UNIVERSITI PUTRA MALAYSIA

PRODUCTION OF POLYURETHANE FROM LIQUEFIED KENAF (*Hibiscus cannabinus* L.) CORE FOR WOOD LAMINATING ADHESIVE

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By

JUHAIDA MOHD FADZIL

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

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This Thesis is Dedicated to My Beloved Mum, Dad,

Sisters, Brothers and All My Friends

with grateful appreciation of their encouragement and love

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in
fulfilment of the requirement for the degree of Master of Science

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Chairman : Associate Professor Paridah Md. Tahir, PhD

Faculty : Forestry

Kenaf is one of the several fibre crops that have been identified as potential source of natural long fibres. The only economical way to use this plant is to extract the long fibres from the bast and used it for fibre reinforced plastic composites to replace glass fibre which are known to be environmental unfriendly. Once the basts have been separated from the stem, the inner, soft and woody section – also known as kenaf core (KC) – can be used for other applications such as biochemicals, due to high amount of holocellulose content and low lignin content. Some of the chemicals that can be derived from KC include polyols, carboxymethyl cellulose, and cellulose esters.

This study was carried out to produce polyurethane (PU) adhesive from liquefied kenaf core (LKC) polyols by reacting it with toluene-2,4-diisocyanate

(TDI). The liquefaction of KC powder was conducted in the presence of polyethylene glycol (PEG) 1000 and sulfuric acid as a catalyst. The optimum reaction condition (i.e., temperature and time) for producing polyol from KC was determined based on the percentage of reaction residues. Lower reaction residues indicate more KC powder being liquefied in the solvent system. The extent of liquefaction in various mixtures of PEG 1000 and glycerol was also analysed. It was found that the percent residue of KC decrease with an increase of liquefaction temperature up to 180°C and time of up to 90 minutes. When the liquefaction reaction was maintained for 120 minutes, the amount of residue, however, increased quite significantly. This increment can be associated with the formation of recondensation of the LKC components as by-product of the reaction. The percent residue of unliquefied KC was found to be relatively lower when the glycerol:PEG ratio was increased from 1:17 to 3:15 suggesting a more complete liquefaction of KC has taken place. At glycerol:PEG ratio of 5:13, however, the amount of residue was slightly increased suggesting recondensation of the lignin during liquefaction process. Hence, it is important to liquefy the KC before the recondensation point was reached.

The PU adhesive was successfully synthesized using polyols from LKC. The LKC polyurethane (LKCPU) adhesive has a molecular weight (MW) of 2,666, viscosity of 5,370 cps, and solids content of 86.9%. In gluing study, the shear strength of the bonded rubberwood with LKCPU adhesive shows an average of 2.9 MPa. No wood failure was observed on the sheared specimens, showing that the adhesive strength is weaker than wood. The thick LKCPU mixture was relatively difficult to be spreaded onto the wood surface so much so reduced the penetration into the wood. Thus, coupled with the uneven pressure during clamping caused the adhesive to fail upon loading. The formation of air bubbles through liberation of carbon dioxide during curing process resulted in weak cohesive strength of the adhesive as can obviously seen on the sheared specimens. Nonetheless, based on the properties of the LKCPU produced in this work, it has great potential as wood laminating adhesive particularly for edge-gluing.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PENGHASILAN POLIURETANA DARIPADA PENCECAIRAN GENTIAN TERAS KENAF (*Hibiscus cannabinus* L.) UNTUK PEREKAT MELAMINASI KAYU

Oleh

JUHAIDA MOHD FADZIL

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Kenaf merupakan satu daripada pelbagai jenis tanaman gentian yang telah dikenalpasti sebagai sumber asli bergentian panjang yang mempunyai potensi. Satu-satunya cara yang ekonomi untuk menggunakan tumbuhan ini ialah dengan mengekstrak gentian panjang daripada kulit kenaf dan digunakan untuk papan plastik diperkukuh gentian bagi menggantikan gentian kaca yang tidak mesra alam. Apabila kulit kenaf ini dipisahkan daripada batang kenaf, bahagian dalamnya yang berkayu lembut –juga dikenali sebagai teras kenaf (KC)- boleh digunakan untuk kegunaan lain seperti biokimia, disebabkan oleh kandungan holoselulosanya yang tinggi dan kandungan ligninnya yang rendah. Beberapa jenis bahan kimia yang boleh dihasilkan daripada KC termasuklah poliol, karboksimetilselulosa, dan ester selulosa.

Kajian ini dijalankan untuk menghasilkan perekat poliuretana (PU) yang dihasilkan daripada poliol teras kenaf cair (LKC) dan toluene-2,4-diisosianat (TDI). Pencecairan serbuk KC dijalankan di dalam kehadiran polietelina glikol (PEG) 1000 dengan menggunakan asid sulfurik sebagai pemangkin. Keadaan tindakbalas (suhu dan masa) yang optimum bagi menghasilkan poliol daripada KC ditentukan berdasarkan peratusan sisa tindakbalas. Sisa tindakbalas yang rendah menunjukkan lebih banyak serbuk KC dicairkan di dalam sistem pelarut. Takat pencecairan di dalam pelbagai campuran pelarut PEG 1000 dan gliserol juga turut dianalisa. Daripada kajian yang dijalankan, didapati peratusan sisa KC yang tidak larut berkurang apabila suhu ditingkatkan kepada 180°C dan masa ditingkatkan kepada 90 minit. Apabila tindakbalas pencecairan dikekalkan selama 120 minit, jumlah sisa didapati agak meningkat. Peningkatan ini dikaitkan dengan pembentukan komponen LKC yang terkondensasi semula sebagai hasil sampingan daripada tindakbalas yang berlaku. Peratusan KC yang tidak larut semakin berkurang apabila nisbah gliserol:PEG ditingkatkan daripada 1:17 kepada 3:15, menunjukkan pencecairan KC yang lebih menyeluruh telah berlaku. Akan tetapi, apabila nisbah gliserol:PEG ditetapkan pada 5:13, jumlah sisa agak meningkat yang mungkin disebabkan oleh lignin yang terkondensasi semula semasa proses pencecairan. Oleh itu, adalah penting untuk mencairkan KC sebelum ia mencapai takat untuk terkondensasi semula.

Perekat PU telah berjaya disintesis dengan menggunakan poliol daripada LKC. Perekat poliuretana LKC (LKCPU) mempunyai berat molekul (MW) 2,666, kelikatan 5,370 cps, dan kandungan pepejal 86.9%. Kekuatan patah kayu getah yang direkat menggunakan perekat LKCPU memberikan purata sebanyak 2.9 MPa. Tiada sebarang kegagalan pada spesimen kayu dapat diperhatikan, yang mana menunjukkan kekuatan perekat yang dihasilkan adalah kurang berbanding kayu. Perekat LKCPU yang pekat menjadikannya agak sukar untuk disapukan pada permukaan kayu dan menyebabkan kurangnya penembusan perekat ke dalam kayu. Tambahan pula, tekanan yang tidak sekata sewaktu dikepitkan menyebabkan perekat gagal semasa dikenakan beban. Penghasilan gelembung udara melalui pembebasan karbon dioksida semasa proses pematangan perekat menyebabkan kekuatan kohesif perekat menjadi lemah sebagaimana yang dapat dilihat pada spesimen yang telah diuji. Walaubagaimanapun, berdasarkan sifat LKCPU yang terhasil daripada kajian ini, ia mempunyai potensi yang baik sebagai perekat untuk melaminasi kayu terutamanya untuk rekatan sisi.

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I certify that an Examination Committee met on 3rd March 2009 to conduct the final examination of Juhaida Mohd Fadzil on her Master of Science thesis entitled "Production of Polyurethane from Kenaf (*Hibiscus cannabinus* L.) Core Fiber for Wood Laminating Adhesive" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the degree of Master of Science.

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

JUHAIDA MOHD FADZIL

Date : 11 May 2009

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LIST OF ABBREVIATIONS

%	Percent
°C	Degree celcius
BDO	1,4 Butane-diol
CPU	Commercial Polyurethane
ECER	East Coast Economic Region
EG	Ethylene glycol
FRIM	Forest Research Institute Malaysia
FTIR	Fourier Transform Infrared
g	gram
HDI	Hexamethylene diisocyanate
KC	Kenaf Core
LKC	Liquefied Kenaf Core
LKCPU	Liquefied Kenaf Core Polyurethane
MARDI	Malaysian Agricultural Research and Development Institute
MC	Moisture Content
MDI	Methylene diphenyl diisocyanate
min.	Minute
MW	Molecular weight
MNTB	Malaysian National Tobacco Board
MPa	Mega Pascal

MTIB	Malaysian Timber Industry Board
NCER	Northern Corridor Economic Region
NUCLEAR MALAYSIA	Malaysian Nuclear Agency
OH	Hydroxyl
PEG	Polyethylene glycol
PU	Polyurethane
PVAc	Polyvinyl acetate
R & D	Research and Development
TEA	Triethylamine
TDI	Toluene diisocyanate
UPM	Universiti Putra Malaysia
US	United States
w/w	weight/weight

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The development of advance technologies is essential to convert renewable resources from plant into new environment-friendly polymeric materials that can be decomposed in a natural environment. This plant biomass serves as alternatives for petroleum which is responsible for the production of various types of petrochemicals. With the high price of petroleum i.e. US$ 138 a barrel in June 2008 (Mouawad, 2008), the economics of such conversion is very attractive. As reported by Anon (2008a), oil hit several new records highs throughout the beginning of year 2008. On February 29, 2008, oil prices hit an inflation-adjusted all time peaks at US$ 103.05 per barrel and have achieved above US$ 133 per barrel on May 21, 2008 (Anon, 2008b). The alteration of oil prices since 1994 to 2008 are presented in Figure 1.1.

Due to continuous increase in petroleum prices, biomass can be a great potential source of material to be used either as replacement or complimentary for petrochemical products. Grass, wood, and non-wood fiber such as kenaf, hemp, sisal, flax, oil palm, and bamboo are some of example biomass that are available in the world that can be used for the production of bio-based products.