BIODEGRADABLE FILMS FROM POLY (LACTIC ACID) (PLA)-CHITOSAN-POLYETHYLENE GLYCOL (PEG): FABRICATION AND EVALUATION OF MECHANICAL PROPERTIES

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ABSTRACT

In this research, the production of biodegradable plastic food packaging from biopolymers poly (lactic acid) (PLA), chitosan and polyethylene glycol (PEG) was investigated. In addition, the objective for this research also wants to study the mechanical properties of biofilms at different percentage of weight of polylactic acid, chitosan, and polyethylene glycol (PEG). The biodegradable plastic food packaging was prepared by blending the films based on these four main chemicals (PLA, chitosan, PEG) and 30 ml of silver nanopaticles for every blend of biofilms. Then tested the films with universal testing machine according to American Standard Test Method (ASTM D882) to investigate the mechanical properties (tensile and elongation) with 1 mm thickness film. Then, the mechanical properties of biodegradable food packaging films optimized by changing the parameters of percentage polyethylene glycol (PEG) and ratio of chitosan to PLA using Response Surface Method (RSM) in order to obtain the good biodegradable food packaging films. Degradation rate test has been determined by using the soil burial degradation rate method by burial the blend films for 14 days. The results show that, at the optimum condition, the tensile strength reached the maximum value of 10.573 MPa when the PEG is 17.6 % and PLA is 71.21%. For the elongation at break point, the optimum condition for the elongation at the break point reached the maximum value of 68% when the PEG is 22.07% and PLA is 50%. For the biodegradation rate indicate that the highest value of the chitosan will have the highest degradation rate among the prepared biofilms. As a conclusion the blend films produces will have a good mechanical properties that and can degraded easily.

BIODERADASI FILEM DARIPADA POLILAKTIK ASID (PLA) KITOSAN-POLYETHYLENE GLYCOL: FABRIKASI DAN PENILAIAN CIRI MEKANIKAL

ABSTRAK

Dalam kajian ini, penghasilan biodegradasi plastik bungkusan makanan telah dihasilkan daripada biopolimer polilaktik asid (PLA), kitosan dan polietilena glikol (PEG) .Di samping itu, objektif kajian ini juga adalah untuk mengkaji sifat-sifat mekanikal biofilm pada komposisi yang berbeza sama ada melalui perbezaan komposisi terhadap Poli laktik asid/kitosan, dan polietilena glikol (PEG). Bungkusan plastik makananan yang mesra alam ini telah dihasilkan dengan mencampurkan empat bahan kimia utama iaitu (PLA, kitosan, PEG) dan 30 ml nanopaticle perak untuk setiap campuran biofilm. Kemudian file mini diuji dengan mesin ujian sejagat menurut Kaedah Ujian American Standard (ASTM D882) untuk menyiasat sifat-sifat mekanikal (tegangan dan pemanjangan) dengan 1 mm ketebalan filem. Kemudian, sifat-sifat mekanikal filem pembungkusan makanan terbiodegradasi dioptimumkan dengan menukar parameter peratusan polietilena glikol (PEG) dan nisbah Chitosan untuk PLA menggunakan Response Kaedah Permukaan (RSM) dalam usaha untuk mendapatkan pembungkusan yang baik dalam menghasilkan filem makanan terbiodegradasi. Degradasi ujian kadar telah ditentukan dengan menggunakan teknik kambusan tanah dan menunjukkan kadar degradasi oleh kambusan tanah telah dikaji selama 14 hari. Keputusan menunjukkan bahawa, pada kondisi optimum, kekuatan tegangan mencapai nilai maksimum 10,573 MPa apabila PEG adalah 17.6% dan PLA adalah 71,21%. Untuk pemanjangan pada titik filem itu terputus,, keadaan optimum untuk pemanjangan filem itu putus mencapai nilai maksimum sebanyak 68% apabila PEG adalah 22,07% dan PLA adalah 50%. Bagi kadar biodegradasi menunjukkan bahawa nilai tertinggi kitosan akan mempunyai kadar degradasi tertinggi daripada biofilm yang telah dihasilkan. Sebagai kesimpulan filem campuran menghasilkan akan mempunyai sifat mekanikal yang baik dan boleh dengan mudah terurai.

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LIST OF SYMBOLS

°C	Degree Celsius
g	grams
h	hour
L	Liter
mL	milliliter
mm	millimeter
min	minutes
% w/w	ratio of weight percentage

LIST OF ABBREVIATIONS

CH_3COOH	Acetic Acid
DD	Degree Deacetylation
PCL	Poly (e-caprolactone)
PEK	Polyethylketone
PGA	Poly (glycolic acid)
PLA	Poly (lactic acid)
PHB	Poly (3-hydroxybutyrate)
PHBV	Polyhydroxyvalerate
PVC	Polyvinyl chloride

CHAPTER 1

INTRODUCTION

1.1 Background of propose study

Development of plastic food packaging that made from fossil fuels can cause harmful to the human bodies and environmental because it have the carcinogen characteristic and take time to degradable maybe hundred year. According to Doi Fukuda (1994), the word “biodegradable” means the materials which can be degrade by the enzymatic action of living organism such as bacteria, fungi, yeast, and the ultimate end-product of the degradation process. Biomass also act as supported degraded agent and can be divided into two that’s biomass under aerobic condition and hydrocarbon, methane and biomass under anaerobic conditions.

The most dangerous thing in plastic food packaging to human bodies when it can caused carcinogen because the material made from the Polyvinyl chloride (PVC). Producing the polyvinyl chloride (PVC) making the vinyl chloride released in to the air and wastewater. Vinyl chloride is known as the human carcinogen chemical and has been linked to increased mortality from liver and breast cancer among workers that involved in its manufacturing. In addition, it can cause the migration between plastic food packaging and food content. Besides that, there are another chemical that has been reported for having a migration when expose to food for example di(2-ethylhexyl) adipate(DEHA). The specific migration limit (SML) set for di(2-ethylhexyl) adipate (DEHA) by the EU is 18 mg/kg food and according to EC (2002), migration values for packaging films must be expressed in term of surface area (mg/dm^2). Because of the adverse impact on the use of plastic food packaging, recent research and development efforts succeeded in producing of biodegradable polymers which can be found from renewable resources.

The plastic that have both characteristics and the biofilms that have less impact on the environment, human bodies is needed. Biopolymers can be defined from the input point of view as polymers that mean biopolymer is polymers produced by living organism. Biopolymers are polymers that have the monomers, which are totally or mainly contained in the biomass, or which can be made from biomass using bio-technological processes. Biodegradable polyester can be divided into four different group based on their chemical structure. Polylactic acid and polygycolic acid are the example of biodegradable polyester generally used to make scaffolds.

In addition due to the biodegradable plastic food packaging, PLA and chitosan are used because the chitosan itself have a good antimicrobial activity, and according by S.Hirano (1996). Chitosan is a monocompenant of microbial agent that has advantages of biodegradability and excellent film forming ability. To make chitosan better as an antimicrobial agent some modification must be made into chitosan with the addition of organic metal such as argentum (Ag), and zinc oxide (ZnO). Therefore it will give the good characteristic on the tensile properties, the moisture of the biofilms and the antimicrobial properties.

1.2 Problem statement

The producing of plastic food packaging by synthetic polymers are not easily degrade and it's produce harmful gases that can cause harmful to human bodies because of the carcinogen characteristic and harmful to environmental pollutants because the degrade of synthetic polymers take hundred years to degrade. To overcome this problem biopolymer has been introduced from polylactic acid combine with polyethylene glycol (PEG) and chitosan in order to improve the strength towards any barrier and have well degradable after disposal.

1.3 Objectives

1. To produce the biodegradable plastic food packaging from PLA, Chitosan and polyethylene glycol (PEG).
2. To investigate the effect of tensile strength and elongation at break point by considering the different percentage of PEG and PLA/chitosan in blending the biodegradable food packaging biofilms.
3. To evaluate the tensile strength properties of the synthesized plastic.

1.4 Research questions

1. What is the advantage of biodegradable plastic food packaging from PLA, chitosan and Ag-nanoparticles?
2. What methods are used to producing the biofilms?
3. What are the parameter needed to be considered in optimize the performance of biofilms?

1.5 Scope of studies

To achieve the objective of the research scope has been identified:

1. Preparing the biofilms from different concentration of PLA/Chitosan(range in 20 to 80 %) and polyethylene glycol (PEG)(ranged in between 5 to 25 % of PEG) by using the fabrication method.

2. Testing the tensile strength properties of the produced biofilms plastic by using the ASTM D882 method.

1.6 Significance of the study

The significant of this study is to produce biodegradable plastic food packaging from PLA and also modified those biopolymers with chitosan and polyethylene glycol to make it resistance to any moisture and also increase the mechanical properties of the biodegradable plastic

CHAPTER 2

LITERATURE RIVIEW

2.1 Conventional Plastic

The demanding for plastics is increasing due to the wide application for human being. Production of plastic from petroleum base increasing with an annual world production of approximately 140 million ton (Masayuki 2001). In other hand, the production of plastic from natural or synthetic materials also can be produced for example the polyvinylchloride (PVC), polylactic acid (PLA) and polyhydroxybutyrate (PHB). There is the conventional plastic made from petroleum that can be degraded by environment and a few of companies trying harder to produces the plastic from the petroleum-based product. The fragments plastic leaves small pieces take hundred years to degrade or can take many decades to fully disappear.

The plastic can be divided into many categories such as polyethylene terephthalate (PET), poly vinyl chloride (PVC),polyester (PET) and others and every category have different risk. The usage of the high-density polyethylene to produce a grocery bag also known as HDPE. PET is used widely to produce plastic because of the manipulation on its size, colour and shape. The usage of plastic can give the impact to environment including air, land and water pollution. The disposal of plastic material also can affect the human and animal health. According to the Badami (2005), at least 1000 death of Mumbai people and additional people suffering injuries when the huge monsoon flooding occurs in the city of Mumbai been blamed by the destructive floods on plastic bags which clogged gutters and drains that prevent the rainwater from leaving the city through underground system. When the drains are blocked by the plastic material cause the water in stagnant position and the water cannot flow freely and the stagnant water will produces the ideals habitat for mosquitoes and other parasites.

In other hand, the disposal of plastics to the ocean will make the animal extinct from the earth for example over a billions seabirds and mammals including turtles die annually from ingestion of plastic (Andrady 2011). It also reported that, the plastic groceries bag have the potential to resulting the health of human being in danger condition with the neurological problems and cancer because of the leaching of the chemical component into our water resources and soil. To overcome this problem many researcher come out with new invention about the biodegradable and antimicrobial of plastic.

2.2 Biodegradable Polymers

The synthetic polymers increasing the demanding due to the need plastics in daily life and the problem is how to dispose or to manage the disposal after it just used. These scenarios become a serious problem and due to this the few researchers try to find alternative about the way to remove, replace or to overcome this problem. When the recycling the synthetic polymers, the plastic food packaging cannot be recycle back into plastic food packaging again and another option left by produce the biodegradable plastic food packaging and sustainability. According to Brundtland commission defined the word sustainability as “social economic advance to assure human beings a healthy and productive life, but one that did not compromise the ability of future generations to meet their needs. Then, the society just starting to understand what the earth needs to avoid any pollution and the biopolymers been increase for the last two decades (Vilaplana, 2010).

Biodegradable polymer can be defined as the polymer that able to undergo hydrolysis at temperature 50^oC (Gupta and Kumar 2007). Besides the biodegradable characteristics the polymer also must be non-toxic. The biodegradable can be divided into two types which are natural polymer or based on renewable starch. These include polysaccharide (starch, cellulose, chitin, chitosan and etc.), proteins (gelatin, silk, and wood) and polyester produced from microorganisms, polyester derived from bioderived monomers including polylactic acid, polyhydroxyalkanoate and polyhdroxybutyrate. Petroleum can be used to produce the biodegradable polymer and a few companies try to make the biodegradable plastic from the petroleum since it consumed by microbes and biodegrade in compost environment. For the example the BASF™ just used the aliphatic-aromatic and ε-caprolactram to make the biodegradable plastic. Polyester is one of the biodegradable polymer and according by (Müller *et al,*. 2001) the structure of polyester can be undergo hydrolysis under certain condition and it can be divided into two major group of polyester, that's aliphatic polyester and aromatic polyester. However, the aliphatic polyester show excellent result in degradation process compare with aromatic polyester because of the stability of the aromatic ring. To break the chain of aromatic will need more energy and time because the ring is stronger and more stable compare to linear chain. By the way, both of them can show the fully biodegradable (Witt *et.al* 2001).

2.3 Chitosan

In order to produce the excellent biopolymers some chemical improvement must be considered by adding the chitosan into biofilms. According to (George *et al.*, 2011) chitin's is the one of polymeric materials that is easier to get and have a lower cost to purchase and it is one of the most abundance polysaccharides and can be found in various invertebrates and lower plants. Chitins also are one of the most abundance polysaccharide that is syntheses in lower animal such as crab shell or shrimp after cellulose. According by (Muzzarelli, 1997), the structural of chitin is quite similar to cellulose but having a different in acetamide group at the C-2 positions in place of hydroxyl group in amino polysaccharide. The different are shown in Figure 2.1.

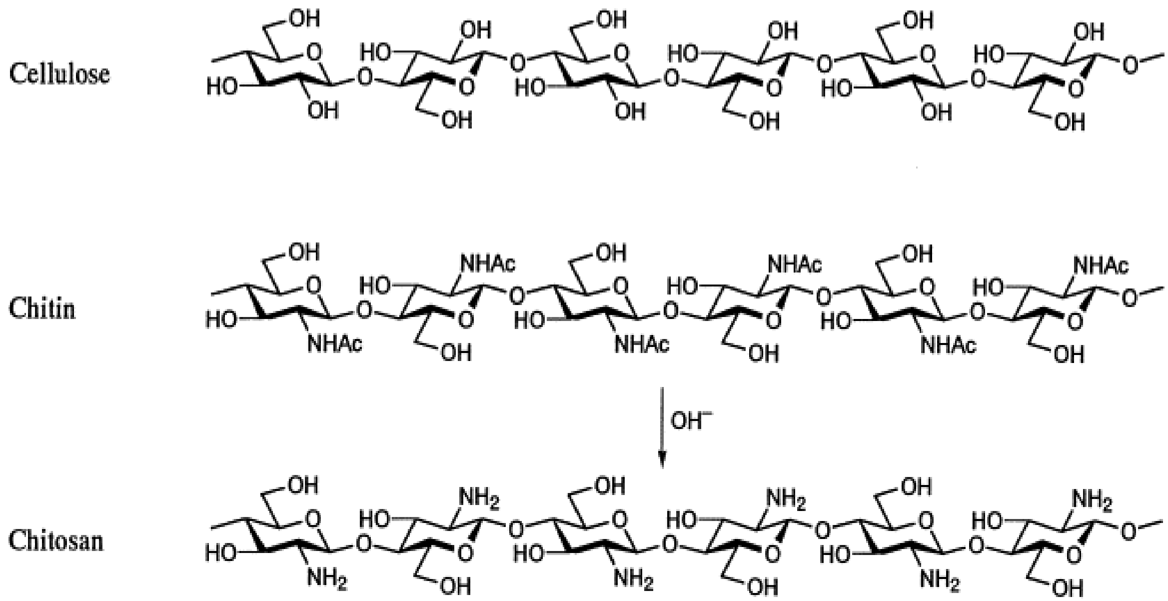

Figure 2.1 The structural formula for cellulose, chitin, and chitosan

For this study, chitosan will be choosen as a polysaccharide to making the biofilms even though it is the second polysaccharide most abundance compare to cellulose because it have the excellent biodegradable, bioactivity and biocompatibility. Chitosan can be prepared by deacetyling α-chitin and the study by Horton (1956) chitosan is commonly prepared by deacetyling α-chitin by using 40-50% aqueous alkali at 100-160°C for a few hours and the process as shown in Figure 2.2.

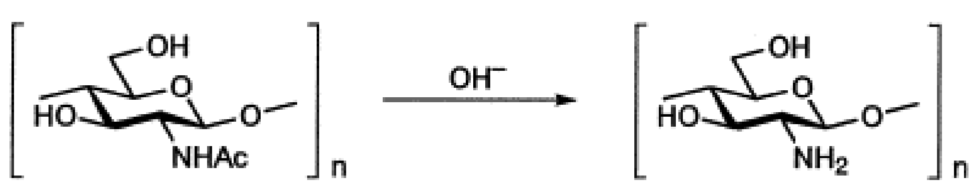

Figure 2.2 The mechanism of chitosan from α-chitin

Chitosan have similar chemical properties with chitin that a most stable substances against acid and alkali and this component also not soluble in ordinary solvent. When chitosan mixed with polylactic acid (PLA), the toxicity of the PLA will be reduced because chitosan can generate acidic degradation product as an implanted site reaction that raised the unwanted product for the tissue reactions.

According to Gandini (2008), chitosan is one of the most important polymer in biomedical application because of the characteristic like biodegradability, biocompatibility and low toxicity, and all the characteristic have led to the development of numerous application in biomedicine like surgical sutures, biodegradable sponge and bandages. According by (Amidi *et al*,. 2010), the important of chitosan in biomedicine including microcapsules and the delivery of drug (glaucoma treatment) and the best thing about chitosan in biomedical is due to excellent properties when interacting in human bodies. For the bandage that come from the chitosan have a ability to accelerate the wound healing effect and due to its biodegradability characteristic, it has been applied in tissue regeneration and tissue restoration. Chitosan also can be improved its properties by combine it with silver nanoparticle or any inorganic metal such as argentum(Ag), zinc oxide (ZnO), silicon dioxide (SiO_2), and titanium dioxide (TiO_2) for improving the degradation rate, mechanical strength and antimicrobial activities.

2.4 Polylactic Acid (PLA)

Biodegradable polymer such as poly (lactic acid) (PLA), poly (glycolic acid) (PGA) and poly (3-hydroxybutyrate) (PHB) are classified as a biodegradable polymer and among of these three, the PLA will give more attention due to its renewable resources, biocompatibility, biodegradation, excellent thermal and mechanical properties and superior transparency biopolymers. PLA can behave likes PET and also perfoms a lot like popypropylene (PP), a polyolefin. PLA also has good organoleptic characteristics and best for food contact and related food packaging application.

Nowadays, PLA can be a successful material in replacing petroleum based plastic in commodity application, with most initial uses limited to biomedical applications such as suture (Sinclair,1986). PLA have been produced by from renewable resources and it is a linear aliphatic thermoplastic polyester and due to the easily to degraded through enzymatic pathways and hydrolytic. It also can be synthesized by using the condensation polymerization of the monomer lactic acid. To obtain the monomer lactic acid through the fermentation process of lower cost material starch including corn, potato, sugar beat and sugar cane. PLA can be produced for a large scale production through injection molding, blow molding and extrusion. To avoid the PLA from undergo degradation, the polymer must undergoes thermal degradation at temperature above 200^oC (Jhamshidi *et al.,* 1988). Catalyst also helping in the degradation processes by decreases the degradation temperature and increase the degradation rate of PLA.

Lactic acid (2-hydroxy proponoid acid) is the simplest hydroxyl acid with an asymmetric carbon atom and exist in two optical configurations. Human bodies and wild mammals will produces the L (+)-isomer, meanwhile the bacterial system will produce the L (+)-enantiomers and D(-). The organisms that predominantly yield the positive –isomers are Lactobacili amylophilis and L. salivarius and both bacteria are used to fermentation to produce the lactic acid. The physical properties of PLA by addition of clay have been extensively report by (Ahmed *et al.,* 2010). The fabrication of PLA with clay nanocomposites were mixed with the PLA matrix and originally-modified clay using melt blending the result indicates the fabricated nanocomposites with the various surface modification of clay in improving the mechanical testing and the degradation rate.

CHAPTER 3

METHODOLOGY

3.1 Materials

Chitosan flakes from crab shells were purchased from Fisher Scientific, Polyethylene glycol (PEG) 400 and Polylactic acid (PLA) (pellet form) were supplied form by Sigma Aldrich. The acetic acid was obtained from Sigma Aldrich and chloroform was provided by Maersk Supplier Company. The preparation of silver nanoparticles from tea extract solution was used by using the tea BOH and mix with the silver nitrate.