UNIVERSITI PUTRA MALAYSIA

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By

ISMAWATI PALLE

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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To My Beloved Mum,

Brothers Ibrahim, Ismail and Ishak

With grateful appreciation for 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

CARBOXYMETHYLATION OF CELLULOSE FROM KENAF (*Hibiscus cannabinus* L.) CORE FOR HYDROGEL PRODUCTION

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Chairman : Associate Professor Paridah Md. Tahir, PhD

Faculty : Forestry

Kenaf is known as fast growing species which is planted mainly for bast fibre which have been used as an alternative raw material for particleboard, medium density fibreboard or pulp and paper industry. On the contrary, the core of kenaf stem which is consist of straw-like and short-length fibres cannot be used exclusively in particleboard and pulp paper industries due to low strength and dimensional stability. Thus, and alternative usage has to be researched. Since kenaf core have relatively high amount of holocellulose, low lignin content and is highly absorbent, these properties make kenaf core a potential material for producing carboxymethyl cellulose (CMC) in hydrogels. This study comprised three main aspects: 1) Evaluation of the basic properties of kenaf core fibres, 2) Carboxymethylation of the kenaf core and 3) Formation of hydrogel from the carboxymethylated kenaf core.

The evaluations of chemical and physical properties of kenaf core fibres were conducted prior to the carboxymethylation process. The samples for fibre morphology and chemical analyses of the kenaf core were prepared from macerized and mechanically refined fibres, respectively. All the chemical analyses were conducted using fibre of 40-mesh size (425 µm size) whilst for fibre morphology (fibre length, fibre diameter, lumen diameter and cell wall thickness) match stick kenaf core samples were used. The study indicates that kenaf core comprises approximately 50.6% alpha-cellulose, 27.1% hemicellulose and 20.5% of lignin. A high percentage of water absorption of kenaf core (i.e., 50%) was recorded due to the presence of a large number of pits along the longitudinal axis of the cell wall as shown by pictures from SEM. The core fibres has low Runkel ratio of 0.36 which is responsible for high water absorption owing to large lumen size and thin fibre wall suggesting good liquid transmission.

Carboxymethylated kenaf core was successfully produced under heterogeneous condition by reacting the core fibres with sodium monochloroacetate as an etherifying agent and isopropanol as reaction medium in the presence of sodium hydroxide as a swelling agent. Several factors affecting the carboxymethylation process such as time, sodium hydroxide concentrations and temperature were studied. The degree of substitution (DS), reaction efficiency (RE) and weight percent gain (WPG) were also determined. Among the three types of kenaf core used, crude kenaf

core (CKC), extractive-free kenaf core (KCFE), and extractive- and lignin-free kenaf core (KCFL), KCFL gives the highest DS value. The purity of the holocellulose was found to be the crucial factor in obtaining high yield. The optimum reaction condition for producing carboxymethylated kenaf core with DS value of 0.87 was based on the following procedures: firstly, by extracting the extractives and lignin from the kenaf core to produce extractive- and lignin-free kenaf core (KCFL) and then reacting the KCFL with sodium monochloroacetate in 30% sodium hydroxide at 55^{o}C for 2 hours. From FTIR spectroscopy analysis, the existence of peak at 1591 cm^{-1} on modified kenaf core revealed that some of hydroxyl groups of cellulose kenaf fibre had been effectively substituted with the carboxymethyl group. The SEM micrograph observation also reconfirmed the substitution process, where the unmodified kenaf core had rough features with the pits still empty. On the other hand, smoother features were observed on the modified kenaf core fibre with the pits has been filled presumably with carboxymethyl of sodium monochloroacetate.

Hydrogels were successfully produced using different concentrations of carboxymethylated kenaf core of extractive- and lignin-free (CMKCFL) at several irradiation doses. A dose of 70 kGy was found to be the optimum irradiation dose for crosslinking of CMKCFL hydrogel with gel content of 37.1%. The optimum crosslinking condition was 50 kGy irradiation and 50% concentration, producing an acceptably good properties CMKCFL hydrogel. The swelling ratio of CMKCFL hydrogel was the highest in de-ionized water

compared to alkaline (1.0 M NaOH) and acidic (1.0 M HCl) at all ranges of irradiation doses except for 10 kGy. Increasing the level of concentration of aqueous CMKCFL resulted in an increased in swelling. This result was however opposite when the swelling test was conducted in acid and alkali mediums. The overall results indicate that kenaf core fibre can be used as raw material for carboxymethyl cellulose and hydrogel production and possess satisfying other properties.

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

KARBOKSIMETIL SELULOSA DARIPADA GENTIAN TERAS KENAF (*Hibiscus cannabinus* L.*)* UNTUK PENGHASILAN HIDROGEL

Oleh

ISMAWATI PALLE

April 2008

Pengerusi : Profesor Madya Paridah Md. Tahir, PhD

Fakulti : Perhutanan

Kenaf dikenali sebagai spesis cepat tumbuh yang ditanam khusus untuk gentian kulit yang telah digunakan sebagai bahan alternatif untuk papan serpai, papan serpai berketumpatan sederhana atau industri pulpa dan kertas. Sebaliknya, gentian teras batang kenaf yang mengandungi bentuk seperti jerami dan gentian yang pendek tidak boleh digunakan dengan sendirinya dalam papan serpai, papan serpai berketumpatan sederhana atau industri pulpa dan kertas kerana rendah kekuatan dan kestabilan dimensi. Oleh itu, penggunaan alternatif perlu dikaji. Memandangkan gentian teras batang kenaf mempunyai tinggi kandungan holoselulosa, kandungan lignin yang rendah dan kadar serapan yang tinggi, sifat-sifat ini membuatkan gentian teras batang kenaf sesuai untuk penghasilan karboksimetil selulosa (KS) dalam hidrogel. Kajian ini terbahagi kepada tiga bahagian utama: 1) Penilaian sifat asas gentian teras kenaf, 2) Karboksimetil gentian teras kenaf dan 3) Pembentukan hidrogel daripada gentian teras kenaf yang dikarboksimetil.

Penilaian sifat kimia dan fizikal gentian teras kenaf dilakukan sebelum proses karboksimetil dijalankan. Sampel untuk morfologi gentian dan analisis kimia disediakan daripada maserasi dan gentian dihalusi secara mekanikal. Semua analisis kimia dijalankan menggunakan gentian bersaiz 40-mesh (saiz 425 µm) manakala untuk analisis morfologi serat (panjang gentian, diameter gentian, diameter lumen dan tebal dinding sel) gentian teras kenaf berukuran mancis digunakan. Kajian ini mendapati gentian teras kenaf mengandungi 50.6% alfa-selulosa, 27.1% hemiselulosa dan 20.5% lignin. Peratus serapan air gentian teras kenaf yang tinggi (50%) telah dicatatkan kerana peratus pit yang banyak dibahagian memanjang dinding sel seperti yang diperhatikan melalui SEM. Gentian teras mempunyai nisbah Runkel yang rendah iaitu 0.36, serta menunjukkan kadar serapan air tinggi kerana saiz lumen besar dan dinding gentian nipis membantu memudahkan pemindahan cecair.

Gentian teras kenaf berjaya dikarboksimetilkan dalam keadaan heteregen terhasil daripada tindakbalas gentian teras dengan sodium monokloroasetat sebagai agen eter dan isopropanol sebagai media tindakbalas dengan kehadiran natrium hidroksida sebagai agen pembengkakan. Beberapa faktor yang mempengaruhi proses pengkarboksimetilan seperti masa, kepekatan natrum hidroksida dan suhu yang digunakan dikaji. Darjah penukargantian (DP), peratus kecekapan (PK) and peratus pertambahan berat (PPB) juga ditentukan. Antara tiga jenis gentian teras kenaf yang digunakan, gentian teras sebenar batang kenaf (GTSK), gentian teras kenaf tanpa ekstraktif (GTKTE)

juga gentian teras kenaf tanpa ekstraktif dan lignin (GTKTEL), GTKTEL memberikan nilai DP tertinggi. Ketulinan holoselulosa didapati faktor penting untuk memperolehi hasil yang tinggi. Keadaan untuk tindakbalas optimum bagi menghasilkan karboksimetil gentian teras kenaf dengan DP 0.87 adalah berdasarkan prosedur berikut: pertama, mengekstrak ekstraktif dan lignin daripada gentian teras kenaf untuk menghasilkan GTKTEL dan tindakbalaskan dengan sodium monokloroasetat dalam 30% natrium hidroksida pada suhu 55^{o}C selama 2 jam. Daripada analisis spektroskopi inframerah transformasi Fourier (FTIR), kewujudan puncak pada 1591 cm^{-1} pada gentian teras kenaf yang dimodifikasi menunjukkan beberapa kumpulan hidroksil selulosa gentian teras kenaf telah diambilalih oleh kumpulan karboksimetil. Kajian mikroskop pengimbasan elektron juga menyokong proses penukargantian terjadi, dimana gentian teras kenaf yang tidak dimodifikasi mempunyai permukaan yang kasar dengan pit yang masih kosong. Sebaliknya, permukaan yang licin dapat diperhatikan daripada gentian yang dimodifikasi dengan menganggap pit terisi dengan karboksimetil natrium monokloroasetat.

Hidrogel berjaya dihasilkan menggunakan larutan yang berkepekatan berbeza-beza terdiri daripada karboksimetil gentian teras kenaf tanpa ekstraktif dan lignin (KGTKTEL) pada beberapa dos sinaran. Didapati dos 70 kGy adalah sinaran optimum untuk tautsilang oleh hidrogel KGTKTEL dengan kandungan gel 37.1%. Keadaan tautsilang optimum adalah 50 kGy iradiasi dan 50% kepekatan, menghasilkan sifat-sifat yang baik hidrogel KGTKTEL. Nisbah

pembengkakan hidrogel KGTKTEL adalah tertinggi dalam air suling berbanding dengan alkali (1.0 M NaOH) dan asid (1.0 M HCl) untuk semua peringkat dos sinaran kecuali 10 kGy. Peningkatan tahap kepekatan KGTKTEL menunjukkan peningkatan pembengkakan. Keputusan ini walaubagaimanapun menunjukkan sebaliknya bila ujian pembengkakan dijalankan dalam media asid dan alkali. Keseluruhan keputusan menunjukkan bahawa gentian teras batang kenaf boleh digunakan sebagai bahan alternatif untuk penghasilan karboksimetil selulos dan hidrogel dan menunjukkan sifat-sifat lain yang memuaskan.

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I certify that an Examination Committee met on 28 April 2008 to conduct the final examination of Ismawati Palle on her Master of Science thesis entitled "Carboxymethylation of Cellulose from Kenaf (*Hibiscus cannabinus* L.) Core for Hydrogel Production" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the degree of Master of Science.

Members of the Examination Committee were as follows:

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Date : 22 July 2008

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date : 14 AUGUST 2008

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.

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ISMAWATI PALLE

Date : 21 July 2008

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