PREPARATION AND CHARACTERIZATION OF POLY(VINYL ALCOHOL) / STARCH COMPOSITE FILMS REINFORCED WITH GRAPHENE AND GRAPHENE OXIDE

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To my beloved father, mother, sisters and brothers,

Thank you for everything

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ABSTRACT

The main objective of this research is to characterize the graphene oxide (GO) prepared by using modified Hummer's method with some modifications which was then used in the poly(vinyl alcohol) (PVA)/starch blends biocomposite film. Results from Fourier transform infrared, scanning electron microscopy-electron dispersive x-ray and x-ray diffraction analyses showed the presence of oxygen functional groups which confirmed the transformation of graphene (G) to GO. PVA/starch film was prepared via casting method at room temperature. The G and GO were added into PVA/starch film with different loadings from 0.5 to 4.0 wt% to determine the best optimum loading that would give the best result of mechanical, thermal and morphological properties. From the scanning electron microscopy, PVA/starch/GO film showed a smoother surface due to the GO filler being more uniformly dispersed in the matrix of PVA/starch film compared to G. The thermal properties, tensile strength, elongation at break and Young's modulus of PVA/starch/G and PVA/starch/GO films showed improvement with increasing filler loading until 2.0 wt%. However, PVA/starch/GO showed better improvements compared to PVA/starch/G. Water barrier properties analysis showed that PVA/starch/GO film had better water resistance than to PVA/starch/G film. From the soil burial test, the biodegradability of films showed that G and GO filler do not gave any significant influence on the biodegradability of film. The addition of 2.0 wt% of filler loading was found to be the best loading to improve the properties of the films, with PVA/starch/GO showed better properties compared to PVA/starch/G film.

ABSTRAK

Objektif utama penyelidikan ini adalah untuk mencirikan grafen oksida (GO) yang dihasilkan melalui kaedah Hummer dengan sedikit pengubahsuaian yang kemudiannya digunakan untuk menghasilkan filem biokomposit adunan poli(vinil alkohol) (PVA)/kanji. Hasil daripada analisa infra-merah transformasi Fourier, mikroskopi elektron pengimbas-sinar-x penyerakan elektron dan pembelauan sinar-x menunjukkan kehadiran kumpulan berfungsi oksigen yang mengesahkan perubahan grafen (G) kepada GO. Filem PVA/kanji telah disediakan melalui kaedah penuangan pada suhu bilik. Pengisi G dan GO telah di tambah ke dalam filem PVA/kanji dengan muatan berbeza daripada 0.5 hingga 4.0 wt% untuk menentukan muatan optimum terbaik bagi menghasilkan sifat-sifat mekanikal, terma, dan morfologi yang terbaik. Berdasarkan mikroskopi elektron pengimbas, filem PVA/kanji/GO mempunyai permukaan yang lebih sekata kerana pengisi GO terserak lebih sekata di dalam matriks filem PVA/kanji berbanding G. Sifat-sifat terma, kekuatan tegangan, pemanjangan pada takat putus dan modulus Young bagi filem PVA/kanji/G dan PVA/kanji/GO menunjukkan peningkatan dengan penambahan muatan pengisi sehingga 2.0 wt%. Walau bagaimanapun, filem PVA/kanji/GO menunjukkan peningkatan yang lebih baik berbanding PVA/kanji/G. Analisa sifat-sifat halangan air menunjukkan filem PVA/kanji/GO mempunyai kadar rintangan air yang lebih baik berbanding PVA/kanji/G. Daripada ujian timbusan tanah, biodegradasi filem menunjukkan pengisi G dan GO tidak memberikan pengaruh utama terhadap biodegradasi filem. Penambahan pengisi pada muatan 2.0 wt% didapati adalah yang terbaik bagi meningkatkan sifat-sifat filem, dengan PVA/kanji/GO menunjukkan sifat-sifat yang lebih baik berbanding filem PVA/kanji/G.

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LIST OF ABBREVIATIONS

ASTM	-	American society of testing and materials
DSC	-	Differential scanning Calorimetry
DTG	-	Derivative Thermogravimetric
FESEM	-	field emission scanning electron microscopy
FTIR	-	Fourier transform infrared
G	-	Graphene
GO	-	Graphene Oxide
PVA	-	Poly(vinyl alcohol)
PVac	-	Poly(vinyl acetate)
rGO	-	Reduced graphene oxide
SEM	-	Scanning electron microscopy
TGA	-	Thermo gravimetric analysis
WVTR	-	Water vapour transmission rate
XRD	-	X-ray diffraction

LIST OF SYMBOLS

%	-	Percentage
$^{\text{o}}$C	-	Degree celcius
ΔH	-	Heat of Fusion
μm	-	Micro meter
gmol^{-1}	-	Gram per mole
g/cm^3	-	Gram per centimetre^3
m^2/g	-	Meter^2 per gram
mL	-	Mili Liter
mm	-	Mili meter
MPa	-	Mega Pascal
Nm	-	Nano meter
T	-	Time
Tg	-	Glass transition temperature
Tmax	-	Temperature at maximum peak
wt%	-	Weight percentage

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, the plastic packaging especially food packaging that is produced is not biodegradable which leads to the environmental problems since it takes thousands of years to be degraded. Biodegradable means the materials can be fully consumed by microorganisms without leaving any harmful pollutants in the environment. To overcome the problems, new bio-based polymeric materials have been exploited to develop the biodegradable plastic packaging films. The use of biodegradable plastics has attracted extensive interest among the researchers to study about the biodegradable material used.

A degradable, non-toxic and environmental material for example, synthetic polymer like PVA and renewable natural polymer resources for example starch, cellulose and chitosan is in interest to the researcher (Chen *et al.,* 2008; Das *et al.,* 2010; Hu, Wang, and Tang, 2013). A great effort has been made to develop biodegradable plastic films by reducing the amount of synthetic polymer materials that can cause environmental problems.

For this research study, a degradable synthetic polymer (PVA) was produced from nonrenewable petroleum resources while starch, one of a renewable natural polymer available in large quantities from renewable resources will be used. PVA is one of the largest water-soluble polymers, non-toxic and environmentally friendly material. PVA is not prepared by the polymerization process of its monomer, vinyl

alcohol since it tends to convert spontaneously into the enol form of acetaldehyde as shown in Figure 1.1.
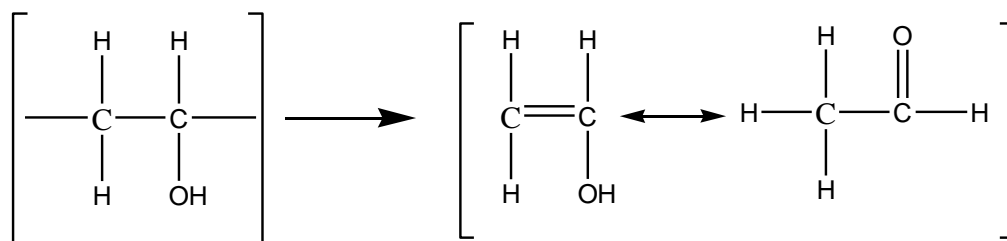
Figure 1.1 Keto-enol tautomerism of PVA

PVA has a polar hydroxyl group that is attached to carbon that makes it highly hydrophilic. Due to the solubility of PVA, it is widely used in the plastic packaging industry. However, PVA is relatively expensive compared to other types of polymers like polyethylene (PE), polypropylene (PP) and poly(vinyl chloride) (PVC). PVA also has a low degradation rate (Chiellini *et al.,* 2003; Chao *et al.,* 2012) . In order to reduce the cost of the matrix, it is necessary for PVA to be blended with a natural and low cost polymer.

The use of tapioca starch as a natural polymer is the most attractive since it is low cost, widespread availability and potential to produce a large scale of product (Smith *et al*., 2005; Chang *et al.,* 2010). Starch is one of the environmental friendly materials where it is completely biodegradable in soil and water. Tapioca starch is the combination of amylase and amylopectin. Starch is well known with high in crystallinity in the chemical structure. Therefore, plasticizer must be added into the blend of PVA and starch to increase the flexibility and work ability (Chao *et al*., 2012). Glycerol was chose as a plasticizer for PVA and starch due to the similarity in chemical structure, close value of polarity and solubility that help in efficiency interactions between PVA and starch.

However, the introduction of starch into the PVA matrix will lower the tensile strength of the film. The result shows that as the amount of starch increased, the tensile strength of the film decreased accordingly. The pure PVA film showed the highest tensile strength with 35.35 MPa compared to the PVA that was introduced

with corn starch with ratio 70/30 PVA/Starch gave the result 9.58 MPa (Azahari *et al*., 2011). The water barrier properties of the PVA/Starch film also show a decrease as reported by the previous research (Guohua *et al*., 2006).

To improve the mechanical and barrier properties of PVA/Starch films, graphene and graphene oxide were added to be act as filler. Nowadays, graphene and graphene oxide have attracted the researchers on its ability to improve the properties of polymer (Zuo *et al.,* 2013). The graphene and graphene oxide are different in chemical structure where graphene does not have a polar hydroxyl group compared to graphene oxide. Therefore, graphene oxide was believes to make a strong interaction with PVA/Starch matrix. For this research study, the effect of graphene and graphene oxide loading into the mechanical, thermal, water barrier, biodegradable and morphological properties of the PVA/Starch film were determined.

Graphene oxide filler was produced from graphene by a modification of Hummer's method using oxidation process. Therefore, graphene oxide will have polar hydroxyl groups that can make strong interaction with PVA/Starch matrix thus make it easily to be dispersed. The strong interaction is from the H-bonding interactions between oxygen–containing groups of graphene oxide and PVA/Starch matrix (Matsuo *et al*., 2005).

Even though graphene and graphene oxide is not popular compared to other carbon nanotubes, some authors have been reported that the incorporation of graphene and graphene oxide with polymers will improve some properties like the thermal stability, electrical and mechanical properties of blends film (Li *et al*., 2011; Peregrino *et al.,* 2014). Thus, the PVA/Starch film reinforced with graphene and graphene oxide filler were prepared by a casting method. The PVA/Starch/Graphene (PVA/Starch/G) and PVA/Starch/Graphene oxide (PVA/Starch/GO) films produced were expected to have good mechanical, thermal, biodegradable and morphological properties compared to the PVA/Starch film.

1.2   Problem Statement

Recently, studies on the possibility of using organic or natural polymer as matrix film to replace synthetic polymer have received much attention.

In this research, PVA was blended with tapioca starch. PVA as a synthetic degradable polymer with excellent film forming properties, high tensile strength and flexibility was blended with tapioca starch in way to reduce cost of the matrix and generating a degradable film. The tapioca starch has been considered as a suitable material source in producing degradable plastic film because of its degradability, low cost, widespread availability and potential for mass production from renewable resources (Chen and Ramaswamy, 1999). However, starch exhibits the poor mechanical and water barrier properties due to the relatively hydrophilic nature of tapioca starch as have been reported by (Chao *et al*., 2012). They reported that, the tensile strength of PVA/Starch film decreased due to the polarity of chlorinated hydrocarbon of starch. Therefore, in this study the incorporation of fillers into PVA/Starch matrix was suggested in order to improve the properties of matrix.

According to the Chang *et al.,* (2013); and Peregrino *et al.,* (2014) the addition of reinforcing fillers to biopolymers matrix has proven to be effective in enhancing their mechanical and water barrier properties. Thus, in this study, graphene and graphene oxide fillers were chosen to act as fillers and incorporated with PVA/Starch film in order to enhance the mechanical, and water barrier properties of composite film. The small amount of graphene oxide was believed to give better results on the stated properties compared to graphene since graphene oxide is able to give strong interactions with the PVA/Starch matrix (Li *et al.,* 2011).

From the previous researches on nanocomposite made of starch and graphene oxide, the young modulus and the thermal stability of starch were increased (Sheshmani *et al.,* 2013; Peregrino *et al.,* 2014). Even though, graphene and graphene oxide are not popular as carbon nanotubes, the application of graphene and

graphene oxide in other polymer showed a significant increase of mechanical, thermal and electrical properties (Zhao *et al.*, 2010; Zhou *et al.*, 2011). Therefore, the main objective of this research project is to prepare and characterize the biodegradable and non-toxic PVA/Starch films reinforced with graphene and graphene oxide filler to produce PVA/Starch/G and PVA/Starch/GO films that gave the different improvements in the properties especially on mechanical and water barrier properties.

1.3 Objectives of study

This research was carried out with the following aims:

i. To prepare and characterize the graphene oxide from graphene by using a modified Hummer's method and the prepared in graphene oxide was characterized using Fourier transform infrared analysis (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy-electron dispersive X-ray (SEM-EDX).

ii. To determine the effect of graphene and graphene oxide loading on the mechanical, thermal, water barrier, biodegradable, and morphological properties on the PVA/Starch film.

1.4 Scope of study

The study is to understand more about the topic. There are steps that were taken wisely in order to achieve the objectives. Firstly, the ratio of the PVA/Starch matrix for both composite films PVA/Starch/G and PVA/Starch/GO must be constant. The ratio used is 2:1 which is 2 for PVA and 1 for starch.

Secondly, graphene oxide was prepared from graphene by using a modified Hummer's method. The graphene will be undergoing an oxidation process by mixing a graphene in strong oxidizing mixtures. A strong oxidizing agent; potassium

permanganate, $KMnO_4$ and a strong acid which is sulfuric acid, H_2SO_4 will be mixed together to form strong oxidizing mixtures. Once the process is completed, the product will be tested using FT-IR and EDX to confirm the formation of graphene oxide by determining the presence of oxygen-functional groups. The difference of the diffraction layer between graphene oxide and graphene will be tested by using XRD. The dispersion of graphene into water can be tested by observing the SEM images.

Lastly is to study the effect of graphene and graphene oxide into the PVA/Starch film. The blend film of starch and PVA was prepared by using the casting method. After that, graphene and graphene oxide were added with a variety of loading that is 0, 0.50, 1.0, 2.0, 3.0, and 4.0 wt% into PVA/Starch film. The films that have been reinforced with graphene and graphene oxide filler were tested for thermal, mechanical, biodegradability and morphological properties. Soil burial and water barrier were done for biodegradability testing. FT-IR, Tensile, TGA and DSC were used to determine the changes in mechanical and thermal properties of the PVA/Starch film. The differences in morphological properties according to the varied loading of graphene and graphene oxide in PVA/Starch film were tested by using the FESEM.

1.5   Significance of study

The significance of this study are:

i.   To produce biodegradable plastics from degradable polymer, PVA and starch which are friendly to our environment.

ii.   To study the differences in improvements of mechanical, thermal and morphological properties between G and GO fillers to the PVA/Starch matrix.

iii. Any interaction between G and GO fillers and PVA/Starch matrix either intramolecular or intermolecular could give a great effect on the properties of the films.

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