UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF NANOCOMPOSITES BASED ON PLASTICIZED STARCH AND KENAF BAST NANOFIBERS

SAMANEH KARIMIMAZRAEHSHAHI

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By

SAMANEH KARIMIMAZRAEHSHAHI

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

January 2014

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DEDICATION

I dedicate this dissertation to my wonderful family who surrounds me with unconditional LOVE.

Especially to:

My lovely husband, Mehdi, who is always pushing me forward and is the source of energy, inspiration and courage.

My uncle, Professor Ali, who without his encouragements, sacrifices and support this work was not possible.

My terrific parents, Ashraf & Hassan, who are the source of love and compassion. I never would have made it here without you!

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

CHARACTERIZATION OF NANOCOMPOSITES BASED ON PLASTICIZED STARCH AND KENAF BAST NANOFIBERS

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January 2014

Chair: Professor Paridah Md. Tahir, PhD
Institute: Institute of Tropical Forestry and Forest Products

Plants cell walls are biological nanocomposites which exhibit high mechanical properties at a light weight. The secret of this rigidity and strength lies in its main structural component; cellulose. Native cellulose exists as highly-ordered microfibrils, which are just a few nanometers wide and have been found to be stiffer than many synthetic fibers. Many critical issues associated with global warming, environmental pollution and the amount of plastic wastes, synergistic with the scarcity and non-renewability of petroleum and petroleum-based products are driving material and composite scientists to focus on development of renewable and sustainable biomaterials. In this quest, using cellulose microfibrils from plant materials as renewable alternatives to conventional reinforcement materials such as glass fibers and carbon fibers is generating particular interest. Cellulosic nanofibers have the potential to reinforce and enhance properties of polymeric matrices, significantly, even at very low volume fractions. According to objectives of this research, by applying a chemi-mechanical approach both unbleached and bleached cellulose nanofibers were extracted from the cell wall of kenaf bast fibers and characterized. Then, the reinforcement performances of these two nanofillers were studied and compared using the starch as a matrix material, to identify the necessity of bleaching procedures in nanofiber isolation process. Subsequently, according to result, nanocomposite with different fiber loadings were prepared with unbleached nanofibers. Structural and mechanical performances of these materials were studied and compared with the composite prepared with micro scale cellulosic fibers from kenaf bast, unders the same conditions, to fully understand the effect of fibers loading and dimension on properties of fabricated materials.

In order to undertake the research objectives, cellulosic fiber hierarchy from kenaf bast were isolated in three stages. Initially raw kenaf bast fibers were subjected to soda-AQ pulping process to eliminate lignin and hemicellulose. Unbleached fibers then undergone a bleaching process and finally both pulped and bleached fibers were mechanically separated into their constituent nanoscale cellulosic fibers. The influence of each treatment on the chemical composition, morphology, functional

groups, crystallinity, and thermal stability of fibers was investigated. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR) showed that lignin and hemicellulose were almost entirely removed during the alkali and bleaching treatments. Morphological studies of fiber hierarchy were done by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-Ray diffraction (XRD) analysis revealed that the crystallinity of fibers increased from 62.9 to 81.5% as subsequent treatments were applied. Comparison with other works demonstrated the effectiveness and superior yield of 62.5% for unbleached nanofibers and 58% for bleached nanofibers, in the applied approach for producing nanocellulose from kenaf bast fibers. The isolated nanofibers displayed about 10% enhancement in thermal stability compare to that of raw kenaf bast fiber. The results of study on the properties of isolated bleached and unbleached nanofibers indicated the probable redundancy of the bleaching process as no significant difference was observed in their characteristics.

The surface chemistry of the unbleached and bleached nanofibers is different and it has led to different behavior when these nanofibers are incorporated into polymeric matrices. In order to evaluate this issue both types of nanofibers were used to reinforce thermoplastic starch matrix and properties of obtained nanocomposite films were characterized using SEM, ATR/FTIR, XRD, thermogravimetric analysis (TGA), tensile and water uptake experiments. The results showed superior overall performance of nanocomposite films made from unbleached nanofibers. Thus the redundancy of bleaching procedures in nanofiber isolation process was cleared.

In the subsequent work, unbleached nanofibers with different loading (0-10 wt%) were incorporated into thermoplastic starch matrix. Thin bionanocomposite films were made by casting and evaporating the mixture of aqueous suspension of nanofibers, starch and glycerol which underwent gelatinization process at the same time. In order to elucidate the importance and the effect of nanoscale cellulosic fibers on the performance of fabricated materials, starch based composite films with the exact same conditions were made by using micro sized pulverized kenaf bast fibers. The resulting composite and nanocomposite films were characterized by SEM, TEM, ATR/FTIR, XRD, TGA, scanning differential calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), tensile and water uptake experiments. Among tested materials, the nanoreinforced composites had significantly greater performance, particularly; increased mechanical strength and reduced water sensitivity. Tensile strength and Young's modulus increased by 313% and 343% and water uptake reduced by 21% with addition of 10% nanofibers. Overalls results demonstrated that applied nanofibers strongly interacted by hydrogen bonding with the starch matrix and showed a favourable compatibility which can be attributed to their chemical similarities.

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

PENCIRIAN NANOKOMPOSIT BERDASARKAN DIPLASTIKKAN KANJI DAN KENAF BAST NANOFIBERS

Oleh

SAMANEH KARIMIMAZRAEHSHAHI

Januari 2014

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Dinding sel tumbuhan nanokomposit biologi yang menunjukkan sifat-sifat mekanik yang tinggi pada berat cahaya. Rahsia ketegaran dan kekuatan terletak kepada komponen utamanya iaitu struktur selulosa.Selulosa asli microfibrils yang wujud sangat tinggi, yang mempunyai luas hanya beberapa nanometer telah didapati lebih keras daripada banyak serat sintetik. Banyak isu-isu kritikal yang berkaitan dengan pemanasan global, pencemaran alam sekitar dan jumlah sisa plastik, yang disinergi dengan kekurangan dan petroleum yang tidak diperbaharui dan produk berasaskan petroleum dalam pembangunan bahan komposit dan saintis memberi tumpuan kepada pembangunan biobahan yang boleh diperbaharui dan mudah diperolehi. Dalam usaha ini, dengan menggunakan microfibrils selulosa dari bahan tumbuhan sebagai alternatif yang boleh diperbaharui kepada bahan-bahan pengukuhan konvensional seperti gentian kaca dan gentian karbon adalah menjana kepentingan tertentu. Nanofibers Cellulosic mempunyai potensi untuk mengukuh dan meningkatkan sifat-sifat matriks polimer, dengan ketara, walaupun pada pecahan jumlah yang sangat rendah. Menurut objektif kajian ini, dengan menggunakan pendekatan bahan- mekanikal kedua-dua luntur dan terluntur nanofibers selulosa dipetik daripada dinding sel kenaf fibers. Kemudian, prestasi pengukuhan kedua-dua nanofillers telah dikaji dan dibandingkan menggunakan kanji sebagai bahan matriks, untuk mengenal pasti keperluan prosedur pelunturan dalam proses pengasingan nanofiber. Selepas itu, menurut hasil, nanocomposite dengan bebanan gentian yang berbeza telah disediakan dengan nanofiber luntur. Prestasi struktur dan mekanikal bahan-bahan ini telah dikaji dan dibandingkan dengan komposit yang disediakan dengan skala mikro serat cellulosic dari kenafbast, dalam keadaan yang sama, untuk memahami sepenuhnya kesan serat memuatkan dan dimensi pada sifat bahan fabrikasi.

Dalam kajian ini, hirarki gentian selulosa dari kulit kenaf telah diasingkan dalam tiga peringkat yang berbeza. Gentian kulit kenaf mentah pada mulanya telah melalui proses pempulpaan untuk mengasingkan lignin dan hemiselulosa. Setelah mendapatkan gentian daripada pulpa, ia melalui proses pelunturan dan akhirnya kedua-dua gentian pulpa dan gentian yang telah dilunturkan diasingkan secara mekanikal kepada konstituen gentian selulosa berskalanano. Kesan setiap rawatan terhadap kandungan kimia, morfologi, kumpulan fungsi, kristaliniti, dan

kestabilan haba gentian telah dikaji. Jumlah pantulan lemah spektroskopi (ATR/FTIR) menunjukkan bahawa hampir semua lignin dan hemiselulosa telah dikeluarkan semasa rawatan alkali dan pelunturan. Kajian morfologi terhadap hierarki gentian telah dijalankan menggunakan mikroskop electron pengimbas (SEM) dan mikroskop electron transmisi (TEM). X-Ray pembelauan (XRD) pula menunjukkan bahawa kristaliniti fiber meningkat dari 62.9-81.5% selepas setiap rawatan yang digunakan. Perbandingan dengan rawatan yang lain menunjukkan keberkesanan dan hasil melebihi 62.5% bagi nanofibers luntur dan 58% untuk nanofiber terluntur, dalam pendekatan yang digunakan untuk penghasilan nano sellulose dari kenaf fiber. Hasil daripada rawatan ini nano fiber yang terpencil menunjukkan peningkatan kira-kira 10% dalam kestabilan terma berbanding dengan kenaf fiber yang mentah. Keputusan kajian terhadap sifat luntur terpencil dan nanofibers luntur menunjukkan lebihan kemungkinan proses pelunturan sebagai tidak ada kesan yang diperhatikan dalam ciri-ciri mereka.

Walaubagaimanapun, sifat kimia permukaan yang diperoleh daripada gentian nano yang tidak dilunturkan adalah berbeza dan ia mungkin disebabkan oleh perlakuan yang berbeza apabila digabungkan kedalam matrik polimer. Dalam usaha untuk menilai kedua-dua jenis gentian nano yang telah digunakan bagi memperkukuh matrik kanji termoplastik dan sifat-sifat filem gentian nano, ia telah dianalisis menggunakan eksperimen SEM, ATR/FTIR, XRD, TGA, kekuatan tarik, dan penyerapan air. Menariknya, keputusan yang diperoleh oleh filem komposit nano yang diperbuat daripada gentian nano tidak luntur menunjukkan prestasi yang lebih baik secara keseluruhannya. Ini adalah hasil kajian yang bernilai tinggi dan menghapuskan prosedur pelunturan yang berlebihan dalam proses-proses pengasingan gentian nano.

Dalam usaha untuk membangunkan nano komposit selulosa berasaskan kanji, gentian nano yang tidak dilunturkan dengan kandungan berlainan (0-10 wt %) dicampurkan ke dalam matrik kanji termoplastik. Filem bionanokomposit nipis telah dihasilkan dengan meletakkan dan meruap campuran gentian nanoterampai, kanji, dangliserol melalui proses pengelatinan dalam masa yang sama. Dalam usaha untuk menerangkan kepentingan dan kesan gentian selulosa berskalanano, filem komposit berasaskan kanji dengan keadaan yang sama telah dihasilkan dengan menggunakan gentian kulit kenaf yang telah dikisar bersaiz mikro. Komposit dan filem nanokomposit yang terhasil kemudiannya dicirikan menggunakan eksperimen SEM, TEM, ATR/FTIR, XRD, TGA, DSC, DMTA, kekuatan tarik, dan penyerapan air. Keputusan yang diperoleh menunjukkan bahawa antara bahan yang diuji, komposit nano diperkukuh mempunyai sifat yang lebih baik secara ketara, khususnya; meningkatkan kekuatan mekanikal dan mengurangkan kepekaan terhadap air. Kekuatan tegangan dan modulus kecil meningkat sebanyak 313% dan 343% dan penggunaan air dikurangkan sebanyak 21% dengan tambahan sebanyak 10% nanofibers.Hasil kajian menunjukkan gentian nano gunaan saling bertindak balas secara kuat terhadap ikatan hydrogen dengan matrik kanji, dan menunjukkan kesesuaian yang disebabkan oleh persamaan kimia.

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Last but not the least, I must give very special thanks to my dear uncle and parents who have taught me to succeed, and for their constant love, patience, calmness, encouragement and believing me in all these years.

I certify that a Thesis Examination Committee has met on 24th January 2014 to conduct the final examination of Samane Karimimazraehshahi on her thesis entitled "Characterization of Nanocomposites Based on Plasticized Starch and Kenaf Bast Nanofibers" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy.

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DECLARATION

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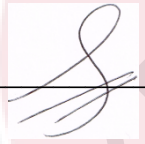
Signature:  Date: 24 January 2014

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