UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF KENAF CELLULOSEPOLYETHYLENE GLYCOL- POLYETHYLENE BIOCOMPOSITES

BEHJAT TAJEDDIN

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By

BEHJAT TAJEDDIN

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

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THIS WORK IS DEDICATED

TO

My HUSBAND (MAHMOOD),
MY LOVELY CHILDREN (MINA & BORNA),

MY FATHER & THE SOUL OF MY MOTHER
WHO SENT ME TO SCHOOL AND ENCOURAGED ME TO FULFILL MY DREAMS,

AND

MY KIND SISTERS & BROTHERS

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in Fulfilment of the Requirement for the Degree of Doctor of Philosophy

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Chairman: Professor Russly Abdul Rahman, PhD

Faculty: Engineering

The possibility of using cellulose as natural fiber for the production of bicomposites was investigated in this study that included two stages. The first stage involved the extraction of cellulose from the cell walls of kenaf (*Hibiscus cannabinus* L.), an annual herbaceous crop with many environmental advantages and good mechanical properties. It was done from the bast part of the crop by chemical treatments. Then, mixture of different weights of low density polyethylene (LDPE) and high density polyethylene (HDPE), as a matrix, with the obtained cellulose, and polyethylene glycol (PEG) were blended in order to produce a biocomposite material suitable for food packaging.

For the second stage, the characterization of LDPE- and HDPE-kenaf cellulose biocomposites was performed in order to develop the optimal blends with optimized thermo-mechanical properties and propensity to environmental degradation. Therefore, the mechanical properties including

tensile strength, flexural and unnotched Izod Impact tests were performed using Instron Universal Testing Machine and Izod Impact Tester, respectively. Thermal properties, biodegradability and water absorption of biocomposites were investigated as well. In addition, a scanning electron microscope (SEM) was used to observe the surface morphology of the tensile fracture surface of the samples before and after biodegradation test.

The results showed that the mechanical properties of the LDPE and HDPE-cellulose composites decreased slightly as the cellulose content increased from 0 to 50 wt % in the biocomposite formulation. It is interesting to note that in all treatments, the mechanical behavior of biocomposites retained in an acceptable level of strength except of HDPE composites with 50% cellulose. In general, there is a good homogeneity between samples with PEG that help to find reasonable and acceptable properties. These findings were confirmed by the SEM study.

Thermal analysis of composites is necessary for determining their end use. Therefore, thermal properties of biocomposites were obtained by a thermogravimetry analysis (TGA) and a differential scanning calorimetry (DSC). Addition of cellulose fillers improves the thermal resistance of these biocomposites. The results also showed that PEG has positive role in thermal behavior of composites. This finding gives a good indication that the addition of kenaf cellulose into the body of LDPE and HDPE was capable to increase their thermal degradation properties.

Biodegradability of these biocomposites was performed based on soil burial test to investigate their degradation during 120 days. The findings illustrated that there is a clear trend of degradation during burial time. The degradability increased as cellulose content was raised in the composite's formulation.

Finally, water absorption was done for biocomposites. The results showed that water absorption value for both composites was higher than those of LDPE and HDPE polymers. Addition of PEG to the formulations reduced the water absorption of the composites.

Generally, it seems that the results of this research may lead to a development of a new type of biocomposites using kenaf cellulose as a natural fiber that can be used to replace plastics for food packaging in the near future.

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

PENYEDIAAN DAN PENCIRIAN SELULOSA KENAF- POLIETILENA GLYKOLA- POLIETILENA BIOKOMPOSIT

Oleh

BEHJAT TAJEDDIN

November 2009

Pengerusi: Professor Russly Abdul Rahman, PhD

Fakulti: Kejuruteraan

Kajian terhadap selulosa sebagai gentian semula jadi bagi penghasilan biokomposit melibatkan dua peringkat. Peringkat pertama adalah pengekstrakan selulosa daripada dinding sel *bast* pokok kenaf (*Hibiscus cannabinus* L.) melalui kaedah rawatan kimia. Kenaf merupakan sejenis tanaman herba tahunan yang mempunyai sifat mekanikal yang baik disamping memberi kebaikan kepada alam sekitar. Selulosa yang telah diekstrak kemudiannya dicampurkan bersama polimer polietilena berketumpatan tinggi dan rendah iaitu HDPE dan LDPE pada berat yang berbeza-beza dimana ia berfungsi sebagai matrik polimer. Manakala, polietilena glikol (PEG) sebagai bahan pemplastik turut dicampurkan bagi menghasilkan bahan biokomposit yang sesuai digunakan dalam pembungkusan makanan.

Pada peringkat kedua, kajian dijalankan terhadap sifat-sifat biokomposit HDPE dan LDPE-ekstrak selulosa bagi mencapai campuran yang optimum

dengan mengambil kira sifat-sifat mekanikal dan terma serta kecenderungan degradasi terhadap persekitaran. Sifat mekanikal seperti kekuatan tegangan, lenturan dan hentaman dianalisis dengan menggunakan alat Instron Universal Testing Machine dan alat Izod Impact Tester. Selain itu, sifat-sifat terma, biodegradasi dan penyerapan air oleh biokomposit turut dianalisis. Kajian morphologi di atas permukaan tegangan patah sebelum dan selepas degradasi dikaji dengan menggunakan pengimbas elektron mikroskopi (SEM).

Keputusan menunjukan dengan meningkatnya penambahan ekstrak selulosa dari 0 hingga 50 (% berat) ke atas polimer mengurangkan sifat-sifat mekanikal biokomposit selulosa LDPE dan HDPE. Bagaimanapun sifat-sifat mekanikal biokomposit adalah kekal pada tahap kekuatan yang boleh diterima kecuali biokomposit dengan campuran 50 % ekstrak selulosa. Ini adalah kerana berdasarkan pengimbas elektron mikroskopi campuran yang sekata dan baik diantara selulosa, polimer dan pemplastikan PEG dikenalpasti.

Analisis termal terhadap biokomposit adalah perlu bagi menentukan kegunaan akhir dan sifat-sifat termal biokomposit ini diperoleh dengan menggunakan analisis thermogravimetri (TGA) dan kalorimeter pengimbas separa (DSC). Berdasarkan keputusan yang diperolehi didapati penambahan selulosa meningkatkan rintangan terma biokomposit dan PEG menunjukkan peranan yang positif di dalam sifat terma biokomposit. Penemuan ini memberi petanda yang baik dimana penambahan selulosa di dalam matrik polimer HDPE dan LDPE meningkatkan sifat-sifat degradasi terma.

Proses biodegradasi dijalankan berdasarkan ujian penanaman ke dalam tanah untuk menganalisis degradasi biokomposit dengan mengambil masa selama 120 hari. Penemuan yang diperolehi menggambarkan aliran dengan jelas terhadap degradasi sepanjang masa penanaman dan didapati penambahan selulosa di dalam biokomposit meningkatkan lagi proses degradasi.

Selain itu, berdasarkan ujian penyerapan air oleh biokomposit didapati nilai penyerapan air bagi kedua-dua biokomposit adalah lebih tinggi berbanding polimer HDPE dan LDPE tulen. Penambahan PEG di dalam formulasi biokomposit dikenalpasti dapat mengurangkan penyerapan air.

Secara umumnya, keputusan yang diperoleh daripada penyelidikan ini boleh membawa kepada pembangunan penghasilan biokomposit baru iaitu dengan menggunakan selulosa daripada kenaf sebagai gentian semula jadi yang boleh dijadikan bahan gantian plastik bagi pembungkusan makanan pada masa hadapan.

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I certify that a Thesis Examination Committee has met on 2 November 2009 to conduct the final examination of Behjat Tajeddin on her thesis entitled "Preparation and Characterization of Kenaf Cellulose- Polyethylene Glycol-Polyethylene Biocomposites" 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.

Members of the Examination Committee were as follows:

Professor Mohd Ali Hassan, PhD
Faculty of Biotechnology and Biomolecular Sciences
University Putra Malaysia
(Chairman)

Associate Professor Mohd Nordin Ibrahim, PhD
Faculty of Engineering
University Putra Malaysia
(Internal Examiner)

Associated Professor Ling Tau Chuan, PhD
Faculty of Engineering
University Putra Malaysia
(Internal Examiner)

Professor Rozman Hj Din, PhD
School of Industrial Technology
University science Malaysia
(External Examiner)

BUJANG BIN KIM HUAT, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the Degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Professor Russly Abdul Rahman, PhD
Faculty of Engineering
University Putra Malaysia
(Chairman)

Associate Professor Luqman Chuah Abdullah, PhD
Faculty of Engineering
University Putra Malaysia
(Member)

Nor Azowa Ibrahim, PhD
Faculty of Science
University Putra Malaysia
(Member)

Yus Aniza Yusof, PhD
Faculty of Engineering
University Putra Malaysia
(Member)

HASANAH MOHD. GHAZALI, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 14 January 2010

DECLARATION

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

Behjat Tajeddin

Date: 13 August 2009

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
Da	Daltons
DP	Degree of polymerization
DSC	Differential Scanning Calorimetry
DTG	Degradation Temperature (Derivative Thermogravimetric)
EU	European Union
FS	Flexural Strength
HDPE	High Density Polyethylene
INTROP	Institute of Tropical Forestry and Forest Products
IS	Impact Strength
KC	Kenaf cellulose
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MA	Maleic Anhydride
MAPP	Maleic Anhydride polypropylene
MARDI	Malaysian Agricultural Research and Development Institute
M_n	The number average molecular weight of the polymer
Mw	Molecular weight (The sum of the atomic weights of all the atoms in a molecule)
OECD	Organization for Economic Cooperation and Development
PCL	Polycaprolactone
PE	Polyethylene
PEA	Polyesteramide
PEG	Polyethylene glycol

PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PLA	Polylactic acid
PP	Polypropylene
RPE	Recycled high density Polyethylene
rpm	Revolution per minute
SEM	Scanning Electron Microscope
T_d	Decomposition Temperature
T_g	Glass transition temperature
TG	Thermogravimetric
TGA	Thermogravimetric Analysis
T_m	Melting Temperature
TS	Tensile Strength
UPM	Universiti Putra Malaysia
WA	Water absorption
WF	Wood flour

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Packaging technology is a mixture of mechanical engineering, mathematics, chemical engineering, physics, packaging science, etc. They make a body of knowledge related to packaging that might be considered the foundation for a technology. Food packaging, for example, is intended to help maintain the quality and shelf life of food products by controlling the transfer of moisture, oxygen, carbon dioxide, lipids, aromas, flavors, and food additives. Han, 2005) said that a good package protects the food quality and also considerably contributes to a business profit. Quality of package depends on its materials. Therefore, the most important function of a packaging material is the preservation of the packed goods quality for storage, transportation and end-use.

Plastic materials are one of the most important materials that are used in food packaging. Plastics are defined as processable materials based on polymers. Because of plastics' advantages in compared with other materials, they have been extensively adopted in food packaging. These advantages are reflected in the physical, mechanical and chemical properties of plastics. They are stable in ambient and many hostile environments and not subject to degradation in normal use. It means that they will not change in properties or performance during the package life (Brown, 1992). Plastics can be formed into end products, such as bottles, containers, films, coatings, etc. The development of self-service stores with their large variety of products is unbelievable without plastics.

Polyethylene (PE) is used as a common and cheap polymer in food packaging. It is one of the usual synthetic polymers with high hydrophobic level and high molecular weight. In natural form, it is not biodegradable. Thus, their use in the production of disposal or packing materials causes many problems (Abd El-Rehim et al., 2004). The main problem is environmental pollution troubles by synthetic polymers and in conjunction with the land shortage problems for solid waste management. Latest and harder ecological policies enforce industries like the automotive, packaging and construction industry to look for new materials (Espert et al., 2004). Thus, attempts have been made to solve these problems and so, the need for environmentally degradable and “environmental friendly” polymers has arisen.

There is a considerable interest in replacing some or all of the synthetic plastics by natural or biodegradable materials in many applications. Since the food industry uses a lot of plastics, even a small reduction in the amount of materials used for each package would result in a significant polymer reduction, and may improve solid waste problems (Chandra & Rustgi, 1998; Han, 2005). It is clear that the use of biodegradable polymers for packaging offers an alternative and partial solution to the problem of gathering of solid waste composed of synthetic inert polymers (Jayasekara et al., 2003).

Plant fibers have attracted more and more research interests owing to their advantages like renewable, environmental friendly, low cost, light weight (low density), high specific mechanical performance (acceptable specific strength properties), easily recyclable, ease of separation, carbon dioxide sequestration, and biodegradability (Zhang et al., 2005).

There are some biocomposites consisting of biodegradable polymers as the matrix material and biodegradable fillers, usually biofibres (e.g. lignocellulose fibers). Since both components are biodegradable, the composite as the integral part is also expected to be biodegradable (Le Digabel & Avérous, 2006). However, these materials may have problems in the mechanical and physical properties.

Nowadays, the blending of biodegradable polymers with inert polymers has been accepted as a possible application in the waste disposal of plastics. In principal, the way of thinking behind this method is that if the biodegradable section is present in enough quantities and if microorganisms in the waste disposal environment degrade it, the plastic or film containing the residual inert component should lose its integrity, fall to pieces and fade away. The best-known renewable resources able to create biopolymer and biodegradable plastics are starch and cellulose (Chandra & Rustgi, 1998; Selke, 2000).

Weber et al. (2002) believed that the only biobased food-packaging materials in use commercially on a major scale are based on cellulose; however, many studies were done on starch-based products including thermoplastic starch, starch and synthetic aliphatic polyester blends, and starch and other polymer blends. Since, starch is a source of energy and it has an important role in human food, research should be focused on new subject that is not human