PREPARATION AND CHARACTERIZATION OF ENVIRONMENTALLY FRIENDLY POLYMERIC BLENDS USING SYNTHETIC AND NATURAL POLYMERS

by

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DECLARATION

I hereby declare that this submission is a result of a work carried out by me and to the best of my knowledge, it contain no material previously written or published by another person nor material which has been accepted for the award of any degree or acceptable qualification of a university, or other Institute of higher learning, except where the due reference to the material is made.

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February 02, 2004

To the best of my knowledge, the above particulars are correct.

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(Dr. B A J K Premachandra)

ABSTRACT

This thesis is consisted of four chapters. Chapter one contains an introductory part including scope and the objectives of the research. Since the present research is divided in to three major parts, chapter two, three and four is arranged accordingly. Each chapter includes an introduction discussing the relevant literature, the experimental work, results and discussions and finally, the conclusions drawn. The contents of this thesis can be best summarized as follows.

Mechanical properties and biodegradability of composites of LDPE with tapioca starch

A series of LDPE/starch composites containing different amounts of starch (as wt %) were prepared using tapioca starch in its native granular form. Mixing was done by dissolving LDPE in cyclohexane pre-heated to its boiling point and subsequently dispersing starch granules by using Silverson emulsifier. The composites were studied by using Fourier Transform Infra-red spectroscopy (FTIR). The failure modes, mechanical properties, water absorption, biodegradation and the biodegradation after thermal incubation were investigated as a function of the composition of the composite. It was found that the incorporation of starch into LDPE matrix has reduced the ductility of the composite. The mechanical properties of the composites, especially the tensile strength and elongation at break were significantly low compared to those of neat LDPE. A significant improvement in modulus was shown by the composites. It was found that the mechanical properties were depended on the composition of the composite.

The extent of the biodegradability, after exposure to α–amylase enzyme solution, was assessed by weight loss measurements and loss of mechanical properties such as tensile strength and percentage elongation. It was found that these composites are biodegradable and the rate of biodegradation increases with increasing starch content. The extent of biodegradation after thermal incubation was assessed by the loss of tensile strength measurements of the composites after incubation of the samples in an

air circulation oven at 70 ^{0}C and subsequently exposing to α–amylase enzyme solution. It was found that the degradability of the samples was not significantly affected by the thermal incubation.

Preparation and characterization of long chain fatty acid esters of tapioca starch

A series of starch esters with different degree of substitution (DS) were prepared and studied. The esters were prepared by acylation of tapioca starch with appropriate acid chlorides such as stearoyl and oleoyl chlorides. Fourier transform infrared (FTIR) spectroscopy confirmed the formation of the starch esters and their DS. As a measurement of the DS of an ester the peak height ratio responsible for O-H bond stretching to C=O bond stretching of the esters were considered. The DS of starch stearates were 5.3, 4.5, 2.6, 2.0 and 1.60. The DS of starch oleates were 3.55, 2.0, 1.90 and 1.21. With increasing DS the color intensities of the esters were improved. Melting temperatures of the esters were determined by using Differential thermal analyzer. The thermo-oxidation degradation of tapioca starch and starch esters, were assessed by using Fourier Transform Infra-red (FTIR) spectroscopy, after the incubation of the samples in an air circulation oven at 70 ^{0}C. The presence of thermo-oxidative degradation was shown in both types of the starch esters. Starch has not shown thermo-oxidative degradation.

Mechanical properties and biodegradability of composites of LDPE with fatty acid esters of tapioca starch

A series of Low Density Polyethylene (LDPE) composites containing different amounts of fatty esters of starch were prepared. Mixing was done by dissolving LDPE, in cyclohexane pre-heated to its boiling temperature, and subsequently, mixing starch esters using Siverson Emulsifier. Two different types of starch esters, starch stearate and oleate with different (DS) were utilized in the preparation of these LDPE composites. Polarized light micrographs were used to assess the miscibility of LDPE with starch esters.

The miscibility of the components was found to be improved with increasing DS of the ester. Water absorption, mechanical properties, biodegradation and biodegradation after thermal incubation were investigated as a function of the composition of the composite. Comparing with the LDPE/starch composites a significant reduction in the water absorption was resulted in the LDPE/starch ester composites. It was found that as the amount of esters increases in the composite, the tensile strength and especially the elongation at break decrease non-linearly. The LDPE/starch ester composites containing starch esters of high DS have shown improved tensile properties than those of LDPE/starch composites. As expected, the fatty ester chains in the starch ester molecules have not shown the plasticizing effect in the composite. The percentage elongation properties were significantly reduced with the introduction of the esters into LDPE.

The extent of the biodegradability of the composites after exposure to α-amylase and lipase enzyme solutions was assessed by weight loss and mechanical properties measurements. The rate of biodegradation of LDPE/starch ester composites was relatively low compared to that of LDPE/starch composites. The rate of biodegradation of these LDPE/starch ester composites further decreases with increasing DS of the ester in the composite. The extent of the biodegradation of the composites after incubation of the samples at air circulation oven at 70 ^{0}C and subsequently immersing in the enzymatic solutions was assessed by the tensile strength measurements. It was found that the degradability of the ester composites was significantly high and the degradation rate increases with the increasing DS of the ester. Highest rate of degradation was observed in the LDPE/starch ester composite containing starch oleate of the highest DS.

To my parents,

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LIST OF ABBREVIATIONS

$CaCO_3$	- Calcium Carbonate
DS	- Degree of Substitution
EAA	- Ethylene Acrylic Acid
EVOH	- Ethylene Vinyl Alcohol
FTIR	- Fourier Transform Infra- Red
h	- Hours
HCl	- Hydro Chloric Acid
HDPE	- High Density Polyethylene
LDPE/PE	- Low Density Polyethylene
MPa	- Mega Pascal
PCL	- Poly Caprolactone
PET	- Polyethylene Terephthalate
PES	- Low Density Polyethylene/ Starch Composite
PESO	- LDPE/ Starch Oleate Composite
PESS	- LDPE/ Starch Stearate Composite
PG	- Poly Glycolide
PHB	- Poly Beta hydroxy Butyrate
PHV	- Poly Hydroxy Valarate
PL	- Poly Lactic
rpm	- Rounds per minutes
TiO_2	- Titanium dioxide
T_m	- Melting temperature
T_g	- Glass transition temperature
wt %	- Weight percentage