CHARACTERIZATION OF CHITOSAN/MONTMORILLONITE HYBRID FILLED TAPIOCA STARCH NANOCOMPOSITE FILMS

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To my beloved father, mother, little brother and sister

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ABSTRACT

Biodegradable nanocomposite films from chitosan/montmorillonite (MMT) hybrid filled plasticized tapioca starch (TPS) were developed using a solution casting method. Chitosan was extracted from local shrimp shell resources with the degree of deacetylation of 60.85%. X-ray diffraction (XRD) analysis showed that the interlayer spacing of the chitosan/MMT/TPS nanocomposite films was slightly increased, indicated that the chitosan molecules were too large to intercalate into clay galleries. However, scanning electron microscopy (SEM) analysis found that the chitosan/MMT/TPS nanocomposite films producing more homogeneous distribution of MMT nanoclay particulate compared to the MMT/TPS nanocomposite films. Fourier transform infrared (FTIR) analysis showed that the shifting in amino group peak of chitosan indicated that the physical interaction occurred between hydroxyl groups (OH) of MMT and amino groups (NH_2) of chitosan. In addition, the broad stretch of OH was also shifted to lower wavelength number proven that hydrogen bonding was formed among starch, MMT and chitosan. It was found that the tensile properties improved in flexibility with moderate strength upon addition of chitosan in MMT/TPS nanocomposite films while the thermal stabilities improved upon addition of MMT in starch films but decreased with the addition of chitosan. The water vapor transmission rate of MMT/TPS films decreased after adding chitosan and the condition was the same for water absorption of the films. The light absorbance was also lowered upon addition of chitosan. Overall, addition of MMT and chitosan improved the TPS film properties that intended for packaging application purposes.

ABSTRAK

Filem komposit nano mesra alam bersumber kitosan/montmorilonit (MMT) hibrid terisi kanji berplastik ubi kayu (TPS) dihasilkan menggunakan teknik acuan larutan. Kitosan dihasilkan daripada kulit udang dari sumber tempatan dengan darjah pendeasetilan yang dicapai ialah 60.85%. Analisis belauan sinar-x (XRD) menunjukkan peningkatan jarak lapisan dalam filem kitosan/MMT/TPS adalah terlalu sedikit, menunjukkan bahawa molekul kitosan terlalu besar untuk masuk ke dalam lapisan galeri MMT. Walau bagaimanapun, analisis mikroskopi elektron penskanan (SEM) menunjukkan filem komposit nano kitosan/MMT/TPS mempunyai pembahagian MMT yang lebih sekata berbanding dengan filem komposit nano MMT/TPS. Berdasarkan analisis spektroskopi inframerah transformasi Fourier (FTIR), pergerakan puncak kumpulan amino kitosan telah menunjukkan berlakunya interaksi fizikal antara kumpulan hidroksil (OH) MMT dengan kumpulan amino (NH_2) kitosan. Sifat regangan didapati telah menunjukkan daya keanjalan yang lebih baik beserta dengan daya kekuatan yang sederhana telah dicapai dengan penambahan kitosan ke dalam filem komposit nano MMT/TPS disamping kestabilan terma meningkat selepas penambahan MMT tetapi menurun apabila kitosan ditambah. Kadar pergerakan wap air MMT/TPS menunjukkan penurunan selepas penambahan kitosan dan keadaan yang sama turut dicapai oleh kadar serapan air filem. Kadar penyerapan cahaya juga turut menurun selepas penambahan kitosan ke dalam filem. Keseluruhannya, penambahan kitosan dan MMT telah berjaya membaik pulih sifat-sifat filem TPS yang digunakan untuk aplikasi bahan pembungkusan.

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LIST OF SYMBOLS

%	-	Percentage
°C	-	Degree Celsius
°	-	Degree
λ	-	Wavelength
Θ_p	-	Diffraction angle
A	-	Area
G	-	Weight change (WVTR analysis)
H	-	Height
L	-	Length
n	-	Integer
R	-	Mean scale
T_d	-	Diffuse transmittance
T_t	-	Total transmittance
t	-	Time
W	-	Width
Wf	-	Final weight
Wi	-	Initial weight
wt%	-	Weight percentage
v/v	-	Volume/volume

LIST OF ABBREVIATIONS

A	-	Absorbance
$CaCO_3$	-	Calcium carbonate
$CaCl_2$	-	Calcium chloride
CO_2	-	Carbon dioxide
DD	-	Deacetylation degree
DSC	-	Differential scanning calorimetry
FTIR	-	Fourier transform infrared
HCl	-	Hydrochloric acid
KBr	-	Potassium bromide
KOH	-	Sodium hydroxide
MMT	-	Montmorillonite
NaOH	-	Potassium hydroxide
Na^+	-	Sodium
OH	-	Hydroxide ion
PTFE	-	Polytetrafluoroethylene
rpm	-	Revolution per minute
SEM	-	Scanning electron microscopy
TEM	-	Transmission electron microscopy
Tg	-	Glass transition temperature
TGA	-	Thermogravimetry analysis
Tm	-	Melting temperature
TPS	-	Thermoplastic starch
WVTR	-	Water vapor transmission rate
XRD	-	X-ray diffraction
%T	-	Transmittance percentage

CHAPTER 1

INTRODUCTION

1.1 Overview

Plastics films are widely used for packaging purposes due to its enormous advantages, such as thermal seal ability, flexibility in thermal and mechanical properties, lightness and low price. Despite various benefits, the bulk of this material was used only for single-use application and was discarded which contributing to environmental problems. Plastic wastes are significantly contributing to environmental pollution and also damaging wild life. Furthermore, recycling plastics wastes lead to some issues for example toxic emission and much energy consumption imply in recycling processes (Avérous and Halley, 2009) . As results, there has been strong interest among national and international levels on the use of biodegradable or biobased materials.

Biodegradable term can be referred to the material that can break down naturally into biogases and biomass (mostly carbon dioxide and water) after being exposed to microbiological environment and humidity (Lagaron and Lopez-Rubio, 2011). Hence, the biodegradable materials reduce waste to landfills. Plants are one of the potential sources of polymers that are renewable and ecologically friendly. One of the potential biodegradable polymers which are obtained from agro resources is starch. Starch has been widely used in packaging application to replace the conventional plastics material (Avérous and Halley, 2009).

Starches have gained interest in polymer industries because they are inexpensive, biodegradable, abundant and renewable resources. There are many types of starch such as maize, tapioca, rice, potato, wheat and sago. According to Howeler (2005), the total production of tapioca in Malaysia is 430,000 tonnes per year. In a tropical country like Malaysia, tapioca has great potential because it can be easily grown in this zone. Other than that, the price for tapioca starch is cheaper compared with the other type of starches.

Tapioca which also called as cassava, manioc or yuca is one of the most important food crops in humid tropics because of its ability to survive in low nutrient availability or drought (Burrell, 2003). The main harvested part of tapioca plant is the tuber or root although leaves are also consumed. Starch is one of the major productions from tapioca roots which are used for various industries and other food products such as in textile industries, pharmaceutical industries, paper production and also main raw material in glue and adhesive industries (Tonukari, 2004). Most of the bioplastics found in the industries are made mainly from starch and the starch based bioplastics represents from 85% to 90% of markets bioplastics (Bastioli, 2001)

Starch can be processed to become a moldable thermoplastic under high temperature and shear which is also known as thermoplastic starch (TPS). During processed, the water content in starch and added plasticizers is play a prominent role because plasticizers can form hydrogen bonds with the starch, replacing the strong interactions between hydroxyl groups of starch molecules and thus making starch thermoplastic (Tang *et al.*, 2008). Introducing high water content or non-volatile plasticizer can decrease the melting temperature and glass transition temperature (T_g) and thus developing a plastic like material (Averous and Pollet, 2012).

There were many types of plasticizer used in starch systems. Some of the plasticizing agents that are widely used in starch systems are glycerol, sorbitol, glycols and sugars (Aouada *et al.*, 2011; Chivrac *et al.*, 2010; Avérous and Halley, 2009). In this study, glycerol will be used as the plasticizer because it has been proven to improve the flexibility better than other type of plasticizer which is one of the requirement properties for packaging application (van Soest *et al.*, 1996).

However, thermoplastic starch has disadvantages such as fast degradation rate, high in hydrophilicity and in certain condition it has poor mechanical properties (Aouada, *et al.*, 2011). In order to overcome these drawbacks, modification was made by adding nanofiller into starch matrix producing nanocomposite film.

The incorporation of montmorillonite (MMT) as reinforcement into plasticized thermoplastic starch improved the properties significantly (Ibrahim, 2011; Majdzadeh-Ardakani *et al.*, 2010; Maksimov *et al.*, 2009). Addition of montmorillonite showed enhancement in mechanical properties, better permeability properties, thermal and flammability (Aouada *et al.*, 2011, Schlemmer *et al.*, 2010, Majdzadeh-Ardakani *et al.*, 2010, Park *et al.*, 2003, Park *et al.*, 2002). Park *et al.*, (2003) reported that MMT has good miscibility with hydrophilic polymers. Therefore, in this study, MMT has been chosen as filler to hydrophilic polymers like starch in producing nanocomposite films.

The most important criteria that need to be achieved in nanocomposite system are intercalation and exfoliation. Solution dispersion is the best method to obtain homogeneous nanocomposites as long as the mixing intensity and duration is well controlled (Medeiros, *et al.*, 2010). The addition of chitosan in montmorillonite filled plasticized starch nanocomposite films is expected to improve the dispersion better because chitosan is compatible with the starch matrix as well as being the ion exchange in the clay (Chung *et al.*, 2010; Kampeerapappun *et al.*, 2007). On the other hand, chitosan itself has the ability to form a good film with favorable properties (Bourtoom and Chinnan, 2008)

Chitosan is one of the polysaccharide materials that are second most abundant after cellulose (Peniche *et al.*, 2008). It can be easily derived from chitin where it is the most abundant organic component of the skeletal structure of animals. In this research, the main resource for chitosan is shrimp shells. Typical chitin is associated with other constituent such as lipids, calcium carbonate, proteins and pigments (Peniche *et al.*, 2008). Some of the well known applications of chitosan are in wastewater treatment, medicine, antimicrobial, seed coating, film forming and other food ingredients and drugs (Bourtoom and Chinnan, 2008). Because of its ability to form good film, widespread availability from stable renewable sources, chitosan was added as hybrid filler to MMT and tapioca starch in order to produce biodegradable films with good properties.

1.2 Statement of Problem

Nowadays, plastics have become indispensable in our daily life for example in packaging, health and hygiene, agricultural, household and consumer goods, transportation, leisure and others. Most of these plastics are non-biodegradable and are produced from non-renewable petrochemical resources. These plastics give huge environmental impact through pollution and poor waste management. Although mankind seeks solution like plastic waste recycling, other issues arise. Recycling could emit toxicity, is non-economical and often gives negative effects to the ecosystem. Hence, the best alternative to overcome these problems is by producing biodegradable polymers, which are from renewable sources.

Starch is one of the biodegradable polymers that can be obtained from agro resources. It is cheap, abundant and renewable. However, starch films are not as good as synthetic polymer films in terms of mechanical and barrier properties. These problems need to be solved so that biodegradable starch plastic can compete with synthetic polymers that already conquer the plastic industries since decades ago.

The main disadvantage of plasticized starch is its hydrophilic character, which leads to poor barrier properties and for some cases it has unsatisfactory mechanical properties (Wang *et al.*, 2008). The solution for this problem is to incorporate nano-sized fillers into the starch matrices which could increase the mechanical properties, thermal stability and water resistance of starch nanocomposite (Aouada, *et al.*, 2011; Dean *et al.*, 2007; Wang *et al.*, 2009; Majdzadeh-Ardakani, *et al.,* 2010).

However, most of starch-clay nanocomposites has been reported to have poor dispersion, which the important aspect to obtain high performance materials (Chung, *et al.,* 2010). According to both of these previous researchers (Chung, *et al.,* 2010; Kampeerapappun, *et al.*, 2007), local chitosan was added as compatibilizer to montmorillonite because chitosan is a natural polysaccharide that is compatible with the starch matrix as well as being ion-exchanged in the clay. So, in this study, chitosan was added as the hybrid filler and it is important to investigate the compatibility between chitosan, tapioca starch and montmorillonite based on the improvement of the acquired properties.

Kampeerapappun, *et al.*, (2007) used chitosan as compatibilizer between starch matrix and montmorillonite as filler. Their study showed that chitosan was a successful compatibilizer through cationic exchange. However, the optimum content involving the combination of montmorillonite and chitosan was not determined by their study. So, in this study, in order to determine the optimum combination of montmorillonite and chitosan, variation content of montmorillonite and chitosan were compared through characterization and properties analysis of nanocomposite films. The thermal properties were not investigated in the previous studies so in this study thermal properties were investigated to determine the thermal stabilities of the material.

1.3 Objectives of The Study

The main objective of this study is to prepare, characterize and investigate the properties of the chitosan/montmorillonite hybrid filled tapioca starch nanocomposite films, namely:

a) To investigate the effect of different montmorillonite content on the physical, mechanical and permeability properties of tapioca starch nanocomposite films and its relation to morphological properties.

b) To investigate the effect of different chitosan content on the physical, mechanical and permeability properties of tapioca starch composite films.

c) To determine the ability of chitosan/montmorillonite hybrid filled starch nanocomposite films on the properties by varying the content of montmorillonite and chitosan.

1.4 Scope of Study

The main scopes of this research are:

i) Sample of chitosan/montmorillonite hybrid filled tapioca starch nanocomposite films were prepared according to the following steps:
   - Chitosan was prepared from chitin derived from prawn shell.
   - Tapioca starch/montmorillonite nanocomposite films were prepared by casting method with the addition of glycerol as the plasticizer.
   - Gelatinized starch solution was cast onto Teflon sheet mold.

ii) Analysis of cast film using X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) analyzer.
   - XRD analysis for the investigation of intercalation existence of montmorillonite.
   - FTIR analysis: To investigate the interaction occurred between tapioca starch, montmorillonite and chitosan and also the functional group exist in chitosan modified tapioca starch/montmorillonite nanocomposite films.
   - FTIR analysis: To determination of degree of deacetylation of chitosan.

iii) Tensile properties: Tensile strength, Young's modulus and elongation at break.

iv) Permeability properties determination based on water vapor transmission rate analysis.

v) Physical properties determination based on water absorption and transparency analysis.

- Water absorption and transparency (cloudy appearance) of films were analysed in order to investigate the effect of montmorillonite and chitosan on the film.

vi) Film surfaces were examined using scanning electron microscopy (SEM)

- Montmorillonite aggregation in the tapioca starch matrix were investigated using SEM.

vii) Thermal stabilities analysis was investigated using Thermogravimetry Analyzer

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