MODIFICATION OF RUBBERWOOD FIBRE BY GRAFT COPOLYMERISATION AND ITS APPLICATION AS ION EXCHANGER AND FILLER IN POLYPROPYLENE COMPOSITE

BY

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DEDICATION

TO ALL MUSLIMS IN THE WORLD

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

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Graft copolymerisation of vinyl monomers such as poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), and polyacrylonitrile (PAN) onto rubberwood fibre (RWF) was carried out by a free radical initiation. Hydrogen peroxide and ferrous ion were used as an initiator system to graft PMA and PMMA onto RWF, while potassium permanganate was used to graft PAN onto RWF. Effect of the reaction parameters (reaction temperature and reaction period, as well as hydrogen peroxide, ferrous ammonium sulphate, potassium permanganate, and monomer concentrations) on the percentage of grafting was investigated. The grafting percentage showed dependence on the initiator, Fe^{2+} and monomer concentrations, as well as the reaction temperature and reaction period. High percentage of grafting was achieved when the optimum reaction conditions were used. Optimum temperature of the

polymerisation of PMA onto rubberwood fibre was found to be about 55 °C for the reaction period 120 minutes. They were 60 °C and 60 minutes for PMMA while they were 70 °C and 180 minutes for PAN. Optimum concentration of H_2O_2 was 0.02 M and the amounts of Fe^{2+} 0.26 mmol when 0.05 mole of MA were used. When 2.36×10^{-2} moles of MMA were used, the concentration of H_2O_2 and amount of Fe^{2+} were 0.03 M and 0.26 mmol, respectively. PMA and PMMA homopolymers were removed from the graft copolymers by Soxhlet extraction using acetone. Optimum reaction conditions for grafting of PAN onto RWF were as follows: monomer amount; 0.18 mole, initiator amount; 4.0 mmol, nitric acid concentration; 0.2 M. PAN as homopolymer was removed from grafted product by DMF. The presence of PMA, PMMA and PAN on the fibre was confirmed by FTIR spectroscopy and gravimetric analysis.

PAN grafted rubberwood fibre was converted to poly(amidoxime) ion exchange resin in order to remove heavy metal ions from aqueous solutions. The cation-exchange resin exists predominantly in the syn-hydroxyamino form. The water uptake by the resin was about 31 g/g dry resin, and hydrogen capacity was 3.6 mmol/g. The absorption capacity for different metal ions from wastewater was determined at different pH's from 1 to 6. The prepared chelating ion exchanger gives highest adsorption capacity for Cu^{2+}, which was 3.83 mmol/g, followed by Cd^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+} and Co^{2+}, respectively. Poly(amidoxime) ion exchanger resin was also used to separate cobalt and nickel ions from copper ion by using column technique. PMA grafted RWF was converted to poly(hydroxamic acid) ion exchanger resin. Adsorption of metal ions was studied at different pH's and it showed that the highest adsorption was for lead ion. The results showed that the absorption capacity depended on the solution pH. FTIR spectroscopy was used to confirm the conversion of grafted fibre to ion exchanger resin.

The percentage of moisture absorbed by the grafted products decreased depending on the grafted polymer. The moisture content in the fibre was reduced from 6 to less than 1% when PMA was grafted onto RWF.

Activation energies (E_a) of RWF and its grafted copolymers were analysed by thermogravimetric analysis (TGA) and dynamic derivatives of the thermogravimetric (DTG). It was found that RWF and RWF-g-PMMA were degraded by one-step decomposition and their E_a are 91 and 96 KJ/mole respectively. On the other hand, RWF-g-PMA degraded by two steps while RWF-PAN degraded by three steps. The highest E_a of RWF-g-PMA was 199 KJ/mole of the second step but it was 200 KJ/mole for RWF-g-PAN at the first step. Temperature of first steps degradation of RWF and its grafted copolymers were as follows: RWF; 352 ˚C, RWF-g-PMA; 362 ˚C, RWF-g-PMMA; 370 ˚C, and RWF-g-PAN; 354 ˚C.

As an application of RWF-g-PMMA copolymer, it was used with RWF to prepare fibre/polypropylene composite. It was found that the tensile strength decreased with increasing of the fibre loading. Tensile strength and modulus were improved when 20% of grafted fibre was used with RWF in preparation of composite when it was radiated by electron beam radiation. However, increasing the fibre loading increased tensile and flexural moduli. On the other hand, toughness of the composite was improved when grafted RWF was used as a filler of PP composite.

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

PENGUBAHSUIAN FIBER KAYU GETAH MELALUI PENGKOPOLIMERAN CANGKUK DAN APLIKASINYA SEBAGAI PENUKAR ION DAN PENGISI DALAM KOMPOSIT POLIPROPILENA

Oleh

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Pengerusi: **Profesor Madya Mansor Ahmad, Ph.D.**

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Pengkopolimeran cangkuk oleh monomer vinil seperti poli(metil akrilit) (PMA), poli(metil metakrilit) (PMMA), dan poliakrilonitril (PAN) ke atas fiber kayu getah (RWF) dilakukan melalui radikal bebas sebagai bahan permula. Hidrogen peroksida dan ion ferus telah digunakan sebagai sistem permula bagi cangkukan PMA dan PMMA ke atas RWF, sementara itu kalium permanganat telah digunakan untuk cangkukan PAN ke atas RWF. Kesan parameter tindak balas (seperti suhu, masa tindak balas, kepekatan hidrogen peroksida, ferus ammonia sulfat, kalium permanganat dan monomer) ke atas peratus cangkukan telah dikaji. Peratus cangkukan didapati bergantung kepada kepekatan bahan permula, Fe^{2+} dan monomer, serta suhu dan masa tindak balas. Peratus cangkukan yang tinggi dicapai apabila keadaan tindak balas optimum digunakan. Suhu optimum pempolimeran PMA ke atas fiber

kayu getah telah didapati pada 55 °C dan masa tindak balas selama 120 minit. Manakala suhu dan masa untuk PMMA adalah pada 60 °C dan 60 minit, sementara untuk PAN adalah pada 70 °C dan 180 minit. Kepekatan optimum bagi H_2O_2 adalah 0.02 M dan amaun Fe^{2+} 0.26 mmol, manakala 0.05 mol MA telah digunakan. Apabila 2.36×10^{-2} mol MMA digunakan, kepekatan bagi H_2O_2 dan amaun Fe^{2+} masing-masing adalah 0.03 M dan 0.26 mmol. Homopolimer PMA dan PMMA telah dikeluarkan daripada kopolimer cangkuk melalui pengekstrak Soxhlet menggunakan aseton. Keadaan optimum tindak balas untuk cangkukan PAN ke atas RWF adalah seperti berikut: Amaun monomer, 0.18 mol; amaun pemula, 4.0 mmol; kepekatan asid nitric, 0.2 M. Homopolimer PAN telah dikeluarkan daripada hasil cangkukan oleh DMF. Kehadiran PMA, PMMA dan PAN ke atas fiber telah disahkan oleh spektroskopi FTIR dan analisis gravimetri.

PAN cangkukan fiber kayu getah telah ditukarkan kepada resin penukar ion poli(amidoksim) untuk mengeluarkan ion logam berat daripada larutan akueus. Resin penukar-kation wujud separa dominan dalam bentuk sin-hidroksiamino. Penyerapan air oleh resin adalah 31 g/g resin kering, dan kapasiti hidrogen adalah 3.6 mmol/g. Kapasiti serapan ion logam yang berlainan daripada air buangan diukur pada pH yang berlainan, iaitu daripada 1 hingga 6. Penukar ion pengkelat yang disediakan memberikan kapasiti serapan yang tinggi untuk Cu^{2+}, iaitu

3.83 mmol/g, diikuti oleh Cd^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+} dan Co^{2+}. Resin penukar ion poli(amidoksim) telah juga digunakan untuk memisahkan ion kobalt dan ion nikel daripada ion kuprum menggunakan teknik kolum. PMA cangkukan RWF telah ditukarkan kepada resin penukar ion asid poli(hidroksimik). Serapan oleh ion logam telah dikaji pada pH yang berlainan dan serapan yang tinggi adalah bagi ion plumbum. Keputusan menunjukkan kapasiti serapan bergantung kepada larutan pH. Spektroskopi FTIR telah mengesahkan penukaran fiber cangkukan kepada resin penukar ion.

Peratus penyerapan lembapan oleh hasil cangkukan menurun, bergantung kepada polimer cangkukan. Kandungan lembapan dalam fiber telah dikurangkan daripada 6% kepada kurang dari 1% apabila PMA dicangkukkan ke atas RWF.

Tenaga pengaktifan (E_a) bagi RWF dan kopolimer cangkukan telah dikaji menggunakan analisis termogravimetri (TGA) dan termogravimetri kamilan (DTG). Didapati RWF dan RWF-g-PMMA telah mengalami degradasi melalui penguraian satu langkah dan E_a masing-masing adalah 91 dan 96 KJ/mol. Selain itu, RWF-g-PMA mengalami degradasi dua langkah sementara RWF-g-PAN mengalami degradasi tiga langkah. Nilai E_a yang tertinggi oleh RWF-g-PMA adalah 199 KJ/mol daripada langkah kedua, tetapi adalah 200 KJ/mol untuk RWF-g-PAN pada langkah pertama. Suhu degradasi langkah pertama oleh RWF dan kopolimer cangkukannya seperti berikut: RWF, 352 °C; RWF-g-PMA, 362 °C; RWF-g-PMMA, 370 °C; dan RWF-g-PAN, 354 °C.

Sebagai aplikasi bagi kopolimer RWF-g-PMMA, ia telah digunakan dengan RWF untuk menyediakan komposit fiber/polipropilena. Penyediaan komposit dengan menggunakan 20% cangkukan fiber dan RWF memberi kekuatan tensil dan modulus yang tinggi apabila telah kenakan iradiasi oleh pancaran alur elektron. Walau bagaimana pun, kekuatan modulus tensil dan fleksural meningkat dengan pertambahan fiber. Selain itu, kekuatan komposit telah meningkat apabila RWF cangkukan telah digunakan sebagai bahan tambah bagi komposit polipropilena.

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I certify that an Examination Committee met on 31 September 2004 to conduct the final examination of Faraj Ahmad Abu-Ilaiwi on his Doctor of Philosophy thesis entitled "Modification of Rubberwood Fibre by Graft Copolymerisation and its Application as Ion Exchanger and Filler in polypropylene Composite" in according 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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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.

FARAJ AHMAD ABU-ILAIWI

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