FABRICATION AND CHARACTERIZATION OF COMPOSITE BIODEGRADABLE FILM MADE FROM EMPTY FRUIT BUNCH

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DECLARATION

"I declare that this thesis entitled *Fabrication and Characterization of Composite Biodegradable Film Made from Empty Fruit Bunch* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree"

Signature : ………………………………….

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Date : ………………………………….

To my beloved mother and father

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ABSTRACT

Composite biodegradable film made from chitosan has been the most potential type of packaging. It has caught many reserches and scientist attention to fully utilize its function as it posses not only great physical properties, it is also environmental friendly. The most suitable additives has not yet to be discovered but organic fibers is the best candidate as it has organic fibers to enhance the film. By using palm oil waste, empty fruit bunches as an additive is the concern of the study in therms of theoritically enhancing the physical and chemical properties of the composite biodegradable film. The film preparation process consist of hydrolisis of empty fruit bunch fibers which was done at a temperature range of 80°C before to be mixed with chitosan based solution. The solution was poured on a glass plate and left at ambient temperature until it has become dry. The film was then peeled off the glass plate after the drying is complete. This work also studied the effect of plasticizer amount added to this solution of biodegradable film as there are several researches suggested that the amount of plasticizer does help enhancing the physical properties of the film. Based on the study, the fibers from empty fruit bunches do gives an extra physical properties for the chitosan-base composite film. The melting point has changed a better value in order to sustain more heat during packaging before it gradually melts compared to chitosan alone. In fact, the temperature for the film to degrade has become more relevant as it is not too high nor too low. Results obtain from FTIR, TGA, DSC and AFM proved that by using empty fruit bunches as an additive, the properties of composite film performance has improved. From the study, it can be concluded that the fibers from empty fruit bunch has great potetntial for being an additive for the composite film and the amount of plasticizer added in the composite film helps to enhance the properties of the film compared to chitosan based film.

ABSTRAK

Filem komposit boleh biodegradasi diperbuat daripada chitosan merupakan antara bahan pembungkus yang berpotensi di pasaran. Sifat fizikal bahan ini dan sifatnya yang kurang membahayakan alam sekitar telah lama menjadi sasaran para saintis untuk menggunakan sepenuhnya kebolehan bahan ini. Bahan tambahan yang sesuai untuk menghasilkan filem komposit dengan kebolehan maksima masih belum ditemui namun ada kajian yang menyatakan bahawa serat organik mampu mengeluarkan potensi penuh filem komposit ini. Dengan menggunakan bahan buangan daripada kelapa sawit, iaitu tandan kelapa sawit kosong sebagai bahan tambahan untuk filem komposit ini menjadi sasaran untuk kajian ini secara teori. Penyediaan filem ini merangkumi hidrolisis untuk serat daripada tandan kelapa sawit yang dijalankan pada suhu sekitar 80°C sebelum ia disebatikan dengan larutan filem berasaskan chitosan. Larutan yang telah sebati dituang pada kepingan kaca dan dibiarkan pada suhu persekitaran sehingga membentuk filem. Filem dikupas dari kepingan kaca selepas ia telah kering dengan sepenuhnya. Kajian ini juga mengkaji kesan kuantiti ejen plastik yang ditambah semasa pembentukan larutan filem kerana terdapat beberapa kajian yang menyatakan bahawa kuantiti ejen plastik mampu meningkatkan sifat fizikal filem. Hasil daripada kajian menunjukkan serat organik dari tandan kelapa sawit meningkatkan lagi sifat fizikal filem. Takat lebur filem yang meningkat membolehkan filem digunakan pada suhu yang agak tinggi berbanding dengan filem buatan dari chitosan sahaja. Suhu sebelum degradasi juga menjadi lebih sesuai selepas penambahan serat organik. Hasil daripada FTIR, TGA, DSC dan AFM menunjukkan penggunaan tandan kelapa sawit sebagai bahan tambahan dalam pembuatan filem mampu meningkatkan lagi sifat fizikal filem. Sebagai kesimpulan, penambahan serat tandan kelapa sawit mampu meningkatkan sifat fizikal filem dan kuantiti ejen plastik juga mampu meningkatkan sifat filem berbanding dengan filem berasaskan chitosan sahaja.

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AFM	-	Atomic Force Microscopy
CGM	-	commercially from corn gluten meal
DSC	-	Differential Scanning Calorimetry
EFB	-	empty fruit bunch
FTIR	-	Fourier Transform Infrared
LDPE	-	low density polyethylene
Mn	-	number average molecular weight
Mw	-	weight average molecular weight
PEG	-	poly(ethylene glycol)
PVA	-	poly(vinyl alcohol)
Ra	-	mean roughness
RH	-	relative humidity
Ry	-	mean difference in the height between the five highest peaks and the five lowest valleys
Rz	-	root mean square of data
TGA	-	Thermogravimetric Analysis
WVP	-	water vapor permeability
%v/v	-	volume percentage for chemical per basis

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Biodegradable film is found to be very crucial in the food industries especially for food packaging as it can extend the storage time of the food and it is also environmental (Kristi and Burns, 2007). This factor is very useful as foods are usually stored in a long time. Food storage has become easier as this biodegradable film will extends the time before any food goes bad. Biodegradable film also has its other benefits in different ways. The fact that it is environmental friendly has always been the top priority whenever it is applied. To minimize food losses and provide safe and sound food products, proper packaging method is required. From a consumer point of view, better quality, fresh-like, and convenient food products have been their top priority as since the last decades. Active packaging is a mode of packaging in which the package, the product, and the environment interact to prolong shelf life or enhance safety or sensory properties, while maintaining the quality of the product (Suppakul *et al.*, 2003). Until today, a variety of active packaging technologies have been developed to provide better quality, wholesome and safe foods. Package-related environmental pollution and disposal problems researches are also done to limit these problems (Rhim *et al.*, 2007).

Based on their origin and use, there has been a lead to the following definition. "Bio-based food packaging materials are materials derived from renewable sources. These materials can be used for food applications" (Suppakul *et al.*, 2003). The packaging materials that are recognized as biodegradable are all according to the standards outlined by the EU Standardization Committee. This standard also included to not to exclude materials which currently, of practical and economical reasons, are based on non-renewable resources, but at a later stage, through research and development, there may be a way to produce these materials based on renewable resources (Chandra *et al*., 1998).

Any packaging that has run out of its packaging capability, a method to dispose this material must be in done carefully as harsh actions to dispose these materials may bring negative environmental effect. The disposal method is always in consideration as this act has become one of the major reasons of pollution. Biodegradable materials are also the same. A consideration of the “cradle to grave” cycle of the packaging material is a critical issue. Hence, the process of disposal of the package at the end of its useful life must also be taken into consideration (Coombs, *et al*., 2000). Though biodegradable material may be environmental friendly, the disposing method must be done with the right method.

1.2 Problem Statement

Today, the main problem of the usage of biodegradable film as food packaging is the materials used to form the biodegradable film. It is true that biodegradable films are formed from bio-based materials. A wide variation of combination of materials to form these biodegradable films has been found. Biopolymers are one of the best materials used for these bio-based materials. Biopolymer-based packaging materials originated from naturally renewable resources such as polysaccharides, proteins, and lipids have become the best candidates to form this biodegradable film in recent years since such biopolymers have their environmental advantages of recyclability and reutilization compared to other conventional petroleum-based synthetic polymer (Lee *et al*., 2007). Biopolymer films can also become barriers of gas and solute barriers and complement other types of packaging by reducing food quality deterioration and extending the life of foods (Debeaufort *et al*., 1998).

However, there are other weakness of this natural biopolymer films as they posses poor mechanical and water vapor barrier properties. Biopolymer films made from proteins and polysaccharides show an excellent oxygen barrier property at low to intermediate relative humidity as well as fairly good mechanical properties. But its most critical disadvantage is its barrier against water vapor due to its hydrophilic nature (Lee *et al*., 2007). Researches have been done focusing on improving its properties especially their mechanical and water vapor barrier through film modification (Rhim and Weller, 2000). Significant improvement can be seen throughout these researches but it is not enough and there are other difficulties in many applications (Rhim *et al.*, 2007).

The usage of chitosan as one of the material for biodegradable film was done thoroughly as we speak. Researchers have studied the antimicrobial action of this polymer on fungal strains (Sebti *et al*., 2005) or on bacterial strains (Coma *et al*., 2002). The only flaw of this material is that its hygroscopic properties of the bio-packaging containing polysaccharides are responsible for their weak moisture barrier and thus have little or no influence on the dehydration or rehydration phenomena of the foodstuffs (Sebastien *et al*., 2006). This property is crucial for maintaining organoleptic and microbiological food qualities. Additives are used to overcome the high sensitivity to moisture of chitosan such as associate it with polysaccharide with a more moisture-resistant polymer, while maintaining the overall biodegradability of the product.

The excessive amount of biomass waste produced by Malaysian country is surprisingly high. Conversion of non-edible biomass such as agriculture residues, wood chips, and fruit bunches, stalks, industrial and municipal wastes into fuels and useful chemicals would solve waste disposal and energy issues (Baratieri *et al*., 2008). Empty fruit bunch is a type of palm oil waste. It is the part where it is used to contain the fruit but since the fruit is removed, it is considered waste. There are some regards which do claim that the empty fruit bunch fibers are physically great for biodegradable film additives. Today, empty fruit bunch is used as fertilizers and some are widely used as solid fuel.

Throughout the years, many researches have been done to improve the performance of biodegradable film in the food packaging area. From all the points above, an attempt is done to investigate the effect of different chitosan concentration in a composite biodegradable film.

1.3 Objective

a. To fabricate composite biodegradable film from empty fruit bunch.
b. To characterize composite biodegradable film in terms of morphology and physical and chemical changes.

1.4 Scope of Study

a. Fabrication of composite biodegradable film from empty fruit bunch with chitosan and PEG 400 as additives.
b. The characterization of the composite biodegradable film using various analysis method:-
    i. Atomic Force Microscope (AFM)
    ii. Fourier Transform Infrared (FTIR) Spectroscopy
    iii. Differential Scanning Calorimetry (DSC)
    iv. Thermogravimetric Analysis (TGA)

CHAPTER 2

LITERATURE REVIEW

2.1 Food Packaging

Food packaging is packaging for food. It requires protection, tampering resistance, and special physical, chemical, or biological needs. It also shows the product that is labeled to show any nutrition information on the food being consumed. Food packaging's functions are as diverse as they are important. They are broken down into several parts. The first is containment. Foods that are granulated, paper-based packages are the best with a sealing system to prevent moisture infiltration of the product (Lai and Padua., 1998). Other products are packaged using metal cans, plastic bags and bottles, and glass. Another factor in containment is packaging durability, meaning the packaged food has to survive transport from the packaging at the food processing facility to the supermarket to the home for the consumer. Next is protection. The packaging must protect the food from biological agents in rats, insects, and microbes, from mechanical damage such as product abrasion, compressive forces, and vibration, and from chemical degradation such as oxidation, moisture transfer, and ultraviolet light (Jagannath *et al*., 2003).

Another function of food packaging is to provide information. Packaged food must be identified for consumer use mainly with label text and graphics. It can also be shown with the food package's shape such as the Coca-Cola bottle or the can of Nescafe. Other well known food package shapes include the potato chip bags and milk bottles (Selke, 2004). These packages also detail nutritional information, if they are kosher or halal-manufacturers and consumers. These products can be purchased all at once such as frozen pizza or as part of a larger package such as a twelve pack of beer. Another use may be to see if the package can go through a microwave process such as a TV dinner. Other items included pour spouts already on the bottles are other methods to ease dispensing of the product.

Another issue about food packaging is the environmental issues. As mention in the Introduction, the issue of food packaging usage is usually come to the decomposition of the package. This means that we must be done to reuse the packaging, reducing the size of the packaging, and then recycling of the products to be remanufactured. Then it will come to the last function of food packaging, product safety. That the package be used for safety of the food from the package or vice versa (Soroka, 2002). This includes any metal contamination issues from a can to the food product.

2.1.1 Composite Biodegradable Film

Composites are engineered materials made from two or more constituents with significantly different physical or chemical properties from their components, which remain separate and distinct within the finished structure. There are two types of constituent materials, which are known as matrix and reinforcement components. The matrix in the material surrounds and supports the reinforcement component by maintaining their relative positions (Rowell *et al.*, 2007). A synergism results in material properties, which are unique prior to used constituents. Names and descriptors arise from the respective experiences of different perspectives and experience. While different industries use different terms to describe the same things, the same term can be applied in vastly different contexts. As for an example, in the case of polysaccharide constituents the final product properties requirements for composites could be fitted without keeping the separate classification for matrix and reinforcement components (Xu *et al.*, 2005). Most of the literature published on composites deals with synthetic polymers. The sources are plant cell walls or some types of living organisms if it is not in conflict with ethical principles. Polysaccharides are environmentally friendly and could be degraded by microorganisms without further assistance. It is believed that their use could be profitable especially when they are by-products of other processes. As there are other natural polymers or related carbohydrate groups like proteins, lignin or cyclodextrins, which are used as constituents of polysaccharide-containing composites, their environmental impact is also covered (Lai and Padua., 1998). Except for plastics related to petrochemical polymers, there are also biodegradable plastics like polylactic acid, but even those could be replaced by polysaccharides due to lower costs and better properties of final composite. Mixing of polysaccharide based materials with plastics means mixing hydrophilic and hydrophobic materials, which requires energy. The goal to replace only a part of the higher-cost plastics with lower-cost polysaccharides is not the best strategy (Rowell *et al.,* 2007).

2.2 Other Methods of Preparing Biodegradable Film

Biodegradable film is in a wide scope. There are various methods to prepare biodegradable films. These methods depend on the materials used as the base component to form the film. Different material brings different method and offers different advantages.

2.2.1 Biodegradable Film Formed from Rice Starch and Chitosan Blend

The unique properties of rice starches are found in its many varieties. Due to different climates, soil characteristics and cultures, over 240,000 registered varieties of rice exist in the world. These varieties lead to a wide range of rice starches with many different characteristics including different starting gelatinization temperatures, textures, processing stabilities and viscosities. Rice starch and its major components, amylose and amylopectin, are biopolymers, which are attractive raw materials for use as barriers in packaging materials. They have been used to produce biodegradable films to partially or entirely replace plastic polymers because of its low cost and renewability, as well as possessing good mechanical properties (Xu *et al.*, 2005).

However, wide application of starch film is limited by its mechanical properties and efficient barrier against low polarity compounds (Azeredo *et al.*, 2000 and Kester and Fennema, 1986). This constraint has led to the development of the improved properties of rice-based films by modifying its starch properties and/or incorporating other materials (Jagannath *et al.*, 2003) blended starch with different proteins to decrease the water vapor permeability of the films and to increase their tensile strength. However, these films still did not perform well compared to synthetic polymer based films.

Chitosan provides unique functional, nutritional, and biomedical properties, and its present and potential uses range from dietary fiber to a functional ingredient and processing aid. Some of the well known applications of chitosan include its use for prevention of water pollution, medicine against hypertension, antimicrobial and hypocholesterolemic activity, flavor encapsulation, seed coating, film-forming, and controlled release of food ingredients and drugs (Struszczyk and Pospieszny, 1997). Relatively low cost, widespread availability from a stable renewable source, that is, shellfish waste of the sea food industry, along with chitosan's ability to form a good film, are primary reasons to seek new applications of this polymer (Bangyekan *et al.*, 2005). Numerous investigations have been reported on the studies of films made from chitosan (Park *et al.*, 2002, and Wiles *et al.*, 2000]) and chitosan blends with natural polymers (Lazaridou and Biliaderis, 2002 and Xu *et al.*, 2005) or synthetic polymers.

2.2.2 Biodegradable Biocomposite Film Formed from Whey Protein and Zein

For this method, materials that can be used for film making include polysaccharides, proteins, lipids and polyesters or combinations of them. Note that these materials are all biopolymer. The barrier properties of the biopolymeric films are important parameters when considering a suitable barrier in foods and food packaging. Protein and polysaccharide films are generally good barriers against oxygen at low and intermediate relative humidity (RH) and, while having relatively good mechanical properties, most of them have poor moisture barrier properties (Lai and Padua., 1998).

The water vapor permeability (WVP) values of protein films are normally 2–4 orders of magnitude higher than that of low density polyethylene (LDPE). This is due to the presence of free hydroxyl groups in the matrix, which interact strongly with migrating water molecules. Moisture considerably affects the WVP and oxygen permeability of protein films. This is attributed to the plasticization effect of water on protein films. Water can increase the free volume and mobility of the polymer chains. Poor moisture barrier properties can be improved by the addition of hydrophobic materials, by laminating a hydrophilic film with another layer or by forming a composite film in which both hydrophilic and hydrophobic components are dispersed in a cosolvent and then dried (Cheng *et al*., 2008).

Zein, the prolamine fraction of corn protein, is produced commercially from corn gluten meal (CGM). CGM is a coproduct material that is obtained during starch production. It is low priced and is used mainly as animal feed (Ghanbarzadeh *et al*., 2006). Zein forms films with high tensile strength and low water vapor permeabilities compared to other protein-based films. It also has a desirable heat seal property. Furthermore, corn zein can be used as a binder to fatty acids as both are alcohol soluble. Zein is insoluble in water. The insolubility of zein in water is due to the low content of polar amino acids and a high content of nonpolar amino acids (Yong *et al*., 2002).

Biodegradability and good gas barrier properties are the main features of the protein-based films. However, the mechanical properties of biopolymers are equally important to maintain the structural integrity of a product as well as provide physical protection and controlled rates of release of additives in the food. Plasticizers, such as polyols and fatty acids, are often added to modify the mechanical properties of biopolymeric films and these may cause significant changes in the barrier properties of the material (Ghanbarzadeh *et al*., 2007).

2.2.3 Biodegradable Film Formed from blends of gelatin and poly(vinyl alcohol)

Films based on biopolymers are generally sensitive to the relative humidity of the air since they are normally hygroscopic and have limited mechanical resistance compared with synthetic films. Nevertheless protein-based films display high deformability. A possible solution to improve the mechanical characteristics of protein-based films could be the mixing of these biopolymers with synthetic polymers (Tharanathan, 2003), such as poly(vinyl alcohol) (PVA), which is also hydrophilic and biodegradable. Some studies on the development and characterization of films based on PVA and protein blends have been published, such as PVA/wheat (Dicharry *et al*., 2006), PVA/collagen hydrolysate (Alexy *et al*., 2003), and PVA/gelatin (Bergo *et al*., 2006) have demonstrated the presumed biodegradability of these blended films.

Gelatin is inexpensive, widely produced in the world, and possesses excellent film-forming properties, and has therefore been widely used as a single biopolymer in studies on edible and/or biodegradable films (Bergo and Sobral, 2007), or blended with other biopolymers (Cao *et al*., 2007). These studies generally involved the development and the physical characterization of the materials. Knowledge of the physical properties of films is of great importance for their subsequent applications. However, it is known that the physical properties are strongly affected by the state of the material: for example, in the glass state the material will be hard and rigid, but in the rubbery state it will be flexible and extendible. Consequently, it is also important to determine the glass transition temperature of the films, a property defining the limit between the rubbery and glassy states.

Normally, the studies on biodegradable biopolymer-based films are carried out to understand the effect of the plasticizer concentration and/or moisture content on the glass transition of the corresponding films. Increases in the moisture content of films provoke a depression in the glass transition temperature of the films. This phenomenon has been observed in films based on different biopolymers, such as pullulan and sodium caseinate (Kristo and Biliaderis, 2006), pullulan (Diab, *et al*., 2001), chitosan–starch and chitosan–pullulan (Lazaridou and Biliaderis, 2002), pullulan–starch (Biliaderis *et al.*, 1999), hydroxy-propyl-starch and gelatin (Arvanitoyannis *et al*., 1998a), chitosan and gelatin (Arvanitoyannis *et al*., 1998b), gelatin (Sobral *et al*., 2001), gluten (Pouplin *et al*., 1999) and myofibrillar proteins (Sobral *et al.*, 2002) amongst others.

Independent of the moisture content, the production of films based on biopolymers normally demands the use of plasticizer agents to improve film workability. Plasticizers, which are low molecular components, increase the free volume of the material or the macromolecular mobility of the polymer, and consequently the polymeric network becomes less dense due to the decrease in intermolecular forces, thus improving the extensibility and flexibility of the films (Sothornvit & Krochta, 2000). In addition, plasticizer agents strongly affect the glass transition temperature of biopolymer-based films (Lazaridou and Biliaderis, 2002; Sobral *et al*., 2001; Vanin *et al*., 2005 and Zhang and Han, 2006).