PREPARATION AND CHARACTERIZATION OF CARBOXYMETHYL SAGO WASTE AND ITS HYDROGEL

By

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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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Faculty : Science

Carboxymethyl sago waste (CMSW) was prepared under heterogeneous condition as the product of the sago waste and sodium monochloroacetate (SMCA) in presence of sodium hydroxide (NaOH). The carboxymethylation of sago waste was optimized respect to degree of substitution (DS) and reaction efficiency (RE). Maximum values of DS and RE were obtained with aqueous isopropyl alcohol as the reaction medium. Data obtained also suggest that water: isopropyl alcohol with 1:15 ratio was most appropriate for the reaction. The concentration of aqueous sodium hydroxide solution, which is used to activate the cellulose and starch was found optimal at 25 % (w/v). The increase of concentration of SMCA leads to an increase of DS, but only in certain extent, approaching a maximum value with anhydroglucose unit of sago waste: SMCA with 1:2.1 in molar ratio. The highest value of DS is being obtained when carboxymethylation was performed at an hour of alkalization and 2 hours etherification at temperature of 55 ^{o}C. The values of DS and RE under optimum condition for CMSW were 1.06 and 61.1% respectively.

Sago waste were fractionated into cold water soluble (2.8%), hot water soluble (7.5%), 5% sodium hydroxide soluble polysaccharides (starch and hemicelluloses) (78.1%), 10% acetic acid and sodium chlorite (3.1%), 24% potassium hydroxide and 2% boric acid soluble hemicelluloses (1.9%) and α-cellulose (10.5%), respectively. Moisture content, density, values of pH and solubility in water of CMSW were found higher than sago waste and these properties were enhanced by increasing the DS of CMSW. Fourier Transform Infrared Spectroscopy (FTIR) of CMSW revealed two new bands with sharp intensity at 1320 and 1422 cm^{-1}, which respectively correspond to the vibration of substituted carboxyl groups (COO). Scanning electron microscopy studies showed that the sago waste consists of surface morphologies of cellulose fibres and smooth surface and oval granules of starch. After carboxymethylation, CMSW were rough and grooved with agglomeration of cellulose fibres and starch granules. Thermogravimetric analysis and differential thermogravimetric of CMSW showed the thermal stability of CMSW was more stable than sago waste from 35 to 900 ^{o}C. Results from differential scanning calorimetric revealed that the carboxymethylation reduced the crystallinity of starch and cellulose and reduced the portion of starch granules being able to be gelatinized in CMSW. Viscometry capillary study indicates that the degradation of the sago waste chains was occurred where the intrinsic viscosity and molecular weight of CMSW were found to be decreased after carboxymethylation. The CMSW hydrogels with various parameter of cross-linking were prepared by using electron beam irradiation. CMSW hydrogel with DS of 1.06, 80 % of CMSW aqueous solution and irradiation dose of 40 kGy showed the highest of gel content. The swelling of CMSW hydrogel decreased with the increase of the dose of irradiation and CMSW concentration. The swelling of CMSW hydrogel in water increases

with increasing of hydrophilic substituents (–CH_2COONa) in CMSW hydrogel. Swelling ratio of CMSW hydrogel in alkaline medium (0.1 M NaOH) and sodium chloride (0.1 M NaCl) were lower than swelling in deionized water but higher than acidic medium (0.1 M HCl). The presence of cations in swelling medium were remarkably affected the swelling ratio of CMSW hydrogel.

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

PENYEDIAAN DAN PENCIRIAN KARBOKSIMETIL HAMPAS SAGU DAN HIDROGEL KARBOKSIMETIL HAMPAS SAGU

Oleh

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Februari 2006

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Karboksimetil hampas sagu (KMHS) telah disintesis dalam keadaan heterogen sebagai hasil tindak balas daripada hampas sagu dan natrium monokloroasetat (NaMKA) dengan kehadiran natrium hidroksida. Proses karboksimetil hampas sagu dioptimum dengan mengkaji keputusan daripada darjah penukargantian (DP) dan keberkesanan tindak balas (KTB). Nilai maximum DP dan KTB telah diperolehi dengan menggunakan isopropanol sebagai medium tindak balas. Data yang diperolehi juga menunjukkan nisbah isipadu air kepada isopropanol 1:15 adalah campuran yang paling sesuai untuk tindak balas karboksimetilasi. Kepekatan larutan natrium hidroksida yang digunakan untuk mengaktifkan molekul kanji sagu dan selulosa didapati optimum pada 25 % (jisim/isipadu). Penambahan kandungan NaMKA juga menyebabkan peningkatan nilai DP dengan mancapai nilai maximum pada nisbah molar unit ringkas glukosa kepada NaMKA pada 1:2.1. Nilai tertinggi untuk DP juga diperolehi apabila proses karboksimetilasi diadakan selama satu jam untuk pengalkalian dan 2 jam untuk pengeteran pada suhu 55 ^{o}C. Nilai DP dan KTB pada keadaan optimum adalah masing-masing ialah 1.06 dan 61.1 %. Hampas sagu

juga diekstrak dengan menggunakan air sejuk (2.8 %), air panas (7.5 %), 5% natrium hidroksida (kanji sagu dan hemiselulose) (78.1 %), 10 % asid asetik dan natrium klorida (3.1 %), 24 % kalium hidroksida-2 % asid borik (1.9 %) dan α-selulosa (10.5 %). Kandungan wap air, ketumpatan, nilai pH, dan keterlarutan dalam air pada KMHS didapati lebih tinggi daripada hampas sagu. Ciri-ciri ini juga meningkat dengan peningkatan pada nilai DP KMHS. Spektra inframerah untuk KMHS menunjukkan terdapat dua puncak baru yang tajam pada 1320 dan 1422 cm^{-1} yang dipercayai hasil daripada getaran kumpulan karboksil (COO). Kajian mengenai imbasan microskopik elektron membuktikan disamping gentian selulosa, hampas sagu juga mengadungi granul kanji sagu yang mempunyai permukaaan yang licin. Selepas proses karboksimetilasi, permukaan yang kasar dan bergerutu didapati pada biji KMHS. Ini menunjukkan penyebatian gentian selulosa dan kanji sagu berlaku pada proses karboksimetilasi. Analisis termogravimetri mendapati kestabilan terma daripada suhu 35 kepada 900 ^{o}C yang ditunjukkan oleh KMHS lebih baik jika dibandingkan dengan hampas sagu. Keputusan daripada kalorimetri pengimbasan pembezaan membuktikan proses karboksimetilasi dapat mengurangkan darjah penghabluran pada molekul kanji dan selulosa serta mengurangkan kecenderungan kanji untuk membentuk gelatin. Kajian kapilari kelikatan menunjukkan degradasi pada rantai molekul hampas sagu berlaku di mana kelikatan intrinsik dan jisim molekul KMHS didapati berkurang selepas prosess pengkarboksimetilasi. Hidrogel KMHS telah disintesis pada pelbagai parameter taut-silang dengan menggunakan teknik radiasi alur elektron. Didapati KMHS dengan DP 1.06, kepekatan larutan CMSW pada 80 % dan dos radiasi pada 40 kGy menghasilkan kandungan gel tertinggi. Pengembungan hydrogel KMHS dalam air didapati berkurangan dengan peningkatan dos radiasi dan kepekatan KMHS. Pengembugan hydrogel KMHS

dalam air bertambah apabila kumpulan penukargantian ($–CH_2COONa$) dalam KMHS bertambah. Darjah pengembungan hidrogel KMHS dalam larutan beralkali (0.1 M NaOH) dan natrium klorida (0.1 M NaCl) didapati kurang daripada pengembugan di dalam air tetapi lebih tinggi daripada pengembungan dalam larutan berasid (0.1 M HCl). Selain ion natrium, kehadiran kation dalam lain larutan menunjukkan pengaruh yang amat ketara ke atas darjah pengembungan hidrogel KMHS.

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I certify that an Examination Committee has met on 17th February 2006 to conduct the final examination of Lim Jew Kiat on his Master of Science thesis entitled "Preparation and Characterization of Carboxymethyl Sago Waste and Its Hydrogel" 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 relevant degree. Members of the Examination Committee are as follows:

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

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DECLARATION

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

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LIM JEW KIAT

Date:27/2/2006

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