extracts proven fruitless, fortification is in many cases the most practical approach to reducing the effect of impurities. Fortification generally consists of copolymerization of the tannin with phenolic of aminoplastic resins.

Compared to synthetic resins, the tannin extracts are more viscous at the concentrations

normally reaquired in adhesives. High viscosity of aqueous solutions of condensed tannins is mainly due to the presence of high molecular weight hydrocolloid gums, hydrogen bonds and electrostatic tannin-tannin, tannin-gum, and gum-gum interactions and the presence of high molecular weight tannins in the extract number of ways: (1) acid and alkaline hydrolysis of the hydrocolloid gums[20-21], (2) the addition of small amounts (up to 3% of extract solids) of hydrogen bond breakers, and (3) sulfitation and bisulfitation which cause the opening of the tannin etherocyclic ring thus increasing tannin molecular mobility, hence decreasing viscosity.

I.3. LIGNIN-BASED WOOD ADHESIVE

Next to cellulose, lignin is the most abundant and important natural products coming from plants. When the plants experience the need for mechanical support of their fibrous tissues, they produce lignin, and deposit it as a reinforcing agent. In addition, lignin performs as a sealant and decay retarder, to name only a few of its many service functions to the woody plant. Lignin is produced in large quantities as an underutilized byproduct during chemical pulping. The amount of lignin present in different plants is quite variable and ranges from 20-40%. In its natural form lignin is a three-dimensional polymer constituted of random polymerized phenylpropane (C9) units by ester and C-C bonds.

During pulping the lignin macromolecule is degraded and modified. The polymeric nature of lignin nevertheless prevails after pulping. Consequently, the development of uses in which the polymeric nature of the by-product lignin is exploited has received widespread attention. The first patent dealing with the application of spent sulfite liquor (SSL) as an adhesive for paper, wood, and other lignocellulosic materials dates back to the end of the last two century.

Chemical pulping can be grouped into two classed, namely sulfite and alkaline pulping. Sulfite pulping is done in the presence of sulfite under acidic or alkaline conditions. The degraded lignin fragments are called lignosulfonate. The polymeric character and the sulfonic acid groups impart surface-active and binding properties to the lignosulfonate. The sulfonic acid groups, however, impart a degree of hygroscopicity to the lignosulfonate. This property and the

poor ability of lignosulfonates to co-crosslink with adhesives, such as phenol-formaldehyde adhesives, probably lead to the poor utilization of this material in wood adhesives.

Alkaline pulping is done with sodium hydroxide as the major pulping chemical. Variations include Kraft pulping, in which about a third of the sodium hydroxide is replaced with sodium sulfide (Na_2S), and soda pulping, in which catalytic quantities of anthraquinone are added. During alkaline pulping the liquid is usually extensively modified. The major degradation reaction is the cleavage of alkylaryl ether (β -O-4) linkages. Concomitant to the cleavage reactions, the lignin fragments also undergo condensation reactions.

The occurrence of lignin as a waste byproduct of woodpulping operations, about 75 million tons produced annually worldwide, has made it an attractive material for adhesives. Over the last hundred years or so, there has been an enormous effort to develop lignin-based adhesives, but this has met with no real commercial success. Presently, most of the spent liquors in pulp mills are burnt. Only about 20% are used for various purposes, such as dispersants, oil-well-dring muds, palletizing materials, molding stabilizers and concrete grinding additives[22-24].

I.3.1. Chemical background

To perceive the polymerization reactions that can make lignin useful in wood adhesives, it is necessary to look at the structure and chemical composition of this material. As mentioned earlier, in its natural form lignin is a three dimensional polymer which is broken into smaller segments during pulping. The following figure shows the formation of Kraft lignin.

In general, lignin is composed of phenylpropane (C9) units (Fig. I.4) that are linked together by carbon-to-carbon as well as ether bonds.

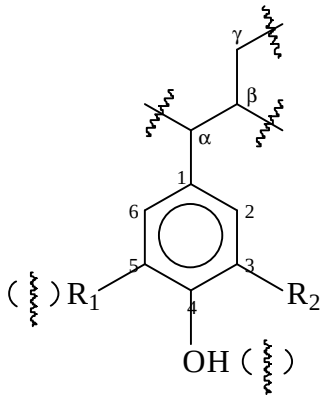


Figure I.4. Phenyl propanoid units of lignin: R1,R2=H, OCH_3, or / and (ζ) = possible linkage to other phenyl propanoid units.

The chemical features of lignin that can be used for polymerization reactions in wood adhesives are as follows.

(1) Phenolic hydroxy groups

(2) Aliphatic hydroxy groups

(3) Structures that can form quinine methide intermediates.

(4) Unsubstituted 3- or 5-positions on phenolic C9 units.

Cross-linking can be achieved either by condensation or by radical coupling reactions. When lignosulfonate is treated with strong mineral acids at elevated temperatures or heated at temperatures above 180°C, condensation reactions leading to diphenyl methanes and sulfones take place. According to its structures as a polyphenol, lignin as an adhesive should be similar to PF resins. This is true for lignin in wood, while technically lignins have to be additionally cross-linked to change them into insoluble resins. However, condensation reactions in lignin by heat or mineral acids cannot be as effective as in synthetic PF resins, due to the lower number of free positions in the aromatic muclei of lignin and their considerably lower reactivity than in PF resins. Besides lignin, in most cases additional cross-linking agents for lignin are necessary, such as epoxides, polyisocyanates, polyols, polyacrylamides, polyethyleneimine, aldehydes, maleic anhydride, amines, proteins, melamine, and so on. However, none of these methods appears to provide enough cross-linking to assure high performance resins. Isocyanates were also combined with lignin for the formation of low cost lignin-based polyurethane foams.

Although very promising results were obtained, the use of organic solvents or complex emulsifying processes restricted further utilization of this method by obscuring the economic advantages of using lignin.

One of the most successful approaches has been the oxidative coupling of lignin. Oxidants such as hydrogen peroxide, and catalysts such as sulfur dioxide or potassium ferricyanide are most effective. The crucial advantage of this type of cross-linking compared with condensation reactions is that it needs neither mineral acids nor high temperatures, due to the recombination of radicals, for which the activation energy is very low. The strongly exothermic reaction causes a uniform temperature profile during pressing of particleboard without external heat.

Although this method appeared to be very promising at its initial stages, no industrial utilization of lignin based on this approach has ever been reported.

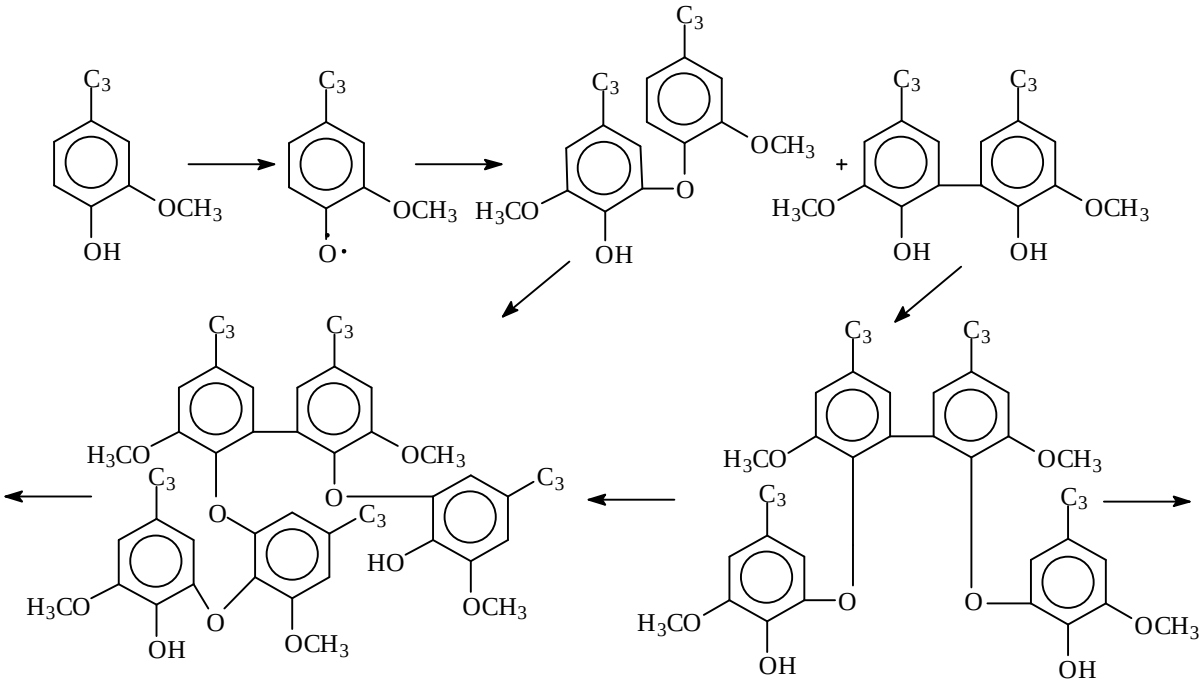


Figure I.5. Cross-linking of lignin by oxydative coupling

I.3.2. Utilization of lignin in phenol-formaldehyde (PF) wood adhesives

The abundance of lignins of different types as a waste product in pulp mills has made such materials an attractive proposition for the preparation of adhesives ever since the pulping of

wood to produce paper. The literature on the use of lignins to prepare wood adhesives is very extensive, and good reviews of it exist [25-30]. In contrast to the great number of articles regarding its utilisation, the record of its industrial use for wood adhesives is instead rather poor. The phenolic character of lignin has made the substitution of PF resins, and particularly PF wood adhesives the most widely-explored avenue of lignin utilization[31-37].

Lignin can react with formaldehyde mainly through unsubstituted 5-positions and form hydroxymethylated species in the same way as phenol does. These species can then form methylene bridges with phenol or other lignin units to form polymers.

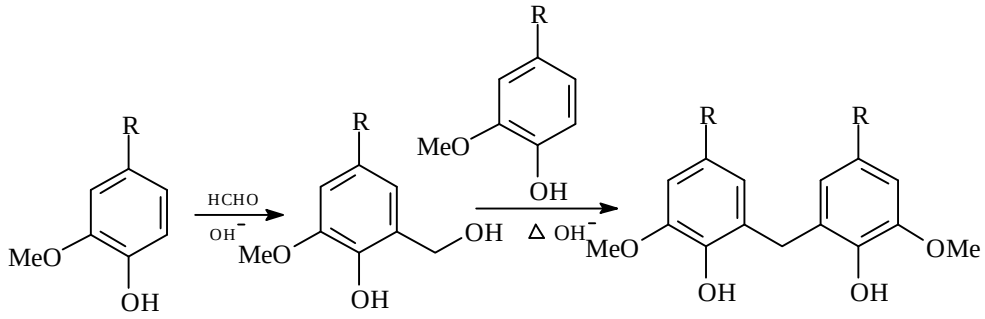


Figure 1.6. Polymerization of lignin with formaldehyde in alkaline solution

The occurrence of unsubstituted 5-position on phenolic C9 units in lignin is however usually low: 0.1 in eucalyptus soda lignin, 0.3 in pine kraft lignin and 0.7 in soda bagasse lignin. Steam explosion and acid hydrolysis lignins appear to have a lower number of reactive sites than karaft softwood lignin. Kraft, the most abundant lignin, containing only 0.3 reactive sites per C9 unit has difficulty in forming acceptable polymerized products by itself or with PF resins. This difficulty is particularly marked for unfractionated lignins which normally contain a substantial portion of low molecular weight fragments. The low molecular weight fractions can be expected to result in the termination of the polymerization reaction of the resin owing to the low content of reactive sites. One way to partially overcome this inherent inability of industrial lignins is by single high molecular weight lignin fractions which can be obtained by ultrafiltration. Due to the larger number of C9 units per fragment, each fragment has a much better chance to contribute to polymerization, compared with the monomeric and dimeric fractions. Forss and Fuhrmann[38] used high molecular weight (MW>5000) lignin from

ultrafiltration and managed to compose a phenolic resin containing 40% to 70% lignin, depending upon the type of application.

One of the main defects of PF/lignin blends as wood adhesives is their slow reactivity which makes the use of extended press times and/or post-treatment at high temperature necessary thus hindering the practical application of such blends.

The combination of lignin with UF resins is proven to be of less importance, probably because of the different characteristics of the UF resins. Although the addition of 10 to 30% UF improves significantly the press time of lignin boards, post-treatment at high temperature is necessary for acquiring the standard mechanical strength requirements.

I.3.3. Chemical modification of lignin

Capacity for condensing with crude lignin itself and with PF resins is nevertheless limited, allowing only about 20% of the phenol in a PF resin to be replaced by the lignin. When the addition is more than 20% of the phenol, lignin acted as a filler and reduced the properties of panels manufactured with the resulting adhesive[39-41]. Higher percentages can be achieved only if the reactivity of the lignin is chemically enhanced, the most promising reactivity-enhancing processes being methylolation[42-45], demethylation[46] and phenolation[47].

Hydroxymethylation of lignin is the most common way to activate lignin. The establishment of methylol groups onto the lignin structure, mainly on unsubstituted 5-positions prepares the material for the final cross-linking and curing during application. This mechanism is parallel to that of phenol-formaldehdye resins. However, much longer reaction periods are required for the establishment of the methylol groups owing to the low reactivity of lignin toward formaldehyde compared to that of phenol. Although hydroxymethylation establishes the chemical groups that can, during application, react further thus causing setting of the resin, their number is limited to that of the few unsubstituted 5-positions on the lignin units. This results in a low density cross-linking and hence a very brittle final resin. One way to resolve this problem is by

chemical activation of the aromatic nuclei of the lignin toward formaldehyde. This can be achieved by demethylation of the methoxy groups on the 3-position of the guaiacyl units or on both 3- and 5-positions of the syringil units of lignin. The 2- and 6-positions of the C9 unit are situated ortho and para to the newly formed aromatic hydroxyl groups and can now contribute in the classical reaction with formaldehyde. Demethylation of lignin can be achieved by several means such as treatment with hydroiodic acid, sodium periodate, potassium dichromate, chlorine and ehanolamine. However, activation of lignin by demethylation did not prove to be viable because of the high cost of the reagents involved.

The feasibility of utilizing the free 2- and 6-positions of the unmodified lignin had also been investigated. It has been demonstrated that under special conditions the C9 lignin units can react with formaldehyde at the 2- and 6-positions to afford a high degree of hydroxymethylation. However, the conditions required, very low pH and the use of dioxane, are not conductive to wood adhesive application.

A different way of increasing the number of reactive sites toward formaldehyde is by grafting reactive species such as phenol onto the lignin C9 units. Under acidic conditions phenol reacts with oxysubstituted α-carbons to afford a phenolated adduct. This method of phenolysis however, is not very efficient due to a limited number of α- hydroxyl groups; most of these groups are eliminated by reacting further during the long pulping periods.

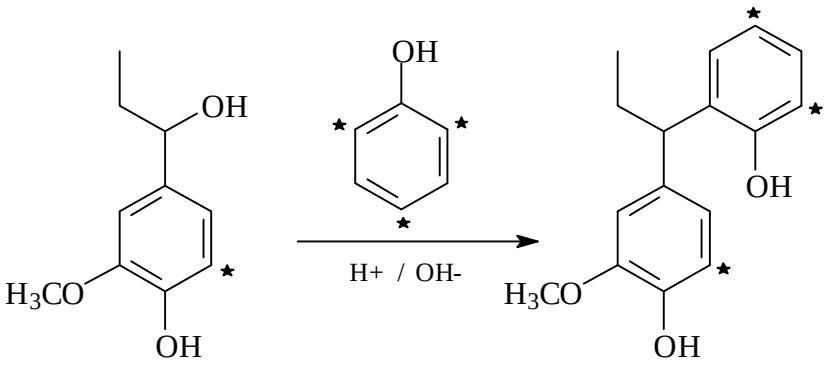


Figure I.7. The increase of reactive sites (*) on lignin fragments by phenolysis

A second way of phenolysis involves the reaction of phenol with hydroxymethylated lignin

under alkaline conditions.

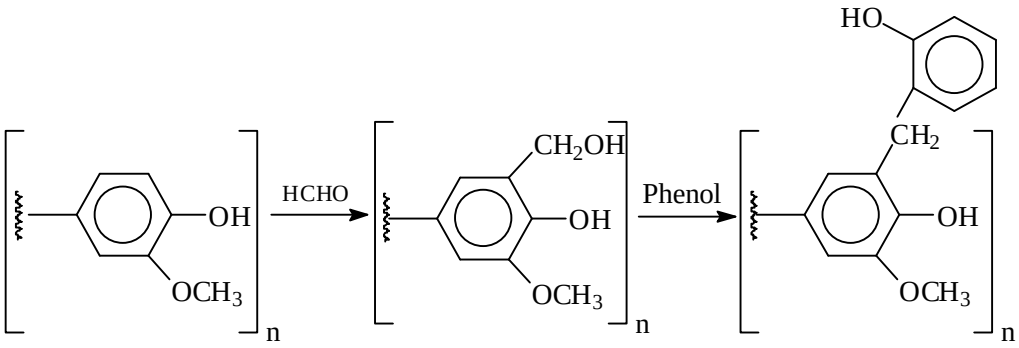


Figure I.8. Hydroxymethylation and phenolysis of lignin

It was found that up to 50% of the phenol in the PF resin could be replaced by phelonated-lignin to give lignin-phenol-formaldehdye wood adhesive having similar or better bonding strength in comparison to a control phenol formaldehyde[48-49].

This method provides two reactive sites for each one of the C9 lignin units. Significant improvement in resin performance has been achieved by alkaline phenolysis of lignin. Boards bonded with phenolated lignin resins have better internal bond strength and durability properties than those bonded with lignin-extended PF resins.

Even cold-cure wood adhesives can be designed by grafting resorcinol onto the relatively high reactive soda bagasse lignin. Because of its high reactivity, 0.7-unsubstituted 3- and 5-positions per C9 unit, soda bagasse lignin is a good candidate to replace phenol-formaldehyde resins in high proportions in polymeric products. Cold-cure wood adhesives were prepared by the hydroxymethylation of the bagasse lignin followed by the reaction of resorcinol onto the hydroxymethylated lignin in the same fashion as demonstrated by Fig. I.7. A high performance adhesive containing only 14% resorcinol on liquid adhesive and 70% hydroxyl-methylated lignin on total solids was obtained. Soda bagasse lignin was also used to prepare acceptable fast-set "honeymoon"-type adhesives. Thermosetting wood adhesives were also prepared by extended hydroxymethylation periods (up to 15 h) at temperatures below 60^{o} C.

Addition of phenol showed no significant improvement in the performance of the methylolated bagasse lignin whereas the addition of the PF (resol) resin resulted in a substantial improvement

in the adhesive performance. Also, addition of phenol to the PF/lignin combination did not improve the strength. It becomes obvious by simply comparing these results with those obtained by other groups that addition of pheol to hydroxymethylated lignin can have advantageous effects only if it is chemically bound to the lignin units by phenolysis reactions. A combination of hydroxymethylated bagasse lignin/commercial PF resin (67:33) gave very encouraging results: three layer 12mm boards pressed for 7.5 minutes could meet the requirements for interior grade. The prospects for a fully exterior grade, bagasse lignin-based adhesive appeared to be very good. It must be noted however, that industrial soda bagasse lignin is only available mainly in third world countries.

On a final analysis, despite its availability in large quantities as a waste product of pulp mills, lignin hitherto has found only scarce utilization as a chemical raw material. Although many efforts have been undertaken in the application of lignin as an adhesive for wood materials, no full-scale industrial application in particleboard, plywood, or fiberboard production is known presently. The search for an economic lignin-based wood adhesive continues.

I.4. SOY-BASED PROTEIN ADHESIVE

The main component of soy-based protein adhesive is soy flour or soy protein isolate (SPI). The former contains 40-60% protein, while the latter more than 90%. Both of them cann't be used as adhesive directly. Before application, cross-linker or other chemicals should be added. Soy protein was once one of the most important adhesives in wood panel industry. Soy-based adhesive products were first developed in 1923 and at that time this kind of adhesive was mainly used for plywood. It flourished in the next twenty years. In America till 1942 about 85% plywood was glued by soy-based adhesive and in west coast almost all of the factories prepared plywood with soy-based adhesives[50]. While with the development of petroleum industry, soy-based adhesives have been displaced by petroleum-based adhesives being developed in the 1940s. At present, petroleum-based adhesives are used predominantly for production of wood composites.Soy protein used as a wood adhesive has acturally declined over the years. However, the research on soy-based adhesive has again attracted considerable attention since 1990s.

America has already done a lot of work in this field.

I.4.1. Characteristics of soy-based adhesive

Advantages of soy-based adhesive:

(1) Soybean is aboundant, sustainable, environment-friendly and low-cost.

(2) Soy-based adhesive can be cured either hot or cold. Hot-curing can be done at temperature between 230 and 270 °C, pressure of 1.21 MPa and curing time of 1.5 min to prepare plywood panel of one-quarter inch thickness. Curing conditions can be varied depending upon the thickness of panels. Cold-curing of soy-based adhesive is recommended at a pressure of 1.03-1.21 MPa for 15 min.

(3) Soy-based adhesive can be used to bond green lumber. The moisture content of wood substrate can be as high as 15%.

Disdvantages of soy-based adhesive:

(1) Low gluing strength;

(2) Poor water resistance;

(3) Poor bio-degradation resistance. Mold will appear once the moisture content of wood panel reaches to 20%.

I.4.2. Modification of soy protein

Soy protein consists of many kinds of functional groups, such as hydroxide group(-OH), amino group($-NH_2$), carboxyl group(-COOH) and so on. Soy protein can be chemically, physically or enzymatically modified to achieve desired properties. The methods of soy modification include hydrolysis, cleavage of disulphide bond, cross-linking, acylation, oxidation, reaction with alkoxy silane and copolymerization.

I.4.2.1. Disruption of soy protein

Soy protein is a natural macromolecule. Its monomers contain the same amino acid residues as many other proteins and are linked by amide bonds into polypeptide chains. The polypeptide

chains are associated and folded into a three-dimensional complicated compacted global structure by disulfide and hydrogen bonds. The resulted globulins can't be used directly as adhesive because of its bad cohesion. To be used as adhesive, the globular structure has to be broken because any good adhesive must consist of relatively large, flexible and interwoven polymer chains. More polar and apolar groups should be exposed for contact. Therefore, it is necessary for soy protein to be disrupted before application[51].

Soy protein has normally been modified by alkaline treatment. Alkali-modified soy protein adhesive was reported to be stronger and more water resistant compared with adhesive containing unmodified soy protein[52]. Alkaline reagents include NaOH、$Ca(OH)_2$、borax、Na_2HPO_4、ammonium hydroxide etc. NaOH is the most commonly used one. The best condition for soy protein disruption were to maintain the temperature at 50 °C and react soy protein with NaOH at pH 10.0. Soy protein treated by slightly alkaline reagents, such as $Ca(OH)_2$、borax、Na_2HPO_4、ammonium hydroxide etc will not change the color of wood, while adhesive strength is smaller than that of NaOH-treated. It can be used as paper adhesive.

The effect of mixing two or more alkaline reagents on the properties of soy protein was investigated by Kalapathy U *et al*[53]. Insoluble protein salts could be attained by the reaction of soy protein and the alkaline mixture, such as NaOH to which $Ca(OH)_2$ or magnesium salts had been added, which led to the improvement in adhesive strength, water resistance and lengthening of pot life.

The degree of hydrolysing depended on pH and time of alkaline treatment. With more alkali and longer time, soy protein hydrolysed further. However, the secondary structure of the protein molecules will help bonding strength[54]. During alkaline treatment, the globulin should be broken as much as possible and at the same time the secondary structure should be kept as much as possible, too. A decrease in soy protein viscosity was reported upon addition of ionic salts [55-56].

I.4.2.2. Chemical denaturation of soy protein

The primary problem with traditional soy adhesives comes from its poor water resistance[57]. As is well-known, most of soy proteins are hydrophilic. Hydrogen bond would be broken when subjected to moisture, leading to bond failure. A limited crosslinking deteriorate the water durability of soy-based adhesive, too. Based on the two causes for poor water resistance, there are two ways to resolve the problem: (1) to expose more hydrophobic groups which are embedded inside the protein before modification and to make the functional groups outside available for bonding to the wood or crosslinking chemicals; (2) to increase the crosslinking degree of soy-based adhesive.

In an alkaline environment, certain reagents such as urea, sodium dodecyl sulphate (SDS), sodium dodecyl benzene sulphonate (SDBS)[58] and guanidine hydrochloride (GuHCl)[59] and DCP[60] could be used to modify soy protein. Actually, most of these reagents could disrupt protein molecules chains. Urea can unfold the secondary helical structure, as well as the tertiary and quaternary structures of a protein. Its oxygen and hydrogen atoms can actively interact with the hydroxyl groups in soy protein. This reaction breaks down the hydrogen bonding in the protein body and unfolds the protein complex, resulting in enhanced adhesion bonding strength [61].

Modification with several chemicals on soy flour was tried by Cheng et al to prepare wheat straw particleboard. The combined effect of the chemical was also studied. The adhesive made from soy flour treated with some amount of urea, urease inhibitor N-(n-butyl) thiophosphoric triamide (nBTPT), citric acid, NaH_2PO_2, boric acid and NaOH produced particleboard with better mechanical strength and water resistance[62].

The effect of varying concentrations of modification agents on adhesion property of modified-SPI adhesives was investigated by Huang and Sun [61]. Soy protein modified by treatment with 1 and 3 M urea, 0.5 and 1 M guanidine hydrochloride, 0.5 and 1% SDS or SDBS gave greater strength and water resistance than unmodified SPI.

Some research was done on the soy protein isolates(SPI) modified by urea and sodium tripolyphosphate(STP). The results showed that viscosity increased when more STP being used. Compared to U-SPI, the U-S-SPI exhibited better shear strength and water resistance[63].

I.4.2.3. Crosslinking of soy protein

Sulphur compounds, such as CS_2, ethylene dior tri-thiocarbonate, thiourea and potassium xanthate, are strong crosslinkers of dispersed soy protein. They have been used to improve their water resistance, working life and consistency. Other crosslinking agents that can be used for alkaline soy dispersions are soluble copper, chromium, zinc salts or aliphatic epoxies[64]. Epoxies are active hardening agents for alkaline soy glues and yield products with improved strength and durability but are expensive. An aqueous solution of cationic polyamidoamine-epichlorohydrin(PAE) could be used as a crosslinker for soy protein and its using increased the strength and water resistance[65-66].

On the basis of the understanding of the adhesion mechanism of mussel protein[67], which served as a strong and water-resistant adhesive, cysteamine was successfully grafted into SPI by amide linkages. Increasing the content of the –SH group significantly improved the wood adhesion for soy proteins. The strength and water-resistance of the wood composites bonded with the modified SPIs depended on the amount of the –SH group in the modified SPIs.

Soy protein isolate (SPI) was first modified with maleic anhydride (MA) to form MA-grafted SPI (MSPI). It was found that MA was grafted onto SPI via amide linkages and ester linkages. Wood composites bonded with MSPI alone had low dry shear strength and delaminated when they underwent a boiling water test. However, a combination of MSPI and polyethylenimine (PEI) dramatically increased the strength and water resistance of the resulting wood composites[68].

Addition of formaldehyde donors or adducts can crosslink or denature proteins and provide

enhanced water resistance. Examples of compounds of this group include: tris-hydroxymethyl nitromethane, dimethylol urea, sodium formaldehyde bisulphite, aldehydic starch, glyceraldehyde, hexamethylene tetramine, urea–formaldehyde, methylolated phenols etc[69]. Formaldehyde and paraformaldehyde are very active crosslinking agents and can cause pre-mature gelation. Therefore, very low concentration of aldehyde-active compounds is sufficient and is added during the final stage of the glue mix.

Soy flour contains 35% carbohydrates besides proteins. The carbohydrate may also contribute to additional durability through copolymerization. Commonly used method is acidic treatment, such as citric acid and boric acid.Citric acid is an important agent for cross-linking cotton cellulose, it contains carboxyl groups that may interact with amino groups in soy protein. With sodium hypophosphite (NaH_2PO_2) as the catalyst, citric acid can interact with the cellulose in soy carbohydrates. Boric acid was reported to interact with carbohydrates in soy flour and create cross-linkings within the carbohydrate complex. This results in a significant decrease in water absorption in the case of soy plastics [70].

I.4.2.4. Enzyme modification

The advantages of enzyme modification include high reaction rates, mild conditions, and, most importantly, specificity. Proteases hydrolyse peptide bonds in proteins to modify their structure. Modification of soy protein isolate with papain was reported to affect hydrophobicity, solubility and emulsifying properties[71]. Modified SPI had significantly higher solubility and emulsifying properties. Trypsin-modified SPI (TMSP) or soybean flour exhibited much higher adhesive strength on soft maple, compared with that of unmodified SPI[72-73].

Other modification methods of soy protein include acylation, oxidation, reaction with alkoxy silane and copolymerization[74-78].

I.4.3. Application of soy-based adhesive in the wood panels industry

The research and development of products made from soy protein is rather limited. Most of them are still on the stage of lab experiment. Study on soy-based adhesive is not exceptional too. Generally, to use soy protein modified by the means mentioned thereinbefore directly as adhesive is not common. In most cases, it should mix with other materials to meet with the relative international requirements. The methods most commonly used are as follows:

I.4.3.1. Soy/urea–formaldehyde or phenol-formaldehyde resins system

Soy protein contains many reactive side-chain amino acid groups that have the potential to react with phenolic adhesives or other adhesives. It is this reactive nature that provides soy flour adhesive systems with the ability to form thermoset networks with a suitable crosslinking agent. A PF-cross-linked soy resin comprising 70% soy flour and 30% PF was developed by Kuo et al. This light-colored soy resin could be used as a liquid resin for preparation of fibreboard and particleboad made from agriculture by-product[79-81]. Subsequent research resulted in soy-based adhesives to be used in fiberboard[82]. They did some work on the modification between soy flour and MUF. The resulted soy/MUF resin had better water resistance, lower formaldehyde emission and lower cost than MUF alone[83]. Hse ***et al.*** also developed a similar PF-cross-linked soy resin for the production of oriented strand board (OSB) [84]. They firstly treated soy flour and phenol with additional percentage from 30/70 to 50/50 with NaOH and heat, and then added formaldehyde to the system. The same performance of OSB had been gotten as that of pure PF used. However, all of these systems were prepared in a lab and there is no report on a soy-based resin system used industrially.

I.4.3.2. Soy flour/methylene diphenyl diisocyanate mixture

The system is based on the high reactivity of MDI. Its reaction with soy protein will increase adhesive's mechanical properties. There is some patents which described the methods for preparing a soybean-based molding compound by cross-linking soy flour with polymeric 4,4-diphenylmethane diisocyanate[85]. When using some amount of alkali-modified SPI and MDI as adhesives, low-density particleboard made from wheat straw and corn stalk pith, had

desirable tensile strength and compressive strength[86]。

I.4.2.3. Soy/phenol-resorcinol-formaldehyde(PRF) adhesive system for finger-jointing green lumber

Kreibich demonstrated the viability of soy adhesive technology in the end jointing of green lumber. In this technology, the hydrolyzed soy protein isolate with paraformaldehyde and a phenol-resorcinol-formaldehyde adhesive are applied to separate ends of two finger-jointed boards, which are then joined together under press when the two kind of adhesive meet with each other, namely so-called honeymoon process. However, this technology requires keeping the soy protein separate from the PRF adhesive, because of high reactivity between the two components. 50% PRF are saved by this technology [87]. Steel did some work on this project too[88].

Because of the higher viscosity compared with other synthetic wood adhesives, before soy protein adhesive normally had been used in the preparation of plywood. Now with more in-depth study, soy-protein based fiberboard and particleboard has been prepared too. And at the same time, the application of soy protein adhesive in the agriculture by-product panel field has showed an attractive prospect. The apolarity and hydrophobility of silicon and wax existing on the surface of most of agriculture by-product, such as wheat straw, make the substrate hard to be bonded with UF or PF. Therefore pMDI is commonly used. The relative results showed that it was possible for soy protein adhesive to displace part of pMDI.

Low-density straw particleboard based on soy protein adhesive was studied by Mo *et al*[89]. The mechanical properties of this kind of particleboard were determined by several factors including the types of adhesives, straw surface structure, and initial straw moisture content. The particleboard with some amount of pMDI had better mechanical properties. Particleboard made from bleached straw with NaOH-modified SPI had the best mechanical properties among those particleboard made from various surface treatments of straw and with different soybean protein-based adhesives. Maximum mechanical strength was obtained at 40% initial straw

moisture content with modified SPI. Mechanical properties of the straw-soy flour particleboard prepared by Cheng *et al* met the requirements of ANSI/A 208.1-1989. Although water resistance of particleboard was poorer than the industry particleboard made from wood fibers bonded with formaldehyde-based resins, it is more environmental sound and can be used in manufacturing core material and other applications where the requirements for water resistance are not stringent[90].

The performance of soy protein adhesive could be affected by press program too. Adhesion properties of SPI on fiber cardboard and effects of press conditions, pre-pressing drying time, and protein concentrations on gluing strength were investigated. Shear strength increased as press time, press pressure, and/or press temperature increased. The effect of temperature on shear strength became more significant at high press pressure. The shear strength of the SPI adhesive on fiber cardboard decreased by 12-25% after water soaking. Shear strength increased as pre-pressing drying time increased and reached its maximal value at about 10 min. An SPI/water ratio of 12:100 (w/w) gave the highest gluing strength[91].

I.4.4. Conclusions

The trend of conversion from petroleum-based to bio-based wood adhesive has been shown recently. It offers a significant opportunity and challenge to develop adhesives from these natural substances[92]. In general, as a member of the family of bio-based adhesive, research on the development and application of soy protein adhesive is limited. Most of relative products are still at the stage of lab and actual industrial usage is rather few. With more and deeper research on soy-based adhesive, the problem on its water resistance and bonding strength will be resolved step by step. It is possible for soy-based adhesive to become a good alternative to formaldehyde-based adhesives for wood and non-wood applications.

I.5. FILLERS

At present, formaldehyde-based adhesives such as phenol-formaldehyde (PF) and

urea-formaldehyde (UF) resins are used predominantly for production of wood composites. UF resin has many advantages, such as low price, absence of color in cured polymer, good mechanical performance and so on, which render it the most widely used adhesive in wood panel industry. However, UF resin can be used only as an interior one because of its poor water resistance. The usage of PF resin is only next to UF resin in wood industry. PF resin has good water resistance and it can be used under more rigorous conditions than UF resin. It is classified as an exterior adhesive. But the application has been limited by its many characteristics too, for example, brown color, brittleness, long curing time, high curing temperature, high requirements on moisture content of veneers and especially the toxicity due to free phenol and formaldehyde[93]. To improve the performance of PF and UF and widen their use, many different modification methods, such as the adjustment of press process, post treatment, the addition of other materials, have been tried. To add fillers to the resins is very simple and has been widely used in industry. It can improve the performance of resins greatly. Filler is used mainly to lower the cost of wood resin adhesives. What's more, in most cases filler can improve the mechanical performance of resins, too. To add filler could alleviate the shrinkage and decrease the stress of glue line, which results in the improvements of toughness and durability. The flowability of glue will be improved due to the locked water in glues by filler. The temperate permeability of glue will do some good to mechanical, physically interlocking of the hardened adhesive into the irregularities of the woods' surface. Therefore, the bonding strength of wood product improves. In general, filler used for modification of resins can be classified into two cateries: activable fillers and inert fillers.

I.5.1. Activable fillers

These fillers are organic compounds, which include cellulose-type fillers (bark powder, wood powder, etc.), starch-type fillers(wheat flour, etc.) and protein-type fillers (soy protein flour, blood powder, etc.). They will swell when dissolving in a solution. It is possible for activable fillers to react with resins. Wheat flour is one of the most widely-used fillers for UF resin in factories. The addition amount is about 10%-30% of total solid resin load. Wheat flour can increase resin's weather resistance, because it can decrease the shrinkage of the glue line, then

the resulted stress of the glue line. And at the same time, the flexibility of the filler itself can increase the toughness of glue, which will weaken the stress and delay the glue's disruption. The reaction between the hydroxyl groups of the starch molecule chains and free formaldehyde to form acetals can lower formaldehyde emission of resulted products. According to Ma et al, using 5%-10% oxidized starch as fillers of UF resin, the formaldehyde emission decreased from 3%-7% to 0.2%-0.5%[94].

While once wheat flour is being used, the poor transparency and flowability make the adhesive loading difficult and the resin with wheat flour will cure faster. Then another starch-type filler oxidized starch was tried recently. Its feasibility and mechanism on resins has been studied. Normal starch will be oxidized by the mixture of H_2O_2, NaOH and water. The main reaction is that hydroxyl groups on the glucose chains will be oxidized to aldehyde ones. At the same time, the glucoside was broken and oxidized starch is depolymerized. During hot press, the reaction between aldehyde groups of glucose of starch and hydroxyl groups leads to the formation of acetal and then a crosslinked three-dimensional structure. Acetals can be gotten by the reactions between chains of oxidized starch too, which will further increase the bonding strength. Compared with wheat flour, oxidized starch filler is better for increasing the strength of UF resin. The good water resistance of acetals will do good to the final glue line, too[95].

I.5.2. Inert fillers

Inert fillers are used to lower the cost and increase the viscosity of resins. They come from inorganic mineral powder. Kaolin, marlite, porcelain clay are the most commonly-used ones. Sometimes sodium silicate, diammonium phosphate, magnesia can be used, too. These hydrophilic powders can be dispersed in the glues.

Mineral fillers are abundant, easily available and of low cost, all of which make them being a promising auxiliary of wood adhesive application. In fact, some work has already been done. Separation into discrete phases caused by the big density of mineral powder is the main drawback to these fillers, which will be resolved by increasing the viscosity of resins or adding

polyvinyl acetate, carboxymethyl cellulose to the resins. For most of mineral fillers, the characteristic of alkaline make the pH itself not accord with a suitable curing condition and the curing speed of resins will be slower. Usually the process of resin preparation has been modified or a latent hardener has been used.

Du *et al* used mineral filler mainly composed of MgO and SiO_2 to prepare plywood[96]. The performance of plywood with mineral filler is better than those with no filler or with filler of wheat flour. Two reasons will account for that: (1) the filler has prevented the over-permeation to the wood substrate of the glue and decreased the inner stress caused by the shrinkage of glue line; (2)oxygen from silicate oxygen and magnesium oxygen can be associated with hydroxymethyl of UF resin, which will do some good to the durability and water resistance of resins.

There is another kind of special mineral filler: nano material. It is a newly-developed material. Nano material has many particular characteristics compared with normal ones. Any nanometer grade material (1-100nm) appeared peculiar or abnormal with interface effect, smaller dimension effect, quantum effect, macroquantum effect, all of which have made them physically and chemically different from the normal ones, such as the characteristic of light, mechanical, thermal, radiation, absorption and so on[97]. Polymer nanocomposite is based on the polymers in which small amount of nanometer grade filler was diffused. The addition of this filler often improves the mechanical, thermal performance of polymers remarkably. Recently, to modify polymer with nano material has attracted more and more attention, especially the research on polymer/layered silicate (PLS). Polymer nanocomposite has combined rigidity, dimensional stability and thermal resistance of inorganic compounds with toughness and well handling of organinc polymer together. Nanocomposite with these characteristics has shown a promising prospective in the field of material.

Some work has been tried to use nano material as fillers of wood adhesives. These nano material include nano-$CaCO_3$, nano-SiO_2 and nano-montmorillonite(MMT)[98-102]. Results have showed that nano material have some effects on gel time, free formaldehyde and strength

of the adhesives. In most of cases, after nano material being used, formaldehyde emission was greatly decreased.

Layered silicate is one of the most important nano materials, especially montmorillite. A significant amount of work has been done on the basic theory and actual industry practice of them. MMT belongs to the general family of 2:1 layered or phyllosilicates.

How to make the filler dispersed at nano lever is the key to the preparation of nanocomposites. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. During the formation of natural MMT, isomorphic substitution within the layers, Al^{3+} in the center has been replaced by other cations with lower charges, generates negative charges that are counterbalanced by metallic cations, such as Na^{+}, K^{+}, Ca^{2+} and Mg^{2+}.

These metallic cations exist on the surface of layerd silicate with weaker electric forces and they can be exchanged with inorganic metallic cations, organic cationic surfactants and other cations, namely intercalator. They are used to convert the normally hydrophilic silicate surface to an organophilic one, and then to make the intercalation of many engineering polymers possible and to render the resulted layered silicates miscible with other polymer matrixes. Additionally, interclator in the organo silicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing. In some cases, some cations can even provide functional groups that can react with the polymer matrix, or initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix.

Intercalation of clays with various organic species is the necessary prerequisite to make sure the formation of nanocomposite. The physical mixture of a polymer and layered silicate may not do well to the improvement of the properties of polymers. In contrast, the poor physical interaction between the organic and the inorganic components leads to separation into discrete phases and resulted poor properties. So intercalator is a key to the preparation of PLS material and it

depends on the polymer matrixes and intercalation reaction process. The most common intercalators include alkylammonium, quartusammonium, pyridine derivant and other cationic surfactants and so on[103].

In nature, there are many other materials which have the similar structure as MMT, such as graphite, mica, and metal oxide. The layered silicates have layer thickness of on the order of 1nm. But only a few of them, such as MMT, kaolin, sepiolite can be used in the preparation of PLS. Most of the layered silicate can't enlarge the interlayer space through the intercalation reaction. This is the reason why graphite fails to be used for the PLS, while the layers space of MMT, kaolin, and sepiolite can be made large enough for polymer matrix entering.

Though many PLS has been used successfully, such as composites made of MMT and epoxy[104-105], polyurethane[106-108], polyacrylic ester[109], and even phenol-formaldehyde resin[110], etc., the reseach on the feasibility and mechanism to modify wood adhesives with MMT is rather limited. It is possible for nano material to be good filler for resins.

I.6. MAIN OBJECTIVES, MAIN WORK AND MAIN INNOVATION

I.6.1. Main objectives and main work

There are two main cases natural materials to be used as wood adhesives: in one case, a natural material is used as the main components of wood adhesives on the basis of adhesion capability of the natural material or similarity of structure characteristic between natural material and synthetic ones. In another case, a natural material is used for the modification of wood adhesives, that is to say, to be as an auxiliary of the wood adhesive.

Therefore, some work has been done on natural material from the two cases. Natural adhesives used in this work include tannin, lignin, and soy-based adhesives, which can be used as the main components to bond wood after being modified or cross-linked. Mineral material montmorillonite, which has been widely-used in nano-composites, is used, too. It is possible to improve the performance of commonly-used wood adhesives, such as urea-formaldehdye and phenol-formaldehyde resins by adding it.

The main work and the main objectives are as below:

(1) Study on environment-friendly tannin/lignin wood adhesive

The feasibility to use non-toxic, non-volatile glyoxal to substitute toxic, volatile formaldehyde in the formulation of lignin-formaldehyde/PF resin/isocyanate resin is judged. Then the suitable addition percentage is determined. Tannin-based adhesive is used to replace PF resins in the formulation considering the similarity of the two adhesives. Through the testing of the performance of the lab-prepared particleboard, the formulation is optimized. The effects of heat-treatment which is widely-used in North America for lignin with high molecular weight on the performance of lignin-based panels are analyzed. With the FT-IR analysis, the structure characteristic of lignin with or without heat treatment is studied and the theoretical explanation on the different performance of panels is given.

(2) Study on environment-friendly soy protein-based wood adhesive

Similar to the study of tannin/lignin-based wood adhesive, formaldehyde is substituted by glyoxal. The structure of soy-formaldehyde adhesive and soy-glyoxal adhesive is compared, and then the feasibility to use glyoxal to substitute formaldehyde is analyzed. The performance of relevant panels is studied. The lab-prepared particleboard procedure is optimized, too. To improve the addition percentage of natural material, glyoxalated lignin is used to replace the PF resin in the formulation and its effects on the performance of soy-based adhesive is studied.

In this study, the main objectives on natural wood adhesive then are:

- To completely eliminate formaldehyde from the adhesive;
- To increase the proportion of natural, envinronmentally friendly materials in these adhesive formulations;
- To determine a suitable addition percentage of these components and optimize the preparation procedure of lignin-based and soy protein-based wood adhesives.

(3) Study on influence of nano-montmorillonite on urea-formaldehyde resin adhesive and its model

The influence of different kind of montmorillonite, such as Na-MMT, Ca-MMT and organic MMT on urea-formaldehyde resins for wood adhesive is studied and one MMT is chosen. The level of exfoliation of the MMT being mixed with UF resin is judged. The thermal characteristic of MMT/UF resin mix system is studied. The effect of different type and different addition amount of MMT on the dry or wet bonding strength of lab-prepared plywood or particleboard is studied. The performance of UF resin with MMT or wheat flour, common filler for wood adhesive, is compared. The modification mechanism for MMT and wheat flour on UF resin is discussed. With the help of relevant analysis method of other models, the suitable addition percentage of MMT to the MMT/urea-formaldehdye resin system is determined.

(4) Study on influence of nano-montmorillonite on phenol-formaldehyde and phenol-urea-formaldehyde resins

This work deals with the addition of different types of montmorillonite nanoclays to thermosetting PF and PUF resins to study:

- The effect of the PF and PUF resin on the level of intercalation or exfoliation of the montmorillonite nanoclays;
- The influence of resin structure on intercalation;
- The improvement in performance of the resin by analyzing the performance of wood panels/composites bonded with PF/ montmorillonite nanoclays.

The main objective of the study of influence of MMT on wood adhesive is to estimate the feasibility of MMT to be used as fillers of wood adhesive, to study the modification mechanism of MMT on wood adhesive, and to optimized the modification procedure.

I.6.2. Main characteristic and innovation of this work

With less of oil reserves and stricter environment regulations, the research on the environment-friendly natural wood adhesive has attracted more and more attention. Though there are lots of literatures on the study of lignin, tannin and soy protein-based adhesive, their actual application in wood industry is rather limited.

Filler is a simple and effective modifier of wood adhesive. Different filler has different effects on the performance of resin adhesive.

The main characteristic and innovation of this work is as below:

(1) Non-toxic, non-volatile glyoxal is used to substitute toxic, volatile formaldehyde being used as cross-linker of lignin and soy protein-based adhesive.

There are a few reports on the study of lignin-based adhesive to which glyoxal being added to substitute formaldehyde, but the feasibility of this method is analyzed only based on the results of panels. There is no relevant theory explanation. While in this work, the resin performance is evaluated on the results of panels and resin structure. The formulation is optimized by decrease the proportion of synthetic materials. This work is the extent of other's work on glyoxalated lignin. However, there is no report on the substitution of formaldehyde with glyoxal in soy protein-based adhesive till now.

(2) The effects of heat treatment, which is normally used to decrease the molecular weight of lignin, on lignin with low molecular weight are studied.

(3) On the precondition of a certain strength performance, different formulations are tried to increase the proportion of natural material for the preparation of environment-friendly wood adhesive. Tannin-based adhesive is introduced to lignin and soy-based adhesive.

(4) Natural mineral material montmorillonite is used as the modifier of wood adhesives. Montmorillonite has some characteristics which are helpful for it to be used as filler of wood adhesives, such as lower cost, capability to increase the viscosity, and so on. At the same time, montmorillonite is one of the most important silicate layer materials for the preparation of nano particles in the field of nano-composite. Through some procedure, nano-composite with good performance can be gotten between montmorillonite and different kind of polymers. However, there is little report on both the study to use montmorillonite as filler of UF resin and PF resin adhesives and the study of nano-composite between them.

I.7. REFERENCES

[1] Pizzi A. Condensed tannins for adhesives. Ind.Eng.Chem.Prod.Res.Dev. 1982,21: 359-369.

[2] Pizzi A. Wood Adhesives: Chemistry and Technology[M], Vol. 1, A. Pizzi (Ed), Chapter 4. Marcel Dekker, New York, NY 1983.

[3] Pizzi A. Handbook of Adhesive Tchnology, 2nd Edn, A. Pizzi and K.L.Mittal(Eds), chanpter 27. Marcel Dekker, New York, NY 2003.

[4] Pasch H, Pizzi A, Rode K. MALDI-TOF mass spectrometry of polyflavonoid tannins. Polymer. 2001,42:7531-7539.

[5] Pizzi A, Horak R M, Roux D G.. Condensates of Phenol, Resorcinol, Phloroglucinol, and Pyrogallol as Model Compounds of Flavonoid A- and B-Rings with Formaldehyde. Journal of Applied Polymer Science.1979,24:1571-1578.

[6] Pizzi A. Hot-setting tannin-urea-formaldehyde exterior wood adhesives. Adhesive Age. 1977,12:27-29.

[7] Pizzi A. H.O.Scharfetter. The chemistry and development of tannin-based adhesives for exterior plywood. Journal of Applied Polymer Science.1978,22:1745-1761.

[8] Pizzi A, Merlin M. A new class of tannin adhesives for exterior particleboard. International Journal of Adhesion and Adhesives. 1981,5(1): 261-264.

[9] Pizzi A. Exterior wood adhesives by MDI crosslinking of polyflavonoid tannin B rings. Journal of Applied Polymer Science.1980,25:2123-2127

[10] Pizzi A, Tekely P. Mechanism of Polyphenolic Tannin Resin Hardening by Hexamethylenetetramine: CP-MAS ^{13}C-NMR. Journal of Applied Polymer Science.1995,56:1645-1650.

[11] Kim S, Kim H.-J. Evaluation of formaldehyde emission of pine and wattle tannin-based adhesives by gas chromatography. Holz Roh Werkst. 2004,62:101-106.

[12] Pizzi A. H.O.Scharfetter. The chemistry and development of tannin-based adhesives for exterior plywood. Journal of Applied Polymer Science.1978,22:1745-1761.

[13] Sun W.D. Chemistry of tannin. China Forestry Publishing House. 1988:368-388.

[14] Pizzi A, Meikleham N. Induced accelerated autocondensation of polyflavonoid tannins for

phenolic polycondensates.II.CP-MAS ^{13}C-NMR of different tannins and models. Journal of Applied Polymer Science.1995,55:1265-1269.

[15] Garcia R, Pizzi A. Polycondensation and autocondensation networks in polyflavonoid tannins.I.final networks. Journal of Applied Polymer Science.1998,70:1083-1091.

[16] Masson E, Pizzi A, Merlin M. Comparative kinetics of the induced radical autocondensation of polyflavonoid tannins. Ⅱ Flavonoid units effects. Journal of Applied Polymer Science. 1997,64:243-265.

[17] Garcia R, Pizzi A, Merlin A. Ionic polycondensation effects on the radical autocondensation of polyflavonoid tannins: an ESR study. Journal of Applied Polymer Science.1997,65:2623-2633.

[18] Pizzi A, Tekely P. ^{13}C-NMR of Zn^{2+} Acetate-Induced Autocondensation of Polyflavonoid Tannins for Phenolic Polycondensates. Journal of Applied Polymer Science.1995,56:633-636.

[19] Pizzi A, Meikleham N, Stephanou A. Induced Accelerated Autocondensation of Polyflavonoid Tannins for Phenolic Polycondensates. II. Cellulose Effect and Application. Journal of Applied Polymer Science.1995,55:929-933.

[20] Pizzi A. Mechanism of viscosity variations during treatment of wattle tannins with hot NaOH. International Journal of Adhesion and Adhesives.1998,4(1):213-214.

[21] Sowunmi S, Ebewele R.O., Conner A.H., *et al*. Differential scanning calorimetry of hydrolysed mangrove tannin. Polym Int 2000,49:574-578.

[22] Gargulak J.G., Lebo, S.E. Commercial use of lignin-based materials. In: Glasser, W.G., Northey, R.A., Schultz, T.P. (Eds.). Lignin: Historical, Biological, and Materials Perspectives. ACSSymposium Series. American Chemical Society, 2000:304-320.

[23] Lora, J.H., Glasser, W.G. Recent application of lignin: a sustainable alternative to nonrenewable materials. J. Polym. Environ. 2002. 10, 39-48.

[24] Gosselink R.J.A, de Jong E, Guran B, *et al*. Co-ordination network for lignin-standardisation, production and applications adapted to market requirements (EUROLIGNIN). Ind.Crops Prod. 2004,20:121-129.

[25] Abe I. Wood adhesives from natural polyphenols. Mokuzai Kyogo. 1987, 42, 151-156.

[26] Feldman D. Lignin and its polyblends: a review, in Chemical Modification, Properties and

Usage of Lignin (T.Q. Hu Ed.), Kluwer Academics/Plenum Publishers, New York (2002)

[27] Lewis N.G., Lantzy T.R. Lignin in adhesives. Introduction and hystorical perspective. ACS symposium series Nr 397. 1989:13-26.

[28] Pecina H., Kuchne G. Lignin-phenol binder based on organocell spent liquor for wood products, Annals of Warsaw Agricultural University, Forestry and Wood Technology. 1995,46: 93-100.

[29] Roffael, E., Dix, B. Lignin and ligninsulfonate in non-conventional bonding-an overview. Holz Roh Werkstoff.1991, 49, 199-205.

[30] Shiraishi, N. Recent progress in wood dissolution and adhesives from kraft lignin, ACS symposium series Nr 397. 1989:488-495.

[31] Muller P.C, Glasser W.G. Engineering plastics from lignin.VIII. Phenolic resin prepolymer synthesis and analysis.J. Adhesion 1984; 17: 157-173.

[32] Budin D, Susa L, Volcic J. Application of modified lignosulfonates in adhesives for insulation board manufacture based on mineral wool. J. Wood Chem. Technol. 1990,10: 531-542.

[33] Barry A.O, Peng W, Riedl B. The effect of lignin content on the cure properties of phenol–formaldehyde resin as determined by differential scanning calorimetry. Holzforschung. , 1993, 47:247-252.

[34] Seller T.J, Kim M.G, Miller G.D, *et al.* Comparison of strandboards made with phenol–formaldehyde resin and modified with TVA acidhydrolysis lignin. Forest Products J. 1994,44, 63-68.

[35] Shinatani K, Sano Y, Sasaya T. Preparation of moderatetemperature setting adhesives from softwood kraft lignin. Holzforschung. 1994,48:337-342.

[36] Zhao L.W, Griggs B.F, Chen, C.L, *et al.* Utilization of softwood kraft lignin as adhesive for the manufacture of reconstituted wood. J. Wood Chem. Technol. 1994,14:127-145.

[37] Turunen M, Alvila L, Pakkanen T.T,*et al*. Modification of phenol–formaldehyde resol resins by lignin, starch, and urea. Journal of Applied Polymer Science. 2003,88:582-588.

[38] Forss K.G., Fuhrmann A. Finnish plywood, particleboard and fiberboard made with a ligninbase adhesive. Paperi ja Puu (Finland), 1976,11:817

[39] Hse X, Hong Q. Effects of phenol-formaldehyde copolymer on gluebond performance of

lignin-phenolic resin systems. In Adhesives from Renewable Resources. ed. R. W. Hemingway and A. H. Conner. ACS Symposium Series 385, 1989:96-109.

[40] Vazquez G., Antorrena G, Gonzilez J, *et al*. Lignin-phenol-formaldehyde adhesives for exterior grade plywoods. Bioresource Technology.1995,51:187-192.

[41] Vazquez G, Gonzalez J, Freire S, *et al*. Effect of chemical modification of lignin on the gluebond performance of lignin-phenolic resins. Bioresource Technology.1997, 60:191-198.

[42] Barry A.O, Peng W, Riedl B. The effect of lignin content on the cure properties of phenol-formaldehyde resin as determined by differential scanning calorimetry. Holzforschung. 1993,47:247-252.

[43] Oh Y, Sellers T, Kim M.G, et al. Evaluation of phenol-formaldehyde OSB resins modified with lignin residues from acid hydrolyzed waste newsprint. Forest Prod. J. 1994, 44(2):25-29.

[44] Sellers T, Kim M.G, Miller G.D, *et al*. Comparison of strandboards made with phenol-formaldehyde resin and resins modified with TVA acid-hydrolysis lignin. For. Prod. J., 1994,44(4):63-68.

[45] Olivares M, Aceituno H, Neiman G, *et al*. Lignin-modified phenolic adhesives for bonding radiata pine plywoods. Forest Prod. J.,1995, 45(1):63-67.

[46] Chia M.Gluability of kraft lignin copolymer resins on bonding southern pine plywood. Holzforschung, 49, 153-157.

[47] Ysbrandy R.E, Sanderson R.D, Gerischer G.F.R. Adhesives from autohydrolysis bagasse lignin, a renewable resource. Part I. The physical properties of laminates made with phenolated lignin novolacs.Holzforschung.1992,46:249-252.

[48] Nihat S.C, Nilgu O. Use of organosolv lignin in phenol-formaldehyde resins for particleboard production II. Particleboard production and properties. International Journal of Adhesion & Adhesives.2002,22:481-486.

[49] Mozaffar A.K, Sayed M.A, Ved P.M. Development and characterization of a wood adhesive using bagasse lignin. International Journal of Adhesion & Adhesives. 2004,24: 485-493.

[50] Beijing Adhesive Academy. Handbook of Adhesive Technology and Application[M].

Beijing: Navigation Publishing House, 1991:115.

[51] Lambuth A.L. Protein Adhesives for Wood. (A.Pizzi, Mittal KL. Eds) Advanced Wood Adhesive Technology. New York :Marcdel Dekker Inc,1994 : 259-281.

[52] Hettiarachchy N.S, Kalapathy U, Myers D.J. Alkalmodified Soy Proteins with Improved Adhesive and Hydrophobic Properties. J Am Oil Chem Soc.1995,72(12):1461-1464.

[53] Kalapathy U, Hettiarachchy N.S, D.J.Myers, *et al.* Alkali modification of soy proteins : effect s of salt s and disulfide bond cleavage on adhesion and viscosity. J Am Oil Chem Soc.1996,73:1063-1066.

[54] Huang W, Sun X. Adhesive properties of soy proteins modified by urea and guanidine hydrochloride. J Am Oil Chem Soc.2000,77:101-104.

[55] Petruccelli S, Anon M.C. Partial reduction of soy protein isolate disulfide bonds. J. Agric. Food Chem. 1995,43:2001–2006.

[56] Shen J.L. Solubility profile, intrinsic viscosity and optical rotational studies of acid precipitated soy protein and commercial soy isolate. J. Agric. Food Chem.1976, 24,784-788.

[57] Wescott J.M, Frihart C.R, Traska A.E. High soy containing water durable adhesives. J Adhesion Sci Technol.2006,20(8):859-873.

[58] Cheng E, Sun X.Z, Greggory S. K. Adhesive properties of modified soybean flour in wheat straw particleboard. Composites Part A: applied science and manufacturing. 2004,35:297-302.

[59] Wen Y.H. Study on the preparation of soy isolate from soy ground. Farm Products Processing.2003,10:161-171

[60] Hu C, Huang L.H,Li W.Z. Effects of 11S/7S ratios of soybean globulin protein on functionalities of soybean protein. Chinese Cereals and Oils Association. 2004,19(1):409-421.

[61] Huang W.N, Sun X.Z. Adhesive properties of soy protein modified by urea and guanidine hydrochloride. J Am Oil Chem Soc 2000,77:101-104.

[62] Cheng E Z, Sun X Z, Greggory S, *et al.* Adhesive Properties of Modified Soybean Flour in Wheat Straw Particleboard . Composites: Part A: Applied Science and Manufacturing,2004, 35 (3) : 297- 302.

[63] Luan J.M, Huang W.N, Zou Q.B. Adhesive properties of soy protein isolate prepared by urea modification and phosphorylation. China Oils and Fats. 2006,31(4):24-28.

[64] Bjorksten J. Cross linkages in protein chemistry. Advances in Protein Chemistry. 1951,6:353-358.

[65] Sun X.Z. Adhesives from modified soy protein [N] .United States Patent: 20050116796, 2005-08-04

[66] Li K.C, Peshkova S, Geng X.L. Investigation of soy protein-kymene adhesive systems for wood composites. JAOCS, 2004,81(5):487-491.

[67] Liu Y, Li K.C. Modification of soy protein for wood adhesives using mussel protein as a model: the influence of a mercapto group.Marcromol. Rapid Commun. 2004,25:1835-1838.

[68] Liu Y, Li K.C. Development and characterization of adhesives from soy protein for bonding wood，International Journal of Adhesion & Adhesives. 2007,27:59-67.

[69] A.L.Lambuth. Soybean glues[M]. Handbook of Adhesives, 2nd ed. (Skeist, I. Ed.). New York.172-180.

[70] Salmoral E, Gonzalez E, Mariscal M, *et al*. Comparison of chickpea and soy protein isolate and whole flour as biodegradable plastics. Ind Crops Prod. 2000,11:227-236.

[71] Wu W.U, Hettiarachchy N.S, Qi M. Hydrophobicity, solubility and emulsifying of soy protein peptides prepared by papain modification and ultrafiltration. J. Am. Oil Chem. Soc. 1998,75:845-850.

[72] Kalapathy U, Hettiarachchy N.S, Myers D,*et al*. Alkali modification of soy protein and their adhesive properties on woods. J. Am. Oil Chem. Soc. 1995,72:507-510.

[73] Ignjatovic N.L, Tomic S.L.J, Vrhovacc L.P, *et al*. Determination of optimal conditions for modification of urea formaldehyde adhesives by enzymatically modified soybean adhesive. Hem. Ind. 1998,52:286-289.

[74] Krinski T.L， Steinmetz A.L. Protein modified with a silanation reagent as a adhesive binder and process of producingit.US:4713116, 1987-12-15.

[75] Coco C.E, Graham P.M. Modified protein adhesive binder and method of producing.US:4474694, 1984-10-02.

[76] Poppe G, Ciesielski E.Method of producing protein products for bright paper coating

applications.US:5364465, 1994-11-15.

[77] He H.B, Chai Q.P, Wang X.G. Study on soy protein emulsion adhesive. China Adhesives. 2008,5:15-19.

[78] Zhao K, Hao X.F, Liu D.Z. Study on the composite adhesion of soy protein isolate. Journal of Zhengzhou University of Technology. 2000,21(1):15-18.

[79] Kuo M.L, Myers D.J, Heemstra H, *et al*. Soybean-based adhesive resins and composite products utilizing such adhesives. U.S.Patent 6,306,997(2001).

[80] Kuo M.L, Stokke D.D. Soybean-based adhesive resins for composite products. Wood Adhesive 2000. Forest Products Society, Madison, WI, 2001:163-165.

[81] Yang I, Kuo M.L, Myers D.J. Bond quality of soy-based phenolic adhesives in southern pine plywood. J Am Oil Chem Soc.2006,83(3):231-237.

[82] Yang I, Kuo M.L, Myers D.J, *et al*. Comparison of protein-based adhesive resins for wood composites. J Wood Sci. 2006,52:503-508.

[83] Kuo M.L, Myers D.J, Stokke D.D. Formulating Soy/melamine-urea-formaldehyde Resins for Medium Density Fiberboard,Iowa Soybean Promotion Board Project,2002

[84] Hse C.Y, Fu F, Bryant B.S. Development of formaldehyde-based wood adhesives with co-reacted phenol/soybean flour.Wood adhesives 2000.Proc. No. 7252. Forest Products Society, Madison, WI,13-19.

[85] Riebel M.J, Torgusen P.L, Roos K.D, *et al*. Bio-composite material and method of making. US patent. 1997,5635123.

[86] Wang D.H，Sun X.Z. Low density particleboard from wheat straw and corn pith，Industrial Crops and Products. 2002,15:43-50.

[87] Kreibich R.E, Steynberg P.J, Hemingway R.W. End jointing green limber with soybond, in proceedings, Wood Residues into Tevenue, Residual Wood Conference, November 4-5, Richmond BC.

[88] Steel P.H, Kreibich R.E, Steynberg P.J, *et al*. Finger jointing green southern yellow pine with a soy-based adhesive. Adhesive Age.1998,10:49-54.

[89] Mo X.Q , Hu J, Sun X.S, *et al*. Compression and Tensile Strength of Low-density Straw-protein Particleboard.Industrial Crops and Product s , 2001 (14) :1-9.

[90] Cheng E.Z , Sun X.Z , Karr S.G. Adhesive Properties of Modified Soybean Flour in Wheat

St raw Particleboard.Composites : Part A : Applied Science and Manufacturing. 2004,35 (3):297-230.

[91] Zhong Z.K, Sun X.Z, Fang X.H. Adhesion Properties of Soy Protein with Fiber Cardboard. JAOCS. 2001,78: 37-41.

[92] Pizzi A. Recent developments in eco-efficient bio-based adhesives for wood bonding:opportunities and issues. J.Adhesion Sci. Technol. 2006,20(8):829-846.

[93] Gu J.Y. Adhesive and Paint.Beijing: China Forestry Publishing House.1998:48-125.

[94] Ma W.W. The preparation of urea-formaldehyde resin modified by oxygenated amylum.Chemistry and Adhesion.1995,3:147-148.

[95] Shi Y.M. Development of the low cost urea-formaldehyde resin adhesive. China Adhesives. 2003,12(4):30-32.

[96] Du G.B, Wu L.Z, Yang Q.X. Development on mineral filler for UF resin. Adhesion. 1995,16(3):9-12.

[97] Cavicchi R.E, Silsbee R.H. Coulomb suppression of tunneling rate from small metal particles.Phys. Rew. Lett..1984, 52:1453.

[98] Ball P, Garwin L. Science at the atomic scale. Nature.l992, 355:761-766.

[99] Yu H.W,Fu S.Y,Wen G.F,et al.The effect of nanometer calcium carbonate on properties of UF resin.China Adhesives.2002,11(6):22-24.

[100] Yang G.D,Lin Q.J,Liu J.H. Study on using nanometer SiO_2 for modifying UF resin.China Wood Industry.2004,18(3):7-9.

[101] Yang G.D,Lin Q.J,Liu J.H. The effect of nanometer silicon dioxide on properties of UF resin. Journal of Fujian Forestry College. 2004,24(2):114-117.

[102] Lin Q.J, Yang G.D, Liu J.H, *et al*. Study on the property of nano-SiO2/urea-formaldehyde resin.Scientia Silvae Sinicae.2005,41(2):129-135.

[103] Ray S.S, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog. Polym. Sci. 2003,28:1539-1641.

[104] Lv J.K, Ke Y.C, Qi Z.N. Synthesis and mechanical properties of epoxy/clay nanocomposites.Acta Materiae Compositae Sinica.2002,19(1):117-121.

[105] Lan T, Kaviratna P.D, Pinnavaia T.J. Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites, Chem. Mater.,1995,7,2144-2150.

[106] Tien Y, Chen T.K., Wei K.H. Synthesis and characterization of novel segmented polyurethane/clay nanocomposites. Polymer. 2000,41:1345-1353.

[107] Carsten Zilg, Ralf Thomann, Rolf Mulhaupt *et al*. Polyurethane nanocomposites containing laminated anisotropic nanoparticles derived from organophilic layered silicates. Adv. Mater. 1999,11(1):49-52.

[108] Zhen W Thomas J. Pinnavaia. Nanolayer reinforcement of elastomeric polyurethane. Chem. Mater.1998,10:3769-3771.

[109] Dong C.L, Lee W.J. Preparation and characterization of PMMA clay hybrid composire by emulsion polymerization. Appl Polym Sci.1995,61:1117-1122.

[110] Choi M.H, Chung I.J, Lee J.D. Morphology and Curing Behaviors of Phenolic Resin-Layered Silicate Nanocomposites Prepared by Melt Intercalation. Chem. Mater. 2000,12:2977-2983.

CHAPTER II

MATERIAL AND METHODS

II.1. RESIN PREPARATION AND MATERIAL SELECT

II.1.1. Phenol-formaldehyde resin preparation and tannin extract used

This PF resin was optimized in previous work on lignin adhesive formulations[1-3]. It was the most suitable found in previous work yet was the simplest to prepare. More complex PF resins could be equally effective. A 500ml flat-bottom flask equipped with a condenser, thermometer and a magnetic stirrer bar was charged with 94 parts by mass phenol, 40 parts (20/80) methanol/water solution, and 55 parts by mass of 96% paraformaldehyde. After stirring was conducted for 30 min at 40 °C, the temperature was slowly, over the period of 30 min, increased to reflux (94°C). A total of 20 parts by mass of 33% sodium hydroxide solution was added in 4 equal parts at 15 min intervals. The mixture was refluxed for 60 min and then cooled in an ice bath to yield a pale yellow transparent resin of 750 cps and 60% solid content.

Commercial mimosa tannin extract in spray-dried, water-soluble powder form supplied by Tanac SA, (Montenegro, Brasil) was substituted for the PF resin in the mixed adhesive. The tannin was predissolved in water, and the pH corrected with 30% NaOH solution to the same pH of the glyoxalated lignin before it was mixed with the latter. In some TMA testing cases free glyoxal to react with the tannin was also added, but as this proved unnecessary the tannin was added without glyoxal to the lignin for all the wood panels made.

II.1.2. Lignin and glyoxalation of lignin

Work on GL/PF/pMDI formulations was previously done with a calcium lignosulfonate, the molecular mass of which was drastically decreased by thermal treatment in a reactor at 170 °C for 90 min at an initial pH of 12.7. This was done to decrease the molecular mass of the lignin, which means some links between lignins to be broken and more reactive places will be gotten. That is to say, thermal treatment will render the material more suitable for reaction. Other types of lignosulphonates, such as ammonium lignosulphonate are in general equally suitable for the types of formulations described when formaldehyde has been used.

In this work instead, two types of already low molecular weight lignins were used. These were (1) a wood lignin produced in India and imported/commercialized under the name of Protobind 100SA by a Swiss company and (2) an acetic acid wheat straw lignin obtained by a paper pulp from an experimental pilot factory in France. The first one of these was used as delivered, as well as after a heat treatment (GLAF) as used previously for higher molecular weight lignins**.**

Lignin powder (29.5 parts by mass, 96% solid) was slowly added to 47.65 parts water, and sodium hydroxide solution (30%) was added from time to time to keep the pH of the solution between 12 and 12.5 for better dissolution of the lignin powder; this was also facilitated by vigorous stirring with an overhead stirrer. A total of 14.1 parts by mass of sodium hydroxide solution (30%) was added, which resulted in a final pH near to 12.5.

A 250ml flat bottom flask equipped with a condenser, thermometer and magnetic stirrer bar was charged with the previous solution and heated to 58 °C. Glyoxal (17.5 parts by mass, 40% in water) was added, and the lignin solution was then continuously stirred with a magnetic stirrer/hot plate for 8 h. The solids content for all GL was around 31%.

II.1.3. Heat and pressure treatment of lignin

10 parts by weight of lignin was mixed with 100 parts by weight of 2% NaOH. The initial pH should be adjusted with 33% NaOH to be equal or higher than 12.7. Then put the glass tube full of the mixture liquid in the reactor. Pre-heat oven to 170 °C, then put the reactor well-closed in the oven for 100 min. Take the reactor out and immense the whole reactor in cold water to let the temperature of the reactor decrease as quick as possible. Open the reactor and take sample out. Neutralize the solution pH to 7 and evaporate in an evaporator of 80-90 °C water vacuum. The solid lignin treated was gotten.

II.1.4. Soy flour –formaldehyde resin preparation[4-5]

The soy flour used was a twice pre-cooked and dried commercial soy flour (CELNAT, St.Germain-la-Prade, France).

In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and condenser was charged with water (709 g), NaOH (28 g), a phase transfer agent ethylene glycol (5.3 g), and silicon oil (10 drops) and heated to 70 ºC. Soy flour (350 g) was then charged to the rapidly stirring solution. The mixture was then heated to 90 ºC over 15 min, with rapid agitation, and held between 88 ºC and 92 ºC for 1 hour. Formaldehyde 37% (134 g) was added to the hot mixture over a 5 min period, less the heat source. The mixture was allowed to stir and maintained between 88 ºC and 92 ºC for an additional 55 min. The mixture was cooled to 35 ºC in an ice bath.

II.1.5. Soy flour-formaldehyde-lignin (or phenol) preparation

In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and condenser was charged with water (709 g), NaOH (28 g), a phase transfer agent ethylene glycol (5.3 g), and silicon oil (10 drops) and heated to 70 ºC. Soy flour (350 g) was then charged to the rapidly stirring solution. The mixture was then heated to 90 ºC over 15 min, with rapid agitation, and held between 88 ºC and 92 ºC for 1 hour. Formaldehyde 37% (134 g) was added to the hot mixture over a 5 min period, less the heat source. The mixture was allowed to stir and maintained between 88 ºC and 92 ºC for an additional 55 min, followed by the addition of lignin solution (pH=12 for better dissolution of the lignin powder) (103 g of lignin and 150 g of water) while cooling to 75 ºC over a 10 minutes period. NaOH (8.8 g) was then added, followed by a second addition of formaldehyde 37% (167.6 g) and two more NaOH charges (4.4 g each). The mixture was held at 75 ºC for an additional 1.5 hours and cooled to 35 ºC in an ice bath. When an equivalent proportion by weight of phenol was added the formulation used was identical and was derived from the work of other authors.

II.1.6. Soy flour-glyoxal preparation

In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and condenser was charged with water (709 g), NaOH (28 g), a phase transfer agent ethylene glycol (5.3 g), and silicon oil (10 drops) and heated to 70 ºC. Soy flour (350 g) was then charged to the rapidly stirring solution. The mixture was then heated to 90ºC over 15 minutes, with rapid agitation, and held between 88 ºC and 92 ºC for 1 hour. Glyoxal (40% in water) (239 g) was added to the hot mixture over a 5 min period, less the heat source. The mixture was allowed to stir and maintained between 88ºC and 92 ºC for an additional 2 hours and 55 minutes. The mixture was cooled to 35 ºC in an ice bath.

The low pH was due to the formation of hydrated sodium salt of glyoxilic acid $(HO)_2CHCOO^-Na^+$ as seen in the NMR spectra. The solid contents, viscosity are shown in Table 2.1.

Table II.1. Characteristics of resins prepared with precooked soy flour by reaction with either formaldehyde or glyoxal.

Resin	Solid content(%)	Viscosity (mPa.s)	pH
(SG)- Soy flour-Glyoxal	0.32	1200	4.5
(SF)- Soy flour-Formaldehyde	0.3	880	11.04
(LBG)- Lignin(Brazil)-Glyoxal	0.31	100	13
(SFL)- Soy flour-Formaldehyde-Lignin	0.32	440	10.35

II.1.7. Blending of glyoxalated glyoxalated lignin and/or soy flour with tannin or phenolic resins and pMDI

The glyoxalated lignin water solution was thoroughly mixed with either a 45% solution of mimosa tannin extract (ex SILVA Italy, origin Tanzania) at the same pH solution or a synthetic phenol-formaldehyde resin with a solid content around 60% as indicated in the Tables. Only non emulsified polymeric pMDI (pMDI = polymeric 4,4' diphenyl methane diisocyanate) was used throughout. The diisocyanate raw polymeric MDI (pMDI) was added before application and mixed in well. In the particleboard preparation all glue mixtures did have a pH between

11.5 and 12.

II.1.8. PUF resin preparation

PUF resins with coreacted urea were prepared with a P:F molar ratio of 1:1.7. The preparation procedure used is as follows for the resin containing 24% molar proportion of urea on phenol coreacted in the resin (thus molar ratio F:[P+U] is 1.37): One mole of phenol is mixed with 0.35 moles NaOH as 30% water solution and 1.2 moles of formaldehyde (as a 37% formalin solution) in a reactor equipped of mechanical stirring, heating facilities and reflux condenser. After stirring for 10 min at 30 °C, 0.24 moles of urea are added and the temperature is slowly increased to reflux (94 °C) over a period of 30 min and under continuous mechanical stirring and kept at reflux for further 30 min. 0.5 moles of formaldehyde (as a 37% formalin solution) are then added. The reaction mix is now at pH 11 and the reaction is continued at reflux until the resin achieves a viscosity (measured at 25 °C) of between 500 and 800 mPa·s. The resin is then cooled and stored. Resin characteristics are then pH = 11, resin solids content = 50% ± 1%.

II.1.9. Montmorillonite nanoclays

The raw Na^+-montmorillonite (MMT) used with a cation exchange capacity (CEC) value of 100 meq/100 g clay, was purchased from Huate Group in ZHE JIANG, China. Organo-montmorillonite (O-MMT) was purchased from same company. This material was prepared by an ion exchange reaction between Na^+-montmorillonite and $CH_3(CH_2)_{15}$-$N(CH_3)_3Br$. Acid-modified montmorillonite(H-MMT) was obtained from Na^+-montmorillonite according to a method already presented in the literature[6]. Montmorillonite in which less than 10% of the particles in the dry clay have a diameter greater than 13 μm was used.

II.1.10. Urea-formaldehyde resins and preparation of UF/nanoclay composites

Three different UF resins were used. For particleboard a commercial UF resin of urea: formaldehyde molar ratio 1:1.1 was used. For plywood both a commercial UF resin and a laboratory manufactured resin both of urea:formaldehyde molar ratio 1:1.5. The laboratory UF

resin was prepared according to the following commercial resin procedure: 478.5 g formurea (a liquid concentrate composed of 57% formaldehyde, 23%urea and 20% water obtained from Dynea, Krems, Austria) were charged under continuous mechanical stirring in a glass reactor equipped with a reflux condenser, thermometer and pH electrode and the temperature raised to 50 °C. Urea (114.1 g) in water (111.5 g) was then charged while the temperature was maintained at 50 °C.

The pH was then adjusted to 4.8-5.0 with a 22% NaOH water solution and 8.4 g melamine were charged in the reactor. The temperature was increased to 70 °C and the pH adjusted to 7.2-7.6. The temperature was then raised as fast as possible to 90 °C. The pH now dropped by itself to 6.3-6.6. Once 90 °C had been reached the pH is adjusted to 5.4-5.6. The temperature was increased to 95 °C and 85.1 g second urea added to the reacting mixture. When the viscosity, measured at 50 °C, reached 220-250 centipoises the pH was adjusted in the 7.0-7.5 range with a 22% NaOH water solution.

Immediately after adjusting the pH, 0.6 g borax was added, followed by 36.4 g third urea, the temperature decreased rapidly to 65-70 °C and maintained at thislevel for 25 min. The resin is then cooled down to 25-30°C and the pH adjusted to 8.0-8.5 with a 22% NaOH solution. The characteristics of the finished resin where pH 8.0-8.5; solids content 64%-66%, gel time of 50-80s at 100 °C; U:F molar ratio 1:1.5. The UF resin was mixed with the montmorillonite clay by mechanically stirring for 5 min at room temperature and then leaving the mixture overnight.

II.1.11. Preparation of PF/nanocaly composites

This study is the only one in the literature so far, involving liquid phase mixing of the wood adhesive phenol formaldehyde resin with clay. Therefore, two different preparation routs of PF/nanoclay composites were tried.

The first route is based on adding montmorillonite during the resin cooking. The phenol-formaldehyde (PF) resins were prepared at molar ratio P:F 1:1.76. The preparation

procedure was as follows: 1.5 moles of phenol were mixed with 2.65 moles formaldehyde (as a 37% formalin solution) in a glass reactor equipped with mechanical stirring, thermometer and reflux condenser. NaMMT was then added at room temperature and the whole mixture was stirred overnight (12 hours). The temperature was then increased to reflux (95°C) in 30 min under continuous mechanical stirring. Once 95 °C reached, 0.25 moles NaOH (as a 30% water solution) were then added in 5 lots with each lot at 10 minutes interval. The mixture was maintained at reflux until the viscosity of resin reached 400-500 mPa·s, measured at 25 °C. The resin was then cooled and stored.

The second route, mixing after resin cooking, was as following: The PF resin was prepared exactly as the same as the first route only without NaMMT being used. The desired amount of clay was then mixed with the PF resin by a thoroughly stirring for 1 h at 45-50 °C.

II.2. CHARATERISTIC OF RESINS

II.2.1. Thermomechanical analysis

The hardening reaction of the glues mixes can be evaluated by TMA by studying the rigidity of a wood-resin joint as a function of temperature. Thus, different glues mixes as indicated in the figures and tables were analyzed by TMA in bending according to a technique already reported[7]. Triplicate samples of two beech wood plys (sliced decorative beech wood (***Fagus sylvatica***) veneers) of 0.6 mm thickness bonded with the test resins as a layer of 350 m , for a total samples dimension of 21×6×1.2 mm were tested with a Mettler 40 TMA apparatus (Mettler-Toledo, Giessen, Germany). In three points 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 (6 s/ 6 s). The classical mechanics relation between force and deflection in bending $E = [L^3/(4bh^3)][DF/(Df)]$, where L is the span, b the width, h the thickness of the specimen, F the force exercised on it and f the resultant deflection, allows the calculation of the Young's modulus E for each case tested. All TMA tests were conducted under the same conditions: heat rate = 10°C / min, 30mg of resin system, temperature range is 25-250°C. The software used for data treatment is STARe

(France). Deflection curves that permit MOE determination have been obtained by three point bending mode. The MOE of a wood-resin system gives a good indication of the end strength of the final application of the glue tested. The MOE max value and its increase as a function of time or temperature for wood-resin systems give a good indication of the possible end performance of the adhesive system tested.

II.2.2. ^{13}C CP-MAS NMR spectra

The hardened soy specimens, lignin specimens, and the original lignin and soy flour were analysed by solid state ^{13}C CP-MAS NMR. Spectra were obtained on a Bruker MSL 300 FT-NMR spectrometer at a frequency of 75.47 MHz and at sample spin of 4.0 kHz. The impulse duration at 90 °C was 4.2 ms, contact time was 1 ms, number of transients was about 1000, and the decoupling field was 59.5 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control. The spectra were accurate to 1 ppm. The spectra were run with suppression of spinning side bands.

II.2.3. FT-IR analysis

Solid state FT-IR spectra of the original lignin, lignin after treatment and the products for them to react with glyoxal were obtained by preparing KBr pills on a Shimadzu FT-IR 8200 infrared spectrophotometer (Champs sur Marne, France).

II.2.4. X-ray diffraction

Wide angle X-ray analysis (XRD) was carried out to investigate the effectiveness of the clay intercalation and if any change in crystalline structure of the UF resin and phenolic resin occurred. XRD samples of UF resins hardened at 103 °C in an oven after mixing with it 0%, 4% and 9% NaMMT were powdered and mounted on a Phillips XRD powder diffractometer for analysis. A 2θ angle range from 2° to 100° in reflection mode was scanned at 2°/min. A computer controlled wide angle goniometer coupled to a sealed tube Cu source K_α radiation (λ = 1.54056 Å) was used. The Cu K_α radiation was filtered electronically with a thin Ni filter.

The interlayer could be calculated when possible from the (001) lattice plane diffraction peak using Bragg's equation[8]. Some consideration on the cristallinity level of UF resins and phenolic resins with and without Na-MMT could be obtained from the XRD investigation.

II.2.5. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was done on UF and phenolic resins. To UF, 2% ammonium sulphate hardener was added as a 30% solution in water and 0% and 4% Na-MMT nanoclay was added. This was done to study the influence of the nanoclay on the hardening rate of the UF resin. To PF resins, 0% and 6% Na-MMT nanoclay was added. DSC scans were carried out with a A Perkin-Elmer DSC spectrometer. PYRIS^{TM} Version 4.0 software was used for data acquisition and processing. The DSC was calibrated with a standard sample before analysis. Large volume capsules containing samples were heated from 25 to 250 °C at a heating rate of 10 °C/min to obtain the exothermic curing reaction curves. Samples were cooled and reheated to establish the baseline.

II.2.6. MALDI-TOF-MS analysis

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF-MS) sample preparation are as follow: the sample was dissolved in water (4 mg/mL). The sample solution was mixed with an acetone solution (10 mg/mL acetone) of the matrix. As the matrix, dithranol was used. NaCl was not added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts, and 0.5 µL of the resulting solution was place on the MALDI target. After the evaporation of the solvent, the MALDI target was introduced into the spectrometer.

The MALDI-TOF mass spectra were recorded on a Kratos Kompact MALDI 4 instrument (Shimadzu Corporation, Kyoto, Japan). The Irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out under the following conditions: a positive polarity, a linear flight path, a high mass (20-kv acceleration voltage), and 100-150 pulse per spectrum. The delayed extraction

technique was with delay times of 200-800 ns. The mass peaks corresponded to M + Na (from natural abundance) and M + H attached cations.

II.2.7. Particleboard manufacture and testing

For natural adhesive, one-layer laboratory particleboard with dimensions of 350×300×14 mm were prepared with only core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) wood mixture at a maximum pressure of 28 kg/cm^2 and a press temperature of 195°C. The resin solids load was maintained at 10% of the total mix of lignin or soy-based adhesive. The total pressing time was maintained at 7.5min. But a series of boards prepared progressively reducing the pressing times was also done for soy-based adhesives. All particleboard were tested for dry internal bond (IB) strength.

For The performance of the UF/nanoclay composites was tested by preparing laboratory plywood and wood particleboard and evaluating respectively their tensile and internal bond (IB) strengths.

For UF/nanoclay composites, duplicate one layer laboratory particleboard of 350×310×16 mm dimensions were prepared by adding 10% total resin solids content on dry wood particles. 28kg/cm^2 was the maximum pressure used, followed by a decreasing pressure cycle. Press temperature at 195 °C and a total pressing time of 5 min were used. The panels' constant thickness was fixed by placing metal stops between the pressing platens. The aimed average density for all the panels was 700 kg/ m^3. The panels, after light surface sanding, were tested for dry internal bond (I.B.) strength. Formaldehyde emission was measured by the dessicator test method according to standard specification AS/NZS 1859.1 2004[9].

II.2.8. Plywood manufacture and testing

Duplicate three-layer laboratory plywood panels of 450×450×6 mm were prepared using two urea-formaldehyde (UF) adhesives of U:F molar ratio = 1:1.5 and beech (*Fagus sylvatica*)

veneers. To all these glue mixes were added (a) 2% ammonium sulphate hardener, solids on UF resin solids, the ammonium sulphate being predissolved to a 30% solution in water, and (b) either wheat flour or sodium montmorillonite (Na-MMT) by weight on the UF resin solids content used, as indicated in the tables and the figures. The glue-spread used was of 300-320 g/m^2 of liquid glue-mix double glue line (dgl). Pressing time was 5 minutes at 120°C and 11 kg/cm^2 pressure. The plywood panels were cut according to EN 314. After being tested for dry tensile strength other specimens were placed in boiling water for 15 and 25 minutes and several of them tested for residual tensile strength. Moisture resistance was evaluated by immersing in boiling water tensile strength specimens for 15 or 25 minutes followed by drying them overnight at room temperature.

II.3. REFERENCES

[1] Stephanou A, Pizzi A. Rapid-curing lignin-based exterior wood adhesives.I. Holzforschung 1993, 47, 439-443.

[2] Stephanou A, Pizzi A. Rapid-curing lignin-based exterior wood adhesives.II. Holzforschung. 1993,47: 501-506.

[3] Batubenga D.B, Pizzi A, Stephanou A, *et al*. Isocyanate/phenolics wood adhesives by catalytic acceleration of copolymerization. Holzforschung. 1995, 49, 84-86.

[4] Wescott J.M, Frihart C.R, Lorenz L. Durable soy-based adhesives, Proceedings Wood Adhesives 2005, Forest Products Society, Madison, Wisconsin 2006.

[5] Lorenz L, Frihart C.R, Wescott J.M. Analysis of soy flour/phenol-formaldehyde adhesives for bonding wood, Proceedings Wood Adhesives 2005, Forest Products Society, Madison, Wisconsin 2006.

[6] Wang H, Zhao T, Zhi L, *et al*. Synthesis of novolac/layered silicate nanocomposites by reaction exfoliation using acid-modified MMT. Macromolecular Rapid Communications. 2002, 23, 44-48.

[7] Yoshikawa T, Kimura K, Fujimura S. The gel permeation chromatography of phenolic compounds. Journal of Applied Polymer Science. 1971,15: 2513-2520.

[8] Yano K, Usuki A, Okada A. Synthesis and properties of polyimide-clay hybrid. Journal of Polymer Science Part A: Polymer chemistry. 1993,31:2493-2498.

[9] Australian/New Zealand standard AS/NZS 1859.1. Reconstituted wood-based panels– Specifications. Part 1: particleboard. 2004

CHAPTER III

ENVIRONMENT-FRIENDLY, MIXED TANNIN/LIGNIN WOOD RESINS

III.1. INTRODUCTION

The great majority of industrial wood products to-day is reconstituted materials held together by synthetic thermosetting adhesives. The resins used to bind them are in general formaldehyde-based adhesives. Environmental and health considerations have prompted the introduction of more severe standards regarding the emission of formaldehyde from bonded wood products. This, coupled with the increase in costs of oil-derived synthetic resins has intensified the interest in alternative resins based on natural, environment-friendly materials for wood adhesives.

The abundance of lignins of different types as a waste product in pulp mills has made such materials an attractive proposition for the preparation of adhesives ever since the pulping of wood to produce paper. The literature on the use of lignins to prepare wood adhesives is very extensive, and good reviews of it exist[1-7]. In contrast to the great number of articles regarding its utilisation, the record of its industrial use for wood adhesives is instead rather poor.

In the approach of adhesive formulations based on the polycondensation products of glyoxalated lignin (GL) with PF resins and isocyanates[8], up to 55%-60% of lignin was used on total resin solids. The rest of the material was composed of a mix of PF resins and isocyanates. The system was based on the reaction of polymeric isocyanate with premethylolated or preglyoxylated lignin, to which about 20% of a PF resol resin was added. It crosslinked both through the formation of lignin-lignin, lignin-phenol and phenol-phenol methylene bridges and by formation of urethane bridges between the hydroxymethyl groups on pre-reacted lignin and PF resin with the isocyanate, with these latter type of crosslinking in the majority. Lignin-based wood adhesives satisfying the requirements of relevant international standards for the manufacture of interior-grade and exterior-grade wood particleboard, in which formaldehyde was not used in their preparation (it was substituted by non-volatile non-toxic aldehyde, namely, glyoxal) were prepared and tested for application to wood panels, such as particleboard. Glyoxal is a non-toxic aldehyde [median lethal dose (LD_{50}) for rats $\geqslant$ 2960 mg/kg; LD_{50} for mice$\geqslant$ 1280 mg/kg] [9] and is non-volatile but less reactive than formaldehyde, which is toxic

(LD_{50} for rats$\geqslant$100 mg/kg; LD_{50} for mice $\geqslant$ 42 mg/kg)[10]. These adhesive systems worked well; panels of good strength were obtained and this at industrially significant short pressing times[11]. In the search to further increase the proportion of natural, envinronmentally friendly materials in these formulations, we tried to eliminate the PF resin from the formulations and to substitute these with vegetable polyflavonoid tannins.

In this study, we first dealt with the optimization of lignin-based adhesives for wood by attempting to eliminate the addition of a synthetic PF resin, substituting it with a natural vegetable tannin extract. The aim then was (1) to completely eliminate formaldehyde from the adhesive and (2) to increase the proportion of natural, envinronmentally friendly materials in these adhesive formulations.

III.2. RESULTS AND DISCUSSION

III.2.1 Study on the performance of different glyoxalated lignin formulations

The initial TMA results of the curing of different GL formulations, shown in Figure III.1, indicated that GL by itself gave relatively low wood-joint strength. GL cann't be used alone as wood adhesive unless it can be cross-linked furtherly. Triacetin (glycerol triacetate) is a generally very effective accelerator of the aldehyde/phenolics polycondensation reaction[15]. But in this work it seemed that its use did not improve the performance of the GL resin when being used alone (Fig. III.1). The addition of a high amount of polymeric 4,4' diphenylmethane diisocyanate (pMDI) to give a 60:40 proportion of GL to pMDI in the formulation yielded a noticeable improvement in the maximum value of the MOE on curing of the joint (Fig. III.1). The addition of triacetin accelerator, also in the case of this formulation, did not improve the performance of the resin; on the contrary, it appeared to interfere severely with its curing (Fig. III.1).

The substitution of the tracetin with the very reactive resorcinol further improved the performance of the formulation (Fig. III.1). The improvement induced by the addition of a

small proportion of resorcinol to the 60/40-GL/pMDI formulation was expected; the highly reactive sites of the resorcinol in defect functioned as condensation sites of the hydroxy methyl groups of GL. The 60/40-GL/pMDI and even more, the 60/40/5-GL/pMDI/resorcinol adhesives cured markedly faster, as can shown by the rapid increase of strength at much lower temperature than for the other adhesive formulations (Fig. III.1).

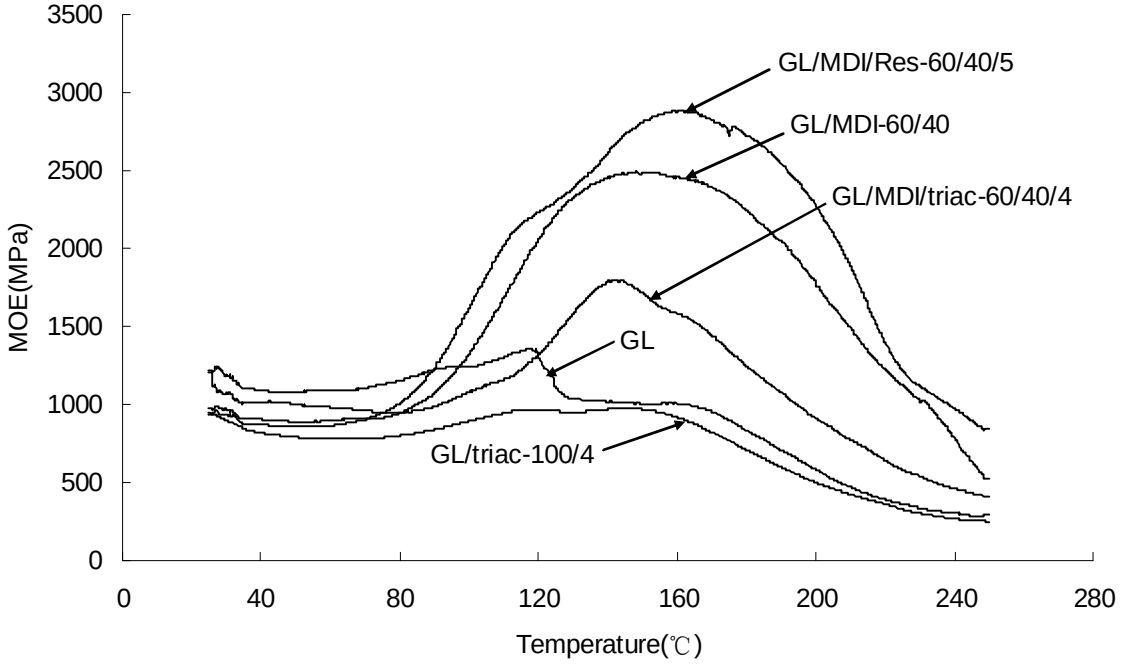


Figure III.1. TMA of different resins of low molecular weight glyoxalated hardwood lignin

The considerable improvement induced by resorcinol on the 60/40 GL/pMDI formulation was only a technical curiosity, with no real applicability in practice, for three reasons:

(1) the proportion of pMDI which is relatively expensive, 40% of the formulation on resin solids basis, was still relatively high;

(2) one should try to increase the proportion of natural material;

(3) resorcinol is far too expensive to be used as such, even in small proportion, for a thermosetting wood panel adhesive.

However, polyflavonoid tannins have reactivities with aldehydes comparable to that of resorcinol[16], and natural tannin extracts are inexpensive. We then tried to add a polyflavonoid

tannin to the formulation in place of resorcinol.

As shown in Figure III.2, a basic adhesive formulation composed of GL/pMDI/Tannin extract showed a comparable performance to the resorcinol-added formulation, but with the added advantage that the proportion of pMDI was decreased to 20% of the total when 25 wt % was tannin extract. The highly reactive sites of the tannin functioned as condensation sites of the hydroxy methyl groups of GL just as resorcinol did for the best adhesive, shown in Figure III.1. The advantages of this adhesive formulation were a much lower proportion of isocyanate (20% instead of 40%) and a greater proportion of natural materials, namely GL plus vegetable tannin extract, for a total of 80%.

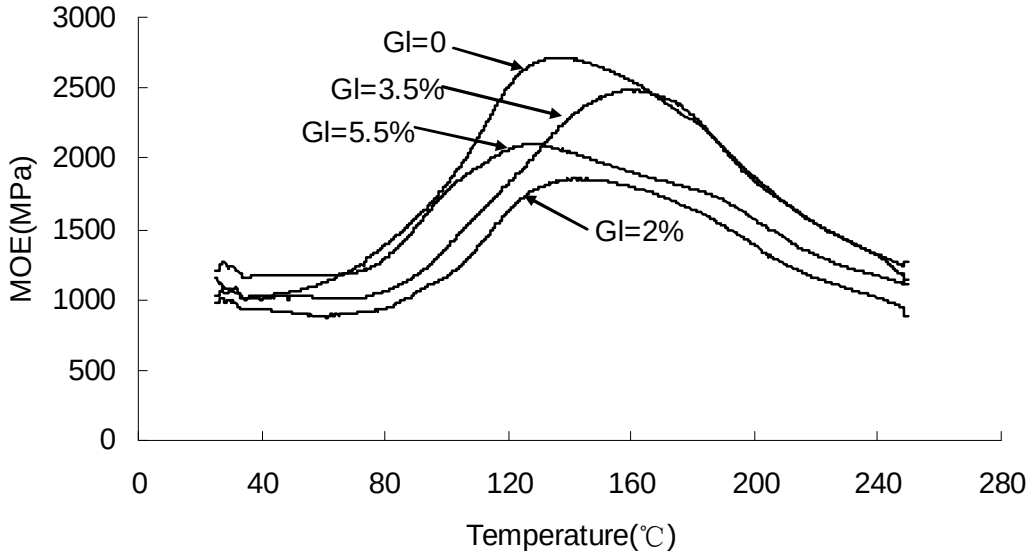


Figure III.2. TMA results of Glyoxalated lignin/pMDI/Mimosa Tannin when different amounts of free glyoxal are added in the glue-mix. The resins are based on low molecular weight glyoxalated wheat straw lignin.

III.2.2. Effects of glyoxal on the glyoxalated lignin formulation

Figure III.3 showed the results of gel time of pine tannin to which 10% paraformaldehyde and glyoxal being added. The results showed that pine tannin cured fast with paraformaldehyde and gel time shortened with the increase of pH. Tannin could react with glyoxal, too. Though the reaction is slower for tannin with glyoxal than with paraformaldehyde, the same relationship between gel time and pH could be seen. At pH 9.3, the gel time was 41s, which was very fast.

Pine tannin, for which the main units was based on phloroglucinol A rings, reacted faster with aldehyde cross-linker than mimosa tannin, for which the main units was based on resorcinol A ring. However, for the two kinds of tannins, the relationship between curing speed and pH was the same. In this work, the pH of glyoxalated lignin was in the range of 10-12, at which tannin could react fast with glyoxal. To increase the cross-linking of resins, glyoxal was added to the glyoxalated lignin formulation with tannins.

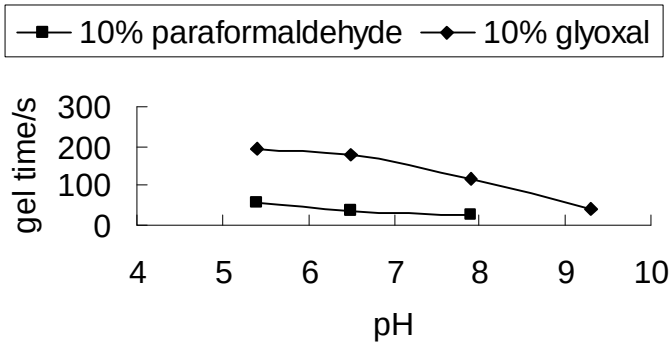


Figure III.3. Gel time of pine tannins mixed with glyoxal or paraformaldehyde

The addition of a further amount of glyoxal in the glue-mix, on the basis of the known reactivity of polyflavonoid tannins with glyoxal did not improve the performance of the adhesive and the joint (Fig.III.2). Such an addition of glyoxal in the glue mix quite apparently changed the reaction mechanism of the adhesive system, with the maximum MOE value being observed for 3.5% free glyoxal added but with the performance worsening at both higher and lower proportion of glyoxal in the formulation (Fig. III.2). What was definite was that no addition of free glyoxal still gave the best result. This reproduced what was observed for resorcinol (Fig. III.1).

As shown in Figure III.2, although the 55/20/25-GL/MDI/Tannin adhesive formulation was the faster curing formulation, as shown by the rapid increase of strength at much lower temperature than for the other adhesive formulations in the same figure, the 55/20/25/5.5 GL/MDI/Tannin/Glyoxal with extra free glyoxal added was also equally fast, which indicated that the lower value of maximum MOE obtained was due to early immobilization of the resin on curing due to the excess of glyoxal added.

III.2.3. Effects of type of lignin on the performance of glyoxalated lignin formulation

The same tendency was shown in Figure III.4 for the second type of lignin, with the formulation based on 55/20/25-GL/pMDI/Tannin giving the best results, which were, again, slightly better than those of the 60/40-GL/pMDI adhesive formulation. However, the maximum MOE values obtained with the formulations based on the second lignin in Fig. III.4, wheat straw lignin, appeared to be lower than those observed in Figure III.2. This means that, notwithsatnding that both the two lignins used were of low molecular weight, differences between each source of lignin induceed a slightly different performance in the adhesives prepared with them.

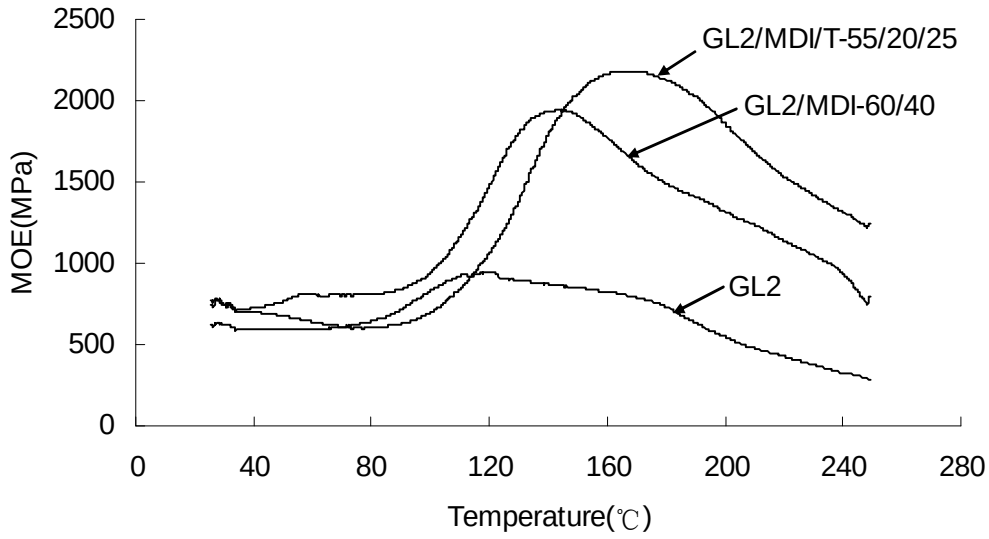


Figure III.4. TMA results of different resins of low molecular weight glyoxalated wheat straw lignin. GL with and without additives.

III.2.4. Effects of pMDI on the performance of glyoxalated lignin formulation

In Figure III.5 are reported the results of the TMA of resins in which the relatively proportion of pMDI was further decreased, namely, the 60/10/30-GL/pMDI/Tannin and 60/0/40 -GL/pMDI/Tannin, with free glyoxal added at 4% and 5.5%, respectively. The results are clearly worse than those of the 55/20/25-GL/pMDI/Tannin formulation. Thus, with this type of lignin adhesives, although the addition of the very reactive tannin allowed a marked decrease in the proportion of pMDI, it does not appear that pMDI could be eliminated completely. However,

the curve of 60/0/40/5.5-GL/MDI/Tannin/glyoxal without pMDI, shown in this figure, showed no decrease in the maximum MOE value in relation to the curve containing 10 parts pMDI, but it started curing at lower temperature; hence, this resin cured faster. Tannin is known to considerably accelerate the curing and setting of any aldhyde-based polycondensatiuon systems, and this could have been the case here, too. If this is so, the lower strength of the formulation may well have been due to early immobilization of the hardened network, and the formulation would have then behaved differently and with better performance once a wood panel was manufactured with it.

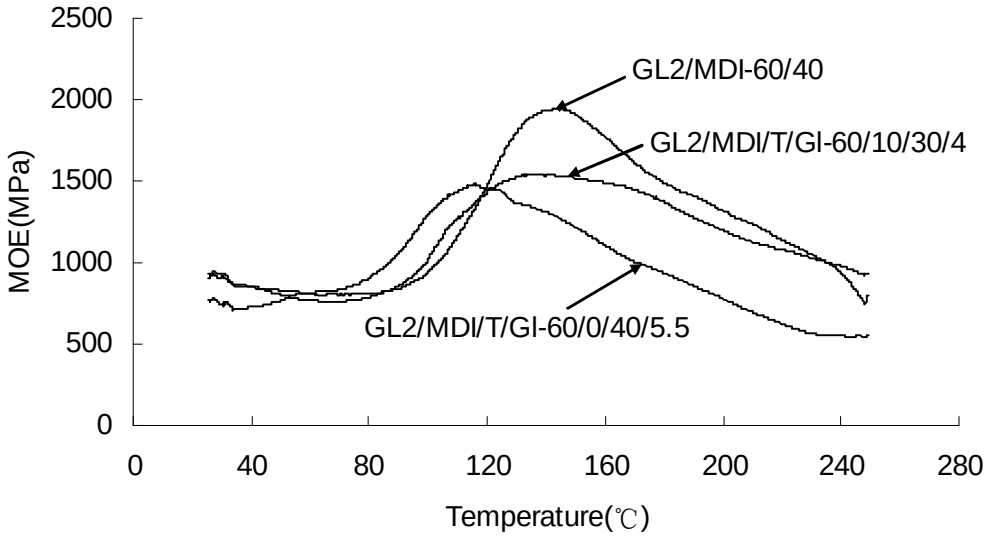


Figure III.5. TMA results of different resins of low-molecular-weight glyoxalated wheat straw lignin.

III.2.5. Strength results of glyoxalated lignin-based particleboard

In Table III.1, we reported the dry internal bond strength results of laboratory one-layer particleboard prepared with the previously defined resins. The results of the 55/25/20 -GL/pMDI/Tannin resin satisfied the requirements of the relevant international standards for dry IB strength ($\geqslant$0.35 MPa), whereas a decrease in pMDI to 15 % of the formulation appeared to decrease strength. The results of the 55/25/20-GL/pMDI/Tannin are comparable to those presented in the same table, in which a synthetic PF resin was used rather than tannin. The dependence of the formulation performance on the proportion of pMDI could be observed in the same table by the much better results of the 60/40-GL/pMDI formulation, even at a

relatively low panel density.

The application of the heat and pressure treatment, as found in the literature[12], also did not appear to improve the performance as adhesives of lignins already of fairly low molecular weight as shown in table III.1. The strength results of boards bonded with the heat treated lignin (GLAF, Table III.1) were worse than that when the original lignin itself was used.

Table III.1. Wood particleboard results of glyoxalated lignin 1 where tannin extract has been substituted to the synthetic phenol-formaldehyde resin

	Board Density(kg/m^3)	Dry IB strength(MPa)
Glyoxylated Lignin 1/pMDI/Mimosa Tannin		
55/25/20	708	0.36±0.05
55/30/15	733	0.36±0.05
60/25/15	694	0.31±0.05
60/40/0	674	0.46±0.04
60/40/0	705	0.53±0.04
GLAF		
55/25/20	733	0.31±0.05
55/25/20	725	0.38±0.09
GL/MDI/PF control		
55/25/20	701	0.35±0.04
55/20/25	673	0.31±0.05

In the formulation of 55/25/20-GL/pMDI/Tannin, there is no formaldehyde being used. Formaldehyde emission is as low as 0.018mg/L measured with the desiccator method, which is lower than F**** requisition lever 0.5mg/L of Japan comparable with E0 lever of China. So it is an environment-friendly wood resin.

Table III.2 showed in the case of another molecular weight lignin, namely wheat straw lignin, that the results obtained were of the same order of magnitude and presented the same trend as observed for the first lignin. The performance of GL/pMDI/PF and GL/pMDI/Tannin was

partly determined by the addition amount of pMDI. After PF resin being substituted by tannin, the performance of this kind of lignin formulation is worse than the first one, which indicated that the performance of resin was different when different lignin being used.

Table III.2. Wood particleboard results of glyoxalated lignin 2 where tannin extract has been substituted to the synthetic phenol-formaldehyde resin.

	Board Density(kg/m^3)	Dry IB strength(MPa)
Glyoxylated Lignin 1/pMDI/Mimosa Tannin/glyoxal		
55/25/20	698	0.36±0.05
55/20/25	673	0.31±0.05
Glyoxylated Lignin 2/pMDI/Mimosa Tannin/glyoxal		
55/25/20/3.5	681	0.19±0.06
55/20/25	692	0.16±0.05

III.2.6. Effects of heat treatment on the glyoxalated lignin

The application of the heat and pressure treatment, as found in the literature, also did not appear to improve the performance as adhesives of lignins already of fairly low molecular weight as shown in TMA results of Figure III.6.

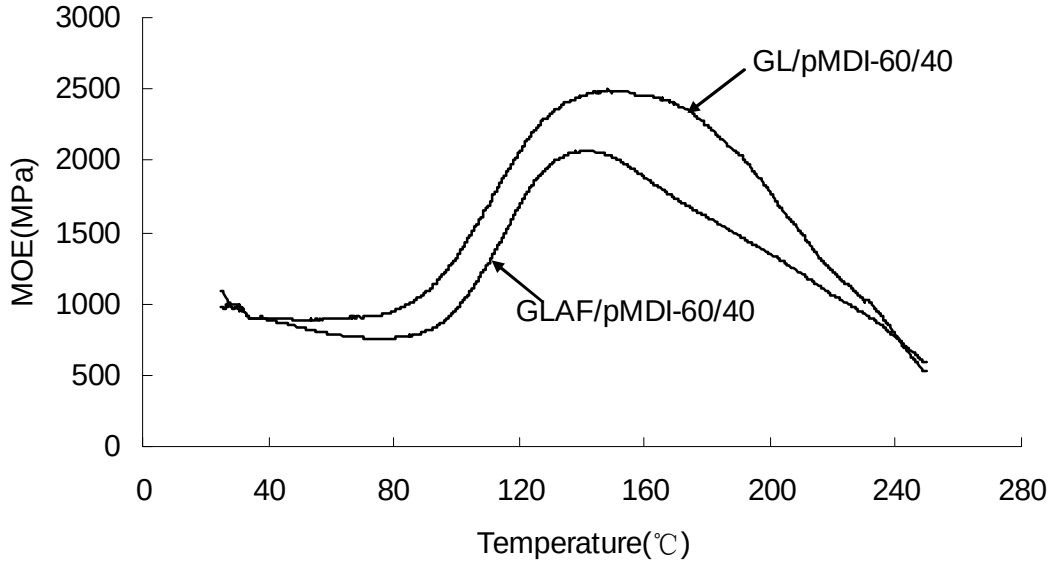


Figure III.6. TMA results of different resins of a low-molecular-weight glyoxalated hardwood lignin. GL to GLAF diffrence

To understand why this appeared to be the case, a sequence of FT-IR spectra were done of the original lignin, the original lignin after dissolution at pH 12.7, the lignin after heat treatment at 170°C for 90min, and the same lignin after redissolution in an alkaline water solution. The relevant spectra are shown respectively in Figures III.7-III.10, respectively.

The FT-IR spectroscopy is an important and forceful technique which can give usefule information about structures. It can provide basic spectra of lignin. 1605-1595cm^{-1} and 1510-1505cm^{-1} bands are assigned as aromatic skeleton structure. 1675-1660cm^{-1} bands are conjugated carbonyl and 1470-1460cm^{-1} are –CH- bending vibration. The assignment of lignin FTIR spectra can be seen the reference[17].

If one compared Figures III.7 and III.8, the disappearance of the 1210 cm^{-1} and 1270 cm^{-1} bands indicated that the heat treatment caused a certain extent of limited depolymerisation by C-O-C cleavage and demethoxylation of the original lignin. This was supported by the decrease and disappearance of 2888 cm^{-1} and 1330 cm^{-1} bands of the –CH- stretch. However, the predominance in Figure III.8 of the 1130 cm^{-1} band indicates that the β-O-4 and α-O-4 bonds were not too affected by the treatment.

The disappearance of the C=O band, a C=O conjugated to an aromatic nuclei, indicated the disappearance of the –COOH and $–COO^-$ groups present on the original structure. The 1,2,3,5-substitution pattern on the aromatic nuclei of lignin decrease was shown by the decrease of the 847 cm^{-1} band. This mainly reflects the cleavage of some of the 5-5 residual bonds between lignin units. Aliphatic $–CH_2OH$ at 1039 cm^{-1} and β-O-β bonds at 917 cm^{-1} were unaffected by the treatment. The relative intensities of the 1500 and 1600 cm^{-1} peaks indicated that this was a hardwood lignin[18].

Comparing Figures III.8 and III.9, the dissolution of the heat-treated material again in alkali showed other changes in the constitution of the lignin. Thus, the 1210 cm^{-1} and 1080 cm^{-1} bands reappeared, which indicated rearangement and some autocondensation by formation of

(Ar)C-O-C bonds, the lignin either recovering part of the limited depolymerization observed passing from Figure III.7 to Figure III.8 or possibly even slightly increasing in molecular weight. This recovery indicated that the strength performance of joints bonded with the heat treated lignin should not have been better than when the original lignin itself was used. This confirmed the results of Figure III.6, where the untreated lignin formulation slightly outperformed the heat-treated one.

The FT-IR in Figure III.10 showed the spectrum of GL. If one compared this with Figure III.7, the 1625 cm^{-1} band characteristic of the C=O of the glyoxal disappears, which indicated that either the aldehyde completely reacted or that its band was simply masked by the dominant and wide C=O band from lignin centered at 1600 cm^{-1}. However, that extensive glyoxal reaction had indeed occurred was confirmed by the dominance and relative increase of the band at 1420 cm^{-1} indicating the increase of $–CH_2-$, or better $–CH_2–CH_2-$ bridges due to the condensation reaction of glyoxal with the aromatic groups of lignin. Again, glyoxalation in a hot and alkaline environment led to cleavage of some β-O-4 and α-O-4 bridges of lignin and to its demethoxylation, as shown by the marked decrease of the 1280- and 1230-cm^{-1} bands. The glycol form HO-CH-OH of the aldehyde group of glyoxal in water was present (1080 cm^{-1}) which indicated that while this could be a cause of the disappearance of glyoxal's C=O signal at 1625 cm^{-1} part of the aldehyde reactive groups were still present in the system under this form. The 1040-cm^{-1} band of the γ -CH_2OH groups of lignin decreased markedly after glyoxalation indicating fairly extensive internal rearrangements of the lignin.

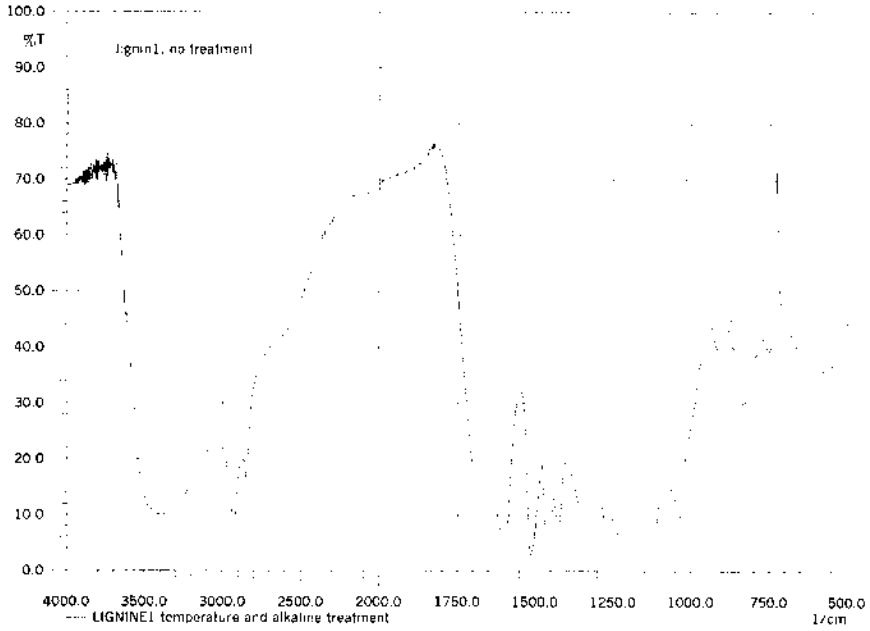
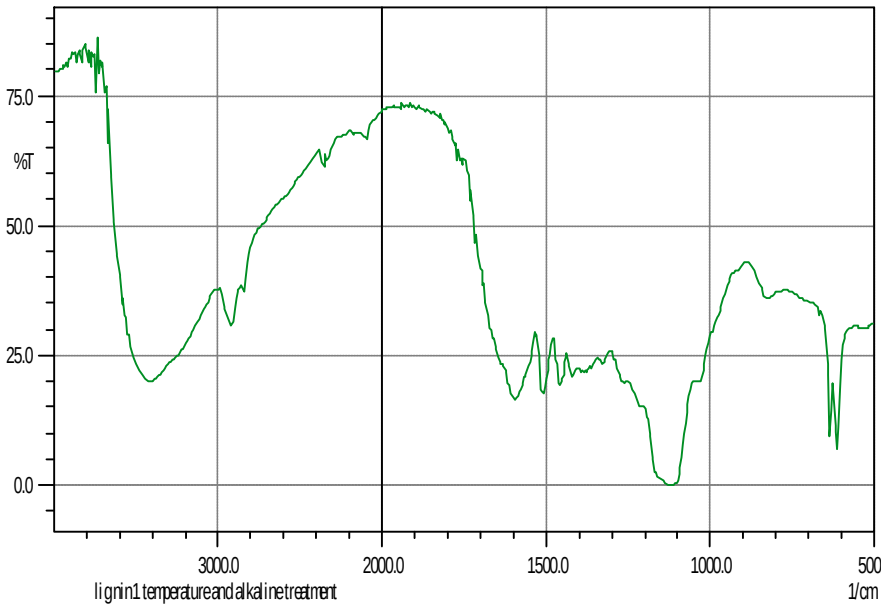


Figure. III.7. FT-IR spectrum of original low molecular weight hardwood lignin before



glyoxalation.

Figure III.8. FT-IR spectrum of low molecular weight hardwood lignin after heat treatment at 170°C for 90 minutes at pH 12.2.

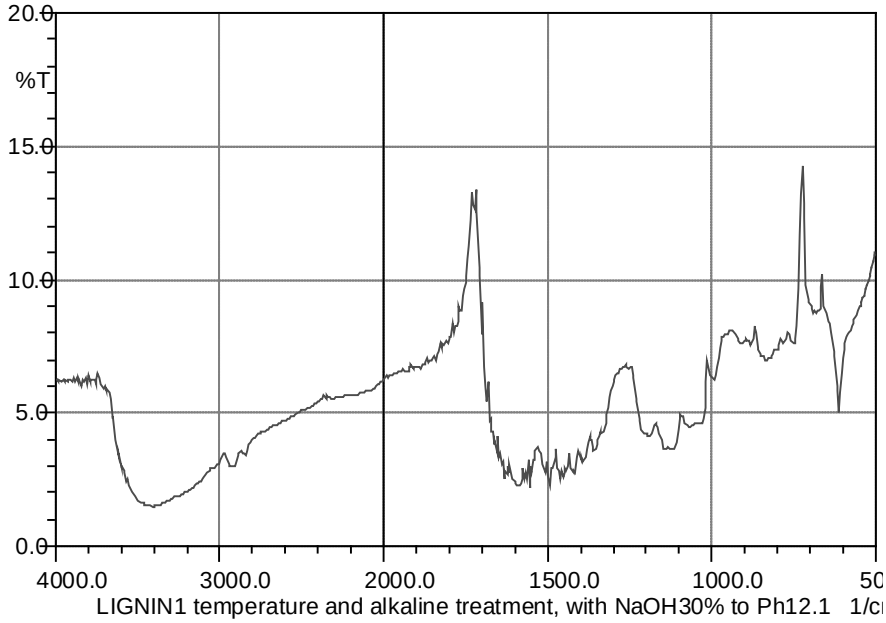


Figure III.9. FT-IR spectrum of low molecular weight hardwood lignin after heat treatment at 170°C for 90 minutes at pH 12.2 and redissolving in water at pH 12.2.

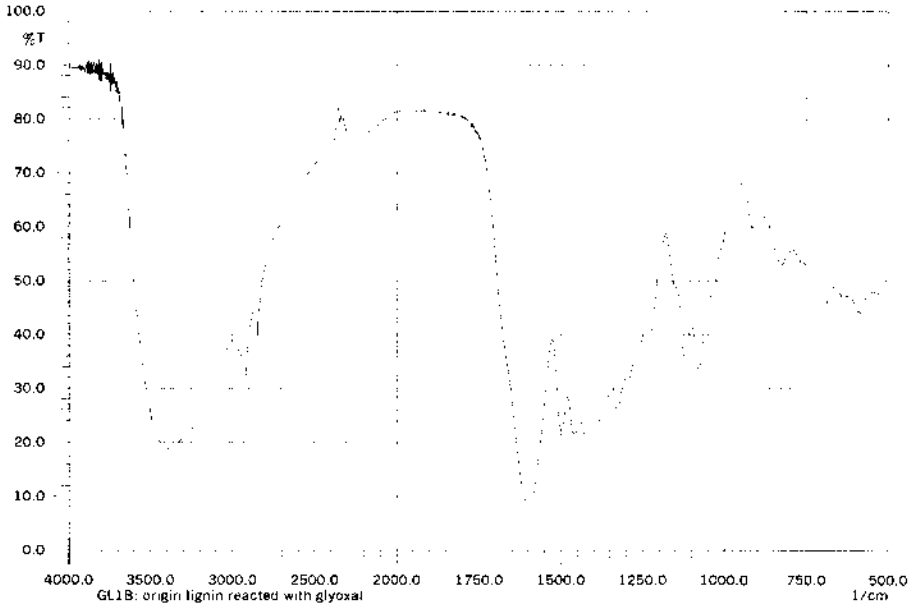


Figure III.10. FT-IR spectrum of low molecular weight glyoxalated hardwood lignin.

III.3. CONCLUSIONS

The results shown in this chapter confirmed few aspects of these fairly new tannin/lignin

formulations, namely:

(1) Triacetin had no obvious effects on the performance of glyoxalated lignin formulation.

(2) Resorcinol could improve the performance of glyoxalated lignin. The TMA results showed that the performance of the same formulation is similar with that of formulations when resorcinol being replaced by tannin.

(3) The addition of a further amount of glyoxal in the glue-mix, on the basis of the known reactivity of polyflavonoid tannins with glyoxal did not improve the performance of the adhesive and the joint. Such an addition of glyoxal in the glue mix quite apparently changed the reaction mechanism of the adhesive system.

(4) The performance of these formulations depends also on the amount or proportion of the MDI used. Although the addition of the very reactive tannin allowed a marked decrease in the proportion of pMDI, it does not appear that pMDI could be eliminated completely.

(5) Lower molecular weight lignins appear to give better IB results than higher molecular weight lignins when formulations with pMDI are used.

(6) Lignin-based wood adhesives made of glyoxalated lignin, pMDI and mimosa tannin satisfying the requirements of relevant international standards for the manufacture of wood particleboard was obtained. These lignin-based wood adhesives did not use any formaldehyde in their formulation, this having been substituted by a non-volatile non-toxic aldehyde, namely glyoxal. In this formulation, 75% the total resin solid was natural material. The formulation with weight ratio glyoxalated lignin:pMDI:tannin=55:25:20 gave a better result.

(7) The IB strength results of boards bonded with the heat-treated lignin(GLAF) are worse than when using the original lignin itself; this result was confirmed by both FT-IR and TMA. Thus, the heat treatment that is so beneficial when applied to reduce degree of polymerization of high-molecular-weight lignin in European and North American countries does not work when applied to already low-molecular-mass lignin.

III.4. REFERENCES

[1] Nimz, H. Lignin-based Adhesives, in Wood Adhesives: Chemistry and Technology, Vol. 1

(A.Pizzi Ed.), Marcel Dekker Inc. 1983.New York.

[2] Abe I. Wood adhesives from natural polyphenols. Mokuzai Kyogo. 1987, 42, 151-156.

[3] Feldman D. Lignin and its polyblends: a review, in Chemical Modification, Properties and Usage of Lignin (T.Q. Hu Ed.), Kluwer Academics/Plenum Publishers, 2002.New York.

[4] Lewis N.G., Lantzy T.R. Lignin in adhesives. Introduction and hystorical perspective. ACS symposium series Nr 397.1989:13-26.

[5] Pecina H, Kuchne G. Lignin-phenol binder based on organocell spent liquor for wood products. Annals of Warsaw Agricultural University, Forestry and Wood Technology. 1995,46:93-100.

[6] Roffael E, Dix B. Lignin and ligninsulfonate in non-conventional bonding-an overview. Holz als Roh-und Werkstoff.1991, 49, 199-205.

[7] Shiraishi N. Recent progress in wood dissolution and adhesives from kraft lignin. ACS symposium series Nr 397. 1989:488-495.

[8] El Mansouri N. -E, Pizzi A, Salvado J. Lignin-based wood panel adhesives without formaldehyde. Holz als Roh-und Werkstoff. 2007,65:65-70.

[9] NTIS** - National Technical Information Service. (Springfield, VA 22161) Formerly U.S.Clearinghouse for Scientific & Technical Information. AD-A125-539.

[10] Niosh. National Institute for Occupational Safety and Health, The registry of toxic effects of chemical substances. December 2000.

[11] Ballerini A, Despres A, Pizzi A. Non-toxic,zero emission tannin-glyoxal adhesives for wood panels. Holz Roh Werkstoff, 2005, 63, 477-478.

[12] El Mansouri, N.-E., Farriol, X, Salvado, J. Structure modification and characterization of lignosulfonate by a reaction in an alkaline medium for its incorporation into phenolic resins.J.Appl.Polymer Sci., 2006, 102, 3286-3297.

[13] Stephanou A, Pizzi A. Rapid-curing lignin-based exterior wood adhesives.I. Holzforschung 1993, 47, 439-443.

[14] Stephanou A, Pizzi A. Rapid-curing lignin-based exterior wood adhesives.II. Holzforschung. 1993,47: 501-506.

[15] Lei H, Pizzi A, Despres A, *et al*. Esters acceleration mechanisms in phenol-formaldehyde resin adhesives. Journal of Applied Polymer Science. 2006,100:3075-3093.

[16] Pizzi A, Tekely P. Mechanism of polyphenolic tannin resin hardening by hexamethylenetetramine: CP-MAS ^{13}C-NMR. J.Appl.Polym.Sci.1995,56:1645-1650.

[17] 中 野 准 三 .Lignin chemistry: bases and application.China Light Industry Press. Beijing.1988.

[18] Fengel D, Wegener G.. Wood: Chemistry, Ultrastructure, reactions, Walter de Gruyter, Berlin,1984.

CHAPITRE IV

ENVIRONMENT-FRIENDLY SOY FLOUR-BASED RESINS WITHOUT FORMALDEHYDE

IV.1. INTRODUCTION

Proteins have been used for long as wood adhesives, based on biomass rich of protein modified or subjected to some process. This kind of wood adhesive can be divided into two groups: one is based on plant-based protein adhesive (such as soy-based adhesive,etc.), the other is based on animal protein adhesive (such as blood-based adhesive, bone-based adhesive, etc.). At present the research work on plant protein adhesive is concentrated on soy-based ones. Industrially usable formaldehyde-free resins based on soy protein and soy flour have been proposed[1-3].

Poor water resistance and bonding strength are the main problems of soy-based protein adhesive. Usually soy protein needs to be modified before being used to formulate adhesives for wood panel products. It would then be used in combination with UF resins, PF resins, isocyanates, or others[4-8]. All of the approaches are good, but they still contain consistently high amounts of synthetic materials, such as formaldehyde, phenol, isocyanate and so on. These adhesives will suffer of the presence of free formaldehyde and free phenol. However, before finding a more effective cross-linking method, the combination with other resins is still a good and easy method for the usage of soy-based adhesive. Thus the main objective of this work is to modify the existing soy-based mixed formulations.

Adhesive resins in which the total content of natural material is much higher than what already achieved, and synthetic materials addition is minimised, would then be of considerable interest. This would be even more interesting if it could be coupled with the total elimination of formaldehyde while still maintaining good performance at hot pressing times of industrial significance. As in Chapter III, non-toxic, non-volatile glyoxal will be used in this chapter.

This chapter deals then with the maximisation of the natural component of the wood adhesive resins, in absence of formaldehyde, while still satisfying relevant standard requirements for wood board and their adhesives.

IV.2. RESULTS AND DISCUSSION

IV.2.1. Performance analysis of soy-formaldehyde resins

The formulations that evolved from the work reported were first scanned by thermomechanical analysis in bending according to a technique already reported. The TMA results are reported in Figs IV.1-IV.4. In Fig. IV.1 are reported the curves of MOE as a function of increasing temperature for three resins in which soy flour was reacted with formaldehyde and the soy-formaldehyde adduct reacted with soda bagasse lignin. The formulation and procedure used to prepare these soy-formaldehyde-lignin resins were the same as reported by other authors in the case of soy-formaldehyde-phenol resin[2-3](soy: phenol by weight = 66:34 to 50:50). In the resin in Fig IV.1 the relative proportions of soy flour and formaldehyde were varied from a soy:lignin weight ratio of 77/23 to 56/44 and 33/67 weight ratios. The results in Fig.IV.1 indicate that (1) sustitution of the phenol in the original resin formulation with a natural material such as lignin is possible, by this increasing the proportion of natural material in the formulation; and (2) that higher proportion of soy in the resin appeared to give better performance of the bonded joint.

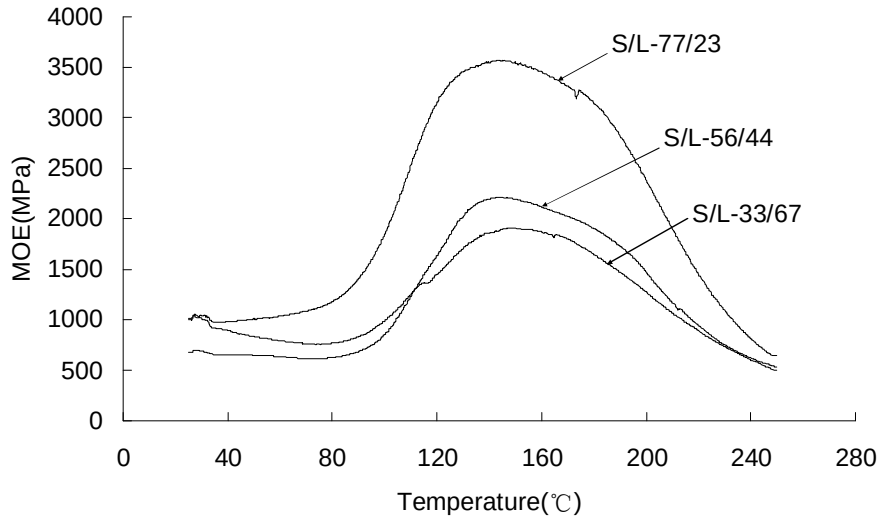


Figure IV.1. TMA results of soy flour (S) + brasilian soda bagasse lignin (L) coreacted in different proportions by weight.

The work of previous authors[2-3] detailing the preparation of soy-formaldehyde-phenol resin

envisaged then their reaction in situ in the wood board with isocyanate (pMDI, polymeric 4,4' diphenylmethane diisocyanate) to yield industrially significant results. These soy-formaldehyde-phenol-pMDI resins presented relative weight proportions of soy:phenol:pMDI = 60:31:9, these proportions yielding the best performing resins. However, at first these results could not be reproduced by substituting lignin to phenol in the original formulation (the performance of the original formulation was checked and found to be good). For this reason the formulation was altered to take into account resins that were developed by adding just in the glue mix both pMDI and natural condensed tannins to lignin prereacted either with formaldehyde or glyoxal[9-10].

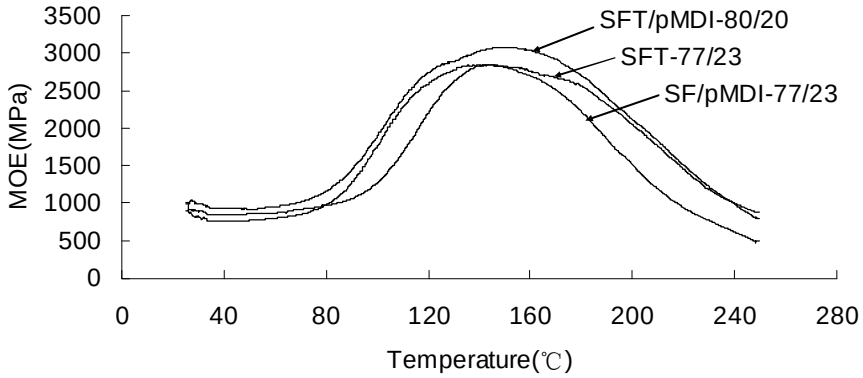


Figure IV.2. TMA results of soy flour reacted with formaldehyde (SF) to which has been added in the glue-mix before application to wood both a water solution of condensed tannin and pMDI. The proportion of natural material to synthetic material are given (SFT/pMDI = 80/20, and SF/pMDI = 80/20), as well as the proportion of SF/tannin when the synthetic resin is absent.

Fig. IV.2 shows the TMA results of soy-formaldehyde-tannin, soy-formaldehyde- pMDI and soy-formaldehyde-tannin-pMDI resins in which the relative proportions of soy-tannin extract = 77:23 by weight, and of soy+tannin: pMDI = 80:20 by weight. The maximum MOE value is a good indication of the final performance of resins. From the cures, it seems that all these show that the results that can be obtained can be acceptable. The maximium MOE of Fig. IV.2 is higher than that of Fig. IV.1, which indicated that the performance of system of soy/tannin/pMDI was better than that of formulations with lignin. In Fig. IV.2, the MOE of the three formulations with tannin increased from about 80ºC, while for formulations with lignin it

increased from about 100 ºC. The addition of tannin and pMDI could accelerate the curing of resins, which accorded with the high reactivity of tannin and pMDI.

It must be pointed out that differently from the lignin that is prereacted with soy and formaldehyde in the reactor, the tannin is not, as it is just added in the glue-mix as for the pMDI.

Table IV.2. Laboratory wood particleboard results of different soy flour resins. Pressing time 7.5 minutes, thickness 14 mm, 190°-195°C press temperature, 10% dry adhesive on dry wood.

Soy flour – Formaldehyde	Viscosity (mPa·s)	Density (kg/m^3)	IB strength (MPa)
(SFLB/p)- Soy flour-Formaldehyde-Lignin Br/pMDI 80-20	440	712	0.37
(SF/p)- Soy flour-Formaldehyde/pMDI 80-20	880	717	0.38
(SFT)- Soy flour-Formaldehyde-Tannin 77-23	1000	713	0.23
(SFT/p)-Soy flour-Formaldehyde-Tannin77-23/pMDI 80-20	1280	718	0.41

[SF: soy-formaldehyde resin; T: tannin; LB: lignin from Brasil]

Table IV.2 reports the results of laboratory wood particleboard obtained using these adhesives. From these it can be seen that the soy-formaldehyde-tannin resin alone does not satisfy the internal bond (IB) strength results required ($\geqslant$ 0.35MPa). However, soy-lignin-formaldehyde-pMDI (soy:lignin:pMDI = 62:18:20 by weight), soy-formaldehyde-pMDI (soy:pMDI = 80:20 by weight) and soy-formaldehyde-tannin-pMDI (soy:tannin:pMDI = 62:18:20 by weight) satisfy the relevant requirements of standard specifications for interior type wood particleboard[11]. In the three systems, the addition amount of natural material (soy, lignin and tannin) is as high as 80% on the total solid resin. This results show that boards in which the binder is 80% composed of natural material are possible. The addition of pMDI partly determined the cross-linking and the performance of final resin. It was obvious that small amount of pMDI could increase greatly the performance of final resin. pMDI was an effective cross-linker of soy protein and tannin adhesive. The strength differences

between different soy-formaldehyde formulations, to all of which pMDI was added, were very small. It indicated that some of the soy-based adhesive could be substituted with condensed tannin or lignin adhesives. With tannin, the strength was better.

IV.2.2. Performance of glyoxalated soy-based adhesives

The problem that remains is the presence of the formaldehyde. However, previous studies on the use of a non-toxic, non-volatile aldehyde, glyoxal, for both tannin and lignin adhesives have shown that glyoxal can well substitute formaldehyde in natural materials for polycondensation resins. Considering the relative conclusions of the Chaper III, the same method is used to diminish the toxicity of resins caused by formaldehyde.

Fig. IV.3 shows the TMA results of formulations in which the reaction product of soy with formaldehyde has been substituted by the reaction resin of soy flour with glyoxal (SG), using the same proportions by weight of aldehyde and natural material. These show that SG/tannin(T) 77/23, SG/pMDI 80/20, SG/pMDI 60/40 formulations but particularly SG/T/pMDI resins 80/20 and 60/40 (in which SG:T = 77:23 by weight) appear to give acceptable results. It seems that with the same addition amount of pMDI to replace part of soy adhesive with tannin will improve the performance of final resin. The maximium of MOE of soy-glyoxal adhesive formulations are comparative to that of soy-formaldehyde adhesive, all of which are between 2000 MPa and 3000 MPa. As the TMA results are only indicative, wood particleboard were also prepared to check the performance of these resins. The results in Table IV.3 indicate that the SG/pMDI 60/40 resin is an excellent one, but the high proportion of pMDI renders it possibly too expensive for application, and with a proportion of natural material which is too low. The SG/T 77/23 formulation without pMDI being used that still appeares reasonable in the TMA gives bad board results, which indicates that it is the same as in soy-formaldehyde adhesives that the performance of soy-glyoxal adhesives depends on the addition amount of pMDI in great degree. Without pMDI, the strength of soy-glyoxal adhesives is not enough for the preparation of particleboard.

The results of formulation SG+T/pMDI-80/20 is similar to that of SG/pMDI-80/20, which indicates that part of soy adhesive can be replaced by tannin. From the results of TMA, the same conclusion has been gotten. However, the low internal strength 0.04 MPa of SG/T-77/23 show that probably there is no reaction between the two kinds of adhesive, soy-glyoxal resin and tannin. The reaction between tannin and pMDI has possibly led to the substitution for soy-based adhesive with tannin. The internal strength of formulations SG+T/pMDI-80/20 and SG/pMDI-80/20 is too low to satisfy the requisition of relevant international standard. In these formulations, the addition amount of pMDI is not enough to make sure the effective reaction between SG and tannin. To increase the addition amount to 30% of total solid resin, the performance of resin increased greatly.

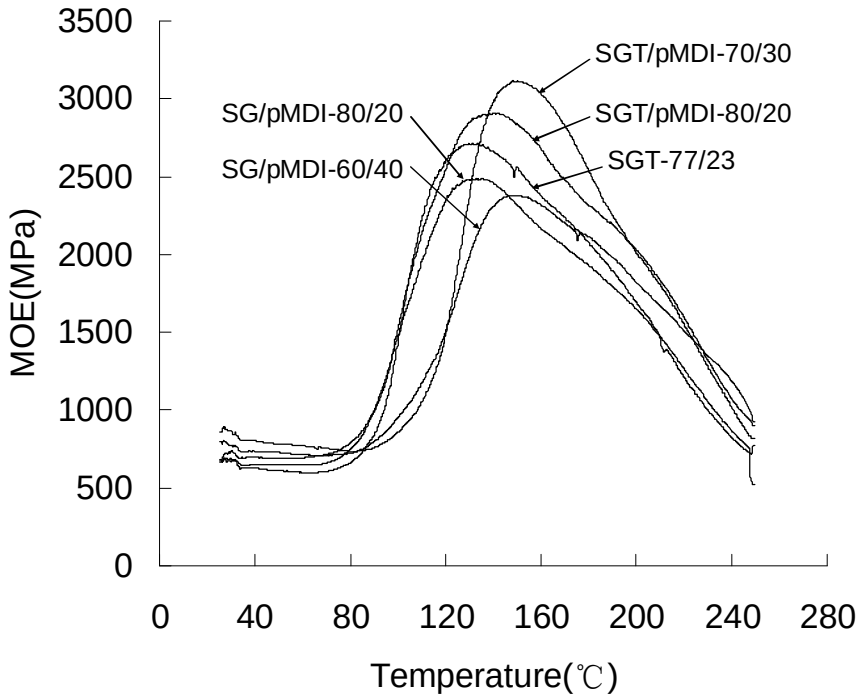


Figure IV.3. TMA results of soy flour reacted with glyoxal (SG) to which has been added in the glue-mix before application to wood both a water solution of condensed tannin and pMDI. The proportion of natural material to synthetic material are given (for example SGT/PMDI = 80/20), as well as the proportion of SG/tannin when the synthetic resin is absent.

The formulation SG/T/pMDI where SG+T/pMDI is 70/30 and the total proportions by weight are 54/16/30, for a still rather satisfactory total of 70% natural material and no formaldehyde gives also a very good result. Due to the lower reactivity of glyoxal[12] in relation to

formaldehyde the need to decrease natural material and to increase pMDI was foreseable.

Table IV.3. Laboratory wood particleboard results of different soy flour resins. Pressing time 7.5 minutes, thickness 14 mm, 190°-195°C press temperature, 10% dry adhesive on dry wood.

Soy flour – Glyoxal	Viscosity (mPa·s)	Density (kg/m^3)	IB strength (MPa)
(SG/p)- Soy flour-Glyoxal/pMDI 80-20	1200	705	0.25
(SG/p)- Soy flour-Glyoxal/pMDI 60-40	1200	712	0.72
(SGT)- Soy flour-Glyoxal-Tannin 77-23	1760	693	0.04
(SGT/p)- Soy flour-Glyoxal-Tannin 77-23/pMDI 80-20	1760	704	0.32
(SGT/p)- Soy flour-Glyoxal-Tannin 77-23/pMDI 70-30	1760	712	0.74

IV.2.3. Structure analysis of soy-based adhesives

The results of Tab. IV.2 and Tab. IV.3 with formulations SF/T-77/23(IB=0.23 MPa), SG/T-77/23(IB=0.04 MPa), SFT/pMDI-80/20(IB=0.41 MPa) and SGT/PMDI-80/20(IB=0.32 MPa) indicate that the performances of soy-glyoxal resins is worse than that of soy-formaldehyde. The SF/T/pMDI and SG/T/pMDI resins show a great difference, too. The reasons for that can be observed by CP-MAS ^{13}C NMR in Figs. IV.4, IV.5, IV.6. In Fig IV.4 is reported the spectrum of the double precooked soy flour used for this study with its characteristic peak at 172.8 ppm characteristic of the –C=O of the keletal peptidic link of the protein (-NH-CO-) and the characteristic pattern of the carbohydrates balance present in the flour suchas C1 (104.9 ppm), C4 (81.6 ppm), C3,C5 (72.5 ppm), C6 (60-62 ppm) and the CH_3-(20-30 ppm). Comparing it with Fig. IV.5 where the spectrum of the reaction product of soy with formaldehyde is shown it can be noted that intense band at 63.9 ppm due to the >N–CH_2OH group due to the reaction of the amide group of the soy protein with the formaldehyde.

There is also the noticeable growth of a band at 33 ppm, this possibly attributed to the formation of formaldehyde-derived methylene bridges linking skeletal amido groups of the protein and/or amino side groups in of certain aminoacids in the protein. Comparing this spectrum (Fig. IV.5) with that of glyoxalated soy flour (Fig. IV.6), we can see that the new peak with the same intense now shifted to 62.6 ppm and representing here the reactive >N-CHR-OH group due to the reaction of the amide group of the soy protein with glyoxal. The peak is even more intense in Fig.IV.6 than in Fig. IV.5 indicating that possibly a greater amount of glyoxal remains reacted in this form than is these for formaldehyde. This is supported by the absence in Fig. IV.6 of a band for the –CHR bridge around 33 ppm equivalent to the -N-CH_2-N- bridge band noted for the soy-formaldehyde resin. This is in accord with the lower reactivity of glyoxal in relation to formaldehyde. The greater proportion of these reactive groups present in SG, due to their lack of further transformation into bridges, explains why soy-glyoxal resins do react better than formaldehyde-based ones with either tannin and pMDI, both of these being very reactive with >N-CHR-OH groups and >N–CH_2OH groups[13-16].In this work, pMDI is a necessary cross-linker to glyoxalated soy protein adhesive. Its addition amount determines performance of final resin.

The results of Fig. IV.6 show us that there is almost no condensation reaction between the reactive groups of soy-glyoxal resins system. It needs more pMDI for soy-glyoxal resin than for soy-formaldehyde resin to get the same strength results since there are more reactive groups in soy-glyoxal system. Small addition amount of pMDI will increase the performance of soy-glyoxal greatly.

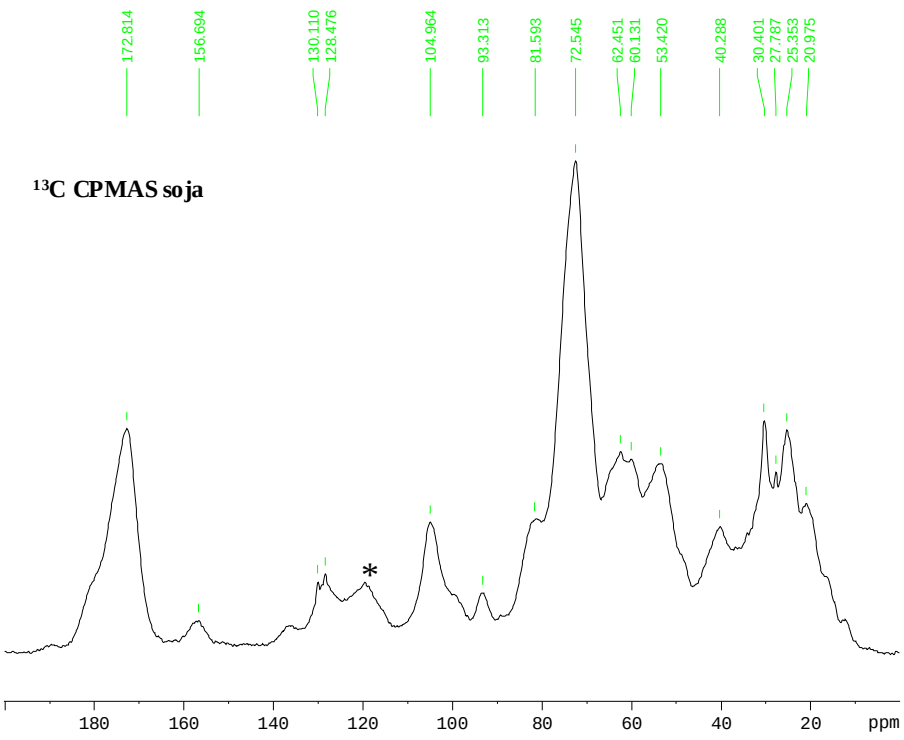


Figure IV.4. CP-MAS ^{13}C NMR of double precooked soy flour raw material.

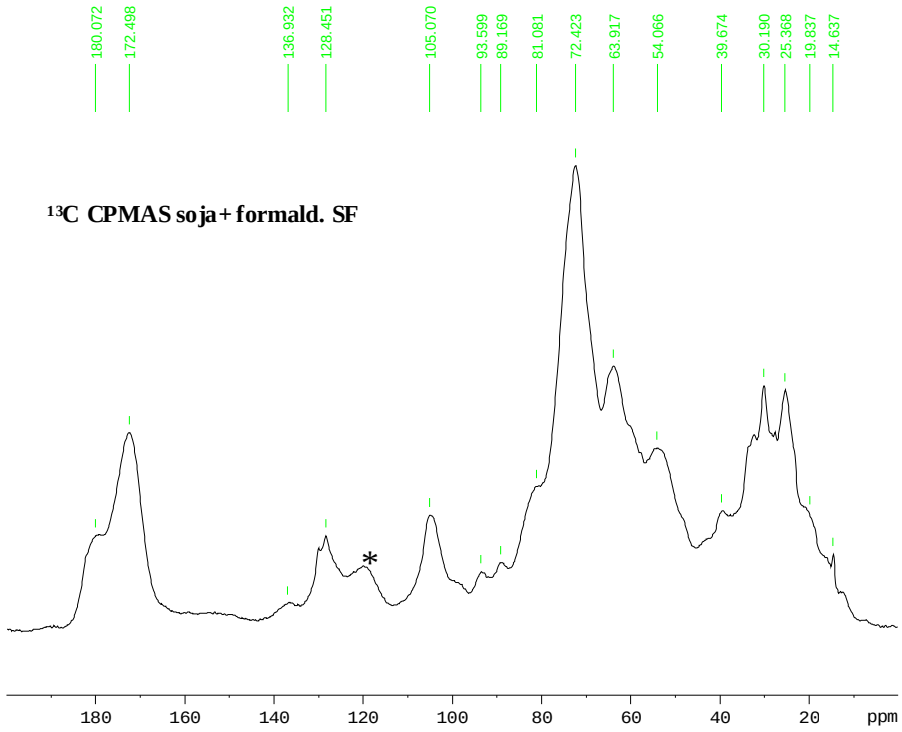


Figure IV.5. CP-MAS ^{13}C NMR of double precooked soy flour reacted with formaldehyde.

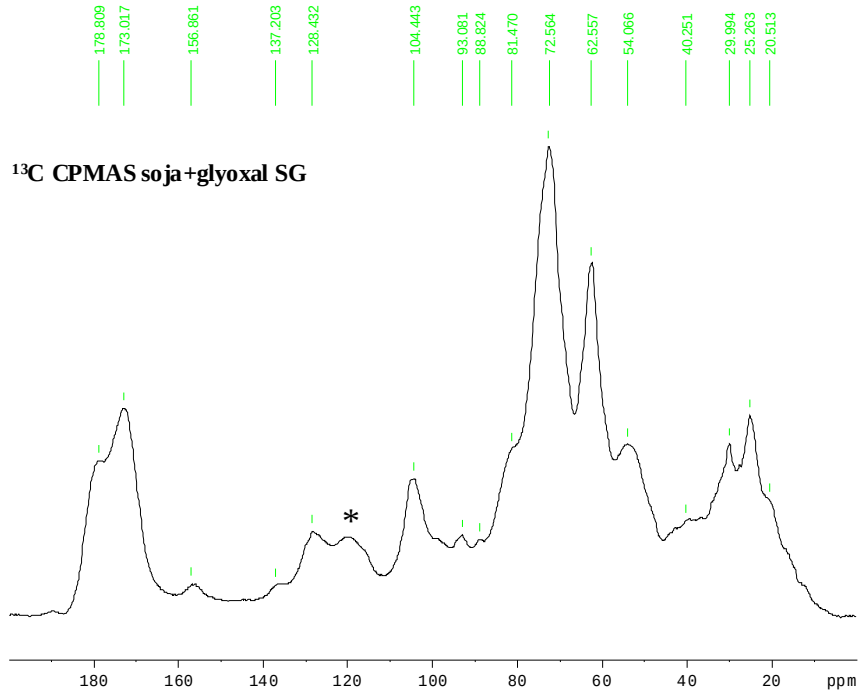


Figure IV.6. CP-MAS ^{13}C NMR of double precooked soy flour reacted with glyoxal.

IV.2.4. Effect of preparation process of particleboard on its performance

There are many factors to interfere the performance of panels, such as press procedure, performance of adhesives, resin load, species of wood, moisture content of particles, and so on. Any change of these factors will have some effects on the final strength of panels. To optimize the preparation process is always a key to panel industry.

The results in Table IV.4 show that the SG/T/pMDI-54/16/30 formulation can be used at lower weight percentages than the 10% used for the results in Tables IV.1, IV.2 and IV.3. Thus, decreasing resin solids content on dry wood from 10% even down to 7% yield, a considerable decrease, still yields IB strength results satisfying the relevant standard specifications for interior grade boards, and this without any formaldehyde being used. In Table IV.5 are also reported the results of a series in which boards using the same formulation are pressed at progressively faster pressing times. Again, pressing time as short as 2.5 minutes for 16 mm thick panels, hence of 9.4 s/mm panel thickness at 190-195°C press temperature is achieved (Table IV.5) while still satisfying the relevant international standard specifications for interior

grade boards. If it is considered that industrial press temperatures are today around 220 °C then the pressing time which derive from this result are industrially significant.

Table IV.4. Effect of percentage resin solids content on board dry wood on the performance of particleboard with best glyoxalated soy flour resin formulation (SG/T/pMDI = 54/16/30 by weight).

Resin load	viscosity(mPa·s)	density(kg/m^3)	IB strength (MPa)
10%	1760	712	0.74
9%	1760	713	0.55
8%	1760	712	0.56
7%	1760	702	0.49

Table IV.5. Effect of pressing time on the performance of particleboard with best glyoxalated soy flour resin formulation (SG/T/pMDI = 54/16/30 by weight).

Press time （min）	viscocity(mPa·s)	density(kg/m^3)	IB strength(MPa)
7.5	1760	712	0.74
6.5	1760	702	0.77
5.5	1760	711	0.75
4.5	1760	696	0.62
3.5	1760	688	0.5
2.5	1760	711	0.47

IV.2.5. Effects of glyoxal on the structure of lignin

The ^{13}C-NMR spectra of lignin can be divided into three main segments: the first (200-165ppm) contains signals assignable to carbonyl carbons; the second (165-100ppm) is ascribable to aromatic and olefinic carbons; the third (100-10ppm) is attributed to aliphatic carbon atoms. Methoxyl carbons signals appear at 56.3±0.2ppm. The assignment can be summarized as Table IV.6.

In Figs. IV.7 and IV.8 are reported the CP-MAS ^{13}C NMR spectra of the brazilian soda bagasse

lignin before and after glyoxalation. Comparing the two spectra, in Fig. IV.8 can be seen different features consequence of the reaction of lignin with glyoxal. The most evident is the appearance of a strong band at 62.2 ppm representing the –CHR-OH group of the benzylic alcohol derived from the first attack of the aldehyde on the aromatic nuclei of lignin. The decrease and disaappearance of the 133.5 ppm (Fig. IV.7) band of one type of meta sites on the crowded aromatic nuclei of lignin indicating that some reaction in meta has ocurred, on the units in which all the ortho and para positions are already blocked, such as SG lignins.

Table IV.6. Assignments of ^{13}C-NMR of lignin

Group assignments	Chemical shifs（ppm）
Acetoxy carbonyls,-C=O	200-160
Aromatic and unsaturated aliphatic carbons,C=C	160-100
Aliphatic carbons, Cα、Cβ、Cγ	90-20
Methoxyl carbons,-OCH3	56.3±0.2

The disappearance of the two bands at 147.4 ppm and 152.9 ppm accompanied by the growth of the single band of the aromatic nuclei carbon (Ar)C-O- at 150.7 ppm. This can be due either to demethylation of the methoxy groups of SG (Syringyl-Gaiacyl) lignin, or to the cleavage of the Beta-O-4 link between two lignin unit, easily cleaved[17], and the appearance of a (Ar)C-OH group increasing the reactivity of the ring towards the aromatic ring of the lignin towards the aldehyde. Equally noticeable is the appearance of the sharp intense 181.9 ppm band atributed to HO-CH_2-COO^-Na^+ and the same form attached to lignin namely L-CH_2-COO^-Na^+ due to the known reaction of glyoxal in water[18-19].

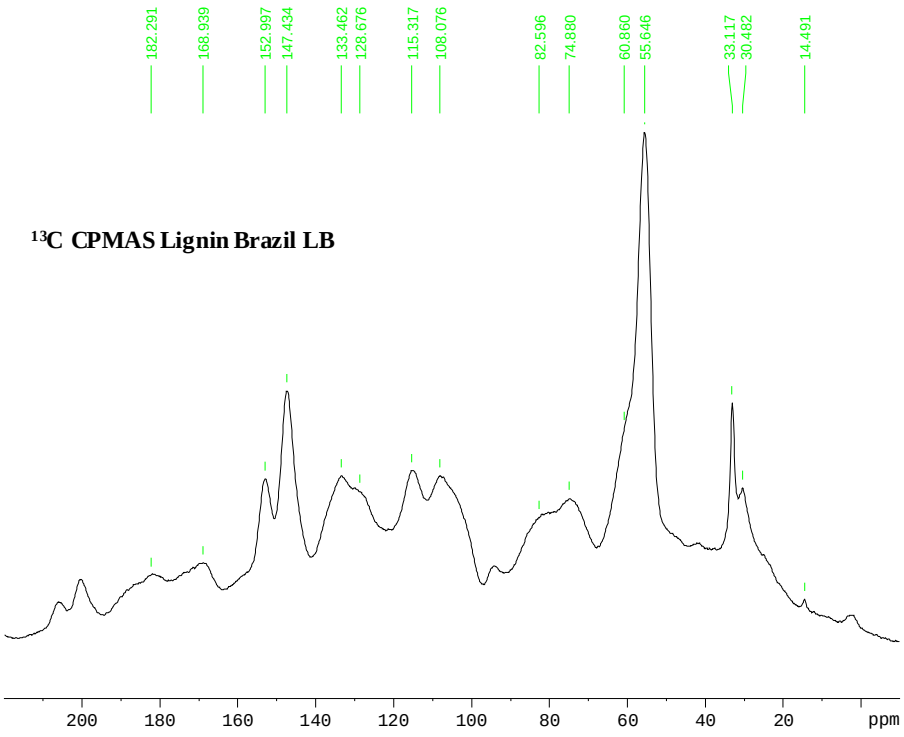


Figure IV.7. CP-MAS ^{13}C NMR of soda bagasse lignin ex Brazil. Starting raw material.

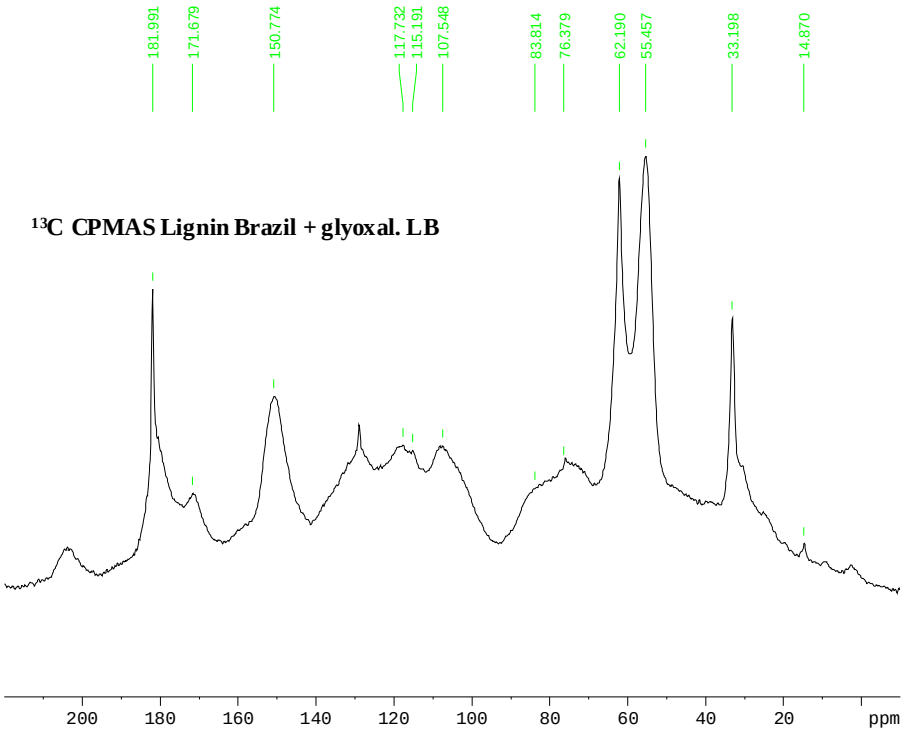


Figure IV.8. CP-MAS ^{13}C NMR of glyoxalated soda bagasse lignin.

IV.2.6. Effects of glyoxalated lignin on the performance of mix-glue

A further, different approach to increase the natural polymers content of the adhesive formulation was tried, by mixing pre-glyoxalated lignin with preglyoxalated soy flour (Table IV.7) in place of either the PF resin or the tannin used in the formulations discussed previously. Two types of lower molecular weight lignins were used, namely soda bagasse lignin ex Brazil and and a partially depolymerized wood lignin ex India. Two resin formulations were used: SG/LG/PMDI 50/25/25 and 25/50/25. The other formulations in Table IV.7 are control formulations obtained from other authors[2-3,10].

Table IV.7. Laboratory wood particleboard results of different mixed glyoxalated soy flour/glyoxalated lignin in relation to control formulations. Two different lignins were used: soda bagasse lignin Brazil ex Brazil (LBG) and low molecular weight wood lignin ex India. Pressing time = 7.5 min, thickness 14 mm, press temperature 190°-195°C.

Mixed soy-glyoxal and lignin-glyoxal	Viscosity (mPa·s)	Density (kg/m^3)	IB (MPa)
(LG/p/PF)- Lignin-Glyoxal/pMDI/PF 55/25/20, control	100	695	0.52
(LG/p)- Lignin-Glyoxal/pMDI 60/40, control	100	704	0.55
(LG/T/p)- Lignin-Glyoxal/Tannin/pMDI 55/20/25, control	1760	710	0.36
(LBG/SG/p) -Lignin-Glyoxal/Soy flour-Glyoxal /pMDI 25/50/25	1760	702	0.48
(LIG/SG/p) -Lignin-Glyoxal/Soy flour-Glyoxal/pMDI 25/50/25	1760	718	0.47
(LIG/SG/p) -Lignin-Glyoxal/Soy flour-Glyoxal/pMDI 50/25/25	1760	708	0.38

The results in Table IV.7 show that all the experimental formulation yield boards satisfying the relevant interior grade standard specifications. They showed too that glyoxalated soy flour gives better results than glyoxalated lignin so that in such mixed SG/LG formulations it is better

to maximize glyoxylated soy than glyoxalated lignin. Finally, there is no difference in behaviour of the two different lignins as regards performance. The thermomechanical results in Fig. IV.7 support the board results shown in Table IV.7.

Figure IV.9. Curves of Young's modulus as a function of temperature obtained by thermomechanical analysis (TMA) of mixed resins baed on glyoxalated soy flour and glyoxalated lignin. Glyoxalated soda bagasse lignin ex Brazil (LBG) and low molecular weight wood lignin ex India (LIG) were used.

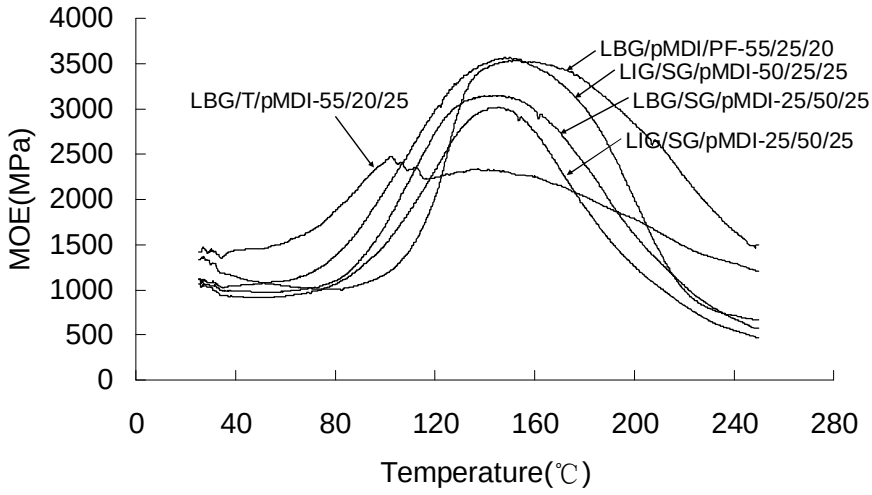


Figure IV.9. TMA results of mixed resins based on glyoxalated soy flour and glyoxalated lignin. Glyoxalated soda bagasse lignin ex Brazil (LBG) and low molecular weight wood lignin ex India (LIG) were used.

IV.3. CONCLUSIONS

Using TMA analysis and particleboard testing, some work was done on soy-based protein adhesive. The effects of tannin, glyoxalated lignin and pMDI on the performance of soy-formaldehyde and soy-glyoxal were testing. With CP-MAS ^{13}C-NMR, the reaction of glyoxal with soy protein and lignin was analized, too. Some conclusion could be gotten:

(1) Glyoxalated soy flour adhesives for wood particleboard added of a much smaller proportion of glyoxalated lignin or of tannin and without any addition of either formaldehyde or formaldehyde based resin are shown to yield results satisfying the relevant standard

specifications for interior wood boards. Adhesive resins formulations in which the total content of natural material is either 70% or 80% of the total resin solids content gave good results.

(2) The performance of soy-formaldehyde and soy-glyoxal adhesives was determined by the addition amount of pMDI in a great degree. It seemed that the addition of pMDI was more important to the latter than to the former.

(3) TMA and particleboard results showed that some soy-based protein adhesive could be replaced by tannin. However, the low strength for the formulation SG/T-77/23 indicated that there was probably no reaction between glyoxalated soy protein and tannin. The improvement of strength when using tannin to substitute soy protein came from the reaction between tannin and pMDI.

(4) The strength of glyoxalated soy adhesive itself is weak. CP-MAS ^{13}C-NMR results showed that the reaction between glyoxal and soy protein existed indeed. But these resulted hydroxy couldn't condensed to a cross-linked structure. Therefore, pMDI is a necessary cross-linker to glyoxalated soy protein adhesive. Its addition amount determines performance of final resin.

(5) The particleboard strength with formulations with glyoxalated soy was better than that with glyoxalated lignin. When both of them being used in one formulation, to increase the addtion amount of glyoxalated soy was helpful to the improvement of the performance of panels. The results of CP-MAS ^{13}C-NMR proved the reaction between lignin and glyoxal.

(6) The best formulation of all the ones tried was the SG/T/PMDI 54/16/30 by weight, which comprising 70% by weight of natural material. This resin can be used in a much lower proportion on wood chips and can afford pressing times fast enough to be significant under industrial panel pressing conditions.

IV.4. REFERENCES

[1] Liu Y, Li K. Development and characterization of adhesives from soy protein for bonding wood. Int. J. Adhesion Adhesives 2007, 27(1):59-67.

[2] Wescott J.M, Frihart C.R, Lorenz L. Durable soy-based adhesives, Proceedings Wood

Adhesives 2005, Forest Products Society, Madison, Wisconsin, 2006.

[3] Lorenz L, Frihart C.R. Wescott J.M. Analysis of soy flour/phenol-formaldehyde adhesives for bonding wood, Proceedings Wood Adhesives 2005, Forest Products Society, Madison, Wisconsin, 2006.

[4] Kuo M.L, Myers D.J, Heemstra H, *et al.* Soybean-based adhesive resins and composite products utilizing such adhesives[P]. U.S.Patent 6,306,997,2001.

[5] Wang D.H， Sun X.Z. Low density particleboard from wheat straw and corn pith. Industrial Crops and Products. 2002,15: 43-50.

[6] Mo X.Q, Hu J, Sun X.S, *et al.* Compression and Tensile Strength of Low-density Straw-protein Particleboard.Industrial Crops and Product s. 2001 (14):1-9;

[7] Cheng E.Z, Sun X.Z, Karr S.G. Adhesive Properties of Modified Soybean Flour in Wheat St raw Particleboard. Composites: Part A: Applied Science and Manufacturing. 2004,35 (3):297-302.

[8] Zhong Z.K, Sun X.Z, Fang X.H, *et al.* Adhesion properties of soy protein with fiber cardboard. JAOCS. 2001,78: 37-41.

[9] El Mansouri N. -E, Pizzi A, Salvado J. Lignin-based wood panel adhesives without formaldehyde. Holz als Roh-und Werkstoff. 2007,65:65-70.

[10] El Mansouri, N.-E., Farriol, X, Salvado, J. Structure modification and characterization of lignosulfonate by a reaction in an alkaline medium for its incorporation into phenolic resins.J.Appl.Polymer Sci., 2006, 102, 3286-3297.

[11] European Norm EN 312-2, Wood particleboard – Specifications, 1995

[12] Ballerini A, Despres A, Pizzi A. Non-toxic, zero emission tannin-glyocal adhesives for wood panels. Holz als Roh-und Werkstoff. 2005,63:477-478.

[13] Pizzi A, Valenzuela J, Westermeyer C.Non-emulsifiable, water-based diisocyanate adhesives for exterior plywood.II. Holzforschung 1993, 47, 69-74.

[14] Despres A, Pizzi A, Delmotte L. ^{13}C-NMR investigation of the reaction in water of UF resins with blocked emulsifiable isocyanates. J.Appl.Polymer Sci. 2006, 99:589-596.

[15] Wieland S, Pizzi A, Hill S, *et al*. The reaction in water of UF resins with isocyanates at short curing times: a 13C-NMR investigation. Journal of Applied Polymer Science. 2006, 100:1624-1632.

[16] Simon C, George B, Pizzi A. Copolymerization in UF/pMDI adhesives networks. Journal of Applied Polymer Science. 2002,86:3681-3688.

[17] Fengel D, Wegener G. Wood: Chemistry, Ultrastructure, Reactions, De Gruyter: Berlin, Germany 1989.

[18] Hine J, Koser G.F. Kinetics and mechanism of the reaction of phenylglyoxal hydrate with sodium hydroxide to give sodium mandelate. Jounal of Organic Chemistry. 1971,36:3591-3592.

[19] Velisek J, Davidek J, Pokorny J, *et al*. Reactions of glyocal with glycine. Forschung A. 1972,149:323-329.

CHAPITRE V

INFLUENCE OF NANOCLAY ON UREA-FORMALDEHYDE RESINS FOR WOOD ADHESIVES AND ITS MODEL

V.1. INTRODUCTION

The wood panels industry heavily relies on the use of synthetic resins and adhesives. Adhesive bonded products constitute about 80% of the wood products on the market to-day. Wood adhesive is a key to the wood industry and plays an important role in the preparation of wood panels with higher quality. Without adhesives and resins this industry would not exist[1]. Since polycondensation resins replaced nature materials to be as wood adhesives, the development of panels has been closely related to the development of synthetic resins.

Now the synthetic resins being widely used in wood panels industry are formaldehyde-based ones, such as UF, PF, MF resins. With the lower cost and good performance, UF resin is the most widely-used wood adhesive. The adhesives used for these panels in 1998 (data from the European Panels Federation) were of 3.2 million tons resin solids, of which 2.6 millions being UF resins used for interior grade applications.

Performance standards have been established throughout the world for wood composite boards. Thus, the percentage on wood of adhesives/resins used for the manufacture of these products to satisfy the requirements of such standards varies little around typical percentage values. These are characteristic for each type of resin and process used. Actually, the resin binder constitutes the more expensive materials cost component and sometimes its cost consists of more than 60% of the total cost. It is one of the parameters of which it is not possible to change markedly the percentage as this will cause a very marked decrease in performance, hence failure to satisfy the relevant standard specifications. Thus, any additive or filler of relatively low cost which can improve the performance of the resin, implying at equal performance lower resin consumption, is of particular interest.

Inorganic filler is one of the most important additives to be used[2]. Usually it is mixed with resins physically. Its addition could not only lower the usage of resins but also improve some properties of resins, such as properties on strength, abrasion resistance, thermal resistance, ageing resistance.

Montmorillonite(MMT) has been used in many industrial fields, especially in producing high-performance intercalation nanocomposites, due to its particular intercalation chemistry and nanoscale layers with high aspect ratio and high strength, high cation exchange capacities, and swellablity. With the high viscosity caused by MMT, the adhesive composites formed by cations exchange reaction between adhesive and MMT will be suspended in the mix system. Once MMT/adhesive composites are formed, the good water resistance of MMT itself will be helpful to the increase of performance of the final resin. According to the work of Yuan[3], MMT can do the same with paints.

Impressive enhancement of properties by inclusion of submicron-size fillers in plastics and elastomers has stimulated considerable research on performance upgrading of thermoplastic resins by addition of such materials. With some research is put up in-depth, the properties of fillers itself and its state in the polymer are found to have important effects on the performance of final resins. As a basic component for polymer/layered silicate, MMT can be dispersed in a polymer at a nano lever. Only with a small amount of MMT, polymer with high strength, good flexibility, and good capability to obstruct gas or liquid can be prepared. Clay nanocomposites of different types yield a marked increase in a number of properties of thermoplastic and other composites[4-9].

This chapter then deals with the addition of different types of montmorillonite nanoclays to thermosetting UF resins to study:

(1) The improvement in performance of the resin by measuring the improved performance of wood panels/composites bonded with UF/nanoclays.
(2) The effect of the resin on the level of exfoliation of the nanoclays.

V.2. RESULTS AND DISCUSSION

V.2.1. Select of MMT

The performance of the resin on the addition of montmorillonite nanoclays is first tested by thermomechanical analysis (TMA). In Fig. V.1 is shown the increase of modulus of elasticity

(MOE) as a function of temperature of joints bonded with a UF resin control and with the same UF resin to which is added 10% (by weight on dry resin) of three different montmorillonite nanoclays (montmorillonite H-MMT, its sodium salt Na-MMT, and O-MMT an organic salt of H-MMT). UF resin is used without acid hardener considering MMT's pH to see the effects of MMT on pure resins. From the figure, the curing temperature for H-MMT is advanced 10ºC than for Na-MMT, which was possibly caused by pH of MMT itself. Generally UF resin could cure under both acid and alkaline conditions. However, for alkaline-cured resins, the curing temperature was increased to 140-150ºC, which was too high and would cause a bad flowability, less chances for the moleculers' contact with each other, less polymerization and less stability of bonds, and then a weaker strength. In all cases the maximum value of the MOE is increased markedly by addition of any of the montmorillonites. The increase is particularly marked for H-MMT and Na-MMT.

Before mixing MMT with polymer, usually MMT's hydrophilic surface should transfer to be a hydrophobic one by treatment with organic compounds, which is favourable for the hydrophobic polymer to enter into the silicate layers of MMT. But from the TMA results, O-MMT can not improve the performance of UF resins greatly. Actually the exist of $–NH_2$ and –OH groups in UF resin have maken the resin hydrophilic, which is totally different from most of polymers with high moleculer weight, such as epoxy, rubber, etc. Therefore, for the preparation of composite of MMT and UF resin, there is no need to change the surface's hydrophilic property to hydrophobic one. The good compatibility between amino resin and silicate layers make the layers to be separated more easily, which may be responsible for the less remarkable change of performance when O-MMT used compared H-MMT and Na-MMT.

In UF resin, there exists $-NH_2$ group. It is the main group for amino acid compound to be used as interclator of MMT. The similarity on the structure between UF resin and amino acid intercalator will probably be helpful to the separation of MMT layers. It is this test that indicated that it is convenient to use the cheaper material Na-MMT, seen its good performance. Since the preparation of H-MMT and O-MMT are complicated, Na-MMT is chosen for this work considering the cost of final resins.

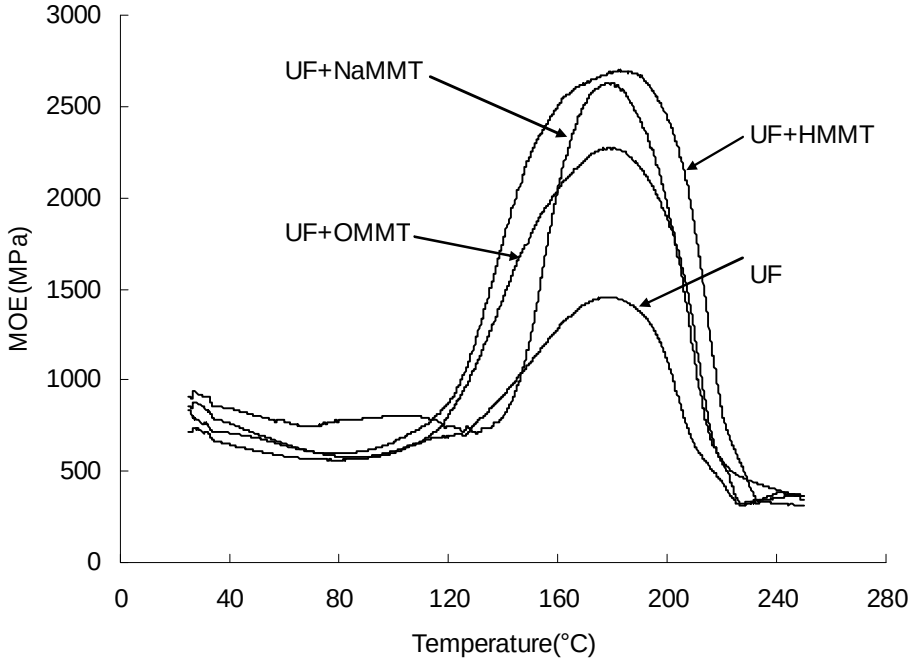


Figure V.1. Thermomechanical analysis (TMA) curve of MOE as a function of temperature for a UF resin with or without different montmorillonite and derivatives added. The amount to be added for all of the samples is 10% of solid resin.

V.2.2. XRD results of MMT/UF resin system

The XRD pattern of the Na-MMT nanoclay, and of the UF resin with and without different amounts of nanoclay is shown in Figs. V.2a,b. Fig. V.2a reports the 2θ angle spectrum 2°-100° and Fig.V.2b the 2°-15° the 2θ angle range. The peaks appearing at 7.03° corresponds to Na-MMT. The strong peaks at about 22.5°, 25.8°, 33.3° and 40.4° are from the lattice planes of the hardened urea-formaldehyde resin[10]. Fig. V.2b shows the measured intensity data over the characteristic 2θ range for Na-MMT. In the case of the pure Na-MMT the strong 2θ peak at 7.03° corresponds to a *d*-spacing of 1.26 nm according to the Bragg equation[4]. For the UF/Na-MMT system the (001) peak disappeared both at 4% and at 8% Na-MMT. This indicates that the periodic atomic structure of ordered zones of the nanoclay does not exist anymore. This has already been interpreted by other authors[5] in other polymer systems by deducing that Na-MMT is completely exfoliated. Accordingly, here too it would appear that Na-MMT is exfoliated when mixed with a UF resin.

The XRD pattern of the UF resin in the 2θ range 20°-40° was not affected by the addition of Na-MMT as the peaks position remained the same. Their intensity however increased when compared to that of the UF resin cured without a hardener. It decreased instead for a UF resin cured by addition of hardener. In the latter case, this suggested the same crystalline structure of the UF resin but at a lower level of crystallinity in the UF/Na-MMT hybrid.

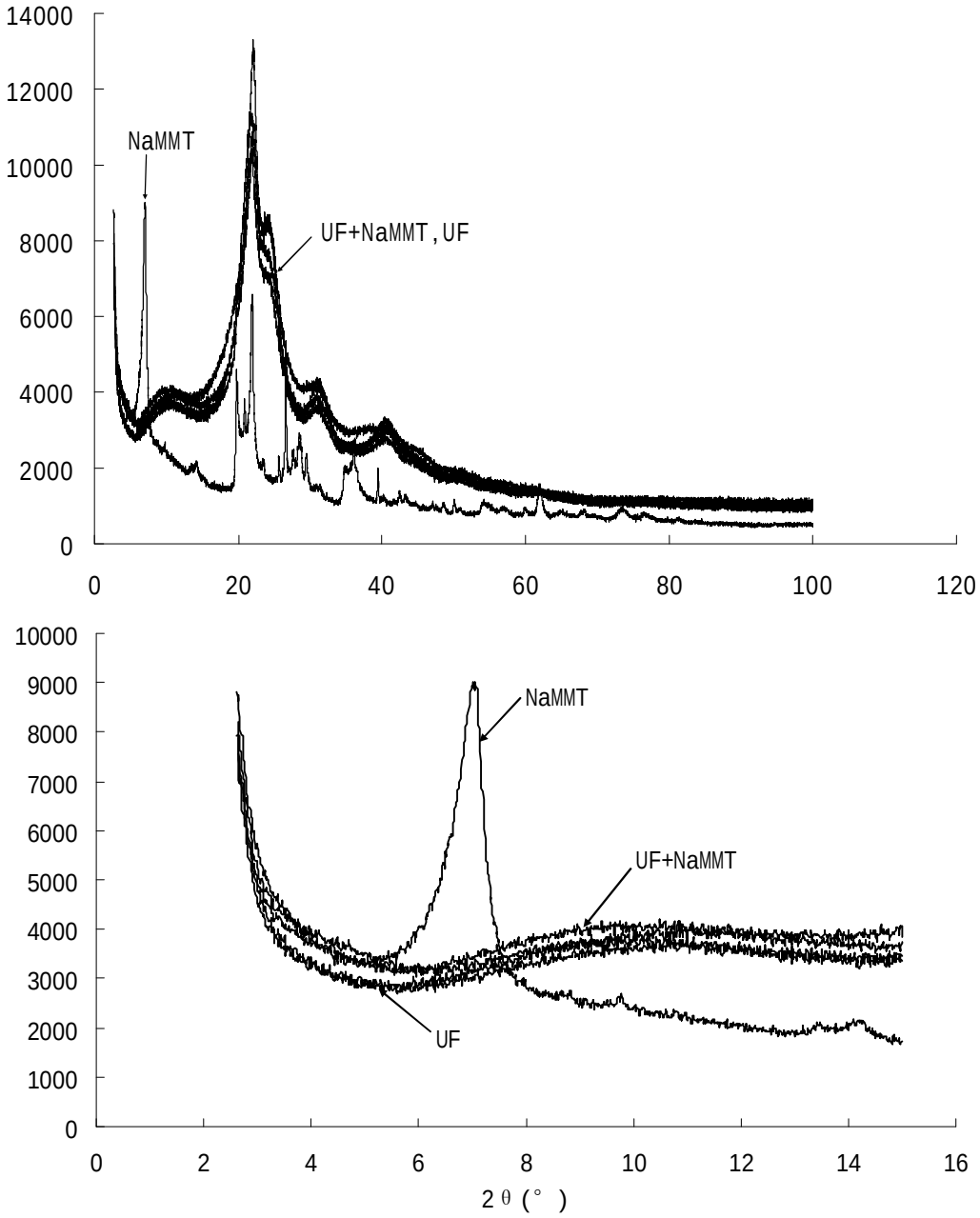


Figure V.2. X-ray diffraction (XRD) spectra for NaMMT, UF resin, and UF+4%NaMMT and UF+8%Na-MMT. (a) in the 2 θ angle range 2-100°. (b) in the 2y angle range 2-15°.

V.2.3. DSC analysis of MMT/UF resin system

The influence of Na-MMT on UF resins was further investigated by DSC. The DSC curves of UF+hardener and UF+hardener+4%Na-MMT are shown in Fig.V.3. This indicates that Na-MMT accelerates hardening of a UF resin. This is shown by the earlier onset and peaking of the exotherm of UF+hardener+NaMMT (onset at 88°C, peaking at 120°C) compared to that of UF+hardener only (onset at 96°C, peaking at 128°C).

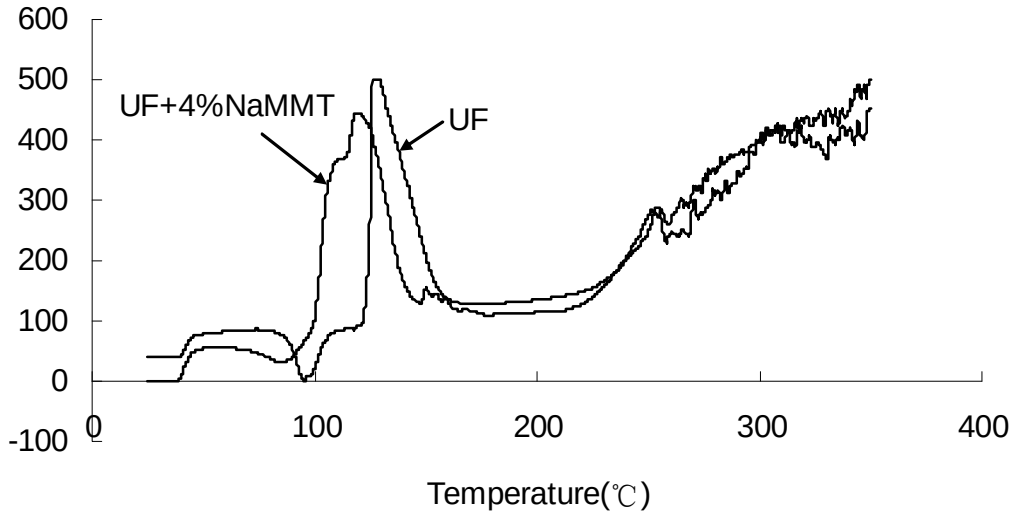


Figure V.3. Differential scanning calorimetry (DSC) thermograms of UF resin+hardener and UF resin+ 4%Na-MMT+hardener.

Of interest is also the appearance of the peak shoulder in the range 100-118°C, which is much higher for the resin with Na-MMT than for the UF resin without nanoclay. This shoulder is probably due to the elimination of water from the system, and the difference in its height for the two cases in Fig. V.3 means that Na-MMT retards water elimination from the system. As wood panels are cured in a hot press, this is likely to give slightly different rheology characteristics to UF resin flow during hot curing when Na-MMT is present, hence it may influence resin performance. Equally interesting is the lower intensity but greater width of the exotherm peak for the two cases in Fig. V.3, indicating a more controlled cross-linking, thus a more regular final network[11] when Na-MMT is present. The endothermic peaks at 90°C for UF+4%Na-MMT system and at 96°C for UF resin are due to the volatilization of water. The endothermic for former is more mild than the latter, too.

V.2.4. Influence of addition percentages of Na-MMT on resin's performance

In Fig. V.4 is indicated the influence of different percentages of Na-MMT on the maximum MOE value during curing of the UF resin, again without addition of a hardener. The maximum MOE value increases up to 4% addition of Na-MMT and then decreases for higher percentage additions. The exfoliated system between UF and MMT should be one of the main reasons for the appearance of threshold of MMT addition amount. In nanocomposites, the addition of MMT for exfoliation composites is much less than for interclation ones, which means with higher addition amount of MMT will do no good to the improvement of performance. What's more, the viscosity of the mixture increases considerably as the percentage of Na-MMT increases to higher than 4% on the resin solid, which would decrease the strength of final resins with consequent diffusion hindrance influencing negatively the curing of the resin.

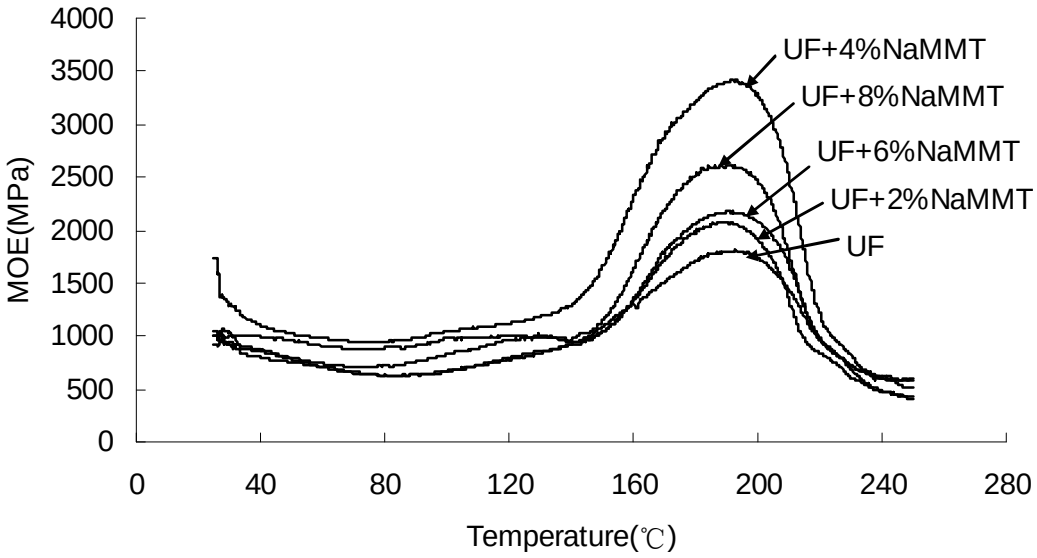


Figure V.4. Thermomechanical analysis (TMA) curve of MOE as a function of temperature indicating the effect on maximum MOE value of different percentages of Na montmorillonite (Na-MMT) added to a UF resin.

V.2.5. Curing characteristic study on MMT/UF resin

Figs. V.5 and V.6 indicate the behaviour of the hardening of UF+Na-MMT systems when in presence of a direct hardener, an acid (acetic acid 30%), used to partly neutralize the alkaline ions generated by Na^+ of Na-MMT. In the case of a direct acid hardener, the progressive

increase in the acid added yields better results up to 1.5 times the acid necessary to neutralize the OH^- generated by the Na^+ of Na-MMT, then the level of max MOE stabilizes. The progressive addition of higher proportions of acid also shifts the increase portion of the MOE curves to progressively lower temperatures (Fig. V.5). Thus, it accelerates the curing of the UF+Na-MMT mix, again up to 1.5 times the acid necessary to neutralize the OH^- generated by the Na^+ of Na-MMT. While the stability of maximium of MOE indicates that excess acid has no obvious effects on the crosslinking or strength of resins, only on curing speed. And with the addition amount of acid, the effects on curing speed become less.

On top of the acid, also a hidden hardener such as ammonium sulphate was added. When different percentage of Na-MMT were used, the maximium MOE value of resins changed a little, all of which are between 3000-3500 MPa and this is in accord with the results of Fig. V.5. However, the further addition of Na-MMT functioning only when the temperature increases over a certain level (Fig. V.6) still shows resin curing acceleration and improved maximum MOE values when comparing UF and UF+Na-MMT, but both of these are much more modest, and stop for NaMMT proportions higher than 4% on resin solids. Fig V.6 indicates that: (1) the addition percentages of Na-MMT have no obvious effects on the strength of final resins; (2) once the acid increased to a degree, hardener has no obvious effects on the cross-linking or strength of final resins and it can only do something to the curing speed. From Figure V.5, the alkaline generated by Na-MMT could be neutralized by acetic acid 1.5 times as much as the amount of Na-MMT. When the addition of Na-MMT is lower than 4% of solid resin, Na-MMT could make the curing of resins accelerated. While the effect is not obvious once the addition is higher than 4%. In all, there is no big change on the strength of the mixing system with hardener with different addition percentage of Na-MMT. The curing acceleration is more modest with hardener. The difference on performance is probably related to the permeation of resins. TMA is a good indication of the strength of final resins. It mainly reflects properties of plywood, which is determined by the process of TMA. Without hardener, the resin cures slower. The curing temperature is about 160℃ and is higher than that of with hardener. Under a press and a higher temperature, MMT which diffused in UF resins could fill parts of the cores of the surface of the plys sampers. Then over-dried was prevented caused by the over permeation of the resins.

However, with hardener the resin can cure faster. The resin begins to cure at about 80 ℃, which is much lower than the 160 ℃ when no hardener being used. The time is not enough for Na-MMT to fill the pores on the surface of the plys. So the addition of Na-MMT has no obvious effects on the strength of UF resins.

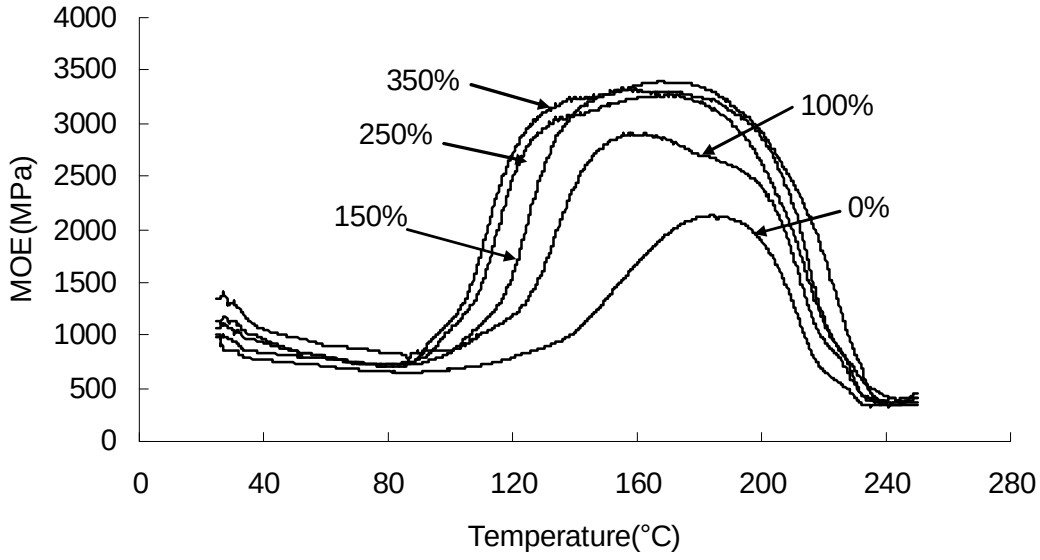


Figure V.5. TMA results of UF resin+2%NaMMT with different percentages of acetic acid on solid resin. Acetic acid content equivalent to neutralization of alkali content of NaMMT (100%), 1.5 times more (150%), 2.5 times more (250%), 3.5 times more (350%).

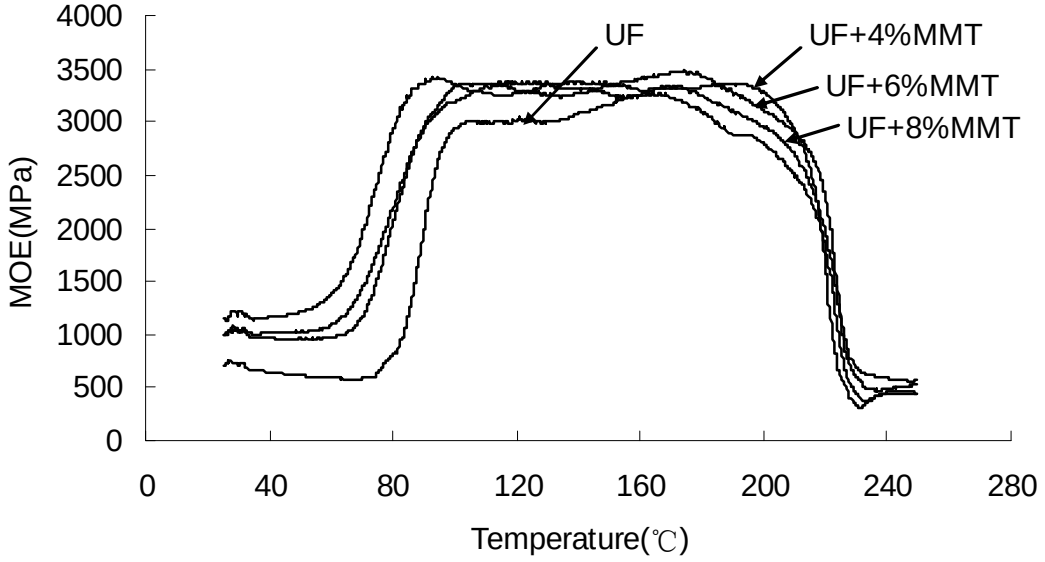


Figure V.6. TMA results of UF resin with different percentages of NaMMT when hardener and acetic acid are added.

V.2.6. Effects of Na-MMT on the performance of plywood

The applied results of two different types of wood panels bonded with UF resins to which Na-MMT was added are shown in Tables V.1 and V.2. In Table V.1 results for plywood indicate that there are no significant differences in dry tensile strength between the UF control and the UF+Na-MMT panels. This is explained by the percentage wood failure being 100% in all cases, indicating that all adhesives mixes are stronger than the wood substrate and consequently the dry strength tested is that of the wood itself. The results are different and of greater interest in the case of the immersion of the panels in boiling water for an accelerated water resistance test. UF resins are not weather and water resistant. This can be noticed in Table V.1 for the control, first by the marked decrease in wood failure observed already after 15 minutes in boiling water and second by the equally noticeable decrease in strength and wood failure after 25 minutes boiling. The behaviour of the panels bonded with UF+Na-MMT is different. First the decrease in strength on boiling is much less marked, the joints being stronger than the control after 25 minutes boiling. Second the decrease in wood failure after 15 minutes boiling is much less marked for the control. This indicates that Na-MMT renders UF bonded plywood more water tolerant, although still far from being of exterior type. This is an interesting result as even slight improvement in water tolerance of UF-bonded joints are much appreciated by the wood panel industry, especially when these are achieved with small amounts of a relatively inexpensive material. The addition percentage of MMT has no obvious effects on the dry strength of plywood. Though it can do something to the wet strength, the relative regulation is unclear, too.

Table V.1. Results of plywood panels prepared with a UF of molar ratio 1:1.5 added of different percentages of Na-MMT

	Dry	Boiled(15min)	Boiled(25min)
NaMMT on dry resin(%)	Tensile strength(N/mm^2)	Tensile strength(N/mm^2)	Tensile strength(N/mm^2)
0	2.45(100)	2.45(27)	1.09(0)
2	2.42(100)	2.68(63)	1.7(0)
4	2.32(100)	2.67(85)	1.33(0)
6	2.39(100)	2.28(51)	1.37(0)
8	2.52(100)	2.58(42)	1.64(0)

V.2.7. Effects of Na-MMT on performance of particleboard

Table V.2 reports the results of laboratory wood particleboard produced by adding increasing percentages of Na-MMT in the UF binder used (molar ratio U:F=1:1). The dry internal bond (IB) strength of the panel, which for particleboard is a direct indication of the performance of the adhesive, progressively increases with increasing proportions of Na-MMT. The greatest improvement occurs with the first 2% NaMMT and then improvements are rather small up to 8% Na-MMT.

Table V.2. Results of wood particleboard panels prepared with a UF of molar ratio 1:1 added of diffrerent percentages of NaMMT

Na-MMT on dry resin(%)	Density(kg/m^3)	Dry IB strength(MPa)
0	700	0.79
2	700	0.94
4	700	0.96
8	700	1.01
10	700	1.00

The influence of nanoclay on the formaldehyde emission was evaluated by the dessicator method according to standard AS/NZS 1859.1 2004[12]. For UF resin without Na-MMT being added, the formaldehyde emission is 0.905mg/l, while for UF resin with 1% addition of Na-MMT, it is 0.827 mg/l, which is lower than the former. It shows that nanoclay can decrease formaldehyde emission even if to a limited extent. The possible reason for that is that MMT has larger specific surface area, especially for the layers being exfoliated. The layers can absorb free formaldehyde existing in UF resin, then decrease the formaldehyde emission of panels.

V.2.8. Comparision study of influence of Na-MMT and wheat flour on UF resin

Wheat flour is one of the most widely-used fillers in the preparation of plywood. In this work, the influence of Na-MMT and wheat flour on the UF resin adhesives was studied. The feasibility to replace flour with Na-MMT was judged, which is helpful to understand the

mechanism of Na-MMT on UF resins.

UF resins for plywood are almost always used after addition of marked amounts of wheat flour (between 20% and 50% by weight on resin solids, with 30% being an average level of addition in industry) both to improve the consistency of the adhesive as well as to cheapen the glue-mix. The dry strength and general dry performance of UF+wheat flour filler resins is generally better than for the same UF resin alone. Unfortunately addition of flour further worsens the resistance of UF-bonded joints to water.

Improvement engendered by the addition of small percentages of Na-MMT as regards water resistance of UF-bonded plywood (Table V.1) led to consider what level of substitution by Na-MMT one could have on traditional wheat flour fillers. Figure V.7 and V.8 reports the TMA results of UF resin alone and to which either different percentages of wheat flour (4% and 30%) or Na-MMT (2% and 4%) have been added, for the two UF resins with different molar ratio, respectively. For Figure IV.7 the molar ratio F/U is 1:1(LUF), and for Figure IV.8 is 1.5:1(GUF).

Both flour and Na-MMT could increase the maximum MOE values. The maximum MOE values obtained by the addition of the small percentage of Na-MMT nanoclay are considerably better than those obtained even with the higher amount of flour, when no hardener is added to the UF resin. When the addition percentage of Na-MMT was as low as 2%, a good performance could be gotten. The difference on MOE between flour and Na-MMT meant that the mechanism for the two fillers to UF resins may be different.

Comparing Figure V.7 and V.8, two informations could be gotten:

(1) For UF with lower molar ratio F/U, the effects of fillers on the performance of resin is much obvious than for UF with higher molar ratio. For LUF, with 2% Na-MMT the maximium MOE increased 45-50% and with 4% Na-MMT MOE increased 65-70% than that without fillers. With flour, the MOE increased less than 40%. While for GUF, with 2% Na-MMT the maximium MOE increased about 30% and with 4% Na-MMT MOE increased about 40%.

With flour, the MOE increased about 15%. The reason for the difference is unclear.

(2) For the resin system without hardener, the curing acceleration for flour is more obvious than for Na-MMT. The possible reason for that is the filler's pH. For flour, it is acid, while for MMT, it is alkaline.

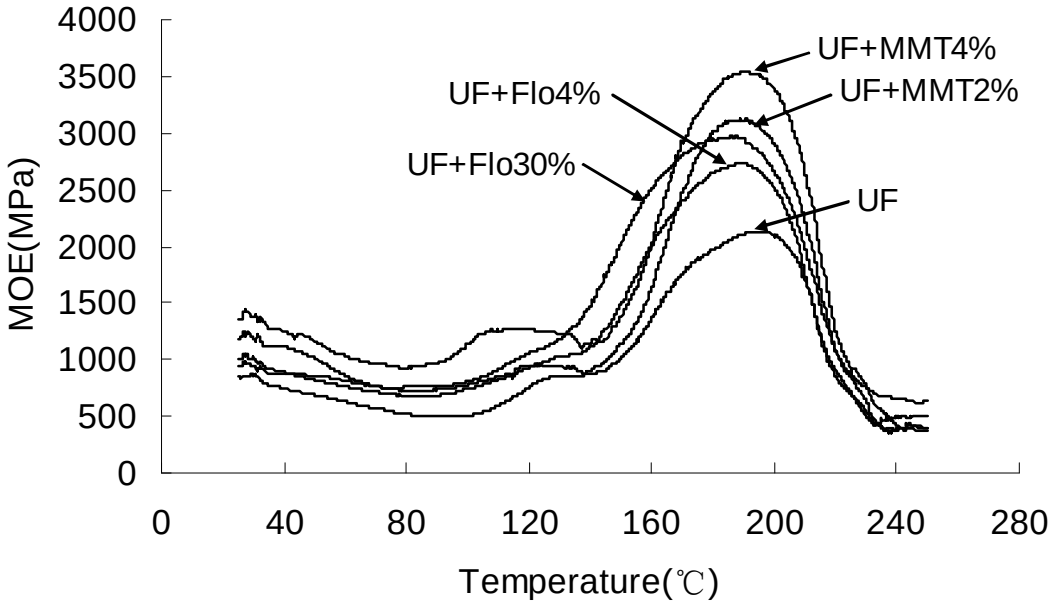


Figure V.7. TMA curve of UF resin with different percentages of Na-MMT and wheat flour.

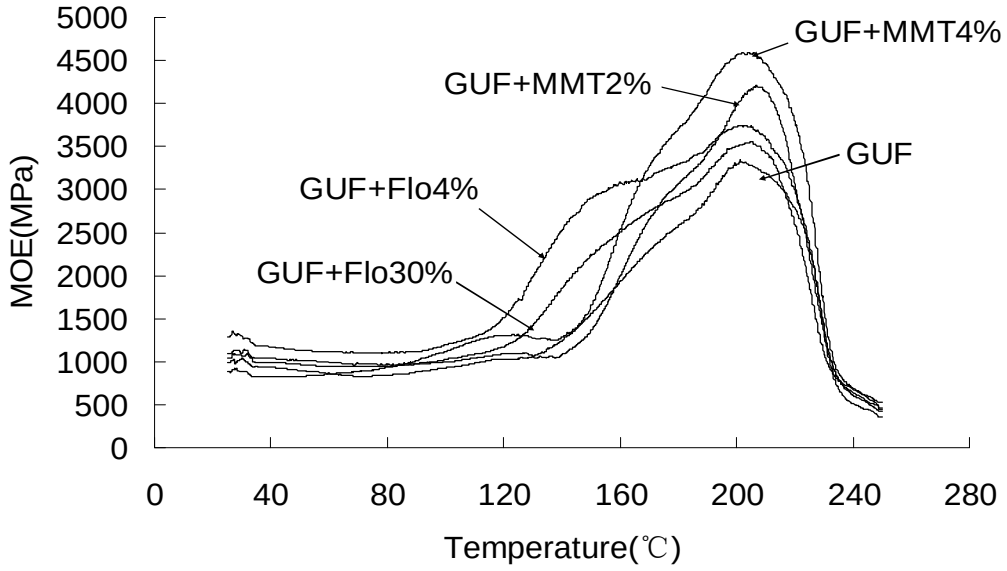


Figure V.8. TMA results of liquid UF added with different amount of Na-MMT or wheat flour, molar ratio F/U=1.5:1.

Figure V.9 and V.10 are TMA results of the two UF resins with hardener with Na-MMT and flour. With hardener, UF resin cross-linked furtherly. The three-dimensional structure would be gotten. With higher molar ratio, the degree of cross-linking is higher. Even when a hardener is added to the resin, UF+4% NaMMT cure much faster than UF+30% wheat flour.

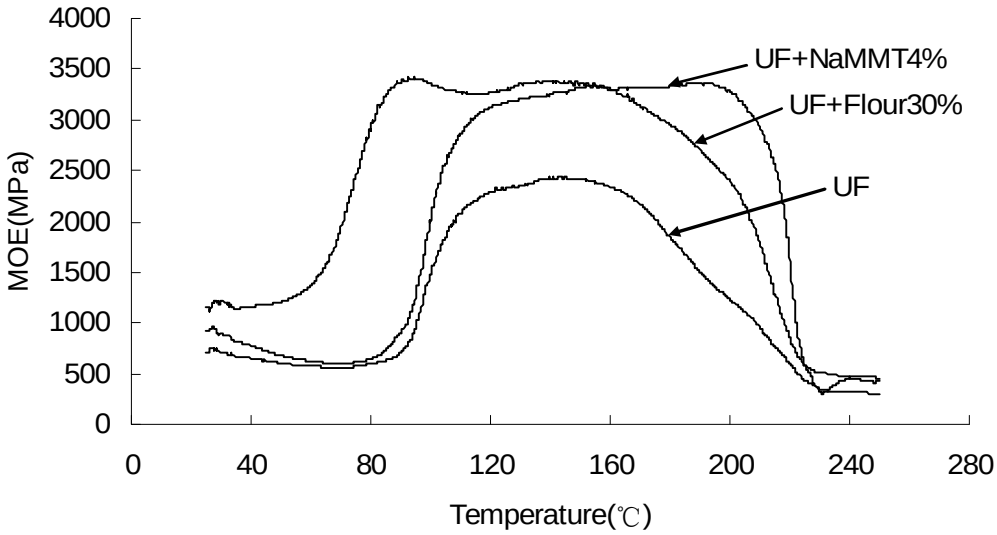


Figure V.9. TMA curve of UF resin with 4% NaMMT and 30% wheat flour when resin hardener is present.

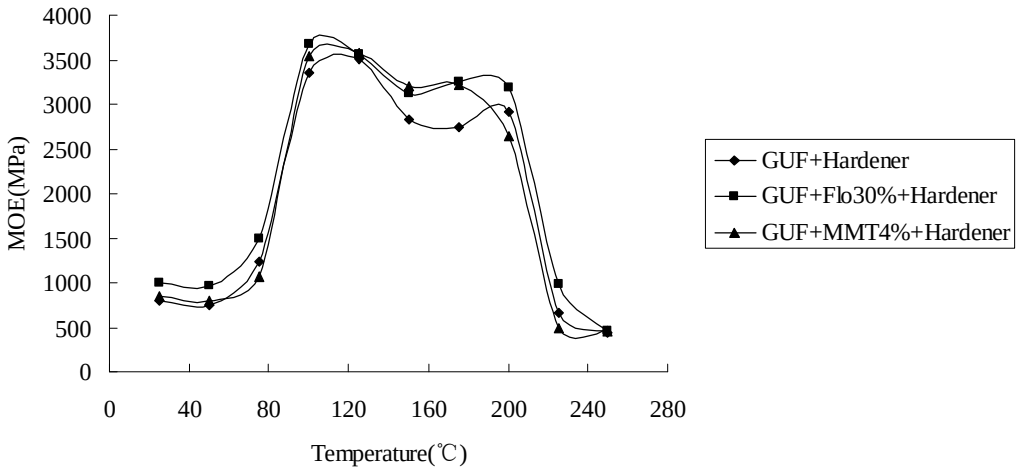


Figure V.10. TMA results of GUF mixed with Na-MMT or wheat flour after adding hardener.

Results of Figure V.9 and V.10 indicate that the effects of Na-MMT on the performance of UF resin relate to the resin structure. For the resin with lower molar ratio with a less cross-linked structure, the effects of Na-MMT on the performance of resin are much obvious. Since the MOE of the system with Na-MMT begins to decrease at a higher temperature than that of

control resin, the addition of Na-MMT could increase also the thermal stabilities of resins. The pH of Na-MMT and flour maybe contribute for that. As a modest alkaline when dissolved in UF resin, Na-MMT is useful for alivieating the hydrolysis of UF resin. For other mineral fillers, the same results can be gotten[13]. However, from the results, it seems that Na-MMT is better than others.

For the UF resin with higher molar ratio (seen Figuer V.10), the MOE and curing time have no obvious differences for resins with Na-MMT and flour. The possible reason is that the effects of Na-MMT or flour on the performance of resins were covered by the cross-linking reaction during which molerculer weight increased rapidly and the performances of UF resin changed a lot[14]. Then the effects of fillers for the UF resin with higher molar ratio cann't be seen.

The comparative results of plywood panels made with wheat flour filler and with much smaller percentages of Na-MMT are shown in Table V.3. Two kinds of UF resins were used. The molar ratio for both of them is 1.5.

Table V.3. Comparison of results for plywood prepared with 30% wheat flour vs.6%Na-MMT using a commercial UF and a laboratory prepared UF

	UF(F/U=1.5 molar)		Commercial UF	
Tensile strength	30%flour	6%Na-MMT	30%flour	6%Na-MMT
Dry(MPa)	2.09(100)	2.39(100)	2.16(100)	2.32(100)
Boil(15min)(MPa)	1.33(0)	2.36(100)	0(0)	2.65(100)

Table V.3 shows that for both a laboratory synthesised UF resin as well as for a commercial resin the water resistance of the joint bonded with 6% Na-MMT is far superior to that of the joint containing 30% wheat flour, both in strength and wood failure. After being immersed in boiling water for some time, the strength became even higher than that of panels without water treatment. There are four reasons for the improvement in water resistance of the resin due to the addition of montmorillonite nanoclay:

(1) The superplasticity of PLS nanocomposites[14].

(2) The strong capability to absorb water by MMT[15]. With this characteristic, MMT can increase the rigidity of glue line, which is good to strength, especially the wet strength.
(3) The characteristic of water repellent of MMT nanoclay itself. By cation exchange, complex between MMT and UF resins can be formed. The hydrophilic of MMT itself will contribute to the improvement of water resistance.
(4) A percolation phenomenon between nanoclay particles may also have some reinforcement effects on the resin performance, specifically water resistance.

V.2.9. Determination of addition amount of Na-MMT for UF resins

The XRD results show that Na-MMT is dispersed in UF resins at nano lever. Therefore, only with a small quantity of Na-MMT a uniform mixture will be gotten. The addition percentage of Na-MMT is analized in this study.

MMT is composed of many layers. As argued below, the corresponding particles may be modelled as thin disks. Similar with the percolation of rigid polymer, there are three ideal percolation forms which according to concentration of these thin disks: low concentration, a transition concentration and high concentration. At low concentration, the thin disks are isotropy. They disperse in a polymer at random. With more disks in the resins, a transition concentration is arrived, which is a transition for the thin disks from dispersing isotropy situation to crystal situation. When the thin disks are at a dispersing isotropy situation, the spacing distance between two adjacent disks is large enough to ignore the interaction of them, though their move was interfered with each other. While at crystal situation, the disks oriented regularly and the adjacent disks have no reaction. To add a small amount of disks, the dispersing disks will connected with the neighbor disk, then oriented automatically. The regular structure will be gotten, namely crystal structure[16].

The nanoclay used in the system of Na-MMT and UF resins is a sodium montmorillonite (Na-MMT), also called bentonite. When dispersed inside a continuous medium like a resin matrix, the particles are expected to touch with each other, thus forming a connected infinite

cluster even at low concentration. It is better for the addition amount of MMT to be lower than the transition concentration. If the addition is too high, the rigidity of the resins will increase. The viscosity is too high to do bad to get a uniform mixture. The critical amount above which a transition from a non-connected to a connected state (i.e., a percolation transition) occurs can be calculated according to the following considerations.

First, the aspect ratio of an average typical particle should be known. The mean diameter, as seen by scanning electron microscope observation, is close to 100 nm. Applying the well known Bragg equation to the main X-ray diffraction peaks of the clay powder led to an interlayer spacing of 1.27 nm. Such a result is remarkably close to what was measured for the first hydration product of bentonite, corresponding to one intercalated layer of water[17], i.e., 12.4-12.6 Å.

XRD diffraction of adhesive-nanoclay composites also revealed that, after dispersion inside the resin, the nanoclay is completely exfoliated. The exfoliation, which is a well-known property of Na-MMT, is caused by the reversible uptake of water by sodium ions. This gives the material a high ability to swell in one dimension, thus effectively cleaving the clay particles and causing a separation of the lamellar units in the form of extremely thin plates[18]. Given the above interlayer spacing, the thickness of the corresponding platelets should be lower than 1.3 nm. Since the stacking of the layers is close compact in the raw nanoclay, and that the intercalated sodium cation has an ionic radius of 116 pm[19], the layer thickness after exfoliation is $1.27 - 2 \times 0.116 = 1.04$ nm, say 1 nm. This result is close to values already published for the thickness of a montmorillonite lamella, i.e. 9.1-9.2 Å [20]. Therefore, the aspect ratio diameter/thickness is assumed to be roughly 100.

The percolation threshold of systems comprising disoriented thin disks was investigated by Celzard *et al*[21], and the resultant equations were successfully applied to a number of composite materials (see for example[22] and refs. therein). Briefly, the critical volume fraction Φ_c at which an infinite cluster is formed throughout a medium filled with randomly dispersed disks of radius r and thickness t reads:

$$\Phi_c = 1 - \exp\left(-\frac{\langle V_{exc}\rangle V}{\langle V_e\rangle}\right) \quad (1)$$

where $<V_{exc}>$ is the so-called total excluded volume; it is a dimensional invariant depending on the shape of the percolating objects (see reference 28 and refs. therein for details). V is the true volume of an average percolating object, and $<V_e>$ is its excluded volume averaged over the orientation distribution. The excluded volume is defined as the volume around an object in which the centre of another similarly shaped object is not allowed to penetrate. For example, the simple case of two identical spheres S1 and S2 having the same volume V may be considered. If S1 is both brought into contact and rotated around S2, it is easily seen that the center of S2 describes a spherical volume with a radius twice that of the sphere. The corresponding excluded volume is thus $<V_e>=4/3*\Pi*(2r)3=8V$. The same approach may be used for any kind of object and particularly in the case of thin discs. The underlying idea is that the percolation threshold is not linked to the true volume of the object itself, but rather to its excluded volume[22]. The mean excluded volume of a disk of infinitely thin radius r is such that[23]:

$$\langle V_e\rangle = 4\pi r^3 \int_0^b \sin^2 a \, da \quad (2)$$

where a is the angle between the planes of two disks in contact with each other, as shown in Fig. 5.11, and b represents the angle of greatest disorientation of the system of disks. In other words, $-b \le a \le +b$. For randomly oriented disks, $b = \pi/2$ and such a system is isotropic. Integration of Eq. (2) leads to:

$$\langle V_e\rangle = \pi r^3 [2b - \sin 2b] \quad (3)$$

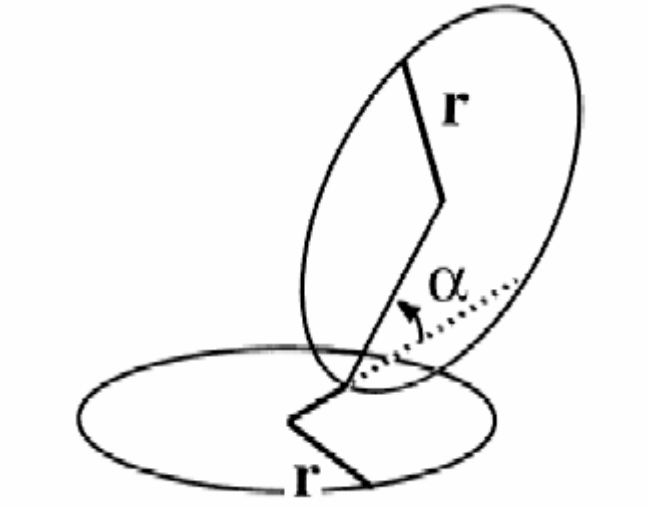


Figure V.11. Excluded volume for thin disks of radius r. The objects touch and their plane make an angle a. $\langle V_e \rangle$ is calculated for any orientation such that $-b \leq a \leq +b$., where b is the maximum disorientation angle of the system. The latter is isotropic for $b=\pi/2$.

thus $\langle V_e \rangle = \pi^2 r^3$ when $b = \pi/2$. Consequently, the percolation threshold of a system of completely disoriented disks, reads:

$$\Phi_c = 1 - \exp\left(- \frac{\langle V_{exc} \rangle t}{p r} \right) \qquad (4)$$

where t is the thickness of the disks. $\langle V_{exc} \rangle$ is known in the extreme cases of infinitely thin disks (1.8)[24] and of spheres (2.8). It is thus expected that the value of $\langle V_{exc} \rangle$ corresponding to disks of finite thickness t lies between 1.8 and 2.8. The following double inequality is then obtained:

$$1 - \exp\left(- \frac{1.8t}{p r} \right) \leq \Phi_c \leq 1 - \exp\left(- \frac{2.8t}{p r} \right) \qquad (5)$$

Since the ratio t/r of the nanoplatelets is 1/50, the percolation threshold verifies the following double inequality:

$$1.14\ \% \leq \Phi_c \leq 1.77\ \% \qquad (6)$$

Such a result may be alternatively recovered through the use of the effective medium theory. It was demonstrated that, assuming platelets as flattened (oblate) ellipsoids, the critical volume fraction Φ_c may be written as[25]:

$$\Phi_C = \frac{9 L_c (1 - L_c)}{2 + L_c (15 - 9 L_c)} \qquad (7)$$

where L_c is the depolarization factor, related to the eccentricity e of the ellipsoid according to the following formulas[26]:

$$e = \sqrt{\left(\frac{2r}{t} \right)^2 - 1}$$
$$L_c = \frac{1 + e^2}{e^3} [e - \arctan e] \qquad (8)$$

Given the aforementioned values of radius and thickness, Eqs (7) and (8) lead to a value of 1.74

% for Φ_c, which is very close to the upper limit given by Eq. (5). Consequently, it can be deduced that percolation occurs in resin – nanoclay systems as soon as the concentration of nanoplatelets is in excess of 1.8 vol. %.

Rather than volume fractions, Φ, the composition of filled adhesives is calculated on the basis of mass fractions, f. It is easy to calculate that both concentrations are related to each other through the following equation:

$$f = \frac{1}{1 + \frac{r_R}{r_N} \times \frac{1 - \Phi}{\Phi}} \qquad (9)$$

in which r_N and r_R are the densities of the nanoclay and of the dry, hardened, resin, respectively. Given that r_N = 1.25 and r_R = 2.35[27], injecting Φ_c = 1.8 vol. % into Eq. (9) shows that the percolation threshold corresponds to f_c = 3.3 wt. %.

Now, the percolation transition is not representative of what happens from a mechanical point of view. Physical properties like elastic modulus or viscosity are not strongly affected by the onset of an incipient cluster made of randomly dispersed particles. The system indeed just undergoes a transition from a non-connected to a connected state, but remains floppy. A second percolation transition should exist at a higher concentration such that the particles form a rigid network. This second critical volume fraction, at which the elastic modulus thus becomes non-zero for the first time, is called rigidity threshold, Φ_r. Therefore, in systems made of dispersed particles, it is obvious that $\Phi_r > \Phi_c$. This situation is met, for example, when expanded graphite particles are pressed into monolithic blocks[28], or in wood-based composites consisting of wood fibres and phenolic resin binder[29]. In the latter case, the binder was randomly dispersed among the fibre-like particles, and its presence was shown to have no influence on the position of the rigidity threshold, thus resembling the actual nanoclay – resin systems.

The rigidity threshold may take various values, depending on the kind of elastic forces acting between the solid particles. Central forces, i.e., being normal to the surface of the particles, like

in most granular systems, are the most probable and must thus be considered in priority among any others. If central forces are strictly alone, the rigidity threshold should be related to the percolation threshold according to[30]:

$$\Phi_r = 2(D-1)\Phi_c \qquad (10)$$

where D is the dimensionality of the system. Since D = 3, then Φ_r = 4 Φ_c, so the onset of the rigidity should occur at 7.2 vol. % or 13.3 wt. % of nanoclay particles in the resin.

If central forces now prevail over any other kind of elastic forces, but are not alone (e.g. beam-like forces and/or angular forces are also present), the rigidity threshold is much lower and now reads[30]:

$$\Phi_r = \frac{D^2-1}{2D-1}\Phi_c \qquad (11)$$

This latter situation is likely to occur because, due to their very low thickness, the nanoclay platelets are prone to bend when forced to come closer to each other. Putting again D = 3 in Eq. (11) leads to Φ_r = 8/5 Φ_c, so the system should be consolidated above 2.88 vol. % or 5.33 wt. % of particles in the adhesive.

Before it dries and hardens, the adhesive is a liquid consisting of 65 wt. % of urea-formaldehyde resin and 35 wt. % of water. For reaching a given value f of mass fraction after hardening, a higher weight fraction f' of nanoclay has to be introduced in the former liquid composition. The relationship between f' and f may be easily calculated, and reads:

$$f = \frac{f'}{0.65 + 0.35f'} \qquad (12)$$

The various compositions that were investigated, namely f' = 2, 4, 6 and 8 wt. % of nanoclay introduced into the liquid resin, led to the following observation. At 2 wt. %, the mixture flows well but, at 4 wt. %, its viscosity diverges. Preparing homogeneous nanoclay – resin mixture thus becomes very difficult above 4 wt. %. For f' = 2 wt. %, Eq. (12) shows that the corresponding weight fraction of particles in the solid resin is f = 3.04 wt. %. This value is below the two rigidity thresholds that may be calculated from Eq. (10) and (11), i.e., 13.3 and

5.33 wt. %, respectively. On the other hand, f' = 4 wt. % corresponds, again according to Eq. (12), to f = 6.02 wt. %. This result is still below the rigidity threshold corresponding to purely central elastic forces, given by Eq. (10), but is slightly above that obtained by Eq. (11). Now, given the divergence of the viscosity at concentrations close to 4 wt. % of nanoclay in the liquid resin, it is clear that the rigidity threshold is already exceeded. Such a finding strongly supports the validity of Eq. (11) for describing the relationship between percolation and rigidity thresholds.

At this point of the paper, it should be noticed that Eq. (11) was justified theoretically[28] on the basis of the so-called Kirkwood-Keating model[31]. While such a model was already confirmed by numerical simulations[32], it is to our knowledge only the third time that it can be applied to a real three-dimensional material.

Finally, a few remarks should be added concerning the observed decrease of elastic modulus at nanoclay concentrations higher than the rigidity threshold. The higher is the concentration above f'_r, the lower is the Young's modulus. Increasing the concentration above the percolation threshold naturally induces, due to the growing number of inter-particle contacts, a mutual orientation of the particles. Given that the aspect ratio of the nanoplatelets is very high, such an orientation is expected to be strong, just like what happens in composites made of polymer filled with micronic graphite flakes having the same as aspect ratio[33]. The effect is expected to be even stronger because of the geometry of the sample, i.e., a thin film of adhesive between two flat pieces of wood. The closeness of the surface should thus prevent the particles to be fully disoriented, especially at increasingly "high" volume fractions.

Through the concept of excluded volume, the disorientation of the nanoclay disk-like particles may be calculated. The excluded volume of a thin disk of radius r and thickness t is given by Eq. (3), and may also be approximated as:

$$\langle V_e \rangle \approx \frac{\text{sample volume}}{\text{number of nanoplatelets}} = \frac{p\, r^2 t}{\Phi} \qquad (13)$$

By identification of Eqs. (3) and (13), one obtains :

$$2b - \sin 2b \approx \frac{t}{\Phi r} \qquad (14)$$

It should be emphasised that Eq. (14) is just an approximation, since (13) is not true at very low volume concentrations of disks (i.e., $<V_e>$ has a constant maximum value when $\Phi \rightarrow 0$), and also Eq. (3) is exact only for infinitely thin disks, which situation does not match the reality, even if t is very low indeed. However, these assumptions were already successfully applied for describing the continuous orientation of a system of disks submitted to an increasing compression[22]. A decrease of inter-particle voids and an increase of particle concentration are expected to present the same behaviour, so Eq. (14) can be used for predicting the way the particles are misaligned throughout the system. However, rather than a maximum disorientation angle, b was experimentally shown to be the mean disorientation angle, thus corresponding to the full width at half maximum of the distribution of angles. Whatever the concentration of disks and/or the thickness of the composite sample, a fraction of nanoplatelets is indeed always misaligned almost randomly. b is thus assumed to be the same as the so-called mosaic spread[28].

Fig. 10 shows the disorientation angle of the nanoclay particles, b, as a function of their volume concentration, Φ, inside the dry, hardened, resin, calculated from Eq. (14). The observed orientation, particularly fast at low volume fractions, is expected to lower the mechanical properties perpendicularly to the bedding layer, i.e., to the surface of the adhesive joint. To a lesser extent, the orientation should also lower the percolation (and hence the rigidity) thresholds. Given that disorientation is only characterised here by a single angle rather than by a distribution, quantifying both effects is not possible. The second one, dealing with the thresholds, is only expected to be weak, because of the non-negligible number of particles remaining fully disoriented, which tend to leave unchanged the values of Φ_c[21].

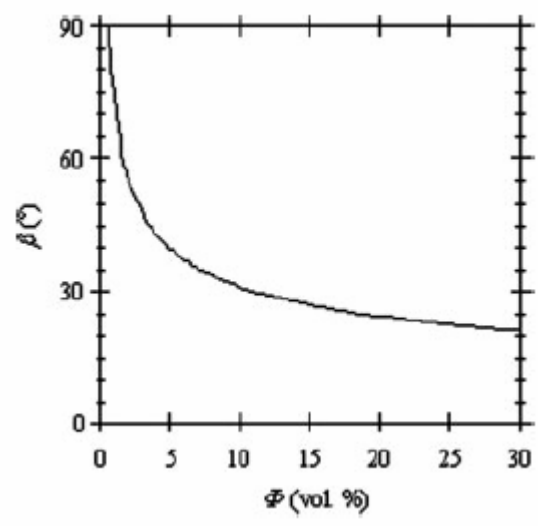


Figure V.12. Mean angle of disorientation, β, of the nanoclay particles as a function of their volume concentration, Φ, in the dry hardened resin.

V.3. CONCLUSIONS

In this work, the effects of Na-montmorillonite (Na-MMT) nanoclay on thermosetting UF resins used as adhesives for panels were studied. Some conclusions could be drawn:

(1) XRD characterization indicated that Na-MMT completely exfoliated when mixed with UF. The layers dispersed in UF resins irregularly at nano lever.

(2) The addition of Na-MMT could accelerate the curing of UF resin and was helpful to the formation of regular cross-linked structure.

(3) The results of TMA showed that the modulus of elastic (MOE) of UF resin/Na-MMT system without hardener increased with the increase of the addition amount of Na-MMT till 4% on the solid resin load. However, for the UF system with hardener, Na-MMT had no obvious effects on the final dry strength performance of resins. The difference on performance is probably related to the permeation of resins.

(4) The addition of small percentages of Na-MMT appeared to increase considerably the water resistance of the UF-bonded particleboard and plywood. Na-MMT could decrease the formaldehyde emission of particleboard, too.

(5) Both dry strength and wet strength performance with Na-MMT as fillers were better than those with wheat flour. The modification mechanisms for Na-MMT and wheat flour on UF

resins probably were different.

(6) A suitable addition percentage could be determined by the modelling method mentioned in this work.

V.4. REFERENCES

[1] Pizzi A. Amino-resin Wood adhesives, chapter 2 in Wood Adhesives Chemistry and Technology (A.Pizzi Ed.). Marcel Dekker Inc., New York, 1983.

[2] Pizzi A, Lipschitz L, Valenzuela J. Theory and practice of the preparation of low formaldehyde emission UF adhesives. Holzforschung 1994, 48:254-261.

[3] Yuan J.S. Application of fly ash floating beads and bentonite in the polymer modified cement-based waterproof paint. Fly Ash Comptehensive Utilization. 2007(6):45-46.

[4] Lei Y, Wu Q, Clemons C.M, *et al*. Influence of nanoclay on properties of HDPE/wood composites. Journal of Applied Polymer Science. 2007, 106:3958-3966.

[5] Yano K, Usuki A, Okada A. Synthesis and properties of polyimide-clay hybrid. Journal of Polymer Science Part A: Polymer chemistry. 1993,31:2493-2498.

[6] Yano K, Usuki A, Okada A. Synthesis and properties of polyimide-clay hybrid films. Journal of Polymer Science Part B : Polymer Physics. 2000,35:2289-2294.

[7] Usuki A, Kojima Y, Kawasumi M, *et al*. Synthesis of nylon 6-clay hybrid. Journal Material Research. 1993,8:1179-1184.

[8] Alexandre, M., Dubois, P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials[J]. Materials Science and Engineering, 2000,28: 1-63.

[9] Vaia R.A, Price G, Ruth P.N, *et al*. Polymer/layered silicate nanocomposites as high performance ablative material. Journal of Applied Clay Science. 1999,15:67-92.

[10] Levendis D, Pizzi A, Ferg E. The correlation of strength and formaldehyde emission with the crystalline amorphous structure of UF resins. Holzforschung 1992, 46, 263-269.

[11] Pizzi A, Lu X, Garcia R. Lignocellulosic substrates influence on TTT and CHT curing diagrams of polycondensation resins. Journal of Applied Polymer Science. 1999,71,915-925.

[12] Australian/New Zealand standard AS/NZS 1859.1. Reconstituted wood-based panels– Specifications. Part 1: particleboard. 2004.

[13] Du G.B, Wu L.Z, Yang Q.X. Development on mineral filler for UF resin. Zhanjie, 1995,16(3):9-12.

[14] Wang Z.L. Measuring methods of nano-material. Chemistry Industry Press. 2005.

[15] Jiang G.L, Zhang P.P. Processing and application of montmorillonite. Chemistry Industry Press.2005.

[16] Qi Z.N, San W.Y. Theory and practice of polymer/layered silicate nano-composite. Chemistry Industry Publishing House.Chapter 2:19-26.

[17] Bourg, C.I. PhD thesis, University of California, Berkeley, 2004

[18] Greenwood N.N, Earnshaw A. Chemistry of the Elements. Pergamon Press. Oxford. 1984:411.

[19] Shannon R.D. Crystal physics, diffraction, theoretical and general crystallography. Acta Crist A. 1976, 32, 751-767.

[20] Shainberg I, Kemper W.D. Hydration status of adsorbed cations. Soil Science Society of America Journal. 1966, 30, 707-713.

[21] Celzard A, Mcrae E, Deleuze C, *et al*. Critical concentration in percolating systems containng a high-aspect-ratio filler. Phys Rev B. 1996,53:6209-6214.

[22] Celzard A, Mareché J.F, Furdin G. Modelling of exfoliated graphite. Progress in Materials Science. 2005,50:93-179.

[23] Charlaix E, Guyon E, Rivier N. A criterion for percolation threshold in a random array of plates. Solid State Commun. 1984,50:999-1002.

[24] Charlaix E. Percolation threshold of a random array of discs: a numerical simulation. Journal of Physics A: Mathematical and General. 1986,19:533-536.

[25] Celzard A, Mareché J.F, Payot F. Simple method for characterizing synthetic graphite powders. Journal of Physics-London-D Applied Physics. 2000,33,1556-1563.

[26] Mendelson K.S, Cohen M.H. The effect of grain anisotropy on the electrical properties of sedimentary rocks. Geophysics. 1982,47:257.

[27] r_R = 2.35 is the average of a number of values (ranging from 2.0 to 2.7) given in the literature for sodium montmorillonite

[28] Celzard A, Krzesiñska M, Mareché J.F, *et al*. Scalar and vectorial percolation in compressed expanded graphite. Physica A. 2001,294:283-294.

[29] Sahimi M. Non-linear and non-local transport processes in hererogeneous media: from long-range correlated percolation to fracture and materials breakdown. Physical Reports. 1998, 306, 213-395.

[30] He H, Thorpe M.F. Elastic properties of glasses. Physical Review Letters. 1985,54,2107-2110.

[31] Celzard A, McRae E, Mareché J.F, *et al*. Composites based on micron-sized exfoliated graphite particals: electrical conduction, critical exponents and anisotropy. Journal of Physics and Chemistry of Solids. 1996,57:715-718.

CHAPTER VI

INFLUENCE OF NANOCLAY ON PHENOLIC RESIN FOR WOOD ADHESIVES

VI.1. INTRODUCTION

Now research on plymer/layered silicate is concentrated on thermal-setting plymers, such as polyamides, polypropylene, polystyrene, poly(methyle methacrylate) (PMMA), thermal-setting polyester, macromolecule polyethylene, and so on. There are a few researches on thermal-curing polymers comparatively. Some work has been done only on polyacrylate[1], epoxy[2-3], polyurethane[4-5], unsaturated polyester[6].

Phenol-formaldehyde (PF) resin is the earliest commercial synthetic resin. It can be easily gotten and has good performance, especially good water resistance. PF resin has been used in various areas and it is the most commonly used resin for exterior grade wood panels in wood industry[7-8]. Progress in research and development in this adhesive industry has shown many successes during the last decades. Considerable research on the upgrading of the performance of thermoplastic resins by addition of submicron-size materials has stimulated the consideration on the feasibility to achieve enhancement of material properties of PF resin with the inclusion of nano-montmorillonite.

Choi *et al.*[9] were the first to prepare phenolic resin/layered silicate nanocomposites with intercalated or exfoliated nanostructures by melt interaction using linear novolac and examined their mechanical properties and thermal stabilities. Lee and Giannelis[10] reported melt interaction method for phenolic resin/clay nanocomposites, too. Although PF resin is a widely used polymer, totally there are not many researches on PF resin/ montmorillolite nanocomposites. And most of the researches are concentrated on linear novolac resins. Up to now, only limited researches on resole-type phenolic resin/layered silicate nanocomposites have been published[12-15] and there is still no literature reported the influence of nano montmorillonite on phenolic resin for wood adhesive.

Novolac resins were formed by the reaction between phenol and formaldehyde with acid catalyst. Wang *et al.*[16] used H-montmorillonite as catalyst and synthesized Novolac/layered silicate nanocomposites by the condensation polymerization of phenol and formaldehyde. It

was found that the silicate layers were exfoliated and the reactants entered the interlayer galleries easily. It turned out that the intra-gallery condensation of phenol and formaldehyde played a predominant role in the exfoliation of MMT. With the reaction went on, layer space became larger. Exfoliated clay plates with interlayer spacings of 10-30 nm were dispersed in the matrix uniformly. Resol resins may be prepared by condensation catalyzed by alkaline Na-MMT, just as what H-MMT has done to novolac resins.

On the basis of PF resin, pheno-urea-formaldehyde (PUF) resin is developed to decrease the cost and accelerate curing. PUF resin consists of three components, namely phenol, urea and formaldehyde. Similar to the standard PF resin, PUF resin is prepared under alkaline conditions[17-20]. Now there are a few reports on its actual application. Some products are even commercialized by Dynea company[21].

The results of Chapter V showed that montmorillonite nanoclays became completely exfoliated which can improve the performance of thermosetting UF resins for interior-grade wood panels. Then urea in PF resin could be possibly useful to the preparation of PUF resin/MMT composites, too. However, little research has been done in this field till now.

This work then deals with the addition of different types of montmorillonite nanoclays, especially Na-MMT, to thermosetting PF and PUF resins to study: (1) the effect of the PF and PUF resin on the level of intercalation or exfoliation of the montmorillonite nanoclays; (2) the influence of resin structure on intercalation; and (3) the improvement in performance of the resin by analysing the performance of wood panels/composites bonded with PF/ montmorillonite nanoclays.

VI.2. RESULTS AND DISCUSSION

VI.2.1. Effects of mixing methods of Na-MMT with PF resins on the performance of resin system

Na-MMT was used as filler of PF resins, which is the same as for UF resin in Chapter V. The performance of the resin on the addition of montmorillonite nanoclays by different mixing route was first tested by thermo mechanical analysis (TMA). In Fig VI.1 is shown the increase of modulus of elasticity (MOE) as a function of temperature of joints bonded with a PF resin control and with the same PF resin to which was added different proportion of Na-MMT with second mixing route, with which Na-MMT was mixed with PF resins after the preparation of PF. Although the degree of improvement with different addition percentage of Na-MMT is different, in all cases the maximum value of the MOE increases by addition of the montmorillonites. However, the results obtained from first mixing route do not show a real improvement for progressively increasing proportions of Na-MMT in the PF resin (Fig. VI.2). Even the higher result with 5% Na-MMT addition was found to be not significant. This result indicates that premixing of montmorillonite clay with phenol and water doesn't do some use to the performance of resin. Then for the following research work the second mixing route was chosen.

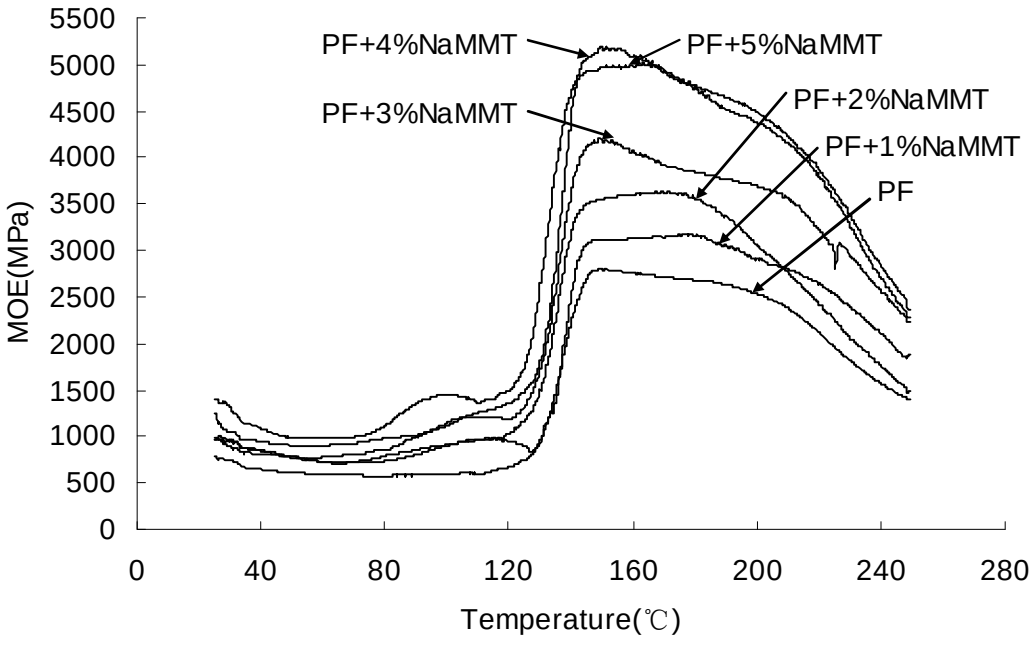


Figure VI.1. Thermomechanical analysis (TMA): curves of MOE as a function of temperature of PF resin with different percentages of NaMMT added by second route.

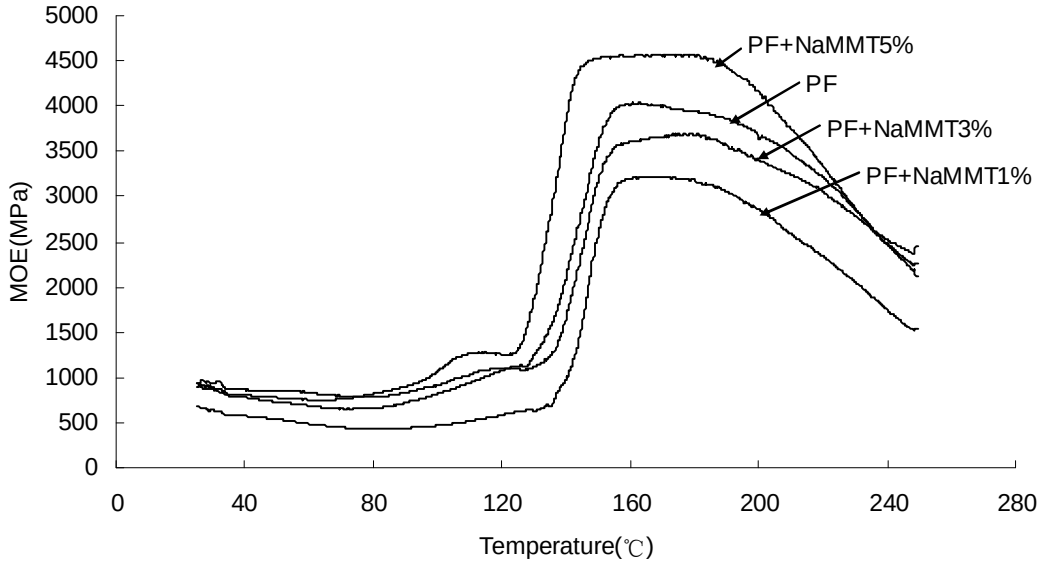


Figure VI.2. Thermomechanical analysis (TMA): curves of MOE as a function of temperature of PF resin with different percentages of NaMMT added by first route.

VI.2.2. XRD results of Na-MMT/PF resin system

The XRD pattern of the Na-MMT, and of the PF resin with and without nanoclay is shown in Fig. VI.3. Fig. VI.3 reports the 2θ angle spectrum in the 0°-16°. The peak appearing at 7.03° corresponds to Na-MMT. In the case of the pure Na-MMT the strong 2θ peak at 7.03° corresponds to a *d*-spacing of 1.26 nm according to the Bragg equation. For the PF/NaMMT system the (001) peak is still present but it does shift to a lower 2θ angle value (6°) to a *d*-spacing of 1.47 nm according to the Bragg equation. This decrease in the value of the 2θ angle indicates an increase, although relatively small, in the distance between the nanoclay planes. It appears that Na-MMT was some degree of intercalation rather than exfoliation to PF resin.

During the preparation of polymer/layered silicate nanocomposites, to improve the compatibility between MMT and polymer, MMT needs to be treated by organic compounds to form so-called organic MMT. In this research, Na-MMT without organic treatment could be intercalated, too. The possible reason for that is the good compatibility between the hydroxy groups of PF resin and MMT. What's more, hydrogen bonds could be formed between the hydroxy groups of PF resin and oxygen on the surface of MMT.

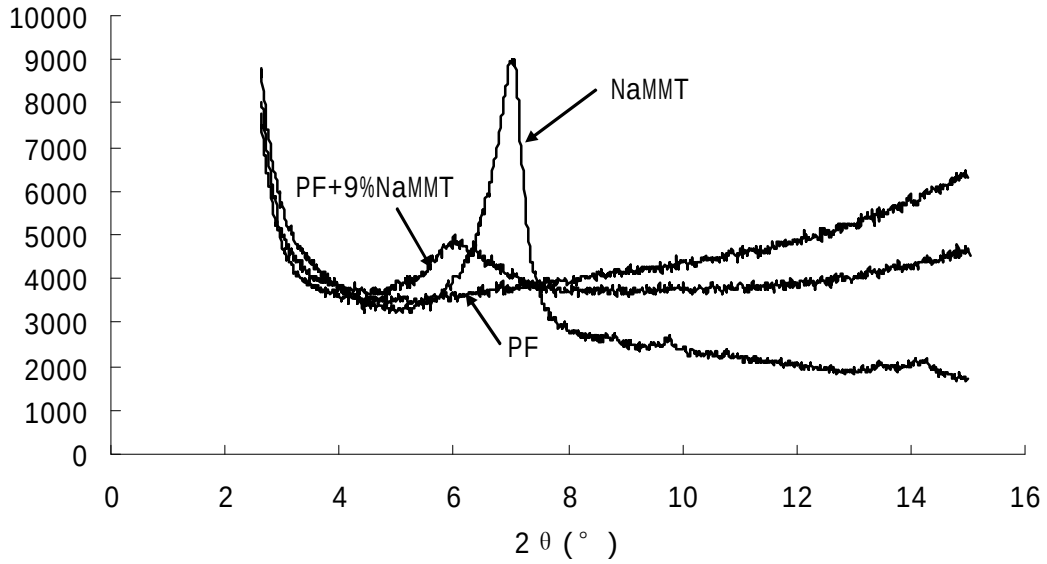


Figure VI.3. X-ray diffraction (XRD) spectra for Na-MMT, PF resin, and PF+9%Na-MMT in the 2θ angle range 0°-16°.

PF mixed with Na-MMT shows some difference to what observed in UF resins where Na-MMT is completely exfoliated with the same mixing process. The different structure of resin polymers is probably responsible for it. There are two main differences on the structure between UF and PF resins. One is that PF resin has a three-dimensional structure even when uncured. The other is that there are some hydrophilic groups existing in UF resins, especially amino groups.

Lots of research indicates that it is very difficult for thermosetting resin to be intercalated into the silicate gallery as a result of its three-dimensional structure and rigidity. Some PLS has been gotten for some thermosetting resins such as epoxy, unsaturated polyester, polyurethane and so on. But only O-MMT was used. While in this research, considering the cost and the hydrophilic groups existing in the adhesives, Na-MMT was chosen. Wu *et al*[22] proved that organic treatment could do use to the compatability between MMT and PF resins. The interclator with benzene ring is the best for the preparation of PF resin/MMT composites. Compared with O-MMT, Na-MMT is much difficult to to be intercalated.

Because of the unreversibility of hardening reaction of thermosetting resins, filling, dispersing

and curing will happen as the resin cures. Therefore, it is better to use synthesis methods to prepare thermosetting resins/nanocomposites. The curing process will cause the intercalation state uncertain, too. In this research, resol was prepared with a higher molar ratio F/P=1.76, which could cured faster than novalac with lower molar ratio. Coupled with the physical obstruction of MMT, resin may cure outside the layers when the time is not enough for it to enter into the space of MMT, which will restrict intercalation of MMT[23]. According to the report of Xu W.B, a kind of nanocomposite of phenolic resin/hexamine/montmorillonite, which was obtained by the treatment of organic montmorillonite, is prepared by casting and curing, and phenol resin exhibit crosslinked chains by chemical bonds forming a three-dimensional network while the mechanisms of phenol resin are different. Resol type of resin can form the intercalated nanocomposite, while novolac phenolic resin can partly form the exfoliated nanocomposite. The curing kinetic of novolac phenol resin gives information that activation energy and reaction order decrease with the addition of organic montmorillonite. With the reduction of the activation energy and the raction order, it is possible to take advantage to the application of nano-composite[24]. Therefore, the interclation of MMT was partly determined by the structure of resin polymer and the compatibility of lamellaes.

Compared with linear polymer structure of low molar ratio UF resin, the general resol phenolic resin has a three-dimensional structure even if the resin is not crosslinked. It is obvious that easier for the lamella of the layered silicate to be intercalated by the former with linear polymers structure while be difficult by latter phenolic resin with three-dimensional structure.

To ascertain if PF resin prepared in this study has three-dimensional structure, MALDI-TOF was used to give some clues on the structure characteristic of phenol formaldehyde (PF) resin. Figure V.5 is the MALDI-TOF mass spectra of PF. 313Da can be assigned as P_2F_4 (P: phenol, F: formaldehyde. The number is that for structure unit), 343Da is P_2F_5, 449Da is P_3F_6, 479Da is P_3F_7, 585Da is P_4F_8, 615Da is P_4F_9, 721Da is P_5F_{10}, and other molecule with high mass can be deduced by the same way. Peak-to-peak mass increments of 136 dominate in spectra which confirm structure being three-dimensional, comparing with novolac line structure has repeated mass increments of 106.

Besides hydroxy groups, the $-NH_2$ on the UF molecules may be another reason for the difference of interaction between UF and PF resin. The main characteristic of MMT is that the metal ions absorbed on the surface of MMT by electrical force can be replaced by organic intercalator, among which alkyl ammonium salt is one of the most communly-used ones. The basic group for the replacement reaction is $-NH_3^+$ at the end of the interclator chain. The similarity on the structure between UF resin and alkyl ammonium salt will possibly be helpful to the intercalation.

Probe PF – Aceton/H_2O -- NaCl; Massenbereich: 200-1900 Da

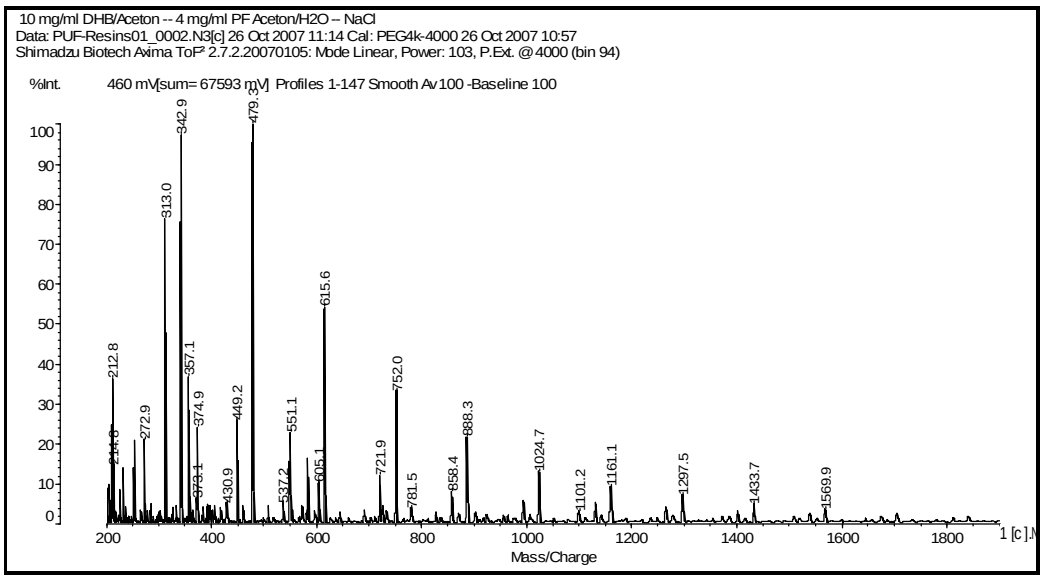


Figure VI.4. Matrix-assisted laser desorption/ionization mass spectrometry

VI.2.3. Plywood performance boned with Na-MMT/PF resin

The lab-prepared plywood results in Table VI.1 indicates that Na-MMT had no obvious effects on the dry shear strength, while it tends to improve the tensile strength after boiling and it is only up to 1% addition of Na-MMT on PF resin solids. Higher addition percentages, although giving higher results compared with the control show a decrease from the maximum value obtained at 1% addition. There is no significant difference in dry tensile strength. These results indicate that addition of Na-MMT does not contribute much to dry performance but improve the wet performance of PF adhesive, which is similar to what has been found in UF adhesives

Table VI.1. Results of plywood bonded with a PF resin added of different percentages of Na-MMT.

Na-MMT(%)	Dry tensile strength (MPa)	Tensile strength 3h boiling (MPa)
0	1.43(22)	1.30(30)
1	1.42(0)	1.65(20)
3	1.40(5)	1.42(10)
5	1.44(20)	1.37(20)

VI.2.4. Influence of Na-MMT with different percentage on the performance of PUF resin

Same interesting accelerating was obtained in PUF resin from TMA analysis: curing is faster as the percentage of Na-MMT increases progressively up to 3%, as can be seen by the curing temperature rise shifting to lower temperatures. While with the Na-MMT addition amount higher than 3%, curing become slower. Then even the cure-acceleration advantage is lost (Fig. VI.3)

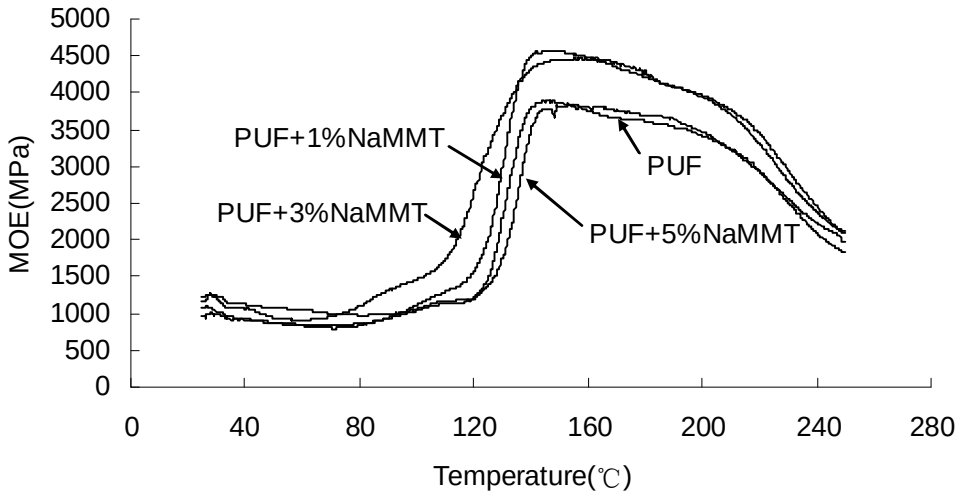


Figure VI.5. Thermomechanical analysis (TMA): curves of MOE as a function of temperature of PUF resin with different percentages of Na-MMT.

VI.2.5. XRD analysis of Na-MMT/PUF resin system

Similar XRD result was found in PUF resin which has similar structure with PF resin. The XRD

patterns of the Na-MMT nanoclay, and of the PUF resin with and without different amounts of nanoclay are shown in Fig. VI.4. For the PUF/NaMMT system the (001) peak is still present but it does shift to a lower 2θ angle value (6.35°) hence to a *d*-spacing of 1.39 nm according to the Bragg equation. This is rather little less even than what observed for PF resins. According to the research of Du G.B et al, PF resin is still the main component of PUF co-condensed resin. Under the alkaline condition, most of the urea-formaldehyde is in the form of methylolurea with low molecule weight. Even UF resin is coupled in a strong alkaline condition, there isn't enough UF resin with higher molecule weight to make the space larger between silicate layers[25].

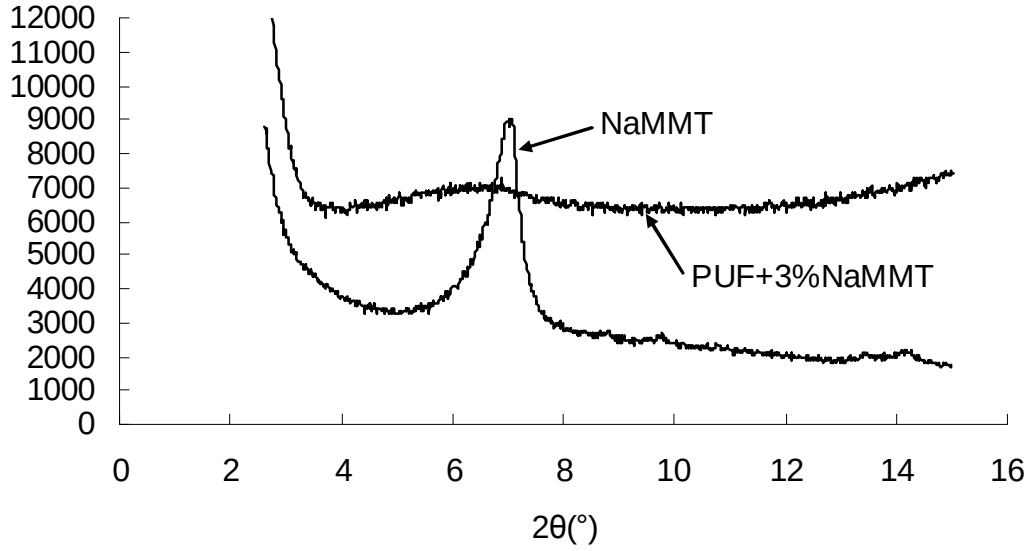


Figure VI.6. X-ray diffraction (XRD) spectra for NaMMT and PUF+NaMMT in the 2θ angle range 0°-16°.

VI.2.6. Performance of Na-MMT/PUF resin

To further ascertain if it is nanoclay that improves water resistance of resin, a phenol-urea-formaldehyde (PUF) resin was prepared. The results of plywood prepared with these resins are shown in Table 5.2. Similar results were found as for PF resin. In this case the performance improves up to 3% addition of Na-MMT. The reason for the performance's decrease once the addition percentage is higher than 3% may be that it is more difficult to get a uniform mixture between more Na-MMT and resin. It is worth noting that all of UF, PF, PUF resin/nanocaly system found increase of water resistance with addition of Na-MMT.

Table VI.2. Results of plywood with a PUF resin added of different percentages of Na-MMT.

Na-MMT(%)	Dry tensile strength (MPa)	Tensile strength 3h boiling (MPa)
0	1.35(23)	1.51(11)
1	1.45(31)	1.55(39)
3	1.55(18)	1.62(23)
4	1.31(26)	1.40(10)
6	1.28(26)	1.41(43)

VI.2.7. DSC analysis of Na-MMT/PF resin

Figure VI.6 shows the DSC curves obtained at heating rate of 10°C/min for the neat PF resin and the PF resin with 6% addition of Na-MMT. These two curves present some differences in the number of peaks. The neat PF resin exhibits a wide exothermic peak which is caused by the condensation either between methylol groups and phenol reactive sites to form methylene bridges or between two methylol groups to form dimethylene ether bridges. There are two differences between the PF resins with and without Na-MMT. One is the pH, namely, 12.6 for the PF resin with 6% addition of Na-MMT and 10 for the neat PF resin. The other is the intercalation state which is confirmed by the XRD results. Both of them could be the reason which will be responsible for the peaks splitting. The difference of pH has some effects on activation energies of reactive groups of PF resin[26]. The difference of the curing speed caused by the intercalation will do some to the the split of exothermic peaks. Since the split is very obvious, the latter reason is much possible.

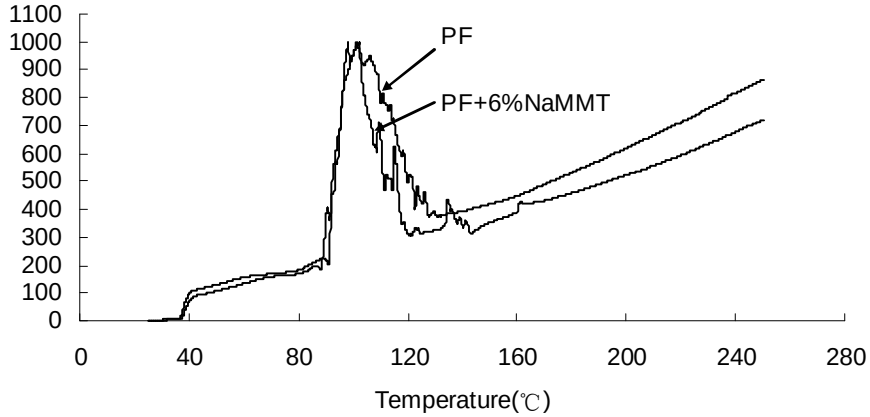


Figure VI.7. Differential scanning calorimetry (DSC) traces of the PF resin alone and of the PF + 6% NaMMT

VI.2.8. Effects of MMT types on performance of PF-based plywood

Table VI.3 reports the results of PF-bonded plywood to which have been added 5% on resin solids of different types of montmorillonite nanopowders. Thus MMT, Na-MMT of two different grades, and O-MMT, were tested. Again, from the results of Table VI.3, there is no significant difference between PF-bonded plywood and inorganic MMT types nanoclays, indicating that all types of inorganic MMTs with 5% addition amount do not contribute to improve the performance of PF adhesive resins. The only exception is O-MMT where an improvement in both dry and after boiling tensile strength can be noticed. The reason why exists the difference on performance between O-MMT and other type of MMTs is possibly that organoclay always shows larger *d*-spacing when compared with unmodified clay composites, that is to say, the degree of performance improvement of nanocaly to thermosetting resin for wood adhesive probably depends on the level of intercalation.

Table VI.3. Results of plywood bonded with a PF resin added of 5% on resin solids of different types of MMT

MMT type	Dry tensile strength (MPa)	Tensile Strength 3h Boiling (MPa)
-	1.43(22)	1.30(30)
MMT	1.38(5)	1.28(7)
NaMMT	1.44(20)	1.37(20)
NaMMT purest	1.51(0)	1.29(0)
OMMT	1.78(0)	1.81(10)

VI.3. CONCLUSIONS

Some conclusion could be drawn from the results on phenol-formaldehyde (PF) and phenol-urea-formaldehyde (PUF) resins of this paper:

(1) XRD results showed that though some Na montmorillonite (Na-MMT) nanoclay had some degree of intercalation after being mixed with PF and PUFresins, it was difficult for resole-type phenolic resin with three-dimensional structure to be composited with nano clay.

(2) When mixed in small proportions in PF and PUF resins, Na-MMT could improve the wet performance of PF and PUF resin, while it does not appear to improve much on dry performance. To increase the amount of Na-MMT to the resins had no obvious effects on the performance of lab-prepared plywood.

(3) However when O-MMT with larger interlayer distance being used with the addition proportion up to 5% on PF resin solid, an improvement in both dry and after boiling tensile strength could be noticed. MMT with a limit increase of interlayer distance had limit effects on PF and PUF.

(4) Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) indicated that NaMMT has an accelerating effect on the curing of PF and PUF resins. Intercalation state of MMT can possibly cause the change of exothermic situation during the curing of resins.

VI.4. REFERENCES

[1] Dong Choo Lee, Lee Wook Jang, Preparation and characterization of PMMA clay hybrid composire by emulsion polymerization. Appl Polym Sci.1995,61:1117-1122.

[2] Lv J.K, Ke Y.C, Qi Z.N, *et al*. Synthesis and mechanical properties of epoxy/clay nanocomposites. Acta Materiae Compositae Sinica. 2002,19(1):117-121.

[3] Fu W.L, Liu J.C, Chen X.F, *et al*. Study on epoxy resin/clay nanocomposite. Zhanjie. 2002,23(2):5-8.

[4] Yi Tien, T.-K.Chen, K.-H.Wei. Synthesis and characterization of novel segmented polyurethane/clay nanocomposites. Polymer. 2000,41:1345-1353.

[5] Zilg C, Thomann R, Mulhaupt R, *et al*. Polyurethane nanocomposites containing laminated anisotropic nanoparticles derived from organophilic layered silicates. Adv. Mater. 1999,11(1):49-52.

[6] Wang L.X, Li J.F, Zhang H.B, et al. Friction and wear behavior of unsaturated polyester/montmorillonite intercalated nanocomposites. Tribology. 2003,23(3):197-200.

[7] Pizzi A. Amino-resin Wood adhesives, chapter 2 in Wood Adhesives Chemistry and Technology (A.Pizzi Ed.). Marcel Dekker Inc., New York, 1983.

[8] Pizzi A, Lipschitz L, Valenzuela J. Theory and practice of the preparation of low formaldehyde emission UF adhesives. Holzforschung. 1994, 48(3), 254-261.

[9] Choi M.H, Chung I.J. Morphology and curing behaviors of phenolic resin-layered siliate nanocomposites prepared by melt intercalation. Chemistry of Materials. 2000,12:2977-2983.

[10] Lee J.D, Emmanuel G.P. Synthesis and characterization of unsaturated polyester and phenolic resin nanocomposition. Polymer Preprints. 1997, 38(2):688-689.

[11] Guo J.S, Zheng Q.M, Wang S.H, *et al*. Research of phenolic resin/modified montmorillonite nanocomposites. Journal of Beijing University of Chemical Technology. 2001, 28(2):34-36.

[12] Manfredi L.B, Puglia D, Kenny J.M, *et al*. Structure-properties relationship in resol/montmorillonite nanocomposites. J Appl Polym Sci, 2007,104(5):3082-3089.

[13] Wang H.S, Zhao T, Yan Y.H, *et al*. Synthesis of resol-layered silicate nanocomposites by reaction exfoliation using acid-modified montmorillonite. J Appl Polym Sci, 2004, 92(2): 791-797.

[14] Lopez M, Blanco M, Ramos J.A, *et al*. Synthesis and characterization of resol-layered silicate nanocomposites. J Appl Polym Sci, 2007,106(4):2800-2807.

[15] Dai L.J. Synthesis and characterization of phenolic resin/montmorillonite nanocomposites. Chemistry and Adhesion. 2006,28(2):79-81.

[16] Wang H.S, Zhao T, Zhi L.J, *et al*. Synthesis of novolac/layered silicate nanocomposites by reaction exfoliation using acid-modified montmorillonite macromol. Rapid Commun. 2002,23(1):44-48.

[17] Pizzi A , Stephanou A , Antunes I, *et al*. Alkaline PF resins linear extension by urea condensation with hydroxybenzyalchohol groups. J. Appl. Polym. Sci.1993,50:2201-2207.

[18] Zhao C.H, Pizzi A, Garnier S. Fast advancement and hardening acceleration of low-condensation alkaline PF resins by esters and copolymerized urea. Journal of applied polymer sciences, 1999,74:359-378.

[19] Du G.B, Li J, Yang Z. Synthsis and structure analysis of phenol-urea-formaldehyde co-condensed resin. Scientia Silvae Sinica. 2000,36(5):73-77.

[20] He G.B, Yan N. Influence of the synthesis conditions on the curing behavior of phenol-urea-formaldehyde resole resins. J. Appl. Polym. Sci. 2005,95:1368-1375.

[21] Osman Z, Pizzi A, Kantner W, *et al*. PUF panel adhesives doped with additional urea and reinforced by isocyanates.Holz Roh Werkst. 2005,63:53-56.

[22] Wu Z.G, Zhou C.X. Synthesis of phenolic resin/montmorillonite nanocomposites by suspension polymerization. Journal of Polymer. 2001,14(4): 449-452.

[23] Lv W.H. Preparation of wood/montmorillonite intercalation nanocomposite. Beijing Forestry University.2004:74.

[24] Xu W.B, Bao S.P, Shen S.J, *et al*. Studies on the preparation and curing reaction kinetics of phenolic resin/montmorillonite nanocomposite.Acta Polymerica Sinica. 2002(4):457-461.

[25] Du G.B, Lei H, Pizzi A, *et al*. Synthesis-structure-performance relationship of cocondensed phenol-urea-formaldehyde resins by MALDI-ToF and ^{13}C-NMR. 2008,110(2): 1182-1194.

[26] He G.B, Riedl B. Phenol-urea-formaldehdye cocondesed resol resins: Their synthesis, curing kinetics, and network properties. J Polym Sci Part B: Polym Phys 2003, 41: 1929-1938.

CHAPTER VII

GENERAL CONCLUSIONS

VII.1 GENERAL CONCLUSIONS

Totally, the main work of this paper can be divided into two parts. One is the study of natural material-based adhesive, specifically tannin, lignin and soy protein adhesives. The other is the study of montmorillonite to be used as extender of wood adhesives. Montmorillonite has already attracted a wide attention in the field of nano-composite.

Environment-friendly tannin/lignin and soy protein-based wood adhesive are studied. The feasibility and mechanism to use non-toxic, non-volatile glyoxal to substitute toxic, volatile formaldehyde in relevant formulations is analyzed. Then the suitable addition percentage is determined. Lab-prepared particleboard procedure is optimized, too. The main objectives on natural wood adhesive then are to completely eliminate formaldehyde from the adhesive and to increase the proportion of natural, envinronmentally friendly materials in these adhesive formulations.

The results shown in this work confirmed few aspects of these formulations, namely:

(1) The performance of these formulations is determined in a great degree by the amount or proportion of the pMDI used. Although the addition of the very reactive tannin allowed a marked decrease in the proportion of pMDI in the lignin-based adhesive, it does not appear that pMDI could be eliminated completely. The strength of glyoxalated lignin and soy adhesive themselves are weak. CP-MAS ^{13}C-NMR results showed that the reaction between glyoxal and soy protein existed indeed. But these resulted hydroxy couldn't condensed to a cross-linked structure. Therefore, pMDI is a necessary cross-linker to glyoxalated soy protein adhesive. Its addition amount determines performance of final resin.

(2) Lignin-based adhesives and glyoxalated soy-based wood adhesives mixed with pMDI and mimosa tannin satisfying the requirements of relevant international standards for the manufacture of wood particleboard are obtained. These lignin-based or soy-based wood adhesives did not use any formaldehyde in their formulation, this having been substituted by a non-volatile non-toxic aldehyde, namely glyoxal. In these formulations, 70%-80% the

total resin solid was natural material. Lignin-based adhesive with weight ratio glyoxalated lignin:pMDI:tannin=75:25:20 gave a better result. The addition of a further amount of triacetin or glyoxal in the glue-mix had no obvious effects oh the performance of glyoxalated lignin formulation. For soy-based adhesive, the best formulation of all the ones tried was the glyoxalated soy/tannin/pMDI 54/16/30 by weight. This resin can be used in a much lower proportion on wood chips and can afford pressing times fast enough to be significant under industrial panel pressing conditions.

(3) The IB strength results of boards bonded with the heat-treated lignin(GLAF) are worse than when using the original lignin itself; this result was confirmed by both FTIR and TMA. Thus, the heat treatment that is so beneficial when applied to reduce degree of polymerization of high-molecular-weight lignin in European and North American countries does not work when applied to already low-molecular-mass lignin.

(4) The particleboard strength with formulations with glyoxalated soy was better than that with glyoxalated lignin. When both of them being used in one formulation, to increase the addtion amount of glyoxalated soy was helpful to the improvement of the performance of panels.

(5) The results of CP-MAS ^{13}C-NMR and FT-IR proved the reaction between lignin and glyoxal.

Some work has been done on the study of the influence of nano-montmorillonite on urea-formaldehyde resin and phenolic resin adhesives. The level of exfoliation of the MMT being mixed with these resins is judged. The thermal and mechanical characteristics of mix system are studied. The main objective of the study of influence of MMT on wood adhesive is to estimate the feasibility of MMT to be used as fillers of wood adhesive, to study the modification mechanism of MMT on wood adhesive, and to optimize the modification procedure. Some conclusions can be drawn.

(1) XRD characterization indicates that Na montmorillonite (Na-MMT) completely exfoliated when mixed with UF, while it only has some degree of intercalation when added to PF and PUF resins. It means that it is difficult for resole-type phenolic resin with three-dimensional

structure to be composited with nano clay.

(2) The addition of Na-MMT could accelerate the curing of UF resin and was helpful to the formation of regular cross-linked structure. Na-MMT has the same accelerating effect on PF and PUF resins, too. Intercalation state of MMT can possibly cause the change of exothermic situation during the curing of resins.

(3) The results of TMA showed that the modulus of elastic (MOE) of UF resin/Na-MMT system without hardener increased with the increase of the addition amount of Na-MMT till 4% on the solid resin load. However, for the UF system with hardener, Na-MMT had no obvious effects on the final dry strength performance of resins.

(4) The addition of small percentages of Na-MMT does not appear to improve much on dry performance, while it seems to increase the water resistance of the UF-bonded and phenolic resin-bond panels. Na-MMT could decrease the formaldehyde emission of particleboard, too. Both dry strength and wet strength performance with Na-MMT as fillers were better than those with wheat flour. The modification mechanisms for Na-MMT and wheat flour on UF resins probably were different.

(5) When O-MMT with larger interlayer distance being used with the addition proportion up to 5% on PF resin solid, an improvement in both dry and after boiling tensile strength could be noticed. MMT with a limit increase of interlayer distance had limit effects on PF and PUF.

VII.2. SUGGESTIONS

In this paper, efforts were concentrated on two topics, namely natural adhesives and mineral fillers of adhesives. Because of the restriction of time and equipments, there are still some questions to be resolved. My suggestions to the future work on the relative fields to this paper are as below:

(1) The lignin material used in this paper was commercialized product, which might show different characteristics as that of practical black liquid from a paper factory. Normally more unstable performance could be seen from black liquid. There is still a lot of work to do on lignin-based adhesive on the view of lignin’s origin.

(2) There are many reagents which can be used as cross-linker of soy protein-based adhesive,

such as aldehyde and its resultants by addition reaction. Besides glyoxal, other chemical reagents, such as glutaraldehyde, urea-formaldehyde resin, phenol-formaldehdye resin could be used to cross-link soy protein molecular. Its mechanism and preparing procedure are deserved to be studied.

(3) For natural adhesive, poor water resistance is another drawback to its development. Therefore, to find a way to improve its water resistance will be an important researching branch in the field of natural adhesive for a long time.

(4) In this paper, some work has been done on the influence of MMT on the performance of urea-formaldehyde and phenol-formaldehyde resins. With the similar methods, the influence on the performance of lignin-, tannin- and soy protein-based adhesive has been studied, too. Though MMT showed no remarkable effects on the final natural adhesive resin system, the possibilities still exist to use them to other types of adhesive, especially thermol-plastic adhesives, such as poly-vinyl acetate, hot-melting adhesives and so on. Some work should be done on the mixing methods of MMT and resin adhesive.

LISTE OF PAPERS IN THE PERIOD OF APPLICATION OF Ph.D DEGREE

1. **Hong Lei**, A. Pizzi, A. Despres, H. Pasch, Guanben Du. Esters acceleration mechanisms in phenol-formaldehyde resin adhesives. Journal of Applied Polymer Science. 2006,100:3075-3093.
2. **Hong Lei**, A. Pizzi, Guanben Du, *et al.* Variation of MUF and PMUF resins mass fractions during preparation. Journal of Applied Polymer. 2006,100:4842-4855.
3. **Hong Lei**, A. Pizzi, Guanben Du. Coreacting PMUF/ Isocyanate resins for wood panel adhesives. Holz als Roh-und Werkstoff. 2006,64:117-120.
4. **Hong Lei**, A. Pizzi, Guanben Du. Environmentally friendly mixed tannin/lignin wood resins. Journal of Applied Polymer Science. 2008, 107:203-209.
5. **Hong Lei**, Guanben Du, A. Pizzi, Alain Celzard. Influence of nanoclay on urea-formaldehyde resins for wood adhesives and its model. Journal of Applied Polymer Science. 2008, 109:2442-2451.
6. Guanben Du, **Hong Lei**, A. Pizzi, H. Pasch. Synthesis-structure-performance relationship of cocondensed phenol-urea-formaldehyde resins by MALDI-ToF and ^{13}C-NMR. Journal of Applied Polymer Science. 2008, 110:1182-1194.
7. **Hong Lei**, Guanben Du, A. Pizzi. Review of tannin-based wood adhesive. China Forest Products Industry (China). 2008(06):15-19.
8. **Hong Lei**, Guanben Du, A. Pizzi, *et al*. Comparative structure development of phenol-urea-formaldehdye resin. Chemistry and Industry of Forest Products (China). 2009,29(2):73-78.
9. Guanben Du, **Hong Lei**, A. Pizzi. Influence of urea addition on phenol-urea-formaldehyde resin. Journal of Beijing Forestry University. 2009,31(2):121-127.
10. Guanben Du, **Hong Lei**, A. Pizzi, *et al*. Structure progressing of phenol-urea-formaldehyde resin under alkaline condition. Chemistry and Industry of Forest Products (China). 2009.
11. Guanben Du, **Hong Lei**, A. Pizzi. Study on curing reaction of urea-formaldehyde resin by thermal mechanical analysis. Journal of Beijing Forestry University. Accepted.
12. **Hong Lei**, A. Pizzi, Guanben Du. Environment-friendly gluten-based mixed resins for particleboard. Journal of Applied Polymer Science. Submitted.