



UNIVERSITI PUTRA MALAYSIA

***OPTIMIZATION OF GLYOXALATION FOR ALKALI LIGNIN USED AS
BULKING AGENT IN WOOD***

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**OPTIMIZATION OF GLYOXALATION FOR ALKALI LIGNIN USED AS
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By

ANG AIK FEI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

April 2016

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DEDICATION

I specially dedicate this thesis to

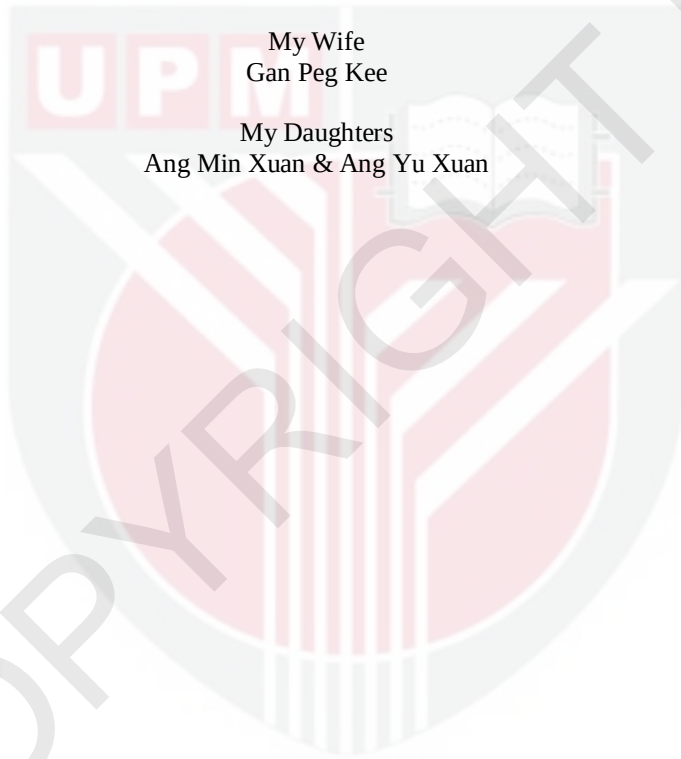
My Supervisor
Prof. Dr. Zaidon Bin Ashaari

My Mother
Kua Ai Lian

My Father
Ang Boon Lip

My Wife
Gan Peg Kee

My Daughters
Ang Min Xuan & Ang Yu Xuan



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

OPTIMIZATION OF GLYOXALATION FOR ALKALI LIGNIN USED AS BULKING AGENT IN WOOD

By

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April 2016

Chairman : Zaidon Ashaari, PhD
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Bulking treatment through the impregnation of low molecular weight phenol formaldehyde (LmwPF) resin is a promising method to enhance the dimensional stability of wood. The development of bulking agent that made of modified alkali lignin, the glyoxalated alkali lignin is crucial to mitigate the concentrations of petrochemical derived phenol and carcinogenic formaldehyde. The objective of this study was to enhance the structural homogeneity and chemical reactivity of alkali lignin through sequential organic solvents fractionation and glyoxalation, and to enhance the dimensional stability of jelutong (*Dyera costulata*) wood using glyoxalated alkali lignin incorporated with low molecular weight phenol formaldehyde resin as bulking agent.

Low molecular weight lignin feedstock was obtained through base catalysed depolymerisation (BCD) treatments from an alkali lignin (OL) with a weight-average molecular weight (M_w) of 11646 g/mol at different combined severity factors. The homogeneity of the OL and BCD treated lignins was altered through sequential fractionation using organic solvents with different Hildebrand solubility parameters i.e. propan-1-ol, ethanol and methanol. The yield of OL and BCD treated lignins dissolved in propan-1-ol (F1), ethanol (F2), and methanol (F3) and their molecular weight distributions and chemical structures were determined and characterized by Gel Permeation Chromatography (GPC), Fourier transform infrared (FT-IR) spectroscopy and ^{13}C -nuclear magnetic resonance (NMR) spectroscopy. The reactivity of the obtained low molecular weight lignin feedstock was then enhanced through glyoxalation using non-volatile and non-toxic dialdehyde, namely glyoxal, instead of formaldehyde. The proportion ratio of glyoxal to sodium hydroxide (NaOH) used in the glyoxalation process was optimised using response surface methodology (RSM) and central composite design (CCD). The glyoxalated alkali lignin (GL) synthesised using the optimum proportion ratio of glyoxal to NaOH was then incorporated with LmwPF resin to prepare bulking agent for wood bulking treatment. Oven dried jelutong (*Dyera costulata*) wood was evacuated under vacuum and then followed by soaking in 15, 20 and 25% concentrations of GL-LmwPF (67% solid of GL:33% solid of LmwPF based on the total solute content) and LmwPF resins, respectively at ambient temperature for 24 h. The impregnated wood was then curing at 180 °C for 30 min. The resin weight percent gain (WPG) and dimensional stability in terms of antiswelling efficiency (ASE), moisture excluding efficiency (MEE) and water absorption (WA) as well as

leachability of bulking agents for GL-LmwPF treated wood were determined and compared with untreated wood and wood treated solely with LmwPF resin. The formaldehyde release for both GL-LmwPF and LmwPF treated wood were also determined.

BCD treatments did not increase the yield of an OL dissolved in propan-1-ol or ethanol but did increase the yield of OL dissolved in methanol. Repolymerization of OL occurred during the BCD treatment. Lower molecular weight, more homogeneous OL tended to dissolve in propan-1-ol and ethanol, but their overall soluble lignin yields were low. The OL dissolved in methanol had higher molecular weight, was less homogeneous, and had a bulkier structure than OL dissolved in propan-1-ol or ethanol. ¹³Carbon-NMR and FT-IR spectroscopy analyses confirmed that F3 in OL exhibits optimum yield and appropriate chemical structures as well as molecular weight distributions for resin synthesis. For glyoxalation of alkali lignin, FT-IR spectroscopy revealed that lower molecular weight of lignin polymers was formed due to the crosslinking of lignin molecules via methylene (CH₂) bridges through the condensation reaction. RSM and CCD showed that the reactivity of GL reached highest when optimum amounts of glyoxal and NaOH, i.e., 0.222 and 0.353 mole, respectively, were used in the glyoxalation process. The WPG of GL-LmwPF treated wood was lower than LmwPF treated wood. GL-LmwPF treated wood exhibited positive ASE but the values were lower compared to LmwPF treated wood. The MEE and WA of GL-LmwPF treated wood were also inferior than LmwPF treated wood and untreated wood. GL-LmwPF resin was leached from treated wood whereas no leaching was found for LmwPF resin after 3 leaching cycles in distilled water. The formaldehyde release of GL-LmwPF resin treated wood was 25.76% lesser than wood treated with LmwPF resin. Wood treated with 25% GL-LmwPF resin yielded highest ASE value compared to 15 and 20% GL-LmwPF treated wood. Hence, wood treated with 25% GL-LmwPF resin together with external coatings could be used in several end applications such as parquet flooring, paneling and furniture component.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGOPTIMUMAN GLYOXALASI UNTUK LIGNIN ALKALI DIGUNAKAN SEBAGAI EJEN PUKAL DALAM KAYU

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Rawatan pukal melalui pengisitepuan fenol formaldehid resin (LmwPF) berberat molekul rendah adalah satu kaedah yang berkesan untuk meningkatkan kestabilan dimensi kayu. Pembangunan ejen pukal yang diperbuat daripada lignin alkali yang diubahsuai iaitu lignin alkali *glyoxalated* adalah penting untuk mengurangkan kepekatan fenol yang diperolehi daripada petrokimia dan formaldehid yang berkasinogenik. Objektif kajian ini adalah untuk meningkatkan keseragaman struktur dan kereaktifan kimia lignin alkali melalui pemeringkatan berurutan dengan menggunakan pelarut organik dan glyoxalasi, dan untuk meningkatkan kestabilan dimensi kayu jelutong (*Dyera costulata*) menggunakan lignin alkali *glyoxalated* yang digabungkan dengan resin fenol formaldehid berberat molekul rendah sebagai ejen pukal.

Bahan mentah lignin berberat molekul rendah diperolehi melalui rawatan *base catalyzed depolymerisation* (BCD) daripada lignin alkali (OL) berberat molekul (mw) 11646 g/mol pada gabungan faktor tahap kekuatan yang berbeza. Kehomogenan struktur OL dan lignin-lignin yang dirawat dengan BCD dikawal melalui pemeringkatan berurutan dengan menggunakan pelarut organik yang mempunyai parameter keterlarutan Hildebrand yang berbeza iaitu propan-1-ol, etanol dan methanol. Hasil OL dan lignin-lignin yang dirawat dengan BCD yang terlarut dalam propan-1-ol (F1), etanol (F2), dan metanol (F3) dan taburan berat molekul serta struktur kimia mereka ditentukan dengan *Gel Permeation Chromatography* (GPC), spektroskopi *Fourier transform infrared* (FT-IR) dan spektroskopi ^{13}C -nuklear resonans magnetik (NMR). Kereaktifan bahan mentah lignin berberat molekul rendah yang diperolehi kemudiannya dipertingkatkan melalui proses *glyoxalation* dengan menggunakan dialdehid yang tidak meruap dan tidak toksik, iaitu glyoxal, daripada formaldehid. Nisbah bahagian glyoxal kepada natrium hidroksida (NaOH) yang digunakan dalam proses *glyoxalation* dioptimumkan dengan menggunakan kaedah *response surface methodology* (RSM) dan *central composite design* (CCD). Lignin alkali *glyoxalated* (GL) yang disintesis dengan nisbah kadar glyoxal kepada NaOH yang optimum kemudiannya digabungkan dengan resin LmwPF untuk penyediaan ejen pukal bagi rawatan pukal kayu. Kayu-kayu jelutong yang telah dikeringkan di dalam oven didedahkan di bawah vakum dan kemudiannya masing-masing direndamkan dalam resin GL-LmwPF (67% pepejal GL: 33% pepejal LmwPF berdasarkan jumlah kandungan bahan larut) dan LmwPF berkepekatan 15, 20 dan 25% pada suhu ambien selama 24 jam. Kayu-kayu yang telah diisitepuan

kemudian dimatangkan pada suhu 180 °C selama 30 menit. Kenaikan peratus berat resin (WPG) dan kestabilan dimensi dari segi *antiswelling efficiency* (ASE), *moisture excluding efficiency* (MEE) dan *water absorption* (WA) serta larut lesap bagi resin-resin LmwPF dan GL-LmwPF ditentukan dan dibandingkan dengan kayu yang tidak dirawat dan kayu dirawat dengan resin LmwPF. Perlepasan formaldehid dari kayu yang dirawat dengan kedua-dua resin GL-LmwPF dan LmwPF juga telah ditentukan.

Rawatan BCD tidak meningkatkan hasil OL yang terlarut dalam propan-1-ol atau etanol tetapi meningkatkan hasil OL yang terlarut dalam methanol. Repolimersasi OL berlaku semasa rawatan BCD dijalankan. OL dengan berat molekul yang lebih rendah, struktur yang lebih seragam cenderung untuk melarut dalam propan-1-ol dan etanol, tetapi secara keseluruhannya hasil lignin yang terlarut dalam larutan-larutan tersebut adalah rendah. OL yang terlarut dalam metanol mempunyai berat molekul yang lebih tinggi, strukturnya adalah kurang seragam dan lebih mampat daripada OL yang terlarut dalam propan-1-ol atau etanol. Analisis spektroskopi ¹³Carbon-NMR dan FT-IR mengesahkan bahawa F3 dalam OL mempamerkan hasil yang optima dan struktur kimia serta taburan berat molekul yang sesuai untuk sintesis resin. Untuk proses *glyoxalation* lignin alkali, spektroskopi FT-IR menunjukkan bahawa pembentukan polimer lignin dengan berat molekul yang lebih rendah adalah disebabkan oleh penyilangan antara molekul-molekul lignin melalui pembentukan lingkaran metilena (CH₂) secara tintak balas condensasi. RSM dan CCD menunjukkan bahawa kereaktifan GL mencapai tertinggi apabila jumlah glyoxal dan NaOH yang optimum, iaitu, 0.222 dan 0.353 mol, masing-masing digunakan dalam proses glyoxalasi. WPG untuk kayu yang dirawat dengan GL-LmwPF adalah lebih rendah daripada kayu yang dirawat dengan LmwPF. Kayu yang dirawat dengan GL-LmwPF mempamerkan ASE positif tetapi nilai-nilainya adalah lebih rendah berbanding dengan kayu yang dirawat dengan LmwPF. MEE dan WA untuk kayu yang dirawat dengan GL-LmwPF adalah lebih lemah daripada kayu yang dirawat dengan LmwPF dan juga kayu yang tidak dirawat. Larut lesap resin GL-LmwPF dari kayu yang dirawat berlaku sedangkan larut lesap resin LmwPF tidak berlaku selepas 3 kitaran larut lesap dalam air suling. Perlepasan formaldehid dari kayu yang dirawat dengan resin GL-LmwPF adalah 25.76% lebih rendah daripada kayu dirawat dengan resin LmwPF. Kayu yang dirawat dengan 25% kepekatan resin GL-LmwPF menghasilkan nilai ASE yang tertinggi berbanding dengan kayu yang dirawat dengan kepekatan 15 dan 20% resin GL-LmwPF. Oleh itu, kayu dirawat dengan 25% kepekatan resin GL-LmwPF diliputi dengan penyalut luar boleh digunakan dalam beberapa aplikasi akhir seperti lantai parket, panel dan komponen perabot.

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The thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirements for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENTS	v
APPROVAL	vi
DECLARATION	viii
LIST OF TABLES	xiii
LIST OF FIGURES	xiv
LIST OF ABBREVIATIONS	xvii
 CHAPTER	
 1 INTRODUCTION	
1.1 General Background	1
1.2 Problem Statement and Justification	2
1.3 Main Objective	4
1.3.1 Specific Objectives	4
 2 LITERATURE REVIEW	
2.1 Dimensional Instability of Wood	5
2.1.1 Wood and Water	5
2.1.2 Problems caused by Shrinkage and Swelling of Wood	5
2.2 Modification of Wood by Impregnation of Chemicals	5
2.3 Wood Treated with Thermosetting Resin (<i>Impreg</i>)	6
2.4 Efforts to Mitigate the Formaldehyde Emission for Formaldehyde based Resin Treated Wood	8
2.5 Lignin	9
2.6 Utilization of Lignin in the Production of Wood Adhesives	9
2.7 Utilization of Glyoxal in the Production of Wood Adhesives	11
2.8 Depolymerization of Lignins through Base Catalyzed Depolymerisation (BCD)	11
2.9 Treatment Severity Parameter	13
2.10 Sequential Solvents Fractionation of Lignins	14
2.11 Hydroxymethylation of Lignins	15
2.12 Glyoxalation of Lignins	15
2.13 Response Surface Methodology (RSM)	16
 3 MATERIALS AND METHODOLOGY	
3.1 Materials	18
3.2 Severity Factor, R_0	18
3.3 Base Catalysed Depolymerisation (BCD) Treatment of Alkali Lignin	18
3.4 Sequential Fractionation with Organic Solvents	20

3.5	Determination of Molecular Weight Distributions of OL, Fractionated OL and BCD Treated Lignins by Gel Permeation Chromatography (GPC)	20
3.6	¹³ C Nuclear Magnetic Resonance (NMR) Spectroscopy	20
3.7	Determination of Functional Groups of OL, Fractionated OL and BCD Treated Lignins by Fourier Transform Infra-Red (FT-IR) Spectroscopy	21
3.8	Response Surface Methodology and Central Composite Design	21
3.9	Glyoxalation of Alkali Lignin	22
3.10	Determination of Glyoxalated Alkali Lignin Solid Content	22
3.11	Determination of Molecular Weight Distributions of Glyoxalated Alkali Lignins by Gel permeation chromatography (GPC)	23
3.12	Determination of Functional Groups of Glyoxalated Alkali Lignins by Fourier Transform Infra-Red (FT-IR) Spectroscopy	23
3.13	Thermogravimetry Analysis (TGA)	23
3.14	Preparation of LmwPF and GL-LmwPF Resins	23
3.15	Characterization of LmwPF and GL-LmwPF Resins by Fourier Transformed Infrared (FT-IR) Spectroscopy	24
3.16	Resin Treatment through Soaking Method	24
3.17	Evaluation of Dimensional Stability	26
3.18	Evaluation of Formaldehyde Release, Flask Value (F_v)	27
3.19	Samples for the Determination of the Flask Value	27
3.20	Determination of Formaldehyde Release	27
3.21	Determination of Formaldehyde Concentration of the Aqueous Solution	28
3.22	Calibration Curve	28
3.23	Formaldehyde Calibration Solution	29
3.24	Determination of the Calibration Curve	29
3.25	Flask Value (F_v)	30
3.26	Leachability Test Procedure	30

4 RESULTS AND DISCUSSION

4.1	Characterization of Base Catalyzed Depolymerization and Sequential Solvents Fractionation of Treated Alkali Lignin	31
4.1.1	Yield and Molecular Weight Distributions of Lignin	31
4.1.2	Semi-Quantitative ¹³ C Nuclear Magnetic Resonance (NMR) Spectra	34
4.1.3	Quantitative FT-IR Spectra	36
4.2	Characterization and Optimization of the Glyoxalation of a Methanol-Fractionated Alkali Lignin using Response Surface Methodology	39
4.2.1	Molecular Weight Distributions of	39

	Glyoxalated Alkali Lignins	
4.2.2	Thermal Stability of Glyoxalated Alkali Lignin	42
4.2.3	Optimization of Reactant Proportions for Glyoxalation of Alkali Lignin	46
4.2.4	Adequacy of the Model	49
4.3	Possibility of Enhancing the Dimensional Stability of Jelutong (<i>Dyera costulata</i>) Wood using Glyoxalated Alkali Lignin-Phenolic Resin as Bulking Agent	50
4.3.1	Characterization of GL-LmwPF resin using FT-IR Spectroscopy	50
4.3.2	Weight Percent Gain (WPG) of LmwPF and GL-LmwPF Treated Wood before and after Leachability Test	52
4.3.3	Dimensional Stability of LmwPF and GL-LmwPF Treated Wood	54
4.3.4	Dimensional Stability of GL-LmwPF Treated Wood after Leaching Cycles	58
4.3.5	Formaldehyde release, flask value (F_v)	59
5	SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH	
5.1	Conclusions	61
5.2	Recommendations for Future Research	62
	REFERENCES	64
	APPENDICES	74
	BIODATA OF STUDENT	80
	LIST OF PUBLICATIONS	81

LIST OF TABLES

Table	Page
1. Severity factor, $\log R_0$, for base catalysed depolymerisation treatment of OL	19
2. The range and levels of the variables	21
3. Experimental condition of central composite design (CCD)	22
4. Concentrations of LmwPF resin used in this study	24
5. Concentrations of GL-LmwPF resin used in this study	24
6. Yield, Number-Average Molecular Weight (M_n), Weight-Average Molecular Weight (M_w), and Polydispersity Index (M_w/M_n) for F1, F2, and F3 in OL and Base Catalysed Depolymerisation Treated OL	31
7. Chemical shift assignments for ^{13}C -NMR spectra and relative intensities of peaks for different chemical structures for OL, F3 in OL, and combined $\log R_0$ 6.72-treated OL	35
8. Band assignments for FT-IR spectra and relative absorbance of bands for each functional group for OL and F3 in OL	37
9. Molecular weight distributions of ML and glyoxalated alkali lignin samples	40
10. TGA data for ML and glyoxalated alkali lignin samples	43
11. Band assignments for FT-IR spectra and intensity of relative absorbance for CH ₂ bridge in glyoxalated alkali lignin samples	46
12. The actual and predicted intensity of relative absorbance for CH ₂ band	47
13. ANOVA for response surface reduced quadratic model	48
14. Changes in ASE, BC, MEE and WA values of GL-LmwPF treated wood before and after 3 leaching cycles	58

LIST OF FIGURES

Figure	Page
1. Diagram Illustrating Different Types of Wood Modification at the Cellular Level (adapted from Norimoto and Gril, 1993)	7
2. Frequencies of Different Linkage Types in Native Softwood and Hardwood Lignin per 100 C9 Units (Source: Henriksson et al. 2010)	12
3. Reactor used for the BCD Process	19
4. Sample Cutting Pattern from Jelutong Veneer. u: Untreated, P15: Treated with 15% LmwPF, P20: Treated with 20% LmwPF, P25: Treated with 25% LmwPF, LP15: Treated with 15% GL-LmwPF, LP20: Treated with 20% GL-LmwPF and LP25: Treated with 25% GL-LmwPF	25
5. Test Apparatus for the Flask Method. 1: 500 ml Polyethylene Bottle with Bottle Top, 2: Hook Out of Stainless Steel, 3: Elastic Rubber Band, 4: Surface of Water	27
6. Calibration Curve for Formaldehyde Determined by Acetylacetone Method	29
7. GPC Chromatogram of OL (without Base Catalyzed Depolymerization and Solvents Fractionation Treatments)	32
8. FT-IR Spectrum of OL (without Base Catalyzed Depolymerization and Solvents Fractionation Treatments)	38
9. FT-IR Spectrum of F3 in OL (OL without Base Catalyzed Depolymerization Treatment but Fractionated with Methanol)	38
10. Chemical Structure of Softwood Alkali Lignin used in this Study	39
11. TGA Thermogram of ML	44
12. TGA Thermogram of R2 Sample	44
13. TGA Thermogram of R3 Sample	45
14. 3D-Surface Plot of Intensity of Relative Absorbance for CH ₂ Bridges in Glyoxalated Alkali Lignin as a Function of Weights of Glyoxal and NaOH	49
15. FT-IR Spectrum of the 25% LmwPF Resin	50
16. FT-IR Spectrum of the 25% GL-LmwPF Resin	50

17. FT-IR Spectrum of the GL	51
18. Mean Values of WPG for LmwPF and GL-LmwPF Treated Wood at Different Concentrations (Before and After 3 Cycles of Leaching Test)	53
19. Mean Values of ASE for LmwPF and GL-LmwPF Treated Wood at Different Concentrations	54
20. Mean Values of ASE and BC for Wood Treated with Different Concentrations of LmwPF Resin	55
21. Mean Values of ASE and BC for Wood Treated with Different Concentrations of GL-LmwPF Resin	55
22. Mean Values of MEE for Wood Treated with Different Concentrations of LmwPF and GL-LmwPF Resins	56
23. Mean Values of WA for Untreated Wood and Wood Treated with Different Concentrations of LmwPF and GL-LmwPF Resins	57
24. Mean flask values (Fv) of wood treated with 25% LmwPF and GL-LmwPF resins	60
A1. First Stage of BCD Treatment Conducted in an Autoclave	74
A2. Second Stage of BCD Treatment Conducted in an Oven	74
A3. Fractionation of OL and BCD Treated OL with Organic Solvents using a Magnetic Stirrer	75
A4. Water Vapour Test for Evaluation of Dimensional Stability of Untreated and Treated Wood	75
A5. Treated Samples were Exposed to Leaching Cycles in Distilled Water, Stirred by a Magnetic Stirrer for 8 h	76
A6. Treated Samples were Exposed to Evaporation cycles in an oven at 60 °C for 16 hours for Leachability Test	76
A7. GPC Chromatogram of OL (without Base Catalysed Depolymerization and Solvents Fractionation Treatments)	77
A8. FT-IR Spectrum of OL (without Base Catalysed Depolymerization and Solvents Fractionation Treatments)	77
A9. FT-IR Spectrum of F3 in OL (OL without Base Catalysed Depolymerization Treatment but Fractionated with Methanol)	78

A10. ^{13}C -NMR Spectrum of OL (without Base Catalysed Depolymerization and Solvents Fractionation Treatments)	78
A11. ^{13}C -NMR Spectrum of F3 in OL (OL without Base Catalysed Depolymerization Treatment but Fractionated with Methanol)	79
A12. ^{13}C -NMR Spectrum of F3 in log R_0 6.72 (BCD Treated and Fractionated with Methanol)	79



LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ASE	Antiswelling Efficiency
BC	Bulking Coefficient
BCD	Base Catalysed Depolymerisation
CCD	Central Composite Design
CPF	Control PF
DMDHEU	Dimethyldihydroxyethyleneurea
DMSO-d ₆	Deuterated Dimethyl Sulfoxide
EFB	Empty Fruit Bunch
EMC	Equilibrium Moisture Content
FT-IR	Fourier Transform Infra-Red
GBI	Green Building Index
GL	Glyoxalated Alkali Lignin
GL-LmwPF	Glyoxalated Alkali Lignin-Low Molecular Weight Phenol Formaldehyde
GPC	Gel Permeation Chromatography
IAQ	Indoor Air Quality
IARC	International Agency for Research on Cancer
IB	Internal Bonding
IMC	Initial Moisture Content
LEED	Leadership in Energy and Environmental Design
LmwPF	Low Molecular Weight Phenol Formaldehyde
LPF	Lignin Substituted PF
ML	Methanol-Fractionated Alkali Lignin
PEO	Polyethylene Oxide

PT	Press Time
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization Time-of-Flight
MC	Moisture Content
MEE	Moisture Excluding Efficiency
MDF	Medium Density Fibreboard
MF	Melamine Formaldehyde
NMR	Nuclear Magnetic Resonance
OL	Alkali Lignin
OSB	Oriented Strand Board
PAM	Pertubuhan Akitek Malaysia
PF	Phenol Formaldehyde
PPM	Part per Million
RH	Relative Humidity
RSM	Response Surface Methodology
S	Swelling Coefficient
SDS	Sodium Dodecyl Sulfate
SI	Severity Index
TGA	Thermogravimetry Analysis
UF	Urea Formaldehyde
VOCs	Volatile Organic Compounds
WA	Water Absorption
WHO	World Health Organization
WPG	Weight Percent Gain

CHAPTER 1

INTRODUCTION

1.1 General Background

Wood chronically is a good material to be used for many applications because of its many excellent material properties. The natural beauty and high strength at low density of wood make it the first choice of material to use in many applications such as roof truss, column, beam, wall cladding, flooring and so on compared to other materials. Although wood possess the excellent properties as mentioned above, but the drawbacks of wood such as the dimensional instability when it is exposed to various atmospheric conditions, susceptibility to biological attack and changes in appearance when exposed to weathering condition limits the potential end-uses of wood.

In fact, the drawbacks of wood can be enhanced through wood modification treatments. Wood modification treatment is a means of altering the material to overcome or ameliorate one of more of its advantages. Wood modification treatments involve the action of a chemical, biological or physical agent upon the material, resulting in a desired property enhancement during the service life of the modified wood (Hill 2006a). Wood modifications either by bulking, internal coating or crosslinking have shown promising results to upgrade low quality timbers for potential applications (Ashaari et al. 1990a and 1990b; Nicholas and Williams 1987; Rowell and Youngs 1981). Some of the modified wood such as phenol formaldehyde resin-treated wood (*Impreg* and *Compreg*) and heat treated-compressed wood (*Lignostone* and *Lignofol*) have been introduced and commercialized since many years ago (Rowell and Konkol 1987).

One of the examples of wood modification using bulking principle is impregnation modifications. Impregnation or diffusion of wood with a single chemical or combination chemicals into wood cell walls followed by polymerization of the chemicals is the most adequate method to enhance the properties of wood with this implication. Impregnation of low molecular weight phenol formaldehyde (LmwPF) compound in the wood followed by full curing under heat may enhance the dimensional stability and strength properties of the treated material (Ang 2010; Furuno et al. 2004; Sham et al. 2004; Ryu et al. 1991; Rowell and Konkol 1987).

However, the utilization of LmwPF resin as bulking agent also brought some disadvantages such as phenol is derived from non-renewable petrochemicals while formaldehyde is a known carcinogen. By using so called 'green' materials, the strong exploitation of fossil resources can be mitigated, reduce the amount of carbon dioxide that enters the atmosphere and take upon the responsibility of using earth's resources in a sustainable manner, thus improving resource management, indoor air quality (IAQ), and generally the overall performance and efficiency of human kind on earth. In Malaysia, the launching of green building rating tool, Green Building Index (GBI) in 2009 by the Pertubuhan Akitek Malaysia (PAM) was an approach to promote sustainability in the built environment and raise awareness among developers, architects, engineers, planners, designers, contractors and the public about environmental issues and our responsibility to the future generations. This was a message to show that the awareness to protecting the environment through energy

savings, water savings and a healthier indoor environment is getting more important in Malaysia.

1.2 Problem Statement and Justification

Wood is an anisotropic material, which means it swells and shrinks to a different extent in the three anatomical directions—longitudinal (vertical direction), tangential (parallel to annual growth rings), and radial (perpendicular to the annual growth rings). Swelling of wood in contact with moisture exerts very large forces. When wood in use swells, the forces developed can cause serious damage. As mentioned earlier, the dimensional instability of wood can be enhanced through bulking treatment i.e. impregnation of low molecular weight phenol formaldehyde (LmwPF) compound (bulking agent) in the wood followed by full curing under heat which yielded treated products with cell walls bulked with insoluble resin polymer.

Although the impregnation modification with LmwPF resin has been studied extensively in past few decades ago (Paridah et al. 2006; Furuno et al. 2004; Wan Ariffin et al. 1992; Kajita and Imamura 1991), but the study of using lignin based-phenolic resin as bulking agent to enhance the properties of wood is rather poor. Phenol is derived from petrochemical benzene and formaldehyde from methanol that is prepared from natural gas. The availability of petrochemicals is finite as it is non-renewable resource and the prices of raw materials for LmwPF resin would increase because the fuel consumption increases as the world's population grows (Sellers, 1985). Formaldehyde has been classified as a known carcinogen by the International Agency for Research on Cancer (IARC), a division of the World Health Organization (WHO). The emission of free formaldehyde from the resin during impregnation process and service life of the treated products will causes health problems to the consumers (Soljagic and Katovic 1988). It has been reported that the formaldehyde emission from LmwPF resin impregnated wood reduced when the wood is impregnated with lower concentration of LmwPF resin (Nur Izreen et al. 2011; Rabi'atol Adawiah et al. 2012). However, it is anticipated that the effectiveness in enhancing some the properties of wood would become inferior if using lower concentration of LmwPF resin as the effectiveness in enhancing the dimensional stability of wood through this method is very much associated with the ultimate cell wall bulking effect (ultimate polymer of chemicals deposited in cell wall) of the impregnated wood (Deka and Saikia 2000; Ang 2010; Rabi'atol Adawiah et al. 2012; Leemon et al. 2015).

The polyphenolic nature of lignin makes it a potential substitute for phenol in the production of ordinary formaldehyde-based resin. In addition, lignin is the most abundant natural and renewable organic polymer in the world after cellulose. Large quantities of isolated lignin can be recovered from various pulping or biomass conversion processes. Therefore, lignin is an inexpensive raw material that potential for the production of environmentally friendly thermosetting resin by substituting the phenol in the ordinary formaldehyde based thermosetting resins (Alonso et al. 2004; Khan and Ashraf 2007; Cetin and Ozmen 2002; El Mansouri et al. 2006; Cavdar et al. 2008). Therefore, impregnation of wood with partial glyoxalated alkali lignin (GL) substituted-LmwPF resin as bulking agent thus offers advantages by reducing the free formaldehyde emission with using lesser neat LmwPF resin while retaining the ultimate WPG in the impregnated wood as majority of the solid content deposited in

the impregnated wood (especially in the cell walls) was comprised of natural and renewable lignin polymer.

To process lignin into various end products, it would be advantageous to use material with a more homogenous structure, chemistry and purity (Stewart 2008). The homogeneity of lignin can be enhanced by sequential fractionation in different organic solvents (Wang et al. 2010; Li et al. 2012). The heterogeneity of lignin can be reduced because different parts of the lignin molecule have different hydrogen-bonding capacity (Hildebrand solubility parameter) in different organic solvents. Low-molecular weight lignin fragments are dissolved in organic solvents with weak or moderate hydrogen-bonding capacities with a wider range of Hildebrand solubility parameters than the higher-molecular weight lignin fragments (Schuerch 1952).

Apart from this, lignins also offer no advantages in terms of chemical reactivity. The low reactivity of lignins is the main obstacle limits their utilization in the production of resins (Vishtal and Kraslawski 2011). Hence, the reactivity of lignins needs to be enhanced in order to increase the possibility of using lignins as feedstock for the production of resins. Hydrolysis of lignin in an alkaline medium has been shown to increase the reactivity of lignin by liberating lower molecular weight phenolic compounds which possess more reactive sites and reduced steric hindrance effect (Cheng et al. 2013; El Mansouri et al. 2006; Thring 1994). Apart from this, depolymerisation of lignin macromolecule into lower molecular weight fragments is also important as one of the requirements for wood bulking treatment is that the molecular weight of bulking agents used should be low to ensure the penetration of bulking agents into wood cell walls (Norimoto 2000). It has been reported that hydroxymethylation is also one of the chemical modification methods applied to enhance the reactivity of lignin toward crosslinking agents such as formaldehyde (Lin et al. 2010; Mu et al. 2009; Malutan et al. 2008; Zhao et al. 1994). Hydroxymethylation enhances the reactivity of lignin by introducing reactive functional groups to the lignin molecules. Instead of using toxic and volatile formaldehyde as crosslinking agent in hydroxymethylation, non-toxic and non-volatile dialdehydes such as glyoxal also has been used as a replacement for formaldehyde (Navarrete et al. 2012; El Mansouri et al. 2011). Glyoxal can be obtained as a by-product from the generation of hydrogen peroxide required by manganese-dependent peroxidase enzymes (Kersten 1990; Hirayama et al. 1984).

Although the modifications of lignin to enhance its structural homogeneity and chemical reactivity may slightly increase the cost of processing, the cost of processing can be reduced by monitoring the concentration of chemicals used by developing the optimum treatment method. Furthermore, the treated products are very potential for commercialization because it is Green Building Index (GBI) and Leadership in Energy and Environmental Design (LEED) complaint material. The treated products could sell with better price as it is value-added product that renders superior performance under service life. The needs of developing thermosetting resin from renewable raw materials as bulking agent for impregnation modification are crucial in order to ensure that the sustainability of thermosetting resins raw materials for this modification.

1.3 Main Objective

The objective of this study was to enhance the structural homogeneity and chemical reactivity of alkali lignin through sequential organic solvents fractionation and glyoxalation, and enhance the dimensional stability of jelutong (*Dyera costulata*) wood using glyoxalated alkali lignin (GL) incorporated low molecular weight phenol formaldehyde (LmwPF) resin as bulking agent.

1.3.1 Specific Objectives

1. To obtain optimal yield of alkali lignin with more homogeneous structure through base catalysed depolymerisation (BCD) and sequential organic solvents fractionation treatments.
2. To optimise the ratios of glyoxal to sodium hydroxide used in the glyoxalation process based on the relative intensity of methylene (CH_2) bridge using response surface methodology (RSM).
3. To determine the molecular weight distributions and thermal stability of glyoxalated alkali lignin (GL).
4. To identify the functional groups in low molecular weight phenol formaldehyde (LmwPF) resin and GL-LmwPF admixture resin.
5. To evaluate the effectiveness of using GL-LmwPF admixture resin as bulking agent to enhance the dimensional stability of jelutong (*Dyera costulata*) wood.

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