PREPARATION AND PROPERTIES OF POLYVINYL ALCOHOL/SOYA BEAN FLOUR BIODEGRADABLE FILM

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles “Preparation and Properties of Polyvinyl Alcohol/Soya Bean Flour Biodegradable Film”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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PREPARATION AND PROPERTIES OF POLYVINYL ALCOHOL/SOYA BEAN FLOUR BIODEGRADABLE FILM

ABSTRACT

In this research, a new polymer blend based on soya bean flour (SBF) and polyvinyl alcohol (PVA) was prepared using solution casting method. Initially, the SBF content was varied from 10 to 40 wt %. Tensile strength and elongation at break of the PVA/SBF blend films were lower, but the tensile modulus was higher than that of unfilled PVA film. This was mainly because of the presence of SBF in the blend. The PVA/SBF blend films showed higher water barrier properties with increasing SBF content. Biodegradability tests revealed that the presence of SBF stimulated the degradation rate and caused the weight loss of the PVA/SBF blend films. Secondly, the effectiveness of hexamethylenetetramine (HMTA) as crosslinker on PVA/SBF blend films was compared to the non crosslinked PVA/SBF blend films. The crosslinked PVA/SBF blend films showed better tensile and water barrier properties. This was attributed to the effectiveness of HMTA in the blend. Natural weathering test revealed that the presence of HMTA did not significantly affect the weatherability of the PVA/SBF blend films. But, in soil burial test the weight loss of non-crosslinked blend films was higher than crosslinked blend films. Thirdly, banana frond flour (BFF) and halloysite nanotubes (HNT) were added as filler to form ternary blend system. PVA/SBF/HNT blend films show better properties in tensile and water barrier because HNT have higher aspect ratio and provided more interaction sites. Degradability for both blend films were increased with increasing filler content after subjected to degradation test. Lastly, BFF was treated by alkaline treatment. Better tensile and water barrier properties were obtained by the treated PVA/SBF/BFF blend films. This result might due to the better compatibility and interaction of treated BFF and PVA/SBF matrix. Besides that, the higher water barrier properties of treated PVA/SBF/BFF blend films were contributed to reduction of the film degradation.

PENYEDIAAN DAN SIFAT ADUNAN FILEM BIOURAI BERASASKAN POLIVINIL ALKOHOL/TEPUNG KACANG SOYA

ABSTRAK

Dalam kajian ini, adunan polimer baru berasaskan tepung kacang soya (SBF) dan polivinil alkohol (PVA) telah disediakan dengan menggunakan kaedah penuangan larutan. Pertama sekali, PVA telah diadun dengan 10-40% berat SBF. Kekuatan tegangan dan pemanjangan pada takat putus filem adunan PVA/SBF adalah lebih rendah, tetapi modulus tegangan adalah lebih tinggi, berbanding filem PVA sahaja. Ini adalah kerana kehadiran SBF dalam adunan filem tersebut. Filem adunan PVA/SBF juga menunjukkan sifat halangan air yang lebih tinggi dengan peningkatan kandungan SBF. Ujian penguraian bio membuktikan bahawa kehadiran SBF mempengaruhi kadar penguraian filem tersebut dengan penurunan berat filem PVA/SBF selepas tempoh ujikaji penguraian dijalankan. Kedua, keberkesanan heksametilenatetramina (HMTA) sebagai ejen sambung silang pada filem adunan PVA/SBF telah dikaji dan dibandingkan dengan filem PVA/SBF tidak disambung silang. Filem PVA/SBF yang disambung silang mempamerkan sifat tegangan dan halangan air yang lebih baik. Ini disebabkan keberkesanan HMTA di dalam adunan. Ujian pencuacaan semula jadi menunjukkan bahawa kehadiran HMTA tidak memberi kesan ketara kepada ketahanan filem adunan PVA/SBF terhadap cuaca, tetapi ujian penanaman dalam tanah menunjukkan filem adunan yang tidak disambung silang mengalami penurunan berat sampel yang lebih tinggi berbanding filem disambung silang . Ketiga, tepung pelepah pisang (BFF) dan tiub nano halloysite (HNT) telah ditambah sebagai pengisi untuk membentuk sistem gabungan ternari. Filem adunan PVA/SBF/HNT menunjukkan sifat tegangan dan halangan air yang lebih baik kerana HNT mempunyai nisbah aspek yang lebih tinggi dan menyediakan lebih tapak interaksi. Peratusan berat kedua-dua filem adunan telah meningkat dengan peningkatan penambahan pengisi selepas dikenakan ujian penguraian. Akhir sekali, BFF telah diubahsuai menggunakan kaedah rawatan alkali. Sifat-sifat tegangan dan halangan air yang lebih baik telah diperolehi oleh filem adunan PVA/SBF/BFF terubahsuai. Kajian ini menunjukkan BFF yang diubahsuai mempunyai keserasian dan interaksi yang lebih baik antara BFF dan matrik PVA/SBF. Di samping itu, sifat halangan air yang lebih baik oleh filem adunan PVA/SBF/BFF terubahsuai telah menyumbang kepada pengurangan kadar penguraian filem tersebut.

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LIST OF ABBREVIATIONS

Abbreviation	**Description**
ASTM	American Society for Testing and Materials
BFF	Banana Frond Flour
CH_4	Methane
CNT	Carbon Nanotubes
CO_2	Carbon Dioxide
MMT	Montmorillonite
SEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
HMTA	Hexamethylenetetramine
HNT	Halloysite Nanotubes
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PET	Poly ethylene tetraphtalate
PVA	Polyvinyl alcohol

PVC	Polyvinyl chloride
PMMA	Poly methyl methacrylate
US	Unted States
UV	Ultraviolet
WVT	Water Vapor Transmission
WVTR	Water Vapour Transmission Rate

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LIST OF PUBLICATIONS

Articles/Manuscript/Books Published

1. Mat Suki, F.M., Ismail, H., Abdul Hamid Z.A. (2012). *Effect of soya bean flour content on mechanical properties and biodegradability of poly (vinyl alcohol) film*. Advanced Materials Research, 626: 360-365.

2. Mat Suki, F.M., Ismail, H., Abdul Hamid Z.A. (2014). *Preparation and properties of polyvinyl alcohol/banana frond flour biodegradable film*. Progress in Rubber, Plastics and Recycling Technology. (Accepted &-in press).

Paper Presentations (International/Local)

1. Mat Suki, F.M., Ismail, H., and Abdul Hamid Z.A. (2012). *Preparation and properties of polyvinyl alcohol/banana frond flour biodegradable film*. In: The Asian International Conference on Materials, Minerals, and Polymer 2012 (MAMIP 2012), 23rd -24th March 2012, Vistana Hotel, Penang, Malaysia. (Poster Presenter)

2. Mat Suki, F.M., Ismail, H., and Abdul Hamid Z.A. (2012). *Crosslinked poly(vinyl alcohol) and soya bean flour blend films: tensile properties, water absorption and water vapour transmission rate.* In: National Symposium on Polymeric Materials 2012 (NSPM 2012), 3rd -5th October 2012, Science and Engineering Research Centre,Engineering Campus, Universiti Sains Malaysia, Penang, Malaysia. (Oral Presenter)

3. Mat Suki, F.M., Ismail, H., and Abdul Hamid Z.A. (2012). *Biodegradation study of poly(vinyl alcohol)/soya bean powder blends.* In: National Symposium on Polymeric Materials 2012 (NSPM 2012), 3rd -5th October 2012, Science and Engineering Research Centre,Engineering Campus, Universiti Sains Malaysia, Penang, Malaysia. (Poster Presenter)

4. Mat Suki, F.M., Ismail, H., Abdul Hamid Z.A. (2012). *Effect of soya bean flour content on mechanical properties and biodegradability of poly(vinyl alcohol) film*. In: The International Conference on Advanced Material Engineering & Technology 2012 (ICAMET 2012), 28th – 30th November 2012, Bayview Beach Resort, Penang, Malaysia. (Oral Presenter)

LIST OF SYMBOLS

Symbol	**Description**
%	percentage
ºC	degree Celsius
A	area of test area
G	weight gain
g	gram
kg	kilogram
mL	mililiter
mm	millimeter
µm	micrometer
nm	nanometer
h	hours
MPa	Mega Pascal
Mtonne	Mega tonne
phr	part per hundred rubber
t	time

W_0	Initial weight of dry samples
Wa	Percentage of water absorption
W_e	Weight of samples at absorbing equilibrium
wt %	Percentage in weight

CHAPTER 1

INTRODUCTION

1.1 Overview

Plastics have become one of the most important materials in our lives and also one of the greatest innovations of the millennium (Danjaji, 2000). The usage of plastic materials was started in 1930 when major thermoplastics such as polystyrene (PS), polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP) and polymethyl methacrylate (PMMA) were developed (Brydson, 1989). Since then, plastics have replaced the conventional materials in many applications ranging from transportation, packaging, building, medical appliances, agricultures and communication. The break-up of these applications in Europe is shown in Figure 1.1. From this figure, 39.4% from 45.9 Mtonne of the total plastics demand came from packaging applications (PEMRG, 2013).

Plastics are one of the major polymer materials used in packaging application because of their matchless characteristics such as low price and can easily be produced in big quantity. In addition, they also exhibit favourable properties such as good mechanical strength and applicable in industrial processing (Tharanathan, 2003; Davis and Song, 2006). In spite of this benefits, plastic industry also significantly contributes to the environmental problem. Disposal of plastic waste is a serious environmental problem. From Figure 1.2, PE, polyethylene terephthalate (PET), PP, PVC and PS from packaging application contribute much to municipal solid waste. Realizing that plastics are prevalent in almost every human activity and the non degradable plastics becoming more and more problematic especially where they are use only a short period of time (Moura and Machado, 2012). In agriculture, plastic films in soil have caused a significant drop in yield. Plastics waste, especially plastics packaging that float in rivers, seas and lakes are endangering the animals that live in those habitats and also threatening the operation of hydropower plants and other public works (Ren, 2003).

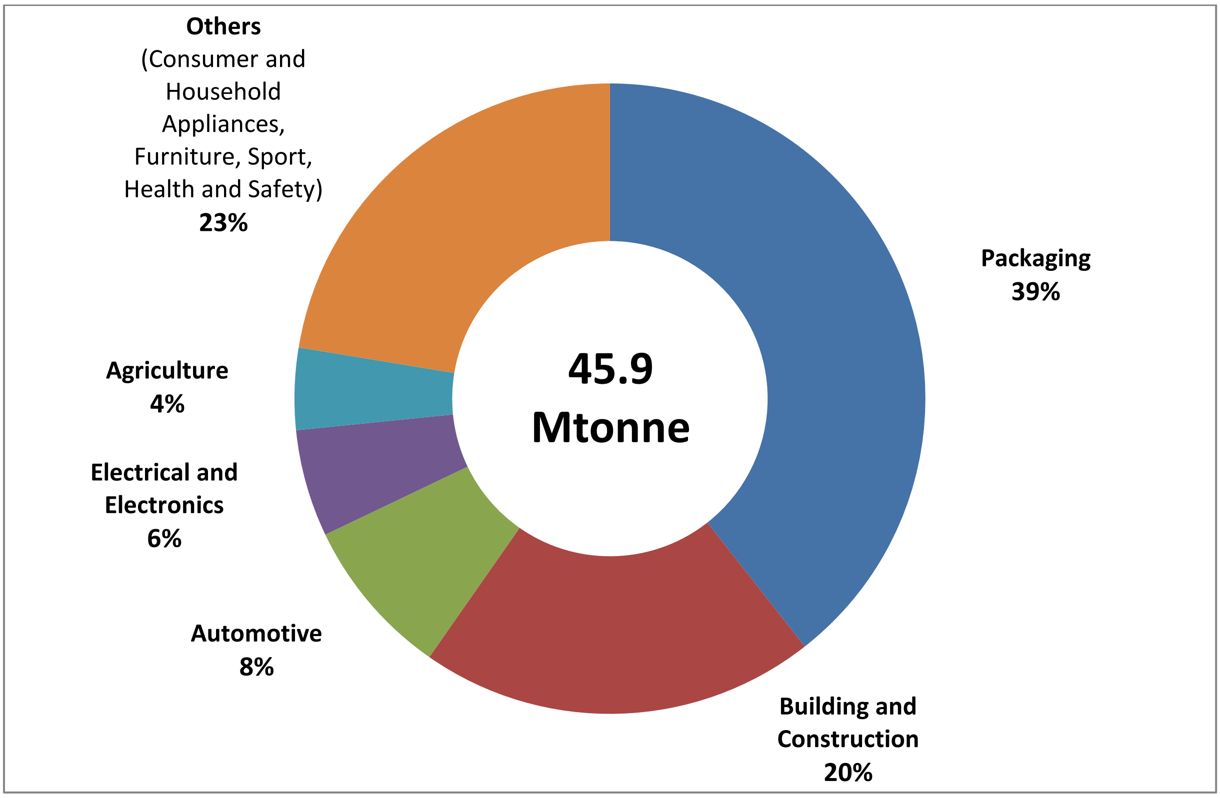


Figure 1.1: European plastic demands by segment in 2012 (PEMRG, 2013).

One of the attempt to overcome the disposal of plastic waste issue is by create a biodegradable polymer. There are several kinds of biodegradable polymers (polylactic acid and polycaprolactone) but polyvinyl alcohol (PVA) is the most promising biodegradable polymer because of its good mechanical properties, excellent chemical resistance, biodegradability, biocompatibility and have potential as water processable polymer (Paradossi *et al.*, 2003; Ramaraj, 2007a; Seldarik *et al.*, 2007). Matsumura *et al.* (1993) reported that PVA has been confirmed to be biodegradable under aerobic conditions. However, degradation process of pure PVA is quite slow under this condition and the degradation rate of PVA is strongly depends on the residual acetate groups (Corti *et al*., 2002). Another limiting factor of PVA usage is its high cost which has to compete with the low cost conventional plastic in practical application (Ramaraj, 2007b). Hence, in order to enhance the biodegradation rate and reduce the cost, polymer blending has been introduced. For this purpose, the highly polar and water soluble of PVA typically used to blend with more biodegradable, cheaper and easily processable natural filler or polymers.

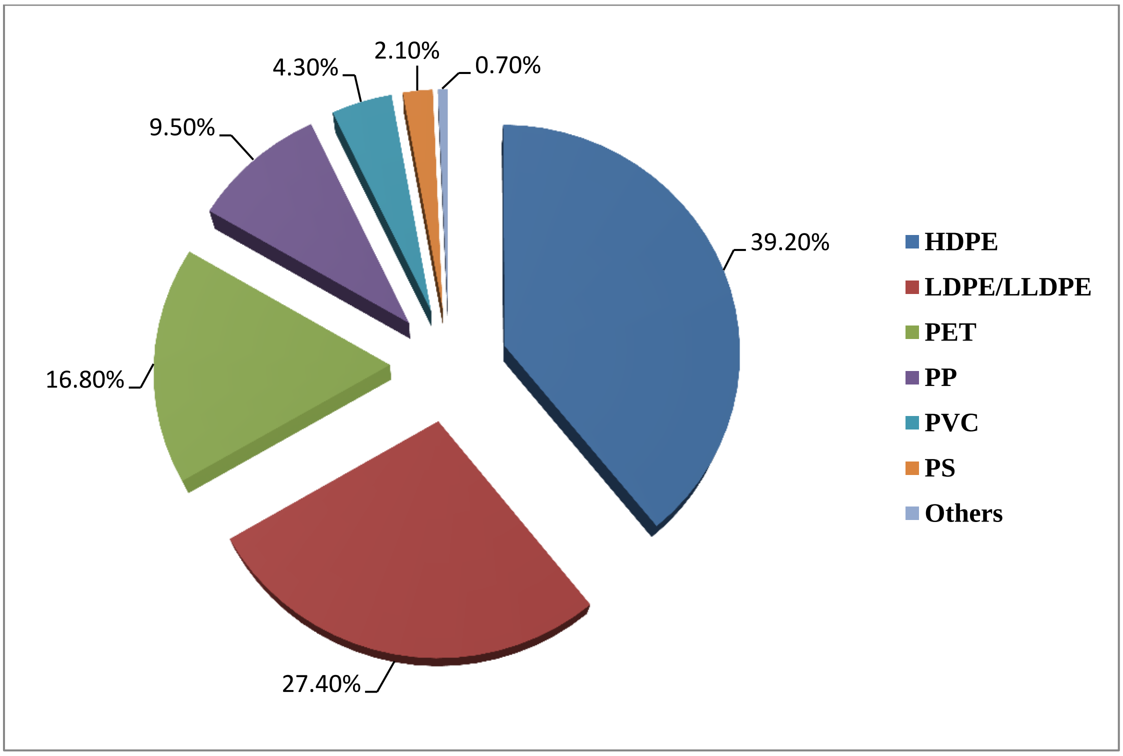


Figure 1.2: Plastic resin in packaging in U.S municipal solid waste stream (PEMRG, 2013).

Various types of starches have been applied in PVA matrices and the biodegradability of the PVA/starches blends has been proven. Beside the starch-based natural polymer, soya protein-based polymer is also a potential natural polymer that can be blended with PVA to reduce the production cost and to accelerate its degradation. Soya bean flour (SBF) actually is a remaining product after removal of soya bean oil (Sam *et al*., 2010). It is not mainly derived from proteins or peptide and less so from carbohydrates (Sam *et al*., 2011). Soya bean is inexpensive, abundantly available and renewability (Jong, 2008). Thus, the investigation of the performance of soya bean products in PVA is a worthwhile effort because the studies of protein in non-food application is still less.

However, the blend of the PVA and SBF has lower tensile properties and water barrier properties. Cajlakovic *et al.* (2002) reported that PVA must be crosslinked in order to be useful for wide variety of application and the crosslinking agents for PVA hydrogel including glutaraldehyde, formaldehyde and acetaldehyde. Besides, crosslinking agents such as boric acid (Yin *et al*., 2005), epichlorohydrin (Sreedhar *et al*., 2006) and glutaraldehyde (Mansur *et al*., 2008) were used to react with the starch and PVA to form the macromolecular network. In addition, Zhou *et al*. (2008) mentioned that the crosslinking agents were usually added into aqueous solution of PVA/starch mixture followed by casting method in order to improve their physical and mechanical properties. Therefore, by preparing the PVA/SBF blend films, the weak tensile properties will be improved through crosslinking reaction. In this study, hexamethylenetetramine was used to create linkages between the hydroxyl group of the PVA and SBF in order to compare the improvement of tensile properties and water barrier properties.

Recently, ternary composite systems have attracted many researchers attention because of their potential to enhance the present of the composite system. The system can be developed either by polymer blend plus filler or hybrid of filler with polymer matrix. In this research, two different types of filler (banana frond flour and halloysite nanotubes) were added to PVA/SBF blend to form ternary blend films. The expanding usage of agricultural material will lead to higher demand of agro based resources, which inherently increase the cost of this material. Therefore, the possible strategy is to utilize the discarded portion from the agricultural material. A number of studies have been reported on the uses of waste from organic industry (Ozaki *et al*., 2005; Ramaraj and Poomalai, 2006; Sedlarik *et al.*, 2007) for the preparation of low cost biodegradable polymer. In this research, banana frond flour (BFF) has been used. Banana frond (*Musacea* family) is known to have high content of cellulose, which can be the substrate for microorganisms reactions. Agricultural activity involving banana generates large amounts of residues, because each plant produces only one bunch of bananas. After harvesting the fruits, banana frond and stem are cut and usually left in the soil plantation to be used as organic material (Abdul Khalil *et al*., 2006). Therefore, by utilizing these wastes, it is hoped to be a way of disposing the waste, it is hoped to be a way of disposing the waste instead of forgo them. Moreover using banana frond/stem can significantly reduce the cost of the biodegradable film production as it is cheap and widely available. Besides agricultural waste, incorporation of nanofiller will hopefully enhance the mechanical and thermal properties of the blend films and decrease the water uptake. The addition of halloysite nanotubes (HNT) will improve the performance of PVA/SBF blend films. HNT are inorganic clay minerals with a unique tubular structure (Liu *et al.*, 2007). The HNT are formed by the hydrothermal alteration of aluminosilicate minerals. These HNT have very high aspect ratios which are critical to the polymer binding process. Alumina and silica groups are located on the surfaces of HNT especially on their crystal edges (Zhou *et al*. 2010).

From the previous series of study, PVA/SBF/HNT blend films show better tensile properties and water capabilty compare to the PVA/SBF/BFF blend films. Therefore, alkaline treatment is needed to impart the properties of PVA/SBF/BFF blend films. Alkali treatment is a common method to clean and modify the fiber surface and enhance interfacial adhesion between a natural fiber and a polymeric matrix. Mohanty *et al*. (2006) reported that fibers are treated with sodium hydroxide (NaOH) to remove lignin, pectin, wax substances and natural oils that cover the surface of the fiber cell wall. Previous studies by several researchers (Edeerozeey et al., 2007; El-Shekeil *et al.,* 2012) have been discussed which alkaline treatment has significantly improved the tensile properties of natural fiber reinforced polymer composites.

1.2 Problem Statement

Today, the petroleum-based plastic takes a long time to degrade, thus caused a serious waste disposal problem to our environment. This is because of the molecular bonds and structure that make them so durable and resistant to natural processes of degradation. Polyolefin are very resistant to hydrolysis and are totally non-biodegradable. As a consequence, the landfill area will have abundance with the plastic waste and definitely lead to another issue including the shortage of landfill availability and soil contamination. Moreover, there are some problems existences from recycling of plastic waste. It was reported that, the recycling process implied to the difficulties of the collection, separation, cleaning and possible contamination on the plastic and hard to find economical viable outlet, where incineration may emit some toxic gas (Averous and Halley, 2009).

As a viable alternative, much effort has been focused in recent years to develop environmental friendly polymer products by incorporating renewable materials. As an added advantage, renewable materials are comparatively less expensive, environmentally friendly and naturally biodegradable. This new polymer cannot replace synthetic polymers in every application but they can result in specific products, especially for those applications in which recovery of plastics is not economically feasible, viable and controllable like one time use plastic (Doane *et al.*, 1993).

Polyvinyl alcohol (PVA) is one of biodegradable synthetic polymers. However, the high production cost and slow biodegradation rate of PVA become limiting factor to compete with the low cost synthetic thermoplastic materials especially in commodity usage. In this regards, PVA is well suited to be blended with the low cost natural polymer, agricultural waste and/or byproducts to overcome the limiting factor. In conjunction of economical and ecological issue has led to the idea of waste utilization. The applications of proteins are commonly in food science. However, the studies of protein in non-food application is still less. From all the point above, an attempt is done in this research to investigate the incorporation of soya bean flour (protein) could enhance the biodegradability of biodegradable polymer.

1.3 Research Objectives

The aim of this research is concerned with the biodegradability of polyvinyl alcohol and soya bean flour (PVA/SBF) blend films by using solution casting method. The primarily objectives for this research work are:

i. To determine the effect of adding SBF on the tensile properties, water barrier properties, morphological studies and degradability of the PVA/SBF blend films under natural weathering and soil burial.
ii. To study the effect of hexamethylenetetramine (HMTA) as crosslinker on the tensile properties, water barrier properties, morphological studies and degradability of the PVA/SBF blend films under natural weathering and soil burial.
iii. To investigate the effect of two different types of filler (banana frond flour (BFF), and halloysite nanotubes (HNT)); on the tensile properties, water barrier properties, morphological studies and degradability of the PVA/SBF blend films under natural weathering and soil burial.
iv. To determine the effect of surface treatment on the tensile properties, water barrier properties, morphological studies and degradability of the PVA/SBF/BFF blend film under natural weathering and soil burial.

1.4 Organization of the Thesis

There are five chapters in this thesis and each chapter gives information related to the research interest as following:

- **Chapter 1** describes the introduction of the project. It covers a brief introduction of research background, problem statement and the objectives of this research.

- **Chapter 2** presents an overview of current issue related to the plastic and development of biodegradable films. This chapter also introduces the literature review of this study and will explain in details about biodegradable polymer, polyvinyl alcohol, polyvinyl alcohol blend, soya bean flour, crosslinking agent, filler addition, and modification of the filler. It also discuss about the research that have been done by other researcher.

- **Chapter 3** contains the information about the materials and equipment used in this research. This chapter also contains the methodology and characterization that related to this research.

- **Chapter 4** presents all the results and discussion of this research. The effect of soya bean flour, crosslinker, various fillers and surface treatment will be explained and discussed in term of its tensile properties, water barrier properties and biodegradability. The films were further characterized by using Fourier transform infrared and scanning electron microscope.

- **Chapter 5** presents some concluding remarks on the present study as well as some suggestion for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodegradable Polymers

Biodegradable polymers are one alternative to the non-degradable of petroleum based polymers in order to decrease the solid waste problems created by the plastic waste. The definition of biodegradable polymer varies greatly among scientists, manufactures and consumers. A biodegradable polymer is defined as a plastic that is degraded primarily by the action of naturally occurring microorganisms, such as bacteria, fungi and algae. The indiscriminate discarding of plastics has increased and the waste does not degrade rapidly because synthetic are inert to the immediate attack of microorganisms. The use of biodegradable polymers provides a promising solution to this problem and this theme has been an objective of many researchers (Rutkowska *et al.*, 2002; Stevens, 2002; Utracki, 2002).

Biodegradable polymers can be divided into two main categories which are natural and synthetic biodegradable polymers. Natural biodegradable polymers or biopolymers are polymers that formed in nature during growth cycles of all organisms (Chandra and Rustgi, 1998), including polysaccharides (starch, cellulose, chitin/chitosan and alginic acid); polypeptides of natural origin and bacteria polyesters (polyhydroxybutyrate). Simple sugar such as glucose, fructose and maltose are the basic units in this compound (Danjaji *et al*., 2000). Some polyester such as polyhydroxylalkanoates is also natural biodegradable polymers. Others naturally occur polymers including proteins, gelatin, silks, shellac and poly (gamma-glutamic acid).

Synthetic biodegradable polymers are normally polymers with hydrolysable backbone or polymers that are sensitive toward photo degradation. Among them aliphatic polyesters, polycaprolactone, polyamides, polyurethanes and polyureas, polyanhydrides and poly (amide-enamine)s (Chandra and Rustgi, 1998). Interestingly, some polymers with carbon backbones such as polyvinyl alcohol (PVA); also categorized as synthetic biodegradable polymers. These polymers (e.g., vinyl polymers) require an oxidation process for biodegradation because they are not susceptible to hydrolysis in general. Most of biodegradable vinyl polymers contain an easily oxidizable functional group and catalysts are added to promote their oxidation or photo oxidation, or both.

2.1.1 Mechanism of Biodegradation

Biodegradation is a chemical degradation of materials provoked by the action of microorganisms. It is expected to be the major mechanism of loss for most chemicals released into the environment (Leja and Lewandowincz, 2010). Its refers to the process of degradation and assimilation of the polymers by living microorganisms to produce degradation products. Fungi, bacteria and algae are the most important organisms in biodegradation (Gautam *et al.*, 2007).

Natural polymers such proteins, polysaccharides, nucleic acids are degraded by oxidation and hydrolysis in biological systems (Kyrikou and Briassoulis, 2007). Biodegradable materials degrade into biomass, carbon dioxide and methane. In the case of synthetic polymers, microbial utilization of its carbon backbone as a carbon source is required (Jayasekara *et al.*, 2005). The biodegradation process can be divided into aerobic and anaerobic degradation (Figure 2.1).

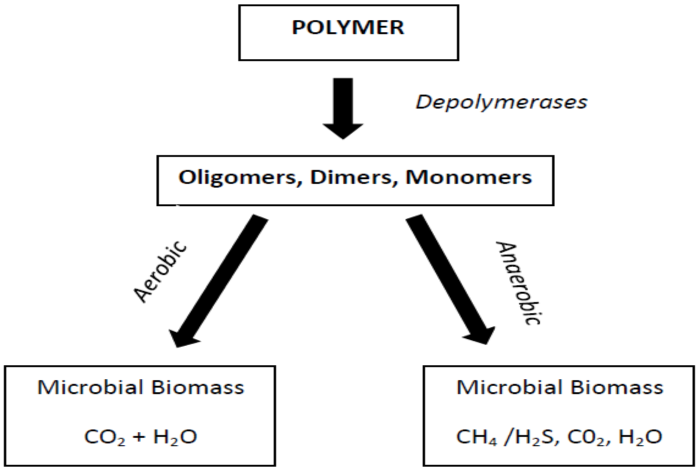


Figure 2.1: Scheme of polymer degradation under aerobic and anaerobic conditions.

Aerobic biodegradation:

Polymer + $O_2 \rightarrow CO_2 + H_2O$ + biomass + residue(s) ....(2.1)

Anaerobic biodegradation:

Polymer $\rightarrow CO_2 + CH_4 + H_2O$ + biomass+ residue(s)......................................(2.2)

An aerobic biodegradation (Equation 2.1) occurs with the presence of oxygen and carbon dioxide is produced. Whereas, an anaerobic degradation (Equation 2.2) occurs when there is no oxygen presence and methane is produced instead of carbon dioxide (Kyrikou and Briassoulis, 2007; Grima *et al*., 2002; Gu, 2003; Swift, 1998). Mineralization is a conversion process of biodegradable materials to gases (carbon dioxide, methane, and nitrogen compounds), water, salts, minerals and residual biomass occurs. Mineralization is complete when all the biodegradable materials or biomass are consumed and all the carbon is converted to carbon dioxide (Kyrikou and Briassoulis, 2007). Biodegradable materials have the proven capability to decompose in the most common environment where the material is disposed, within one year, through natural biological processes into non-toxic carbonaceous soil, water or carbon dioxide.

2.1.2 Factors Affecting Polymer Biodegradability

At this present, there are two main types of plastics degradation being researched which are chemical, physical and both are closely inter-connected. Chemical degradation included the reactions of oxidation and hydrolysis (Tidjani *et al*., 1997; Usarat *et al*., 2006; Baljit and Nisha, 2008) while physical degradation involved environmental stress cracking and plasticizer migration and loss (Baljit and Nisha, 2008). Polymer structure, polymer morphology, radiation, chemical treatments and molecular weight are the several factors that affecting the degradability of the polymers.

Polymer structure (amorphous, crystalline and semi crystalline) are really affected the degradability of the polymers. Bastioli (2005) and Lee (2007) mentioned that other chemical properties including the chemical linkages in the polymer backbone, the position and chemical activity of the pendant groups and the chemical activity of the ends groups also important in affecting polymer degradability. Some polymers degrade at a faster rate than others because of their different chemical structures. The chemical structures of the common commodity plastics like polyolefin, which contain the carbon-carbon single bonds in their backbones makes them particularly resistance to degradation (Steven, 2002). Nevertheless, polyvinyl alcohol (PVA) also have the carbon-carbon single bond in their backbone chain, but the presence of hydroxyl groups on the alternate carbon atoms make it hydrophilic. Thus, this hydrophilicity helps to promote degradation of PVA through hydrolysis mechanism.

According to Chandra and Rustgi (1998), morphology will affect the biodegradability of the polymer too. Synthetic polymers that have a short repeating unit will enhance the crystallization to make the hydrozable groups inaccessible to the enzymes. Shape, size and number of the crystallites will pronounced effect on the chain mobility of the amorphous regions and thus affect the biodegradation rate.

The molecular weight distribution of the polymer can have a dramatic effect on rates of degradation. This effect has been demonstrated for a number of polymers, where a critical lower limit must be present before the process will start. The molecular origin for this effect is still subject to speculation, and has been attributed to a range of causes such as changes in enzyme accessibility, chain flexibility, fits with active sites, crystallinity, or other aspects of morphology (Bastioli, 2005; Lee, 2007).

Photolysis, irradiation and oxidation affect the polymer biodegradability by the chain scission and the reduction of molecular weight. The biodegradability rate increase until most of the fragment polymer is consumed. Crosslinked polymer will show a lower biodegradability rate due to the crosslink network present (Chandra and Rustgi, 1998).

2.1.3 Ways to Increase Biodegradability of Polymer

Most of synthetic polymers have very high molecular weights and contain only carbon-carbon bonds. Thus, these types of polymers show little or no susceptibility to enzyme-catalyzed degradation reactions. 'Weak links' can be attached or inserted within the polymers that are not readily degraded due to the high molecular weight. These weak links are designed to control the degradation of an initially high molecular weight and hydrophobic polymer into a lower molecular weight oligomer that can be attacked and consumed by the microorganism through the biodegradation process (Chandra and Rustgi, 1998; Baljit and Nisha, 2008). Figure 2.2 shows the inserting main chain ester groups into vinyl type polymers.

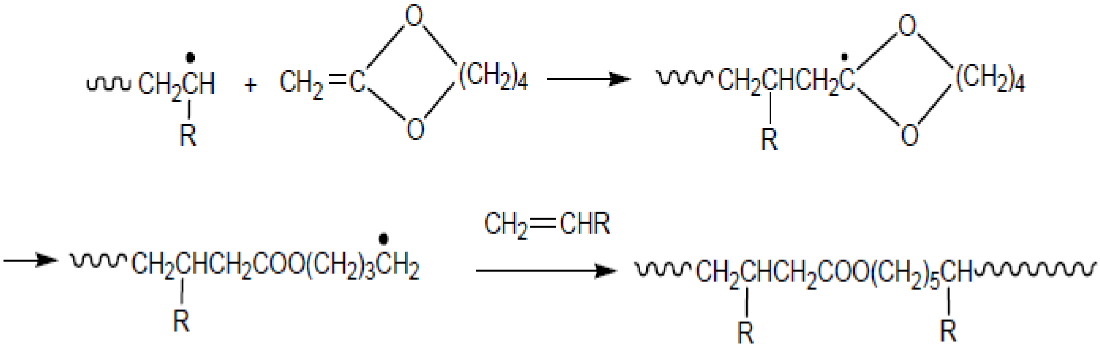


Figure 2.2: Insertion of ester group into vinyl polymer (Baljit and Nisha, 2008).

Preparation of the photodegradable copolymer follows by oxidation is shown in Figure 2.3 and Figure 2.4. These are some of the methods to insert the weak link into a high molecular weight and hydrophobic polymers.

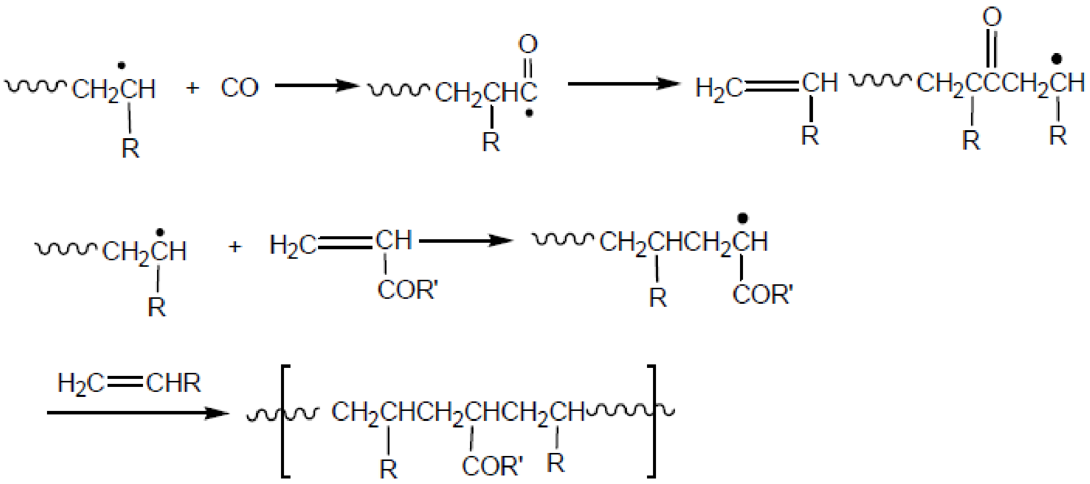


Figure 2.3: Insertion of ketone group into vinyl polymer (Baljit and Nisha, 2008).

From Figure 2.4, Norrish I is the free radical generation and no chain cleavage, and Norrish II is the chain cleavage. Ketones are introduced onto the backbones of polymers by photo oxidation. Under exposure to light, these ketone groups absorb photons of appropriate energy; break the carbon-carbon bonds, and scission the polymer backbone (Feldman, 2002).

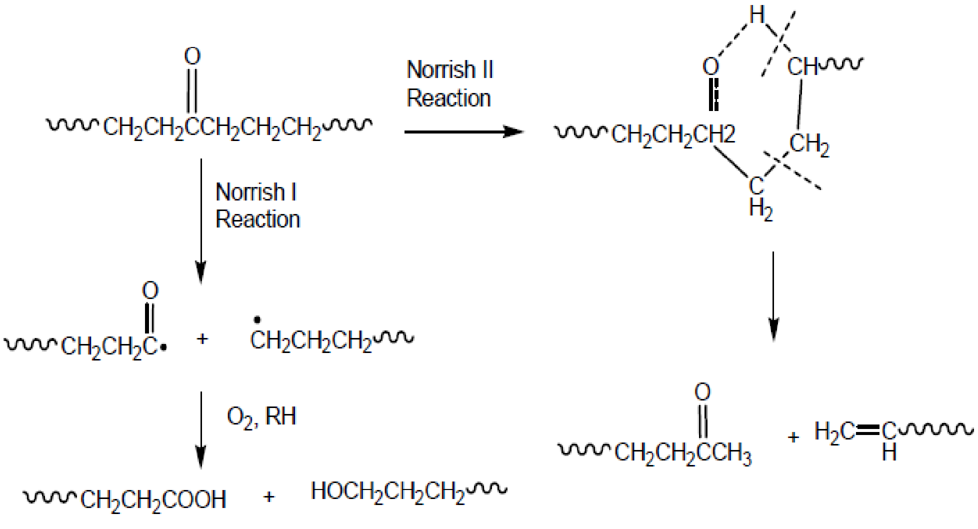


Figure 2.4: Norrish I and Norrish II reaction mechanisms for the degradation of copolymers of ethylene (Baljit and Nisha, 2008).

Blending of biodegradable polymers such as poly (ε-caprolactone) and starch with an inert polymer such as polyethylene is another method to produce a degradable polymer. The idea in this concept is if the biodegradable component is present in sufficient amounts and it is potentially removed by the microorganism, the plastic or film containing the remaining inert will lose its integrity, disintegrate and disappear (Chandra and Rustgi, 1998; Baljit and Nisha, 2008).

2.2 Polyvinyl alcohol

Polyvinyl alcohol (PVA) was discovered in 1915 by F Klatte and the stoichiometric saponification of polyvinyl acetate with caustic soda to yield PVA was first described in 1924 by W. O. Hermann and W. Haehnel. The name of PVA is based on the repeating structural unit, and it is not monomer based (Stevens, 2002). This is because the polymerization takes place on the principle of free radical polymerization of vinyl acetate, followed by alkaline alcoholysis of the functional acetate groups (Chiellini *et al.*, 2003). Unlike most of the polymer, PVA faces difficulties to be formed by its own monomer due to the restriction caused by the unstable vinyl that tends to form stable tautomer of acetaldehyde. Molecular structure of PVA is schematically presented in Figure 2.5 and the scheme for industrial production of PVA is given in Figure 2.6.

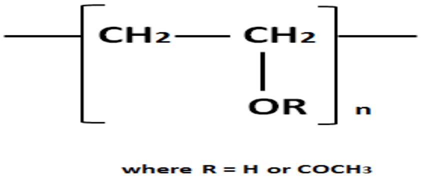


Figure 2.5: Molecular structure of PVA

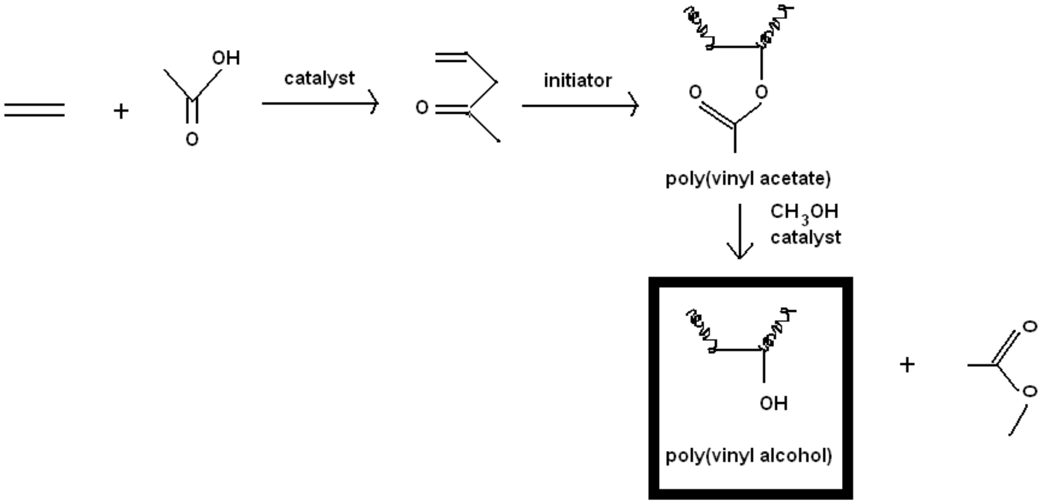


Figure 2.6: Manufacturing route to PVA (Rudnik, 2008**).**

Different grades of PVA were depending on the degree of hydrolysis. Degree of hydrolysis indicates the number of residual acetate group that presence in the polymer which saponification or alcoholysis has not taken place (Goldschmidt and Streitberger, 2003). According to Hutten (2007), there are four different range of hydrolysis are 98 - 99.5 % (fully), 90 – 97 % (intermediate), 86 – 89 % (partially) and 76 - 87.6 % (specialty grades). But, commercially PVA only can be classified into fully or partially hydrolysed as shown in Figure 2.7 (Goswami *et al*., 2005).

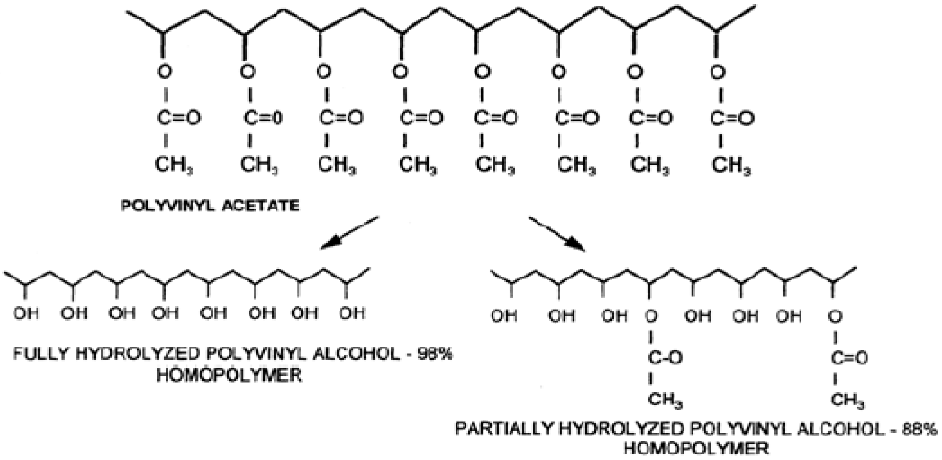


Figure 2.7: Hydrolysis of polyvinyl acetate (PVAc) (Goswami *et al.*, 2005).

The effects of degree of hydrolysis (Hutten, 2007) are shown in Table 2.1. As degree of hydrolysis increased, increment of solvent and water resistance, tensile strength and viscosity can be seen. But, the reduction in stability, hygroscopic and flexibility can be observed as increased in degree of hydrolysis. Figure 2.9 shows a closer look into the effect of degree of hydrolysis on solubility; water molecule would require addition breakage of interchain hydrogen bonding for fully hydrolysed PVA while penetration of water molecule is easy for partially hydrolysed PVA due to the presence of bulky acetate radical which distances the neighbouring chains (Goswami *et al.*, 2005).

Table 2.1: The effect of degree of hydrolysis on the properties of PVA.

Property effect on	Degree of hydrolysis	
	High	Low
Solvent resistance	+	-
Water resistance	+	-
Solubility	-	+
Hygroscopicity	-	+
Tensile strength	+	-
Flexibility	-	+
Viscosity	+	-

Note: "+" indicates the property gets higher or stronger
"-" indicates the property gets lower or weaker

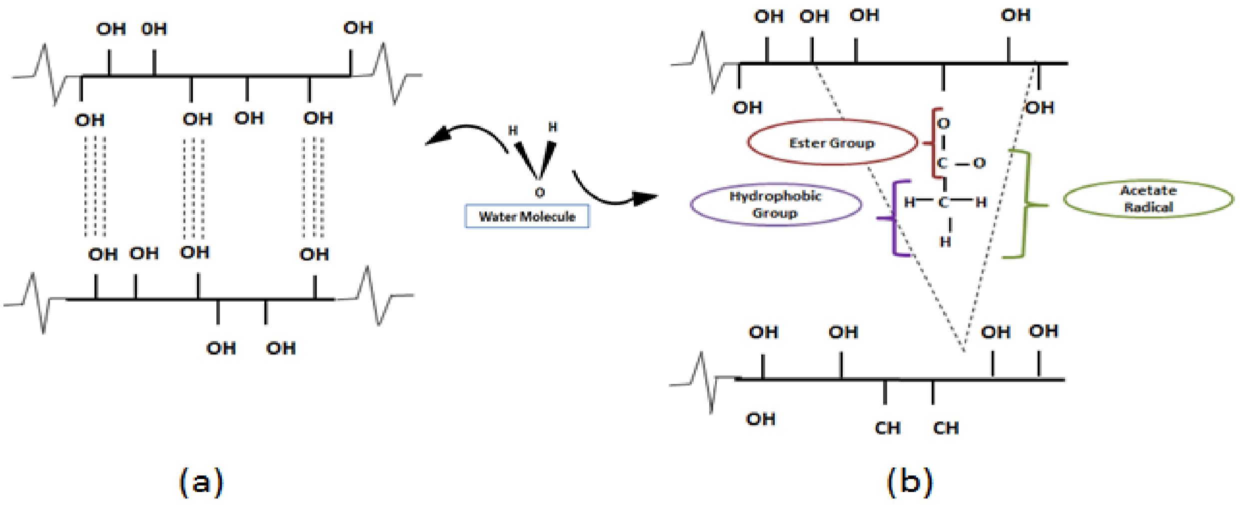


Figure 2.8: Effect of degree of hydrolysis on solubility of PVA; (a) fully hydrolysed segment and (b) partially hydrolysed segment

PVA is a synthetic polymer with its excellent characteristic such as water solubility, good barrier properties to oxygen and oil, good optical and tensile properties, good thermal properties, resistance to organic solvents and oils, non-toxicity and biodegradability under certain conditions (DeMerlis and Schoneker, 2003; Siddaramaiah *et al*., 2004; Li *et al*., 2005, Ramaraj, 2007). Siddaramiah *et al.* (2004) reported that PVA also a water processable polymer, thus it allowing the PVA to be produced using solution casting method. Another uniqueness of PVA is its film-forming ability. Therefore, the exceptional properties of PVA have been employed in various application like dip coating, adhesive and solution casting film (Zaikov and Lomakin, 1997; El-Shinawy *et al*., 1998; Seldarik *et al*., 2007; Ramaraj, 2007).

PVA is the only synthetic polymers which having carbon-carbon linkages in its backbone and show the biodegradability behavior. This is due to the occurrence of hydroxyl groups on alternate carbon atoms causing enzymatic oxidation of hydroxyl groups from carbonyl groups in the polymer backbone, followed by the hydrolysis of two carbonyl groups causes polymer chain cleavage which resulting to a decrease in molecular weight of PVA (Kale *et al*., 2007). However, the biodegradability of PVA is low compared to other biodegradable polymer such as poly(lactic acid) and poly(caprolactone) (Ishigaki *et al*., 1999). The degradation process of pure PVA is quite slow, particularly under anaerobic conditions (Pseja *et al*., 2006) and the rate of degradation is strongly depends on the residual acetate groups (Corti *et al*., 2002). However, Lenz (1993) has reported that PVA with an average molecular weight as high as 10^6 could be completely degrade by soil bacteria, especially by *Pseudomonads.*

There are two technologies involved in PVA film production from viscous water solution casting and blown extrusion. Traditionally, most of the plastic are produced by casting method. Recently, with the development in polymer compounding, PVA can be melt-processed. Yang *et al.* (2008) and Zou *et al.* (2008) have applied this process in the extrusion technique for PVA film productions. However, processing at high temperatures is very sensitive to the degradation of PVA. Both solution casting and blown extrusion has its own advantages when it comes to production of PVA film. Solution casting only allows small scale of production and often takes longer time to dry the film. However, it would provide better optical properties, stiffer instant-quenched-film and better gauge control. On the contrary, blown film will have larger variation of 3 % to 4 % of gauge control range as compared to solution casting of only 1 % to 2 %. Furthermore, blown film would be able to produce biaxial orientation with lesser scrap and also permits some post-processing in one continuous process such as heat seal and winding up for stock keeping (Giles *et al*., 2005).

2.3 Polyvinyl Alcohol Blend

The commercial development of polymer blends was rapid growth in the late 1960's by gaining major interest for many researchers, especially in polymer industry since the polymer blend could potentially offer a large number of different commercial products with the desirable properties (Robeson, 2007). The main reason for blending is to meet the desirable properties with adjusting the cost-performance balance and tailor with the current technology to fabricate product for end use application. According to Utracki (2002), there are several important factors that contribute to the interest in polymer blends. Polymer blends offer useful and economic means of upgrading recycled and off-specification polymers. Polymer blending is a way to develop a new product by blending of two or more commercially available polymer. This is more cost-effective way than totally develop a new polymer which involving high research and cost to meet the customer and market requirements. Moreover, polymer blending allows custom production of different blends in a wide range of production volumes. Contrarily, the polymerization plant for a new polymer is not as flexible and not economical for small volumes production. Polymer blending can be done at relatively low cost conventional equipment compared to new polymer requires high investment risk to develop intensive plant and reactor for the production and research purpose. Other than that, polymer blends can be generated, formulated, optimized and even commercialized at a faster rate than new polymer.

Developments of environmental friendly polymer material have been classified into two categories based on their raw material; degradable synthetic polymer and renewable natural polymers (Yang *et al.*, 2004). The renewable natural polymers include starch, gelatin, protein, cellulose, chitosan are tested alone or blend with other polymer to enhance the polymer properties and biodegradability.

2.3.1 Polyvinyl Alcohol Blend with Starch

PVA/starch blend plastics are one of the most popular types for biodegradable plastics application, and are widely used in packaging and agricultural mulch films (Bastioli *et al.*, 1993). Many researchers have been developed for PVA/starch blend and improvements have been done in the formulation to increase its compatibility, strength and modulus of the film (Chen *et al.*, 1997, Tudorachi *et al.*, 2000 and Jayasekara *et al.*, 2004). Compatibility between starch and synthetic polymers can be improved by adding a compatibilizer to the blends (Avella *et al.*, 2000) and chemical modifications of the synthetic polymers (Bikiaris and Panayiotou, 1998) and starch. These techniques have been proved as effective measures to improve the film properties. A number of methods are available in starch modification including esterification, oxidation, etherification and cross-linking. From these methods, methylation, as one esterification method, was used widely in elucidating the structure of polysaccharides and the substitution pattern in polymer chains (Van der Burgt *et al*., 2000 and Bergsma *et al.,* 2000). A good properties can be observed when blending PVA with starch but in term of biodegradability, it has been reported that PVA/starch have low biodegradability compared with other biodegradable plastics. Bastioli *et al.* (1993) reported that an amylose-PVA composite (PVA-starch blend) was very slowly biodegraded and that 75% weight loss required 300 days in a degradation test with activated sludge.

2.3.2 Polyvinyl Alcohol Blend with Miscellaneous

Besides starch, PVA is also blended with other materials to look for the possible synergy effect like wastewood and *Amaranthus cruentus* flour. Ozaki *et al.* (2005) reported that PVA/wastewood can improve surface properties and mold ability rather than reduce the wastewood disposal in environment. In addition, Elizondo et al. (2009) also studied the blending of PVA with a renewable resource (*Amaranthus cruentus* flour). From this report, the mechanical properties of the blend films improved and the water solubility of the blend films decreased as the PVA content increased.

2.4 Soya Bean Flour

Soya bean are one of the most abundant crops in the world and has attracted attention in recent years because of its versatile uses in many cultures. Soya bean are considered functional foods since they contain high amounts of protein, complex carbohydrates, soluble fibers, micronutrients, and phytochemicals. Availability of soybeans is high in the United States (US) since the US produces almost half of the world's soybeans and they are the second most important cash crop. There was 2.79 million hectares of soya bean being planted in 1940 (Swain *et al.*, 2004). After 50 years, the soya bean production reach a record of 2.8 billion bushels.

Soya bean flour (SBF) is obtained from soybeans oils and it is commonly being defined as the flour prepared from fine grinding of soya bean which will be used as high protein food, thickener for gravy and sauce (Ash and Ash, 2004). The characteristic of SBF is yet being discovered in polymer industry. However, some predictions on the behavior of SBF can be made based on the compositions of SBF (Liu, 1997) as mentioned in Table 2.2. Triglycerides, an example of lipid exist in SBF was constructed from fatty acid and glycerol; while protein is constituted by saturated and unsaturated fatty acid. According to Liu (1997), the functional properties and oxidative stability of SBF are governed by characteristic and composition of fatty acid.

Table 2.2: Proximate composition of soya bean and their parts.

	Percentage in Whole Seeds	Chemical Composition (% dry matter)			
		Protein	Lipid	Carbohydrate	Ash
Hull	8	9	1	86	4.3
Hypocotyl axis	2	41	11	43	4.3
Cotyledons	90	43	23	29	5.0
Whole seeds	100	40	20	35	5.0

SBF appears in semisolid, solid or liquid form is determined by its melting point which is ultimately determined by the chain length of fatty acid and the presence of double bond in fatty acid. Fatty acid with longer chain length and lower amount of unsaturated bond in fatty acid brings up the melting point of SBF. In addition, bonding in fatty acid will affect the oxidation susceptibility and stability of SBF; the higher double bond, the lesser the stability. Moreover, the geometric configuration and positional distribution of double bond in fatty acid will cause some changes on the physical and chemical properties of SBF (Liu, 1997). Nevertheless, existence of polar lipids such as phospholipids and protein in SBF also affect the polarity of SBF (Liu, 1997).

2.5 Soya Bean Blend

SBF is cheap and widely abundance as starch, thus it is potentially can reduced the production cost of any materials upon blending. Since SBF falls under the category of naturally occurring material, it will be easily biodegraded as other starches. Currently, the blending of SBF with other polymer has not much been studied. For linear-low-density polyethylene/soya bean powder (LLDPE/SBP) blend, Sam et al. (2009) proved that soya bean powder helps in mixing process due to the lowering of stabilizing torque. Similar to starch blend, tensile strength and elongation at break were decreased as the soya bean powder content increase in the blend. Moreover, thermal stability, melting temperature, crystallization temperature and heat of fusion are reduced after the addition of soya bean powder into linear-low-density polyethylene. This research also showed that the effect can be compensated by utilization of compatibilizer such as polyethylene-g-(maleic anhydride) and epoxidized natural rubber (Sam et al. 2009).

2.6 Crosslinking Agent

Crosslinking agent is useful to create linkages between the functional group of each polymer to for the macromolecular network in order to improve the mechanical properties for the various applications. There are varieties of crosslinking agent nowadays, but the common crosslinking agents that used in the PVA blending are acetaldehyde, formaldehyde (Cajlakovic *et al.*, 2002), boric acid (Yin *et al*., 2005), epichlohydrin (Sreedhar *et al*., 2006), glutaraldehyde (Mansur *et al*., 2008) and hexamethylenetetramine (Ooi *et al.*, 2011). When the crosslinking agent was used, the acetal bridges will form between the pendant hydroxyl groups within the PVA chains (Mansur *et al*., 2008).

2.6.1 Hexamethylenetetramine

Hexamethylenetetramine (HMTA) also known as hexamine or methanamine is formed in nearly quantitative yield from the condensation of ammonia and formaldehyde in liquid phase. In reversed, HMTA will gradually decompose to yield formaldehyde and ammonia under hydrothermal conditions as in Equation 2.3 (Liu et al, 2011). It can be considered as one such simple heterocyclic compound with a cagelike structure (Figure 2.9 and 2.10) which, due to its inexpensiveness, commercial availability and high solubility in water and polar organic solvents. It has found a broad variety of applications, ranging from the production of phenolic resins and solid fuel tablets to uses in organic synthesis, medicinal and material chemistry (Zhend *et al.*, 2003).

$$6\ CH_20 + 4\ NH_3 \rightarrow C_6H_{12}N_4 + 6\ H_20 \quad \text{(2.3)}$$

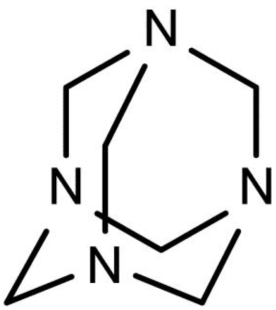


Figure 2.9: Structural formula of HMTA, $(CH_2)_6N_4$

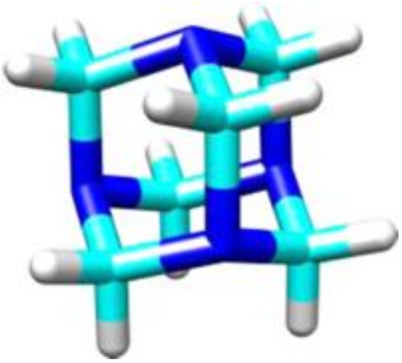


Figure 2.10: X-ray crystal structure of HMTA, $(CH_2)_6N_4$

2.7 Filler

In general, filler can be classified by their geometries, broadly in three classes, which is particle, layered and fibrous material (Hussain *et al.*, 2006). Filler is a material that is added to a polymer formulation to lower the compound cost or to improve properties. It can be in the form of solid, liquid or gas. By the appropriate selection of these materials, not only the economics but also the properties such as processing and mechanical behavior can be improved.

Few decades ago, many polymer composites have been prepared and combined with various types of synthetic reinforcing filler in order to improve the mechanical properties and to obtain the characteristic demanded in actual applications (Yao *et al.*, 2008; Tabari *et al.*, 2011). But recently, the use of natural filler for the reinforcement of the composites has received increasing attention by the academic and industry sector.

Natural filler have many significant advantages over synthetic filler and fibres such as lightweight, low cost, non-toxicity and have ability to reduce abrasion of machinery. (Hardinnawirda and SitiRabiatul, 2012). Currently, many types of natural fillers have been investigated to be used in the industry due to their potential advantages over synthetic fillers and fibres.

2.7.1 Banana Frond

There are various types of raw materials can be chosen for a production of biodegradable plastics, namely starch, corn, sugarcane, rambutan, chitosan and even the types of renewable materials such as paper mills, forestry and etc. Banana frond is known to have high content of cellulose, which can be the substrate for microorganisms reactions. Agricultural activity involving banana generates large amounts of residues, because each plant produces only one bunch of bananas. After harvesting the fruits, banana frond and stem are cut and usually left in the soil plantation to be used as organic material. It has estimated that for every 60 kg of banana grown, 200 kg of waste stem is thrown away. In Malaysia alone, the area of banana plantation is estimated to be 34, 000 hectars (Abdul Khalil *et al.*, 2006). Therefore, by utilizing these wastes, it is hoped to be a way of disposing the waste, it is hoped to be a way of disposing the waste instead of forgo them. Moreover using banana frond/stem can significantly reduce the cost of the biodegradable film production as it is cheap and widely available.

2.7.2 Halloysite Nanotubes

Halloysites have been used as a new type of filler for polymers such as epoxy, polypropylene and polyvinyl alcohol, recently (Du *et al.*, 2006; Ye *et al.*, 2007; Liu *et al.*, 2007). They are an economically and abundantly viable clay material that can be mined from deposits (Lvov *et al.*, 2008). It is mainly composed of aluminosilicate and has a predominantly hollow tubular structure with chemical composition, $Al_2(OH)_4Si_2O_5(2H_2O)$, chemically similar to kaolin. Commonly halloysites can be found in the form of fine, tubular structures with a length of 300 ~ 1500 nm, and with inner and outer diameters of 15-100 nm and 40-120 nm, respectively (Du *et al*., 2010).

Application of natural occurring nanotubes as reinforcing materials for preparing polymer composites is still new. But the usage of halloysite nanotubes (HNT) are considered as the ideal materials for preparing polymer composites due to the fact that halloysites are rigid material and the unique crystal structure of halloysite nanotubes (HNT) resembles that of carbon nanotubes (CNT) in term of aspect ratio. Compared with other nanoparticles such as fumed silica, montmorillonite (MMT) and CNT, HNT are more easily dispersed in polymer matrix by shearing due to their rod-like geometry and limited intertubular contact area (Du *et al*., 2010).

Chemically, HNT are recognized for their relatively lower hydroxyl density on the outer surfaces compared with fumed silica and other layered silicates like MMT (Liu et al., 2008). Therefore, the aggregation induced by the intertubular hydrogen bonding in susceptible to the shearing force. In fact, HNTs are widely available, biocompatible and cheaper compared with other nanofillers. Consequently, it can be concluded that HNT are ‘green’, unique and promising reinforcing material for polymers (Prashanta *et al*., 2011).

CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Polyvinyl Alcohol

Biodegradable films have been prepared by using polyvinyl alcohol (PVA), Elvanol from Sigma-Aldrich (M) Sdn. Bhd. with 99 % hydrolyzed, with molecular weight average of 146 000 to 186 000 g/mol. This PVA powder has density of 1.26 g/cm^3. The melting temperature and thermal decomposition temperature are above 200 ºC and 300 ºC respectively.

3.1.2 Soya Bean Flour

Soya bean flour (SBF) was obtained from Hasrat Bestari (M) Sdn. Bhd. The granular size was in the range of 50-100 nm with an average granular size of 80 nm. The proximate composition in SBF is shown in Table 3.1.

Table 3.1: Proximate composition in SBF

Constituent	**Content (%)**
Protein	46.7 ± 0.6
Carbohydrates	25.4 ± 0.6
Lipid	21.2 ± 0.6
Starch	10.7 ± 0.6
Moisture	8.7 ± 0.6
Ash	5.8 ± 0.6

3.1.3 Banana Frond Flour

Banana plants are categorized under family of *Musacease.* The flour used in this study is extracted from banana frond and dried under sunlight for one week until all the moisture is removed from the fronds. The dried fronds are then was grinded by using a small crusher (Rong Tsong Precision Technology Co.) to have fine powder particle size. *Bilba et al.* (2007) has determined that the composition of a typical banana flour obtained by elemental analysis as shown in Table 3.2.

Table 3.2: Proximate composition in banana flour

Constituent	**Content (%)**
Cellulose	31.27 ± 3.61
Hemicellulose	14.90 ± 2.03
Lignin	15.07 ± 0.66
Extractive	4.46 ± 0.11
Moisture	9.74 ± 1.42
Ash	8.65 ± 0.10

3.1.4 Halloysite Nanotubes

The halloysite nanotubes (HNT) were supplied by Imerys Tableware Asia Limited, New Zealand. The elemental composition of HNTs is as follows (wt%): SiO_2-49; Al_2O_3-34.8; Fe_2O_3-0.35; TiO_2-0.12; Na_2O-0.25 and MgO-0.15. The HNT have typical dimensions of 150 nm – 2 μm long, 20–100 nm outer diameter, and 5–30 nm inner diameter and their most common morphology is hollow tube. Before mixing with other materials, these powders need to be dried at 80 °C in an oven for 24 hours.

3.1.5 Hexamethylenetetramine

Hexamethylenetetramnine (HMTA), ACS Reagent, ≥ 99 % with molecular weight of 140.19 g/mol was used as a crosslinking agent. It was used to react with the hydroxyl group in PVA and SBF. It was purchased from Sigma-Aldrich Pte Ltd. It is a water soluble material with density of 1.331 g/cm^3 and melting temperature of 280 °C.

3.1.7 Deionized Water

Deionized water was used as a solvent to dissolve all the water soluble ingredients and also acts as a plasticizer in the blend.

3.2 Equipments

The major equipment that used in this study are:

3.2.1 Vacuum Oven (EV 018)

Vacuum oven was used for dry and remove the moisture content in the raw material.

3.2.2 Grinder (Micro Universal Bench Top Grinder)

Grinder was used for grinding the dry banana frond to flour.

3.2.3 Hot Plate (FAVORIT)

Hot plate was used for mixing the solution of PVA, SBF, BFF, HNT and HMTA with controlling the temperature.

3.2.4 Glass Plates

Glass plate was used for preparing the cast film in fixed dimension (275 mm x 130 mm x 2 mm).

3.2.5 Analytical Weight Balancing (Precisa XT 220A)

Weight balancing was used to measuring the weight of raw material and weight of films before and after water absorption and degradation testing.

3.2.6 Scanning Electron Microscopy (Zeiss Supra 35VP)

Scanning Electron Microscopy (SEM) is used to study the morphology of blend films such as particle distribution and surface after degradation test.

3.2.7 Fourier Transform Infrared Spectroscopy (Perkin Elmer)

Fourier Transform Infrared Spectroscopy (FTIR) was used to obtain some qualitative information about the functional groups and chemical characteristics of the prepared cast films.

3.2.8 Instron Testing Machine (Instron 3366)

Instron machine was used for determining the tensile properties for the prepared cast films.

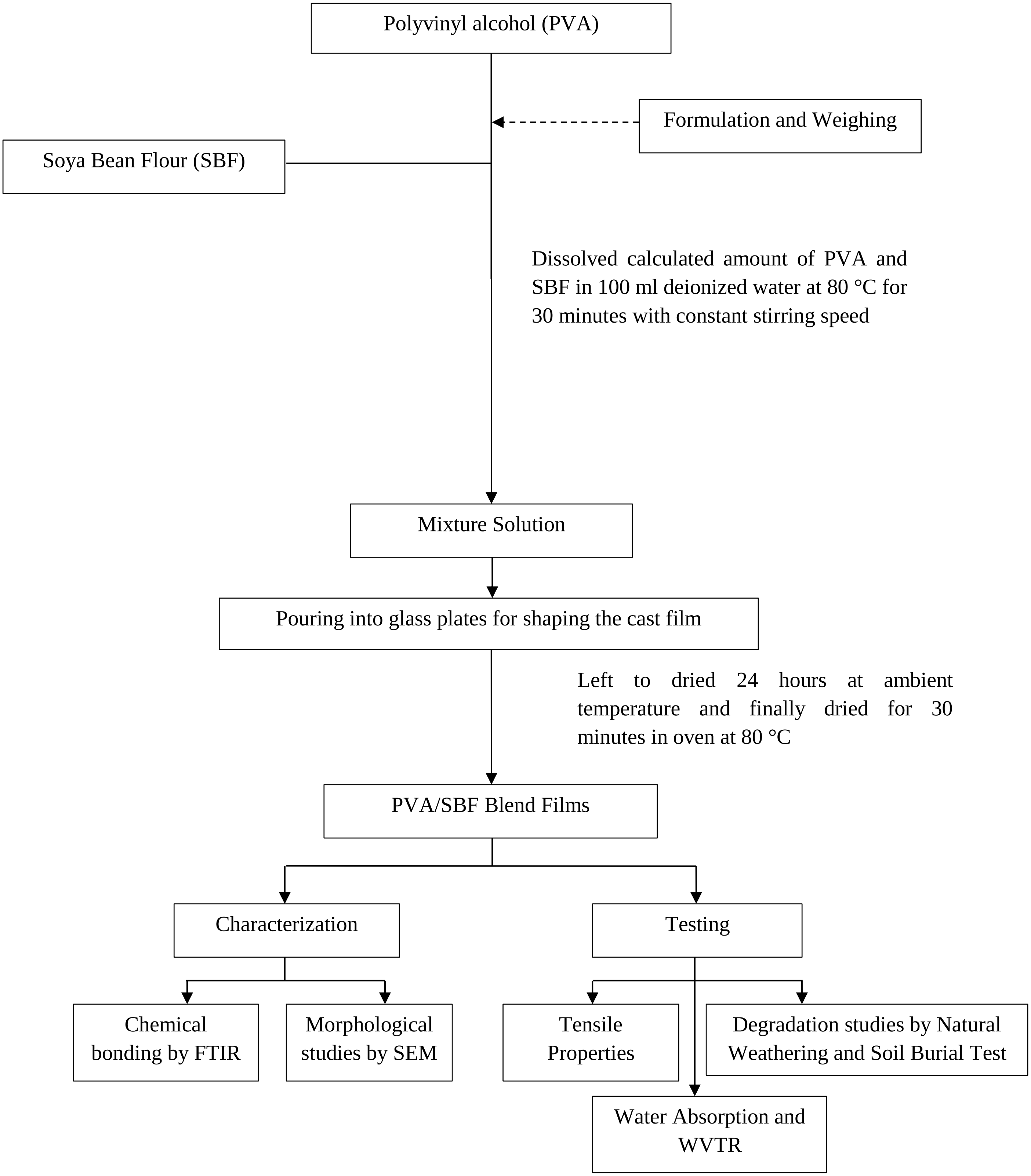
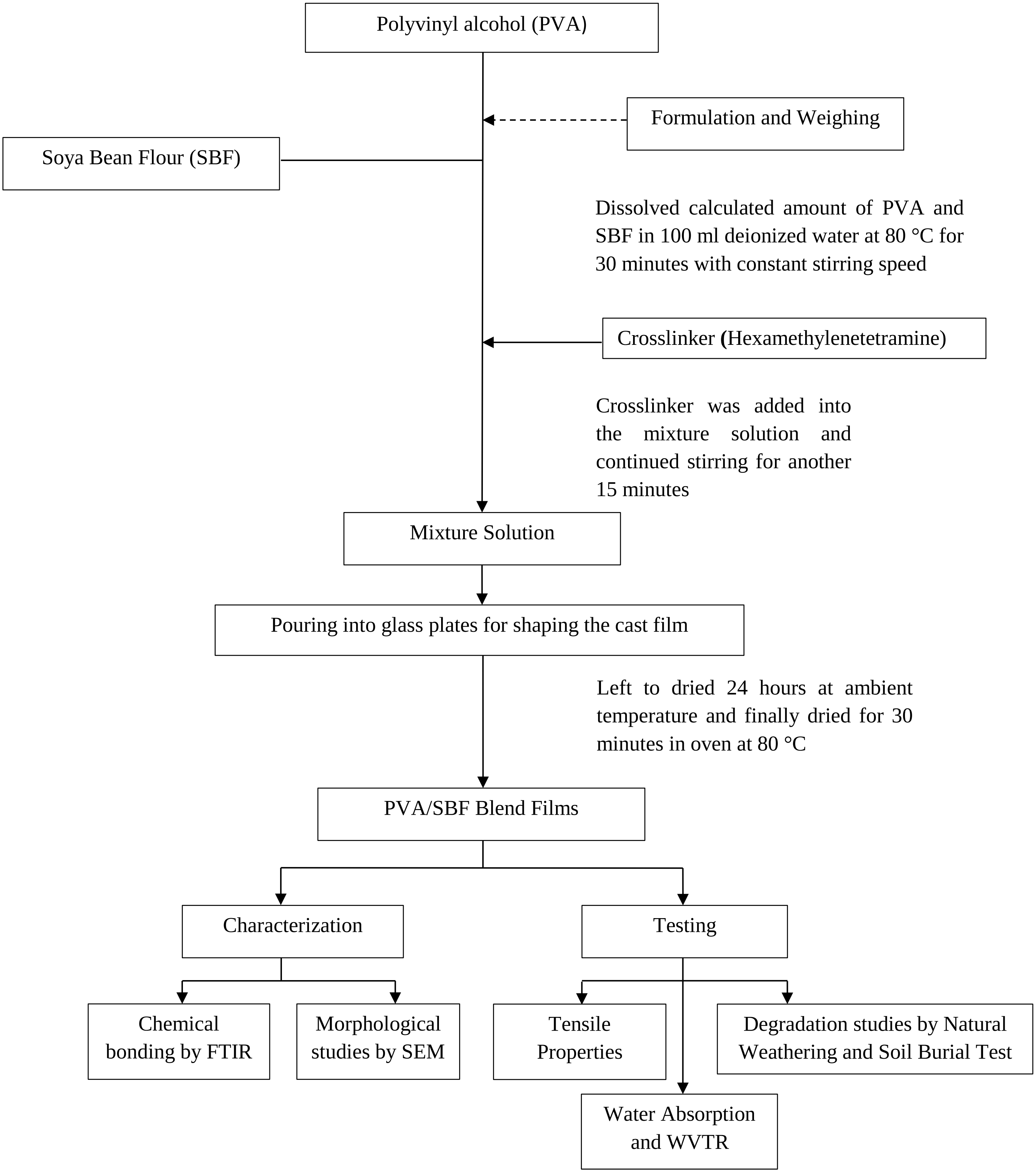


Figure 3.1: Flow chart of 1st series study.



Dissolved calculated amount of PVA and SBF in 100 ml deionized water at 80 °C for 30 minutes with constant stirring speed

Crosslinker was added into the mixture solution and continued stirring for another 15 minutes

Left to dried 24 hours at ambient temperature and finally dried for 30 minutes in oven at 80 °C

Figure 3.2: Flow chart of 2nd series study.

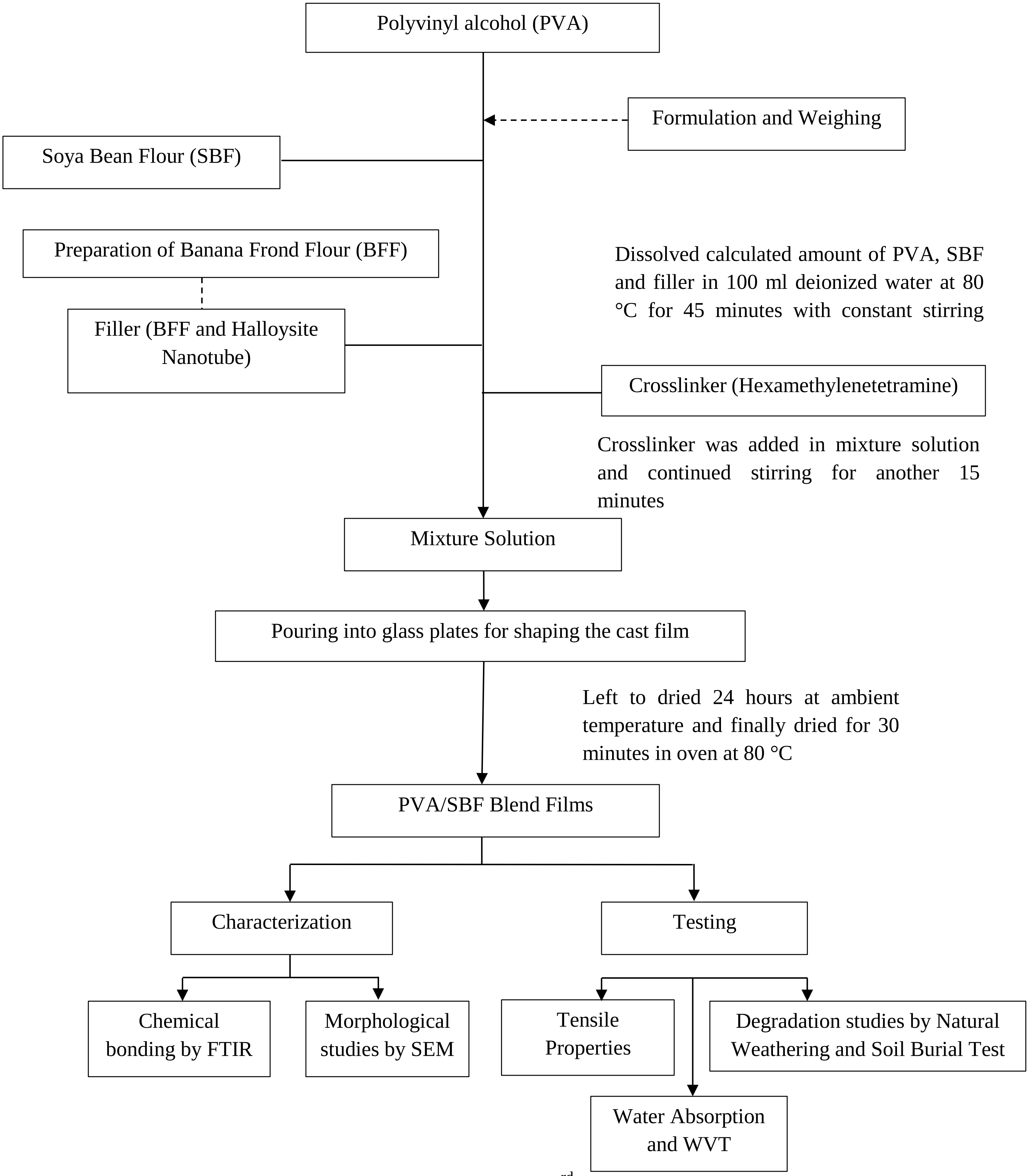


Figure 3.3: Flow chart of 3rd series study.

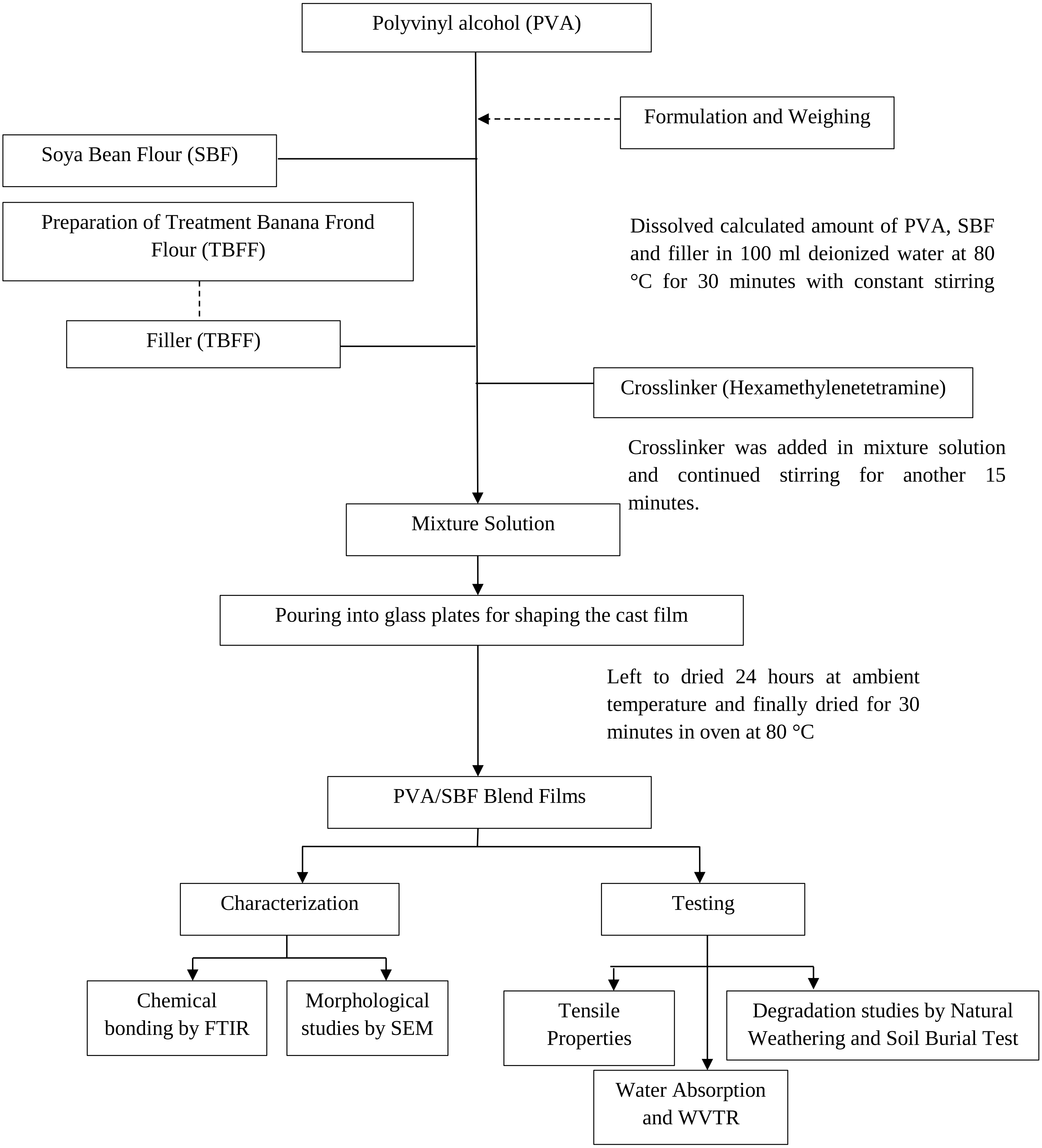


Figure 3.4: Flow chart of 4th series study.

3.3 Film Preparation

3.3.1 Preparation of Polyvinyl Alcohol/Soya Bean Flour (PVA/SBF) Blend Films

Figure 3.1 shows the flow chart of fabricating 1st series PVA/SBF blend films followed by the characterization and testing method. The physical properties consist of tensile properties, water absorption, water vapour transmission and biodegradability by natural weathering and soil burial test. Characterization of cast films was studied by FTIR and SEM.

PVA/SBF blend films were made by the solution casting technique. Calculated amount of PVA and SBF (Table 3.3) was added into deionized water to make a homogenous solution by a magnetic stirrer and heated to 80 °C for 30 minutes. Before casting, bubbles from the solution mixing were removed by using a vacuum oven. Then, the films were casted onto each glass plate which was placed on a leveled flat surface and left to dry at ambient temperature for 24 hours before finally dried in an oven at 80 °C. The films were then peeled off and stored in desiccator 24 hours before further testing.

Table 3.3: Material designation and composition for PVA/SBF blend films.

Sample Designation	**Composition**	
	PVA (wt%)	**SBF (wt%)**
PVA	100	0
PVA/SBF10	90	10
PVA/SBF20	80	20
PVA/SBF30	70	30
PVA/SBF40	60	40

3.3.2 Preparation of Crosslinked Polyvinyl Alcohol/Soya Bean Flour (PVA/SBF) Blend Films

Figure 3.2 shows the flow chart of fabricating 2nd series of PVA/SBF blend films followed by the characterization and testing method. For preparation of non-crosslinked and crosslinked PVA/SBF blend films, the calculated amount of PVA and SBF (Table 3.4) was added into deionized water to make a homogenous solution by a magnetic stirrer and heated to 80 °C for 30 minutes. Yin et al. (2005) had reported that 1.5 wt % (based on the dry basis of total weight of starch and PVA) was the optimum dosage to increase the tensile strength of the film. Thus, 1.5 phr of HMTA was added into the mixture solution and continued stirring for another 15 minutes. Another longer stirring time needed to have a homogenous solution. Before casting, bubbles from the solution mixing were removed by using an aspirator. Then, the films were casted onto each glass plate which was placed on a leveled flat surface and left to dry at ambient temperature for 24 hours before finally dried in an oven at 80 °C.

Table 3.4: Material designation and composition for non-crosslinked and crosslinked PVA/SBF blend films.

Sample Designation	**Composition**		
	PVA (wt %)	**SBF (wt %)**	**HMTA (phr)**
Non-crosslinked PVA	100	0	-
Non-crosslinked PVA/SBF10	90	10	-
Non-crosslinked PVA/SBF20	80	20	-
Non-crosslinked PVA/SBF30	70	30	-
Non-crosslinked PVA/SBF40	60	40	-
Crosslinked PVA	100	0	1.5
Crosslinked PVA/SBF10	90	10	1.5
Crosslinked PVA/SBF20	80	20	1.5
Crosslinked PVA/SBF30	70	30	1.5
Crosslinked PVA/SBF40	60	40	1.5

3.3.3 Preparation of Polyvinyl Alcohol/Soya Bean Flour/Banana Frond Flour (PVA/SBF/BFF) Blend Films and Preparation of Polyvinyl Alcohol/Soya Bean Flour/Halloysite Nanotubes (PVA/SBF/HNT)

Banana frond need to convert into flour types before use in the film preparation. Firstly, the banana frond was undergo sanitizing process. They were rinsed under running tap water to remove the dirt. The cleaned banana frond were chopped to an average length of 50 mm and dried in an oven at 70 °C for 24 hours to remove moisture. Then, the dried banana frond was grinded into finer flour particles. Then, the dried banana frond flour (BFF) was stored in desiccators at room temperature prior to use.

Figure 3.3 shows the flow chart of fabricating 3rd series of PVA/SBF blend films followed by the characterization and testing method. For preparation of PVA/SBF/BFF and PVA/SBF/HNT blend films, the calculated amount of PVA, SBF and BFF or HNT (Table 3.5) was added into deionized water to make a homogenous solution by a magnetic stirrer and heated to 80 °C for 45 minutes. Then, HMTA was added into the mixture solution and continued stirring for another 15 minutes. Before casting, bubbles from the solution mixing were removed by using an aspirator. Then, the films were casted onto each glass plate which was placed on a leveled flat surface and left to dry at ambient temperature for 24 hours before finally dried in an oven at 80 °C.

Table 3.5: Material designation and composition for PVA/SBF/BFF blend films and PVA/SBF/HNT blend films.

Sample Designation	**Composition**				
	PVA (wt %)	**SBF (wt %)**	**HMTA (phr)**	**BFF (phr)**	**HNT (phr)**
PVA80	80	20	1.5	-	-
PVA80BFF5	80	20	1.5	5	-
PVA80BFF10	80	20	1.5	10	-
PVA80BFF15	80	20	1.5	15	-
PVA80BFF20	80	20	1.5	20	-
PVA80HNT5	80	20	1.5	-	5
PVA80HNT10	80	20	1.5	-	10
PVA80HNT15	80	20	1.5	-	15
PVA80HNT20	80	20	1.5	-	20

3.3.4 Preparation of Treated Polyvinyl Alcohol/Soya Bean Flour Blend/Banana Frond Flour (PVA/SBF/BFF) Blend Films

Firstly, the banana frond was undergo sanitizing process. They were rinsed under running tap water to remove the dirt. The cleaned banana frond was chopped to an average length of 50 mm. Then, the cleaned banana fronds were immersed in 1% solution of sodium hydroxide (NaOH) for 1 hour. Washing was continued till the banana frond was alkali free. The washed banana frond was then dried in the oven at 70 °C for 24 hours to remove moisture. Then, the dried treated banana frond was grinded into finer flour particles. Then, the dried treated banana frond flour (BFF) was stored in desiccators at room temperature prior to use.

Figure 3.4 shows the flow chart of fabricating 4th series of PVA/SBF blend films followed by the characterization and testing method. For preparation of untreated and treated PVA/SBF/BFF blend films, the calculated amount of PVA, SBF and BFF (Table 3.6) was added into deionized water to make a homogenous solution by a magnetic stirrer and heated to 80 °C for 45 minutes. Then, crosslinker was added into the mixture solution and continued stirring for another 15 minutes. Before casting, bubbles from the solution mixing were removed by using an aspirator. Then, the films were casted onto each glass plate which was placed on a leveled flat surface and left to dry at ambient temperature for 24 hours before finally dried in an oven at 80 °C.

Table 3.6: Material designation and composition for untreated and treated PVA/SBF/BFF blend films.

Sample Designation	**Composition**				
	PVA (wt %)	**SBF (wt %)**	**HMTA (phr)**	**Untreated BFF (phr)**	**Treated BFF (phr)**
Untreated PVA80BFF5	80	20	1.5	5	-
Untreated PVA80BFF10	80	20	1.5	10	-
Untreated PVA80BFF15	80	20	1.5	15	-
Untreated PVA80BFF20	80	20	1.5	20	-
Treated PVA80BFF5	80	20	1.5	-	5
Treated PVA80BFF10	80	20	1.5	-	10
Treated PVA80BFF15	80	20	1.5	-	15
Treated PVA80BFF20	80	20	1.5	-	20

3.4 Characterization

3.4.1 Tensile Properties

Tensile properties were evaluated for each film using an Instron 3366 testing machine (Plate 3.1). Five dumbbell shaped samples (ASTM D638) were cut from each film. Each piece was measured for thickness in three places along the test length using a Mitutoyo (Japan). The crosshead speed was 50 mm/min and load cell was 10 kN. The gap between the upper and lower clamp was set at 50 mm. The tests were carried out at room temperature and an average value five repeated tests were taken for each blend composition. Tensile properties like tensile strength, elongation at break and tensile modulus were evaluated from the stress strain data.

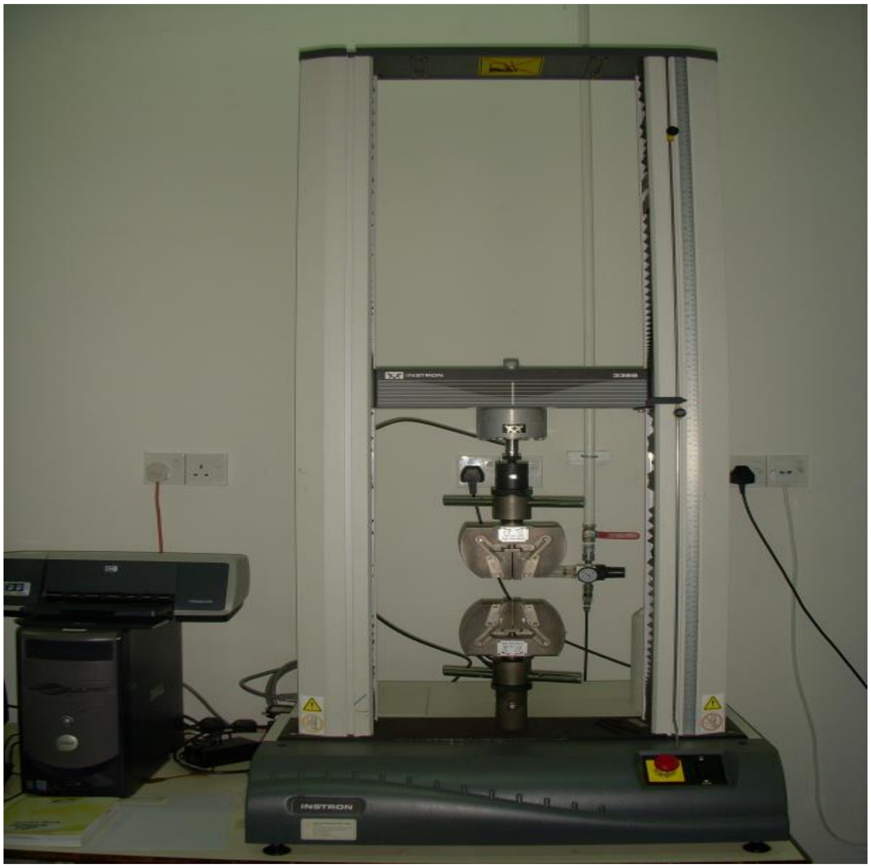


Plate 3.1: Instron 3366

3.4.2 Morphology Studies

Studies on the tensile fracture and surface morphology of the blended films, before and after degradation, were observed with a scanning electron miscrocope (SEM) (Plate 3.2). The specimen was mounted on aluminium stubs and sputter coated with a thin layer of gold (Plate 3.3) to avoid electrostatic charging and poor resolution during examination.

Plate 3.2: Scanning electron microscope (SEM, Supra35VP-24-58, Germany)

Plate 3.3: Sputter coater

3.4.3 Fourier Transform Infrared Spectroscopy

Plate 3.4 shows Perkin Elmer FTIR Spectrometer which was used in this study to obtain some qualitative information about the functional groups and characteristics of the blended films. The Fourier Transform Infrared (FTIR) spectra of blended films were collected on a Perkin Elmer FTIR Spectrometer in a range of 400-4000 cm^{-1}. For the films, a dumbbell shape sample was directly used for the FTIR test. A reflectance (%) FTIR spectrum was obtained from the analysis. The means of the peaks in the FTIR spectrum were used to determine the chemical structure of the samples.

Plate 3.4: Perkin Elmer FTIR Spectrometer (IR Spectroscopy V 5.0.2, United State)

3.4.4 Water Absorption

The kinetics of water absorption was studied using a water absorption test. The sample dimensions were 20 mm x 30 mm. Prior to the test, the samples were dried in an oven at 50 °C for 30 minutes in order to remove the water content. Then, the samples were totally immersed in distilled water for 24 hours. After this period of immersion, samples were removed at fixed time intervals, wiped with dry cloth to remove surface water and weighed using an analytical weight balance to the nearest 0.001 g. The average of five values was recorded. The percentage of water absorption, W_a (%) was calculated to the nearest 0.01% as Equation 3.1:

$$\mathrm{Wa}\ (\%) = \frac{(\mathrm{We} - \mathrm{Wo})}{\mathrm{Wo}} \times 100 \quad \text{..}(3.1)$$

where, W_e is the weight of samples at the absorbing equilibrium, and W_o is the initial weight of dry samples.

3.4.5 Water Vapour Transmission Rate

Water vapour transmission (WVT) was measured by performing testing according to ASTM E96-80. An impermeable cup with silica gel was closed with 10 cm x 10 cm square film firmly fixed on top. The cups then were weighed with their contents and were placed in a desiccator containing distilled water at ambient temperature. The film was weighed every 24 hours until a steady increase on weight achieved. The water vapour transferred through the films and absorbed by the gel was determined from the weight gain of the cup daily using analytical weight balance until constant weight. The water vapour transmission rate, WVTR ($gh^{-1}m^{-2}$) was calculated as Equation 3.2:

$$\mathrm{WVT} = \frac{G}{t} \times \frac{1}{A} \quad \text{..}(3.2)$$

where, G was the weight gain, t was the time tested (h) and A was the area exposed to water transfer (m^2).

3.4.6 Natural Weathering Exposure

Natural weathering tests were performed according ASTM D1435. Specimens were attached to a rack with a specimen holder. The rack (Plate 3.6) was adjusted to face the equator at angle of 45°. The rack is situated at an open area and free from being overshadowed by other object. Moisture on the surface of the sample were removed with a dry cloth and left in air for 24 hours at room temperature before mechanical testing were conducted.

Plate 3.6: The specimen holder rack used for weathering test

3.4.7 Soil Burial Degradation

The soil burial test was conducted for in the vicinity of the School of Materials and Mineral Resources Engineering, University Sains Malaysia. This burying time period was primarily chosen to study the effect of biodegradation after the short period of time. In this method, the samples in a dumbbell shape specimens were buried in 10L polybag filled with compost soil. After a month, the specimens were removed, washed in distilled water and dried at 50°C in an oven for 4 hours and then kept in desiccators.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Soya Bean Flour Content (SBF) on the Properties of Polyvinyl Alcohol/Soya Bean Flour (PVA/SBF) Blend Films

Mechanical properties are important criteria for many practical applications of materials. In order to investigate the influence of soya bean flour (SBF) content on the polyvinyl alcohol (PVA) blends, the SBF were added (from 1 wt% to 5 wt%) into the blends. In this research, the solution casting were adopted to study the effect of SBF content in PVA blends in term of tensile properties, water absorption, water vapour transmission rate, Fourier transform infrared (FTIR), natural weathering test, soil burial test and morphology analysis.

4.1.1 Tensile Properties

Figures 4.1 - 4.3 show the effect of SBF content on tensile strength, elongation at break and tensile modulus of PVA/SBF blend films. As shown in Figure 4.1, it is clearly seen that the tensile strength decreased from 46 MPa to 16 MPa as increasing of SBF content. The same trend also can be seen in Figure 4.2 for elongation at break. The elongation at break of the PVA/SBF films decreased from 158 % to 103 % as increasing SBF content. The reduction of both tensile strength and elongation at break were due to the weak intermolecular hydrogen bonding between the SBF and PVA. This could be due to the lack compatibility between the two components. PVA is hydrophilic, whereas SBF is semi-hydrophilic due to the presence of fats and lipid in SBF (Engel, 2009). SBF acted as filler in PVA matrix but as the blends subjected to the tensile load only the PVA matrix will mainly bear the load due to the less effective cross sectional of SBF at high SBF content (Ramaraj, 2007a). The granules of SBF will acted as stress concentrators and will induced the cracks and resulted low strength and elongation at break.

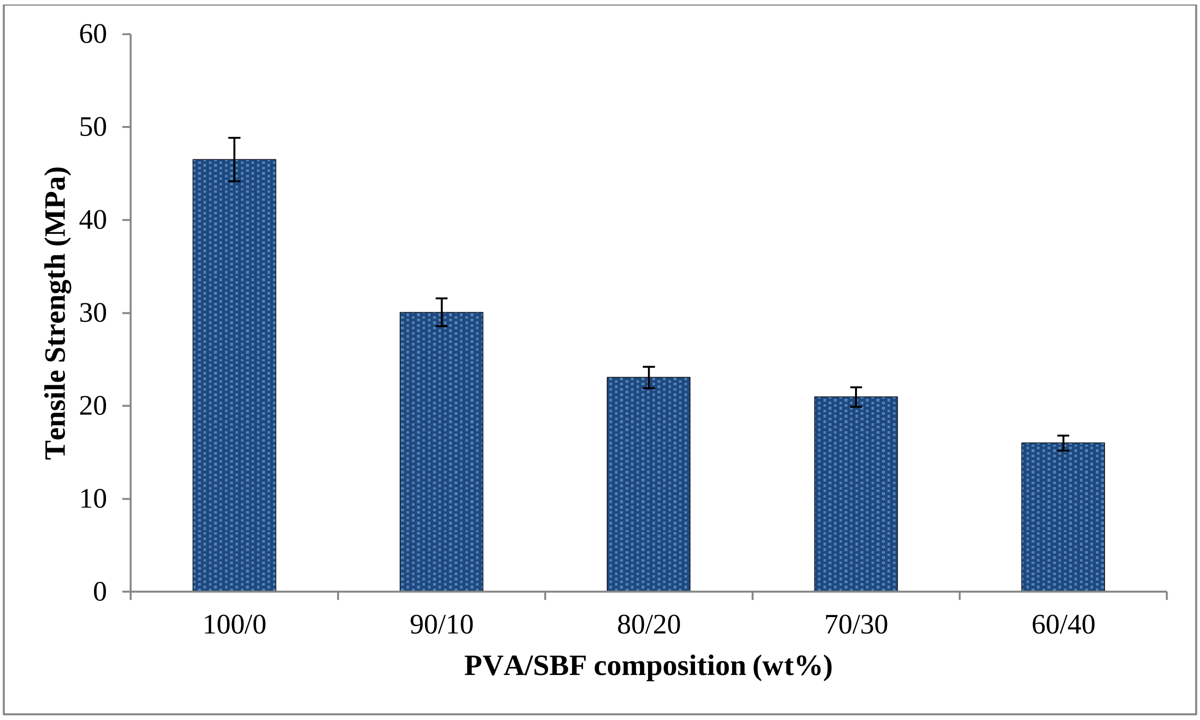


Figure 4.1: Effect of SBF content on the tensile strength of PVA/SBF blend films.

The tensile modulus of the PVA/SBF blend films as a function of SBF content is presented in Figure 4.3. The experimental results show that the tensile modulus increased with increasing SBF content in the blends. This trend is due to the stiffening effect by the particulate nature of SBF granules. The rigid SBF granules were expected to restrict the molecular mobility of PVA chain, thus the higher resistance of the PVA molecules against straining resulted the higher tensile modulus values. This results shows that the presence of SBF did not improve the tensile properties of the blend films. This was due to PVA's excellent mechanical properties and the poor compatibility of PVA and SBF.

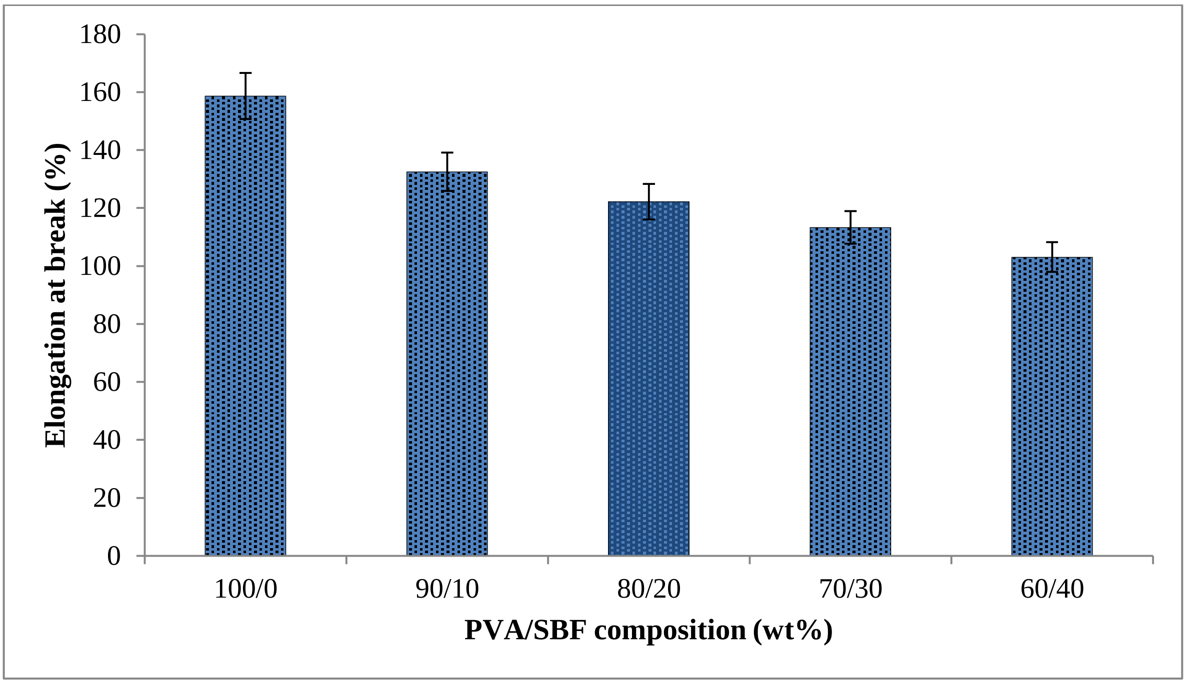


Figure 4.2: Effect of SBF content on the elongation at break of PVA/SBF blend films.

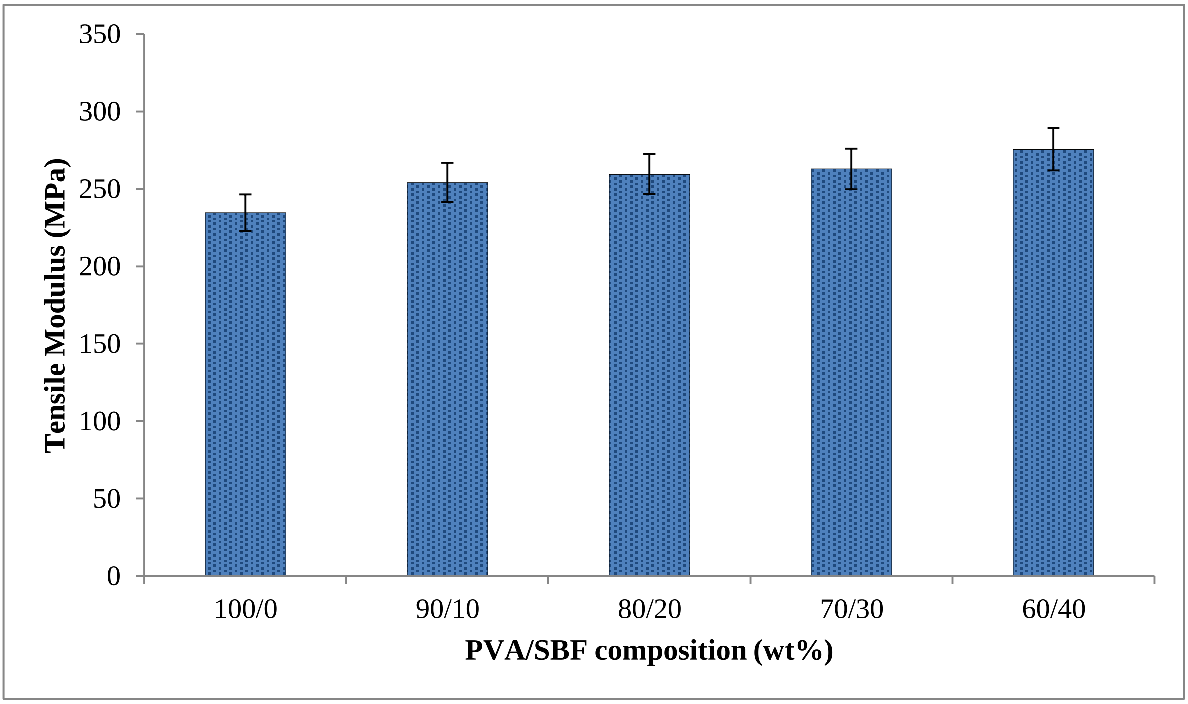


Figure 4.3: Effect of SBF content on the tensile modulus of PVA/SBF blend films.

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4.1.2 Water Absorption

The water absorption characteristic of films was determined by conducted a water absorption test. The tendency of film to absorb moisture cannot be overlooked especially for packaging application because the slight amount of moisture or water can significantly change its properties. Figure 4.4 shows the variation of water absorption of PVA/SBF blend films with different SBF content. The water absorption values increased from 135% to 154%. The increased in water absorption for PVA/SBF blend films, with increasing SBF content was due to the increase in hydrophilicity of the blend films caused by the many hydroxyl groups contained in both PVA and SBF. This was proven by the FTIR results that would be discussed later. Presence of small amount of SBF in the blend film will significantly increase the percentage of water absorption compare to the unfilled PVA film. The reason for this could be attributed by the water sensitivity nature of SBF. This phenomenon of increasing percentage of water absorption with increasing SBF content has been reported previously by Chen *et al*. (1997) on the PVA/starch films. As mentioned by Das *et al*. (2010), the water absorption is also depends on diffusion rate of water molecules through the thickness of the polymer film.

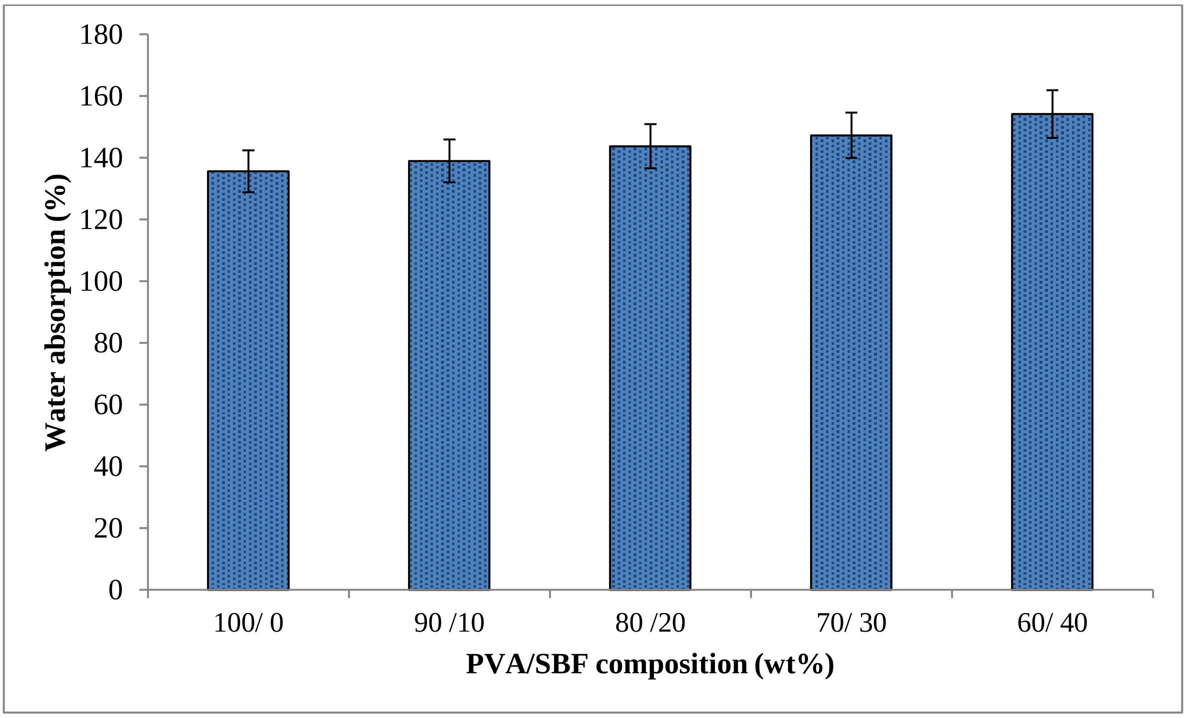

Figure 4.4: Water absorption of PVA/SBF blend films with different SBF content.

4.1.3 Water Vapour Transmission Rate (WVTR)

Water vapour transmission rate (WVTR) is useful to measure the capability of water vapour to pass through the material (Tang *et a*l., 2008). Gontard and Guilbert (1994) mentioned that the WVTR of a hydrophilic film depends on both the diffusivity and solubility of water molecules in the film matrix. The WVTR of the PVA/SBF blend films at different SBF content is shown in Figure 4.5. The results showed a similar trend as the results of water absorption that previously discussed. The WVTR values range from 3.46 to 6.54 ($x10^{-1}$ gh^{-1} m^{-2}) and it is significantly affected by the addition of SBF in the PVA/SBF blend films. This was mainly due to the high sensitivity and hydrophilicity of the SBF in absorbing moisture. In this case, the moisture could act as plasticizer and causes the greater mobility (Tudorachi *et al*., 2000) of the SBF and PVA macromolecules. Thus, it will automatically increase the interchain distance and facilitate the passage of the molecules through the films. Consequently, the presence and content of SBF had increased the WVTR of the PVA/SBF blend films and showed poor water barrier properties.

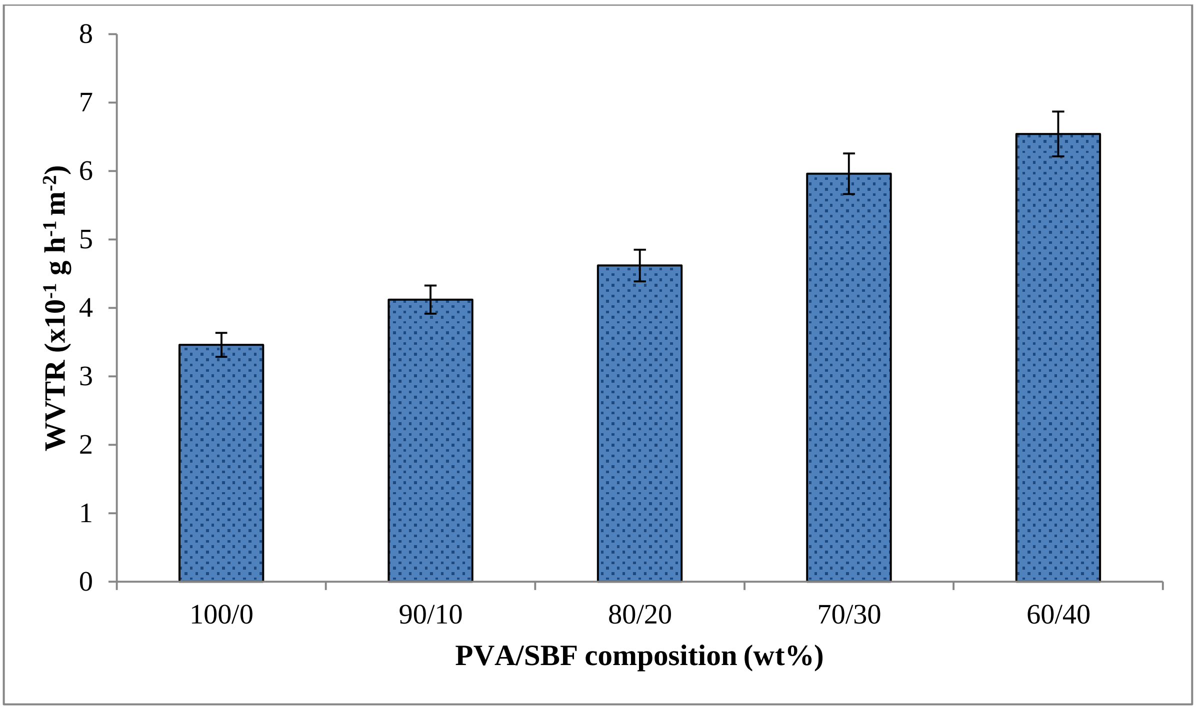

Figure 4.5: Water vapour transmission rate (WVTR) of PVA/SBF blend films with different SBF content.

4.1.4 Fourier Transform Infrared Spectroscopy (FTIR)

In Figure 4.6, FTIR spectra of SBF, unfilled PVA film and PVA/SBF (80/20 wt%) blend films are shown. For SBF spectrum (Figure 4.6(a)), the broad stretching vibration peaks for hydroxyl group appeared at 3369 cm^{-1}. This is due to the presence of aspartic acid and glutamic acid in the SBF (Yan *et al.*, 2004). The peak at 2927 cm^{-1} and 1657 cm^{-1} indicated the existence of alkane and alkene in SBF which were due to the saturated and unsaturated fats in SBF. Peaks from 800 cm^{-1} to 950 cm^{-1} were due to the bending vibration of vinyl C-H out of plane while broad peaks around 700 cm^{-1} were caused by the bending vibration of cis C-H out of plane.

The spectrum of unfilled PVA film (Figure 4.6(b)) show the characteristic of C-H stretching bands at 2910 cm^{-1} and 1327 cm^{-1} and medium strong C-H bending at 844 cm^{-1}. The stretching vibration of hydroxyl groups was observed at 3266 cm^{-1} and asymmetrical vibration peaks of C-O-C occurred at 1141 cm^{-1} and 1087 cm^{-1}. All the characteristics observed were similar as reported by Yin *et al.* (2005) and Ooi *et al.* (2011). Comparing the spectra of SBF and unfilled PVA film, the absorption peaks of the PVA/SBF (80/20 wt%) blend film (Figure 4.6(c)) is almost similar pattern with only a slightly change and shift. The vibration peak of the hydroxyl group appeared at 3266 cm^{-1} (unfilled PVA film) and 3369 cm^{-1} (SBF), but the PVA/SBF (80/20 wt%) blend films show the peak at 3270 cm^{-1}. This indicated that there were weak interactions of different hydroxyl groups occurring between PVA and SBF during the preparation process (Ooi *et al.*, 2011). From all spectra, it can be assumed that the interactions among PVA molecules are dominant and stronger than those for PVA-SBF molecules and SBF-SBF molecules because the blend films show almost similar shape and location of the characteristic peak to those of PVA film (Yin *et al*., 2005; Ooi *et al.*, 2011)

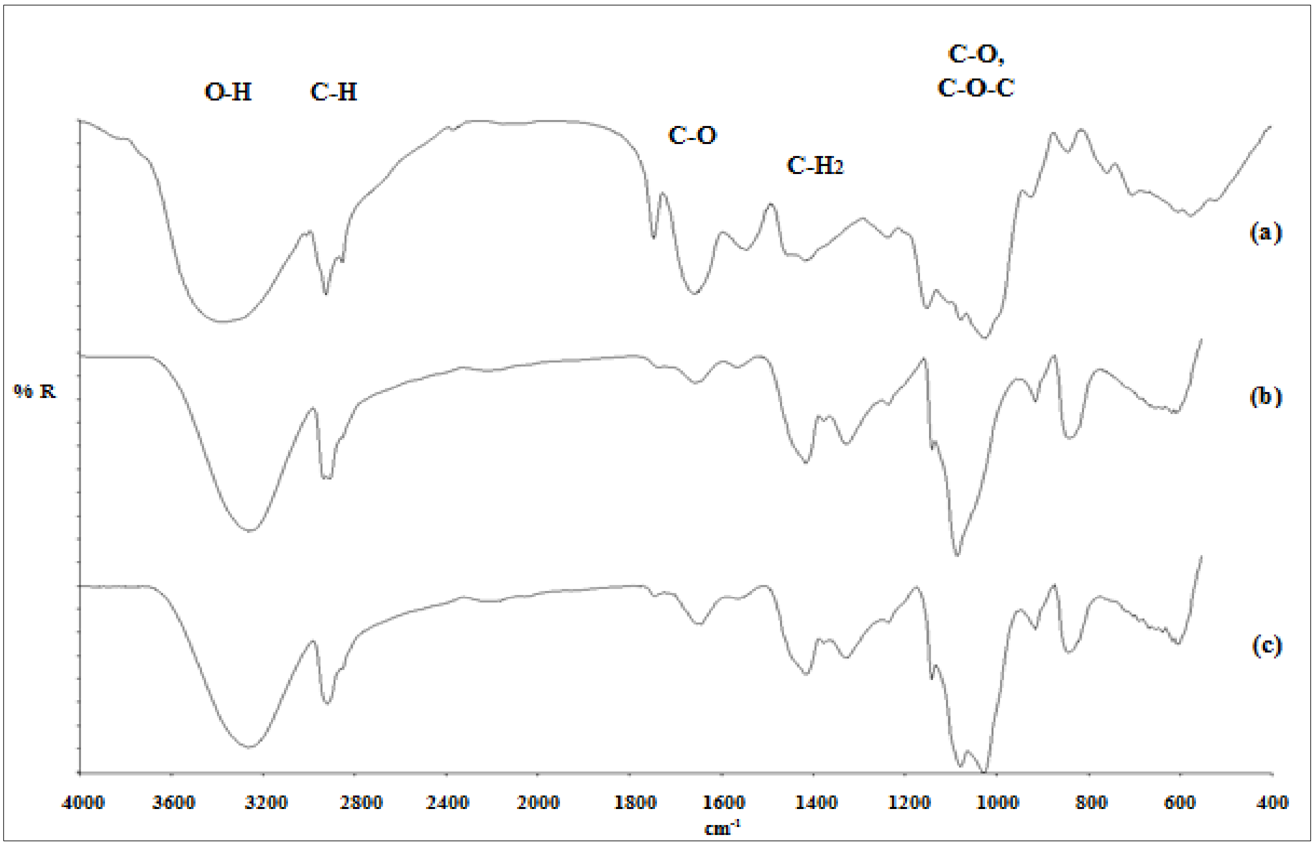

Figure 4.6: FTIR spectra of (a) SBF, (b) unfilled PVA film and (c) PVA/SBF (80/20 wt %) blend film.

4.1.5 Soil Burial Degradation

Soil burial is probably the most appropriate test to examine the biodegradability (Danjaji *et al.*, 2002) of the PVA/SBF blend films. According to Guohua *et al*. (2006), the soil burial test can provide a realistic environment where temperature, pH and humidity are less in control and change with the season by the reduction in the weight. Thus, the unfilled PVA film and PVA/SBF blend films were buried in the soil for 3 months under prevailing environmental conditions. After the burying time, films eventually diminished in size and appeared hard. Film deterioration was also accompanied by loss in their total weight which can be used to determine the biodegradability. It was noted that SBF was more biodegradable than PVA. From Figure 4.7, it can be seen that the PVA/SBF blend films degraded more rapidly than the unfilled PVA in every month. From this figure, it can be seen that the weight loss of the blend film rapidly increased with increasing SBF content in the PVA matrix.

Both PVA and SBF are hydrophilic in nature, thus the water molecules in soil tends to diffuse into the film and allowing the microorganisms to grow and utilize it. Finally, it results in weight loss and disruption of the films. In general, all PVA/SBF blend films lost almost 20% of their original weight and indicated that they degraded more than the PVA film. This is due to the presence of carbohydrate content in SBF which had contributed to the increase in the rate of film deterioration. This finding is similar to Shi *et al*. (2009) in their studies on degradation of starch/PVA films.

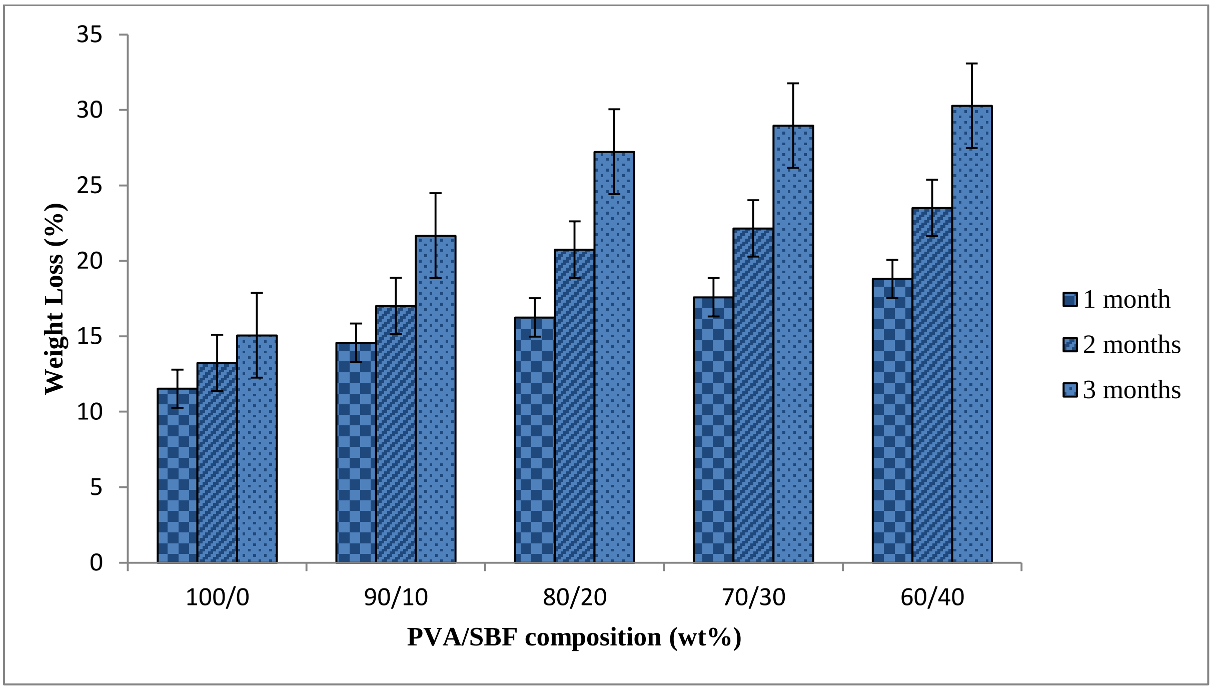

Figure 4.7: Weight loss of unfilled PVA film and PVA/SBF blend films at different weight ratio during biodegradation natural soil conditions.

The surface morphologies of unfilled PVA and PVA/SBF (80/20 wt%) blend film, before and after biodegradation are shown in Figure 4.8 and 4.9, respectively. Before the degradation, the PVA film has a smooth surface (Figure 4.8(a)) while the PVA/SBF blend film has some SBF particles on the rough surface (Figure 4.9(a)). But, after buried in soil for 3 months, both film surfaces show a rough and indicating some deterioration (Figure 4.8(b)) and (Figure 4.9(b)).

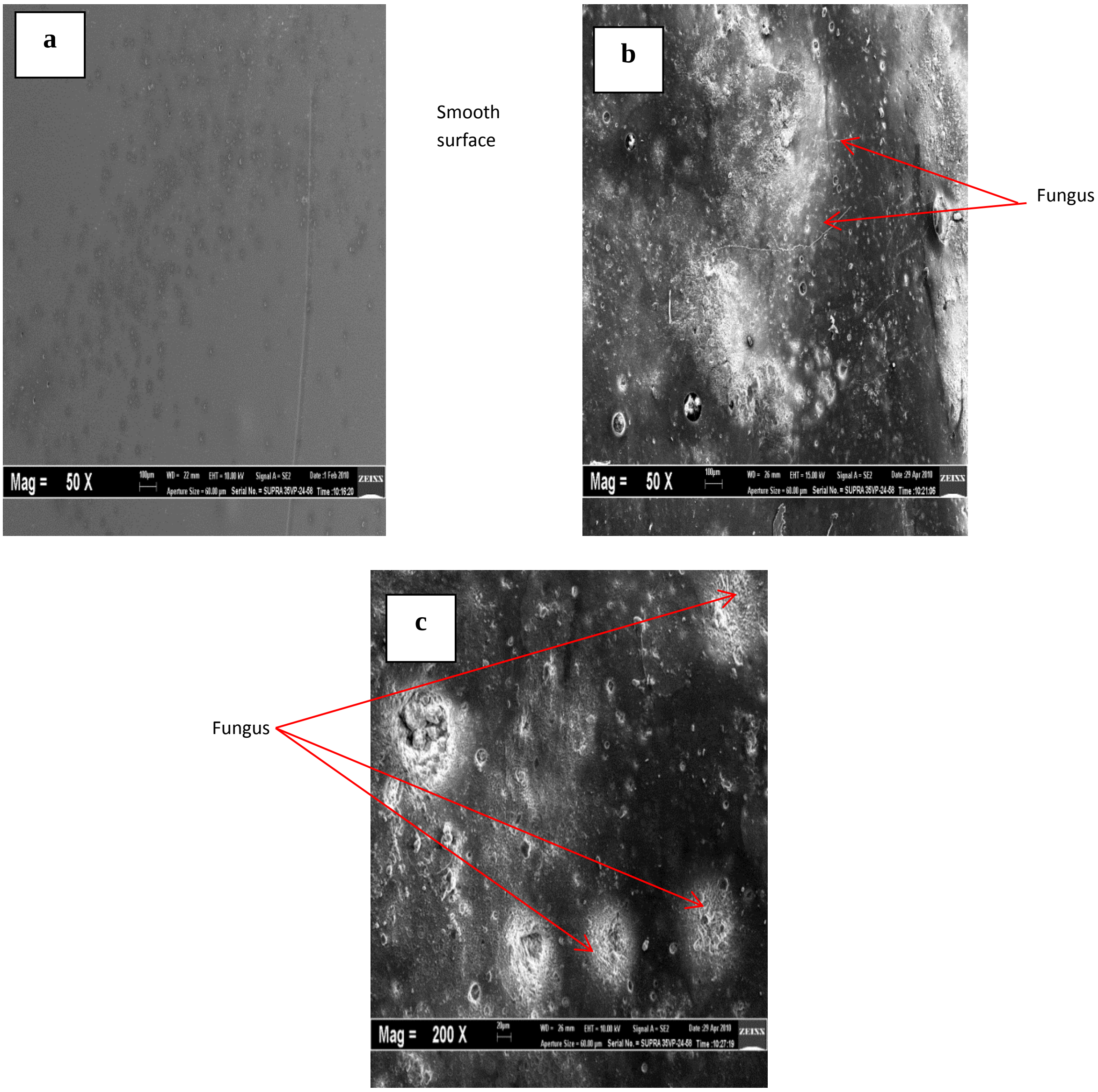

Figure 4.8: SEM images scanned from the surface of unfilled PVA film (a) before and (b) after 3 months; (c) detailed micrograph at 200X magnification after 3 months burial in natural soil conditions.

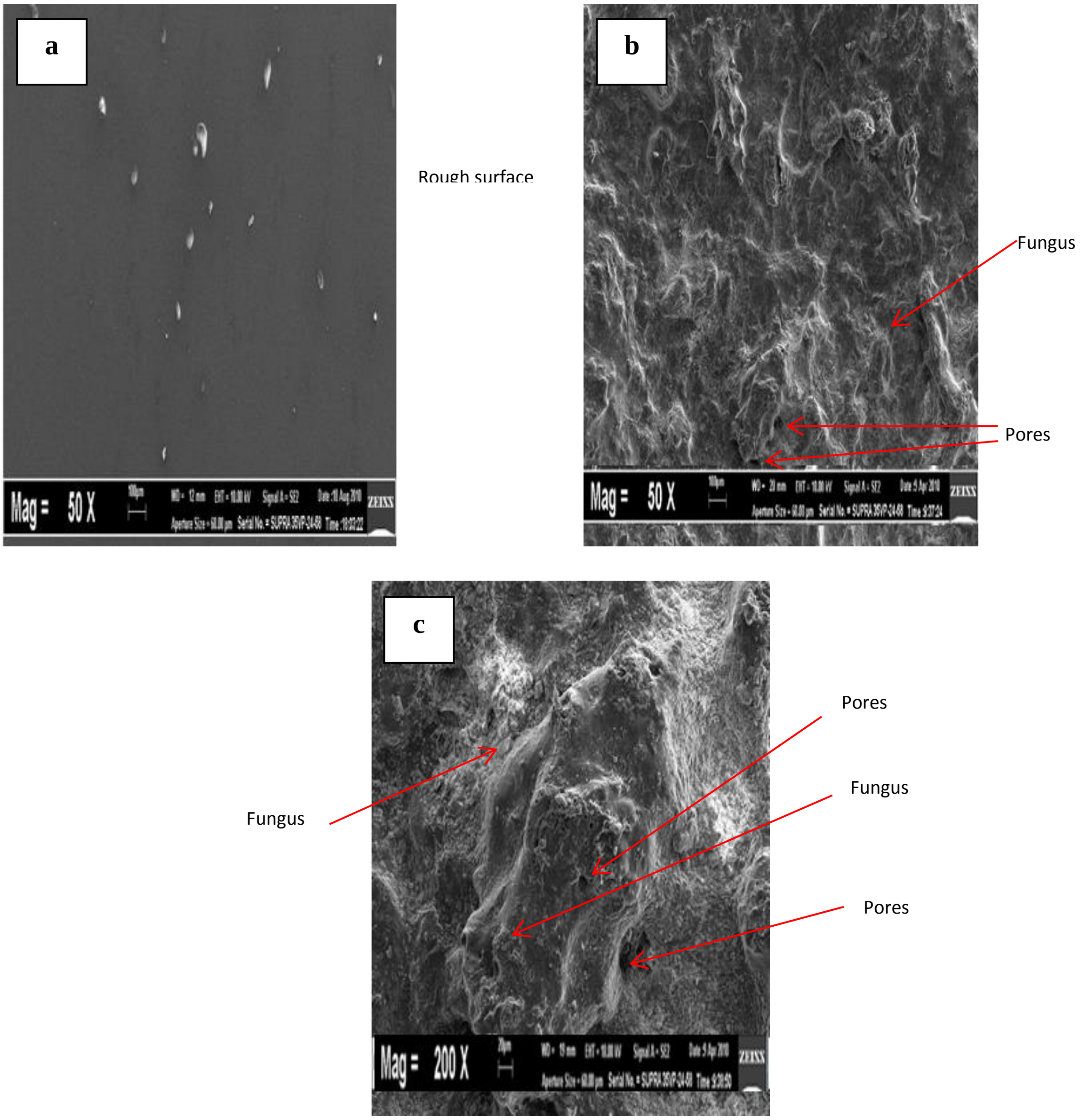

Figure 4.9: SEM images scanned from the surface of PVA/SBF (80/20 wt%) blend film (a) before and (b) after 3 months; (c) detailed micrograph at 200X magnification after 3 months burial in natural soils conditions.

4.1.6 Natural Weathering

Natural weathering is one of the degradation tests used by most of researchers to examine the degradation rate. Figure 4.10 shows the weight loss of unfilled PVA and PVA/SBF blend films after being subjected to natural weathering for 3 months. After subjected to natural weathering, all the films were found to be highly deteriorated with a reduction value of weight. In general, all PVA/SBF blend films lost almost 25% of their original weight which is better than the unfilled PVA film. The reduction in weight of the unfilled PVA film might be attributed to the photo-oxidation of UV exposure and hydrolysis cause by the rainfall and dew. Recall that the PVA contains hydroxyl groups tend to absorb water due to the effect of raining and thus resulting in hydrolysis depolymerisation. Bastioli (2005) mentioned the long polymer chain was converted into oligomer fragments due to hydrolysis depolymerisation process. With addition of SBF into PVA blend, the weight loss of the PVA/SBF blend films were further increased after 3 months expose to natural weathering. The weight loss of the PVA/SBF blend films increased as the increasing of SBF content. Based on previous FTIR spectra of SBF, there was hydroxyl groups which similar with PVA that prone to water absorption. Recall that the natural weathering test was conduct on the hot and wet tropical climates. Thus, the blend films get moistened by raining and dried by sunlight. Beside, this may be attributed to the combination of two or more antagonistic factors such as sunlight, UV radiation, rainfall, heat, wind, moisture, humidity and etc. Schiers (2000) and Yew *et al.* (2009) reported that these factors lead to the embrittlement or catastrophic failure of the product once it was exposed to natural weathering.

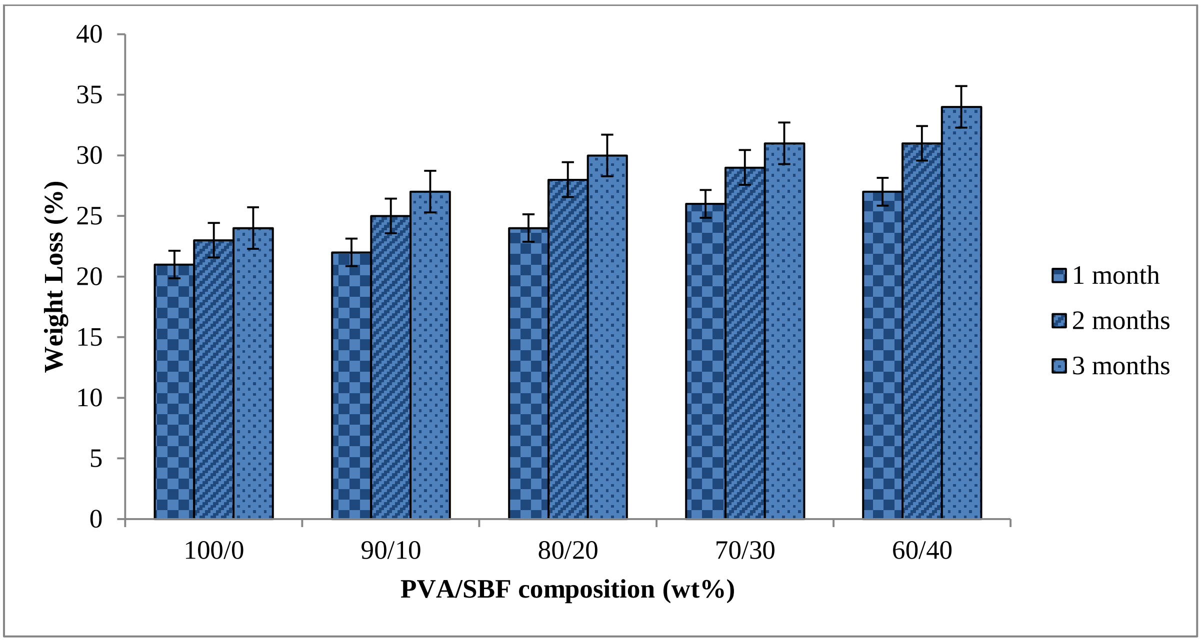

Figure 4.10: Weight loss of unfilled PVA film and PVA/SBF blend films at different weight ratio after exposure to natural weathering for ups to 3 months.

Further evidence of the degradation of PVA and PVA/SBF blend films was provided by the SEM micrographs. Figs. 4.11 and 4.12 show the SEM micrograph of PVA and PVA/SBF blend films after 1 month of natural weathering. Severe deterioration occurred on the surface of both PVA and PVA/SBF blend films, and cracks in Figure 4.12 (b) are more widely spread throughout the surface compared to the PVA film in Figure 4.11 (b) and this correlates with the reduction of tensile properties of the films.

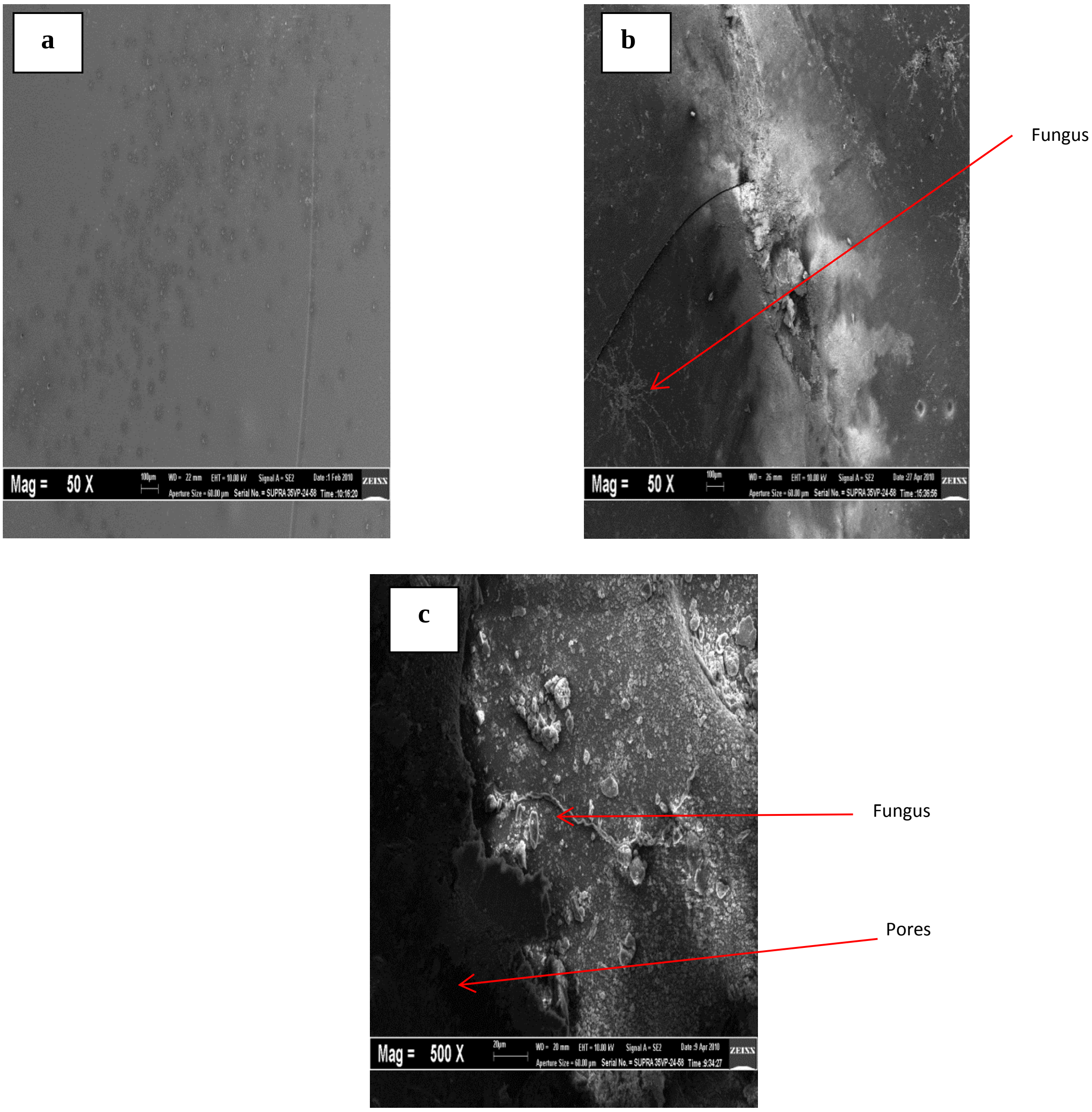

Figure 4.11: SEM images scanned from the surface of unfilled PVA film (a) before and (b) after 3 months of exposure to natural weathering; (c) detailed micrograph at 500X magnification after 3 months of exposure to natural weathering.

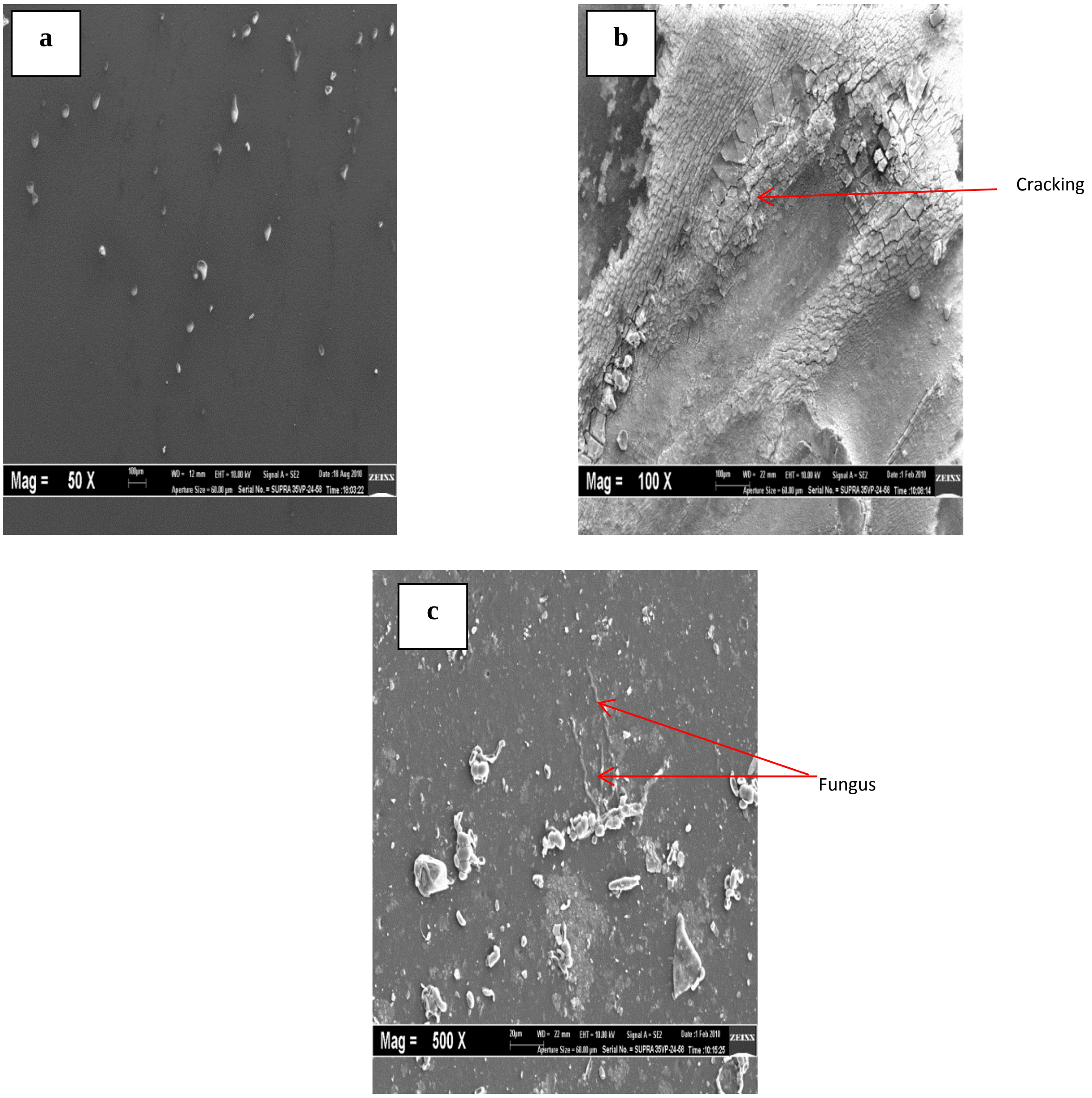

Figure 4.12: SEM images scanned from the surface of PVA/SBF20 blend film (a) before and (b) after 3 months of exposure to natural weathering; (c) detailed micrograph at 500X magnification after 3 months of exposure to natural weathering.

4.2 Effect of Crosslinker on the Properties of Polyvinyl Alcohol/Soya Bean Flour (PVA/SBF) Blend Films

The adding of crosslinking agent is a common practice in polymer science to enhance the physical properties of the film. In this research, the effect of crosslinking agent, hexamethylenetetramine (HMTA) in the polymer blend was investigated in term of tensile properties, water absorption, water vapour transmission rate, Fourier transform infrared (FTIR), natural weathering test, soil burial test and morphology analysis.

4.2.1 Tensile Properties

The tensile properties of PVA/SBF blend films with and without the addition of HMTA are shown in Figure 4.13 to Figure 4.15. According to Morreale *et al.* (2008), tensile strength is the maximum tensile stress sustained by the sample during tension test and elongation at break is an indication of the samples flexibility and stretchability. As shown in Figure 4.13, the tensile strength of non-crosslinked PVA/SBF blend films gradually decreased as increasing SBF content from 46.5 MPa to 16 MPa. This was due to the weak intermolecular hydrogen bonding between PVA and SBF. However, with the addition of crosslinker the similar trend also can be observed on tensile strength of the crosslinked PVA/SBF blend films (decreased from 47.5 MPa to 18.8 MPa). But, between the non-crosslinked and crosslinked films, the crosslinked films have slightly higher tensile strength over the crosslinked films. The increased in tensile strength for crosslinked films was due to the covalent bonding between SBF and PVA formed after addition of HMTA. This proved that the presence of HMTA as a crosslinker able to form strong covalent bonding that required additional force to break the film.

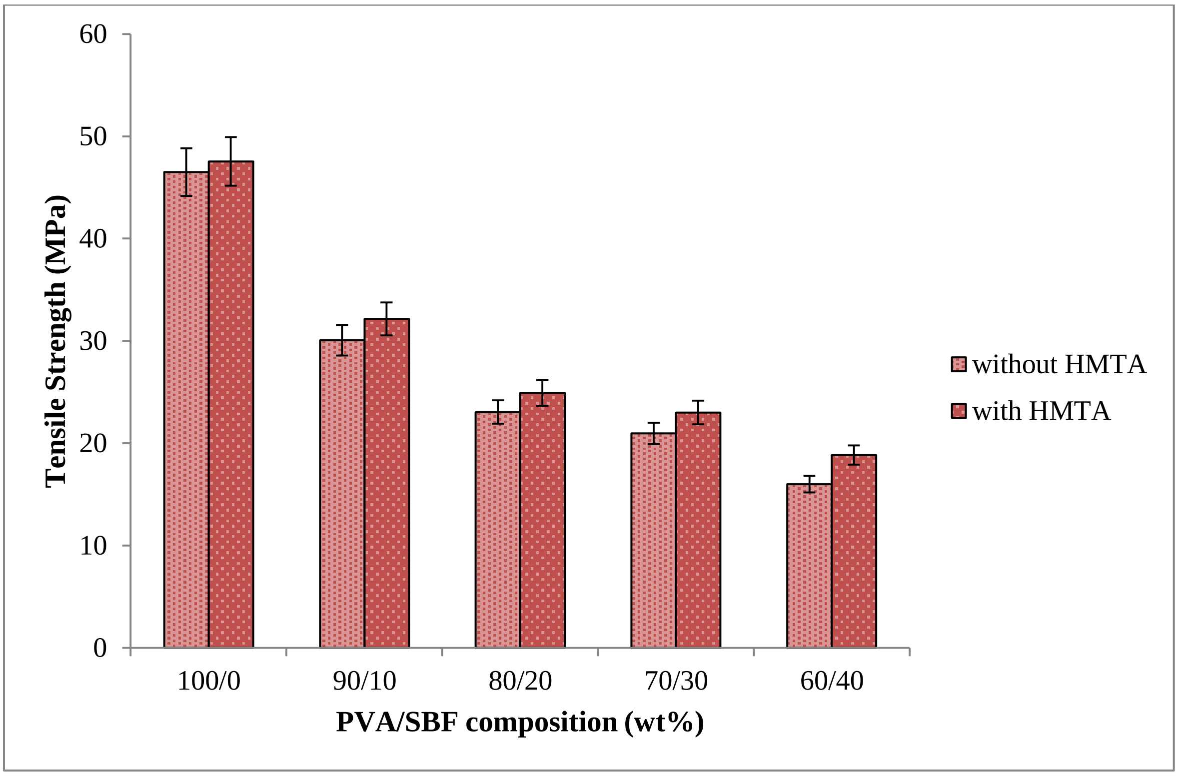

Figure 4.13: Effect of crosslinking agent on the tensile strength of PVA/SBF blend films.

Elongation at break of crosslinked and non-crosslinked PVA/SBF blend films were investigated. Both blend films show a decreasing trend of elongation at break as increasing SBF content. From Figure 4.14, it can be seen that the elongation at break of non-crosslinked PVA/SBF blend films decreased from 158.7% to 103.1% while the elongation at break of crosslinked PVA/SBF blend films decreased from 157.3% to 109.3%. Reduction in elongation at break was attributed to the increase of brittleness in the films. This was due to less of effective cross sectional area of the PVA continuous phase (Ramaraj, 2007). In addition, the poor interaction between SBF and PVA gives rise to weak interfacial regions and will permits easier crack propagation. Thus, the films have lower elongation at break value at higher SBF content. Elongation at break of crosslinked PVA/SBF blend films shows better value as compared to the non-crosslinked PVA/SBF blend films and this is because of the effectiveness of HMTA used in this study. Anis *et al.* (2008) has reported that the formation of a crosslinked network which restricted the mobility of the polymer chain.

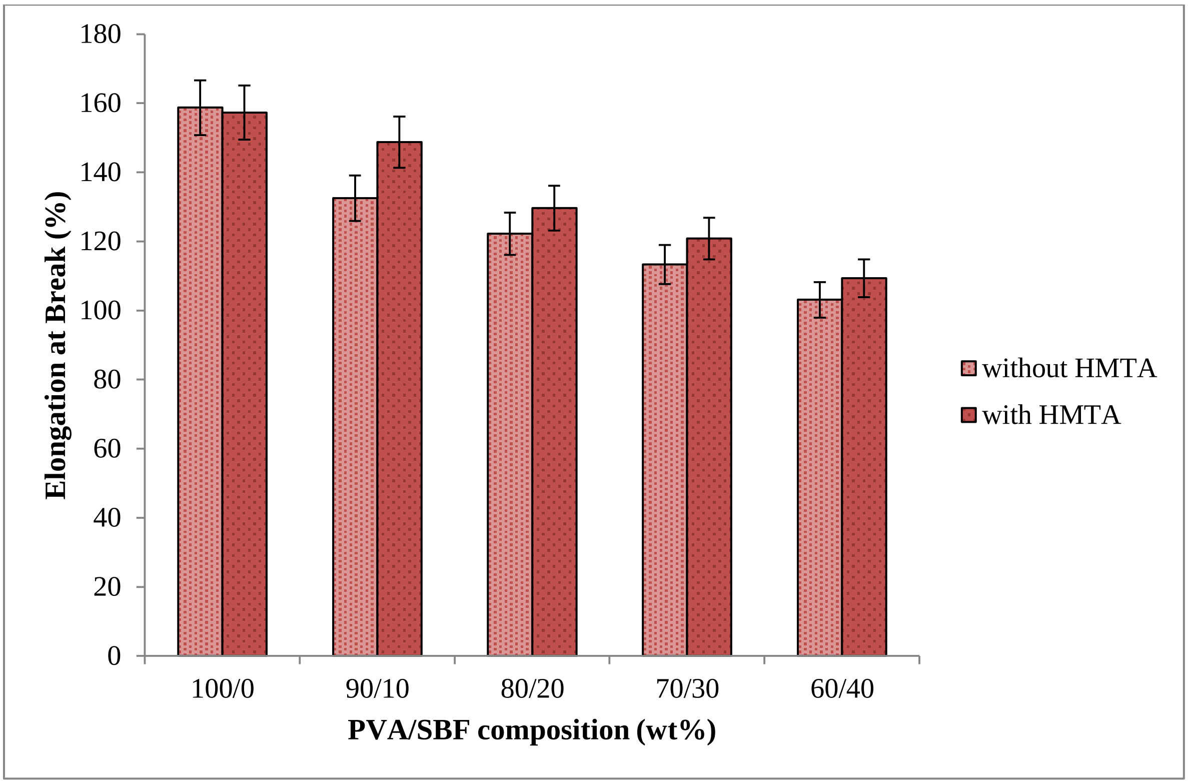

Figure 4.14: Effect of crosslinking agent on the elongation at break of PVA/SBF blend films.

The variation of tensile modulus with SBF content of the PVA/SBF blend films is shown in Figure 4.15. For both non-crosslinked and crosslinked PVA/SBF blend films, the tensile modulus increased from 234.6 MPa to 275.6 MPa and from 250.8 MPa to 280.9 MPa respectively. The increment of tensile modulus after addition of SBF was attributed by the stiffening effect (Ramaraj, 2007 and Vandelli *et al.*, 2001) of SBF granules. In comparison, crosslinked blend films have better tensile modulus compared to the non-crosslinked blend films because both HMTA and SBF had a positive effect on tensile modulus. In the blend, molecular mobility of PVA chain is restricted by rigid SBF granules, which have high modulus and covalent HMTA bonding at the interface. The high resistance of PVA molecules to stretch the film resulted in a higher tensile modulus. Huang and Netravali (2007) reported that stiffness of the film increased due to the crosslinking restriction of the molecular motion and reduction of the free volume. Further evidence of the interaction between PVA and SBF in the presence of HMTA is discussed later in FTIR spectroscopy results.

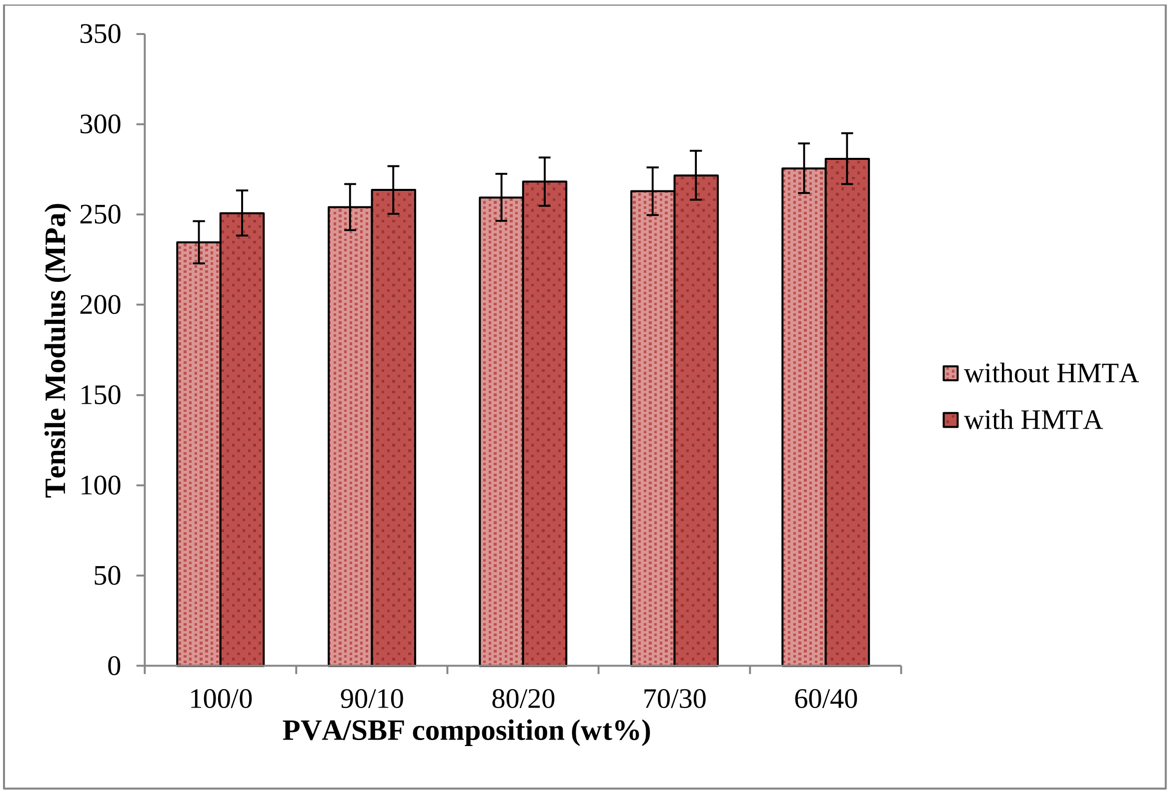

Figure 4.15: Effect of crosslinking agent on the tensile modulus of PVA/SBF blend films.

4.2.2 Water Absorption

The water absorption capacity and the degradability are the most important properties for biodegradable materials (Arajuo *et al*., 2004). Figure 4.16 illustrates the effect of crosslinker on the water absorption of the PVA/SBF blend films. It could be observed that the water absorption of the crosslinked PVA/SBF blend films was slightly lower than the non-crosslinked PVA/SBF blend films. It was attributed by the crosslinking reaction by HMTA (Ooi *et al*., 2012) as a crosslinking agent. This reaction could decrease the interchain distance as well as to improve their water barrier properties. According to Elizando *et al*. (2000), the capacity of the polymer film to absorb water was reduced because of the strong interaction between two polymers and homogenisation of the blends. Besides, Zou *et al*. (2007) and Das *et al*. (2010) also mentioned that the crosslinking reaction could decrease the interchain distance as well as reduce their water absorption behaviour. Based on the resulted shown in Figure 4.16, the incorporation of HMTA was effective to reduce the interchain distance due to covalent bonding formed between the filler and matrix. Thus reducing the water/moisture from penetration into the crosslinked blend films. Huang and Netravali (2007) reported that the crosslinked structure of crosslinked soy protein resin reduced the moisture sensitivity due to the reduction of the hydrophilic group in the composite.

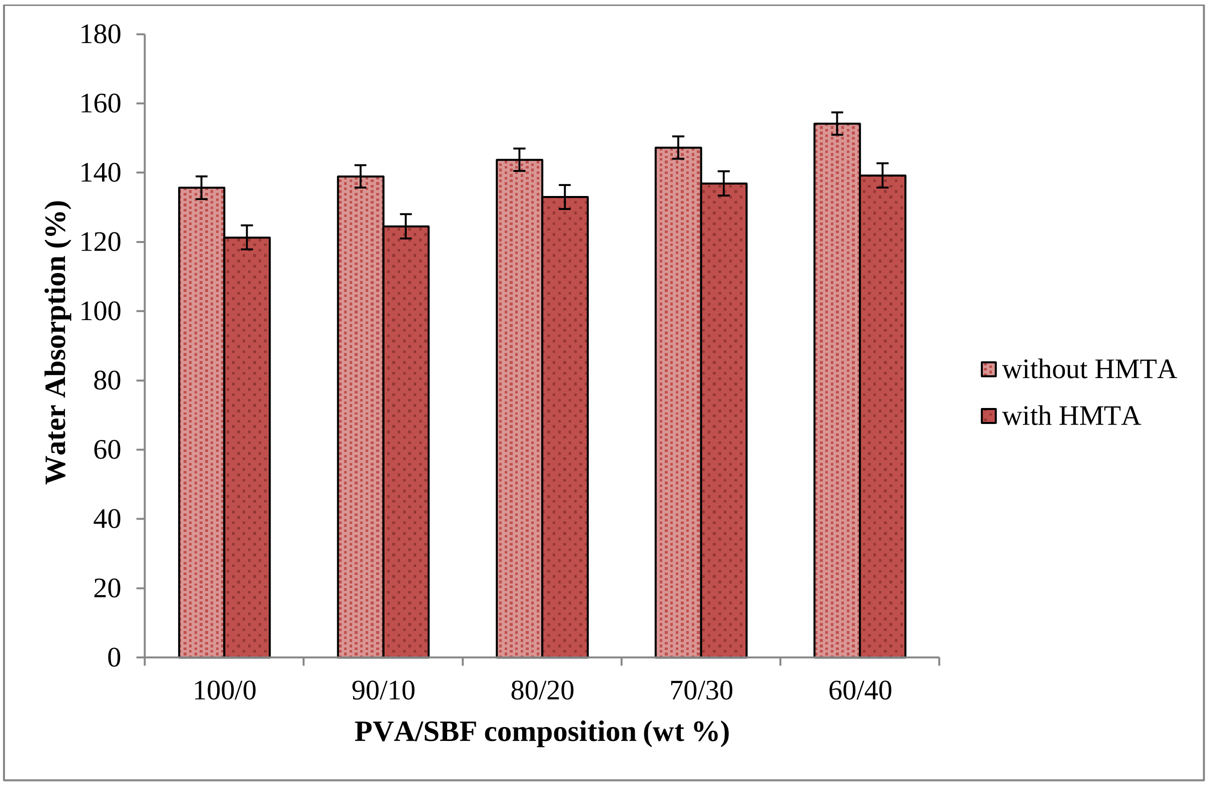

Figure 4.16: Water absorption of PVA/SBF blend films with and without addition of crosslinking agent.

4.2.3 Water Vapour Transmission Rate (WVTR)

Based on the Figure 4.17, the WVTR of non-crosslinked PVA/SBF blend films increased with increasing SBF content. However, with the presence of HMTA, the WVTR of the crosslinked PVA/SBF blend films decreased with increasing SBF content. This is due to the effectiveness of HMTA in strengthened and reduced the interchain distance of PVA and SBF. Thus, the water vapour molecules were having some difficulties to diffuse via the films and resulting better water barrier properties. Zhou *et al*. (2008) mentioned that generally, in the crosslinked structure, the crosslinking points restrict the molecular mobility of the polymer chains.

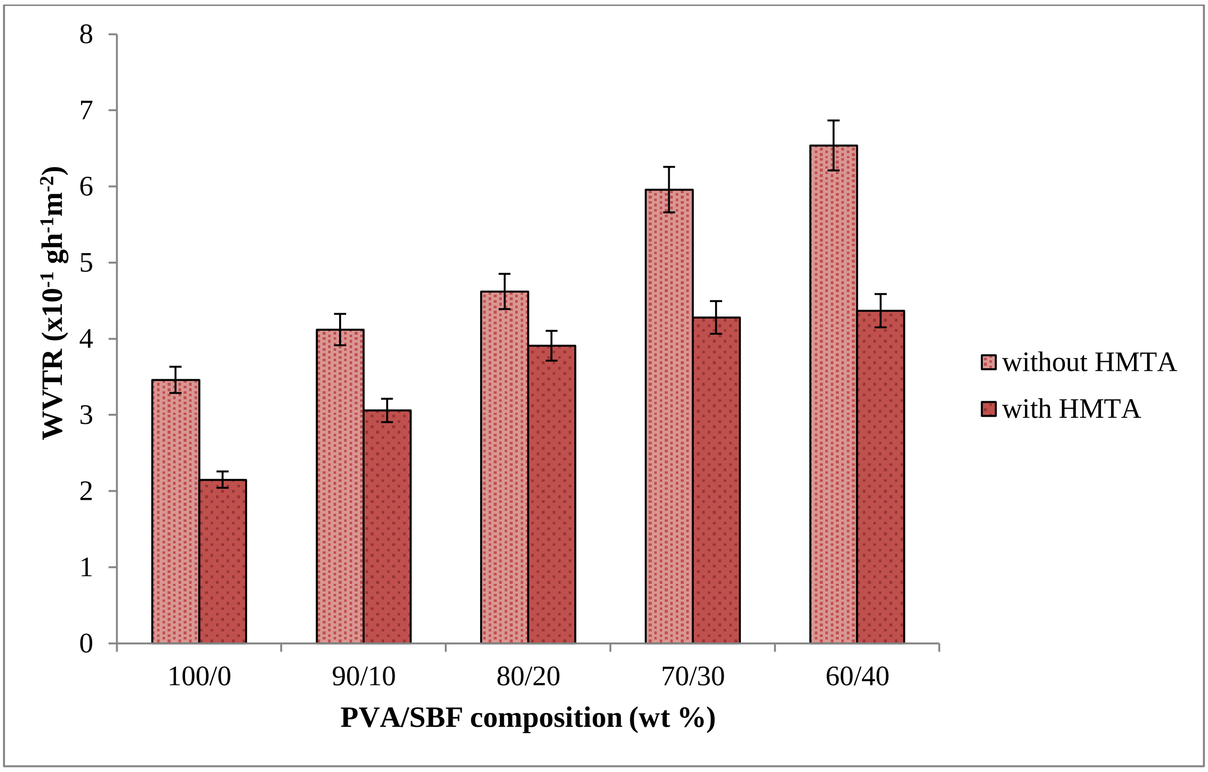

Figure 4.17: Water vapour transmission rate (WVTR) of PVA/SBF blend films with and without addition of crosslinking agent.

4.2.4 Fourier Transform Infrared (FTIR)

The spectra of the crosslinked films were studied and compared with the non-crosslinked films. The major characteristic bands that observed in all the spectra (Figure 4.18) were hydroxyl groups, methyl groups, amine groups, carbonyl groups and ether groups. The non-crosslinked PVA film spectra (Figure 4.18 (a)) show the stretching vibration of hydroxyl groups at 3266 cm^{-1}, C-H stretching bands at 2910 cm-^{1} and 1327 cm^{-1} and medium strong C-H bending at 844 cm^{-1}. The vibration peaks of C-O-C as reported by Ooi *et al.* (2011) and Yin *et al.* (2005) also can be observed at 1141 and 1087 cm^{-1}.

As compared to the FTIR spectra of Figure 4.18 (a) and (b), there is no occurrence of new peak that can be observed on the FTIR spectra of crosslinked PVA (Figure 4.18 (c)) and PVA/SBF40 (Figure 4.18 (d)) blend film except for the different in band intensities. Presence of HMTA shows that the intensities and characteristic peaks were found to be sharper and stronger. This was due to the crosslinking effect that built or formed new structure of hydrogen bonding. In Figure 4.18 (c) and (d), the stronger and broader band around 3280 and 3278 cm^{-1}, respectively were due to the association of hydrogen bonds with the stretching vibrations of N-H. Sharper peak intensities around 1084 cm^{-1} could be attributed by an increase of intermolecular bonding of C-O in the C-O-C groups.

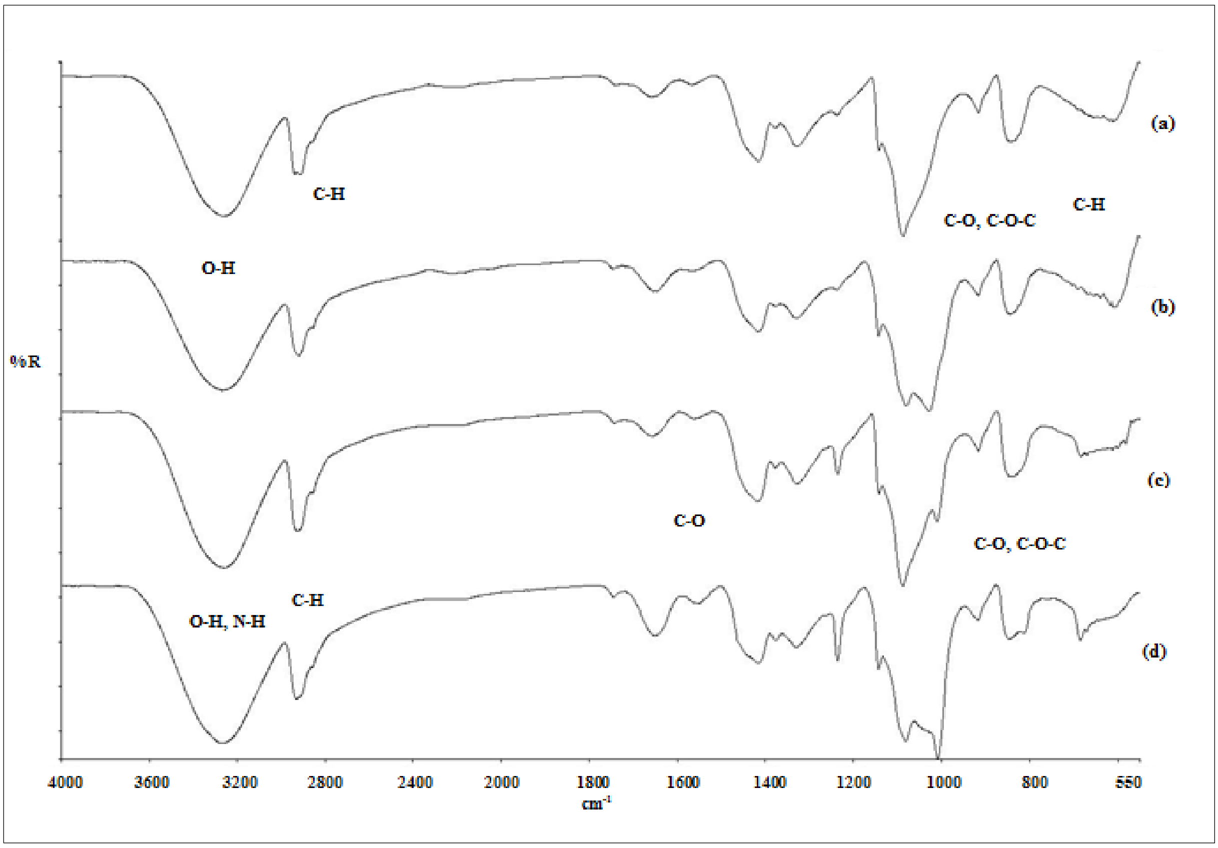

Figure 4.18: FTIR spectra of the (a) PVA film without HMTA, (b) PVA/SBF20 blend film without HMTA, (c) PVA film with HMTA, and (d) PVA/SBF20 blend film with HMTA.

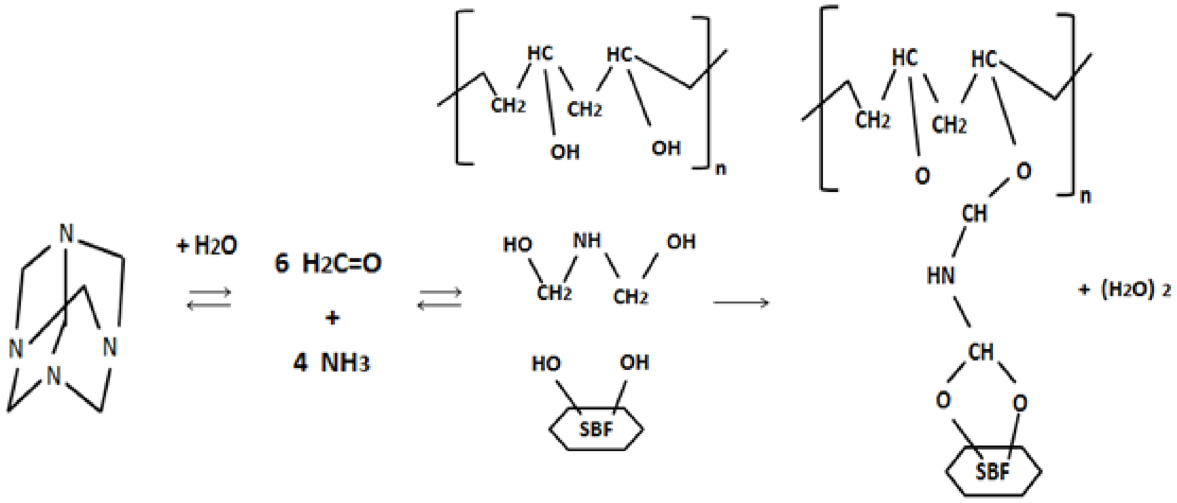

Figure 4.19: Possibly interaction between PVA and SBF through HMTA.

4.2.5 Soil Burial Degradation

Soil burial test could provide realistic environment where pH, temperature and humidity are less in control and change with season (Guohuo *et al*., 2006). Rutkowska *et a*l. (2000) demonstrated that the different conditions should have an effect on the process of biodegradation of polymer samples because the parameters such as pH, temperature and humidity have a significant effect of living microorganism, thus caused the biodegradation to occur. The results of the weight loss of unfilled PVA film and PVA/SBF blend films in the presence of HMTA crosslinking agent compared to the non-crosslinked blend films are shown in Figure 4.20. As expected, the SBF was more rapidly biodegraded compared to the PVA. As can be seen from Figure 4.20, weight losses of all the buried films are increased with the degradation time.

From the Figure 4.20, crosslinked PVA/SBF blend films show an increase of weight loss during the burial time, but its lower than non-crosslinked PVA/SBF blend films. The lower weight loss for the crosslinked PVA/SBF blend films was due to the crosslinking effect and water absorption capacity, which were further proved by SEM observation. In addition, both PVA and SBF had overall hydrophilic properties and tends to absorb water. Thus, moist environment enable will enable more microorganisms to survive, growth and able to break down the biopolymers by enzymes (Khachatourians and Qazi, 2008).

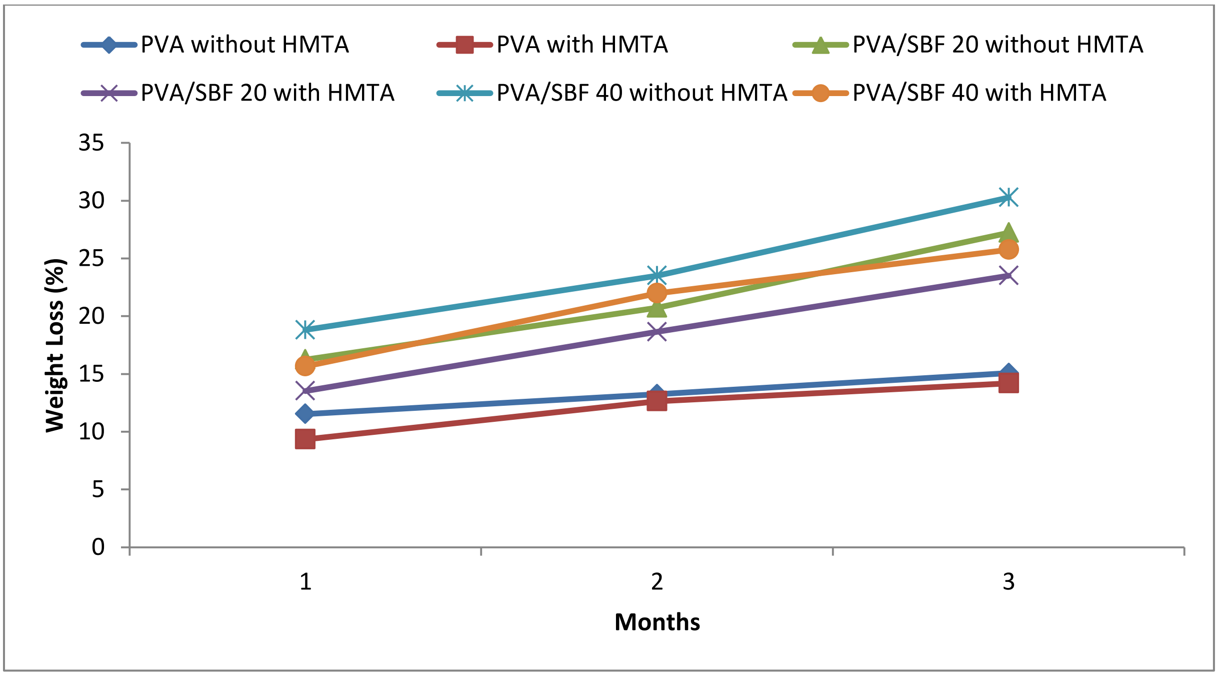

Figure 4.20: The weight loss of PVA and PVA/SBF blend film with and without HMTA crosslinking agent during biodegradation in natural soil burial test.

The SEM micrograph on the surface degradation of PVA/SBF blend films without and with HMTA were shown in Figs 4.21 and 4.22, respectively. During degradation time, the traces of soil could be observed on the buried PVA/SBF blend films. But the microorganism was not observed on the SEM micrograph because the microorganism might be removed during the sanitizing purpose. The surface cracks, holes could be observed on the surface of all the buried PVA/SBF40 blend films. This was due to the natural soil environment effect that causing the buried PVA/SBF blend films was deteriorated to swell and shrink. However, the surface degradation occurred on the non-crosslinked PVA/SBF40 blend films were deteriorated more than the crosslinked PVA/SBF40 blend films. As can be seen from Figure 4.21 (c), the cracks and holes were bigger than crosslinked PVA/SBF40 blend films. Since the weight loss for the non-crosslinked PVA/SBF blend films was highest compared to others after 3 month of buried time, it can be conclude that the non-crosslinked PVA/SBF blend films able to delayed the natural soil environment effects.

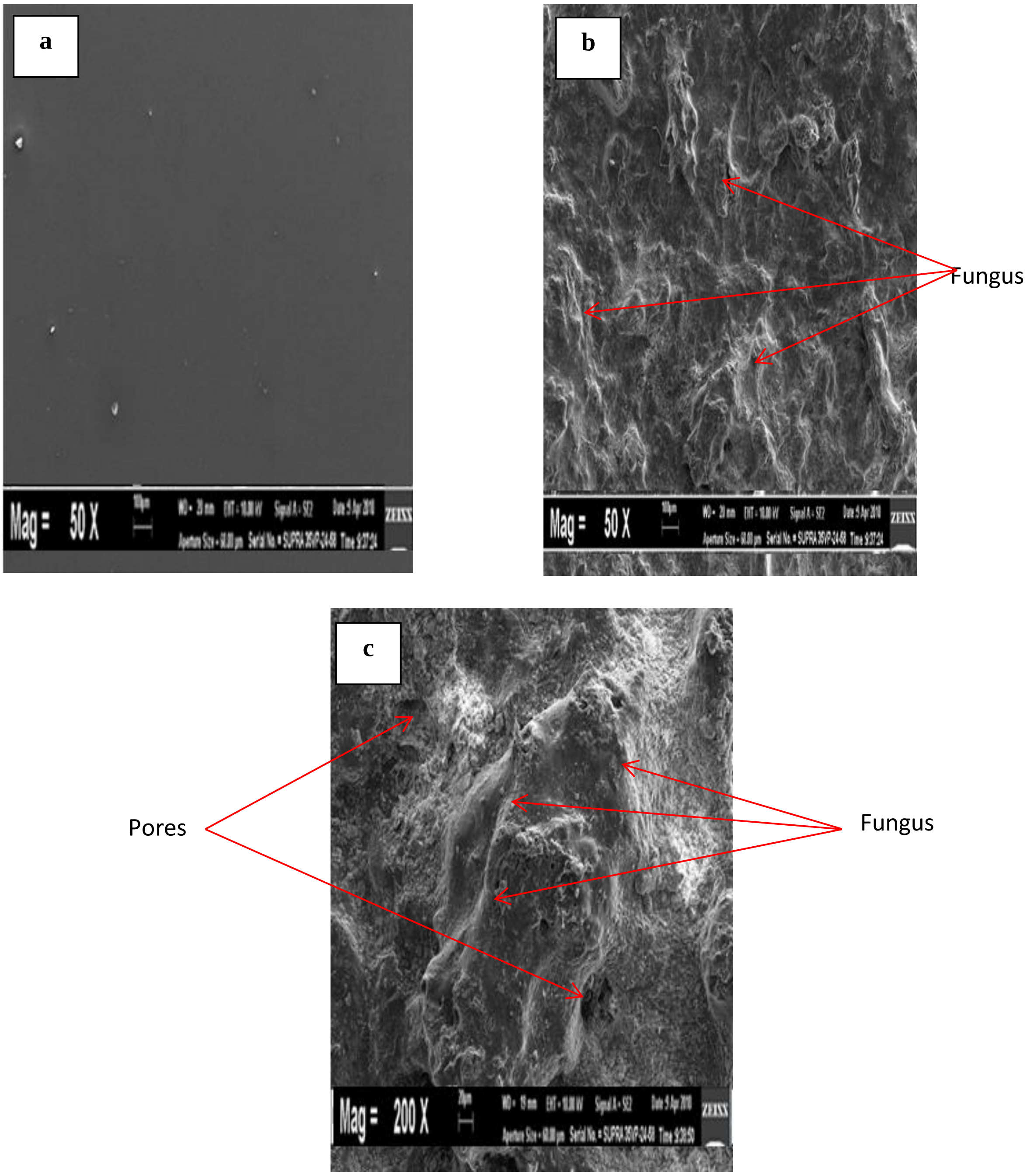

Figure 4.21: SEM images scanned from the surface of non-crosslinked PVA/SBF40 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 200x magnification after 3 months burial in natural soil conditions.

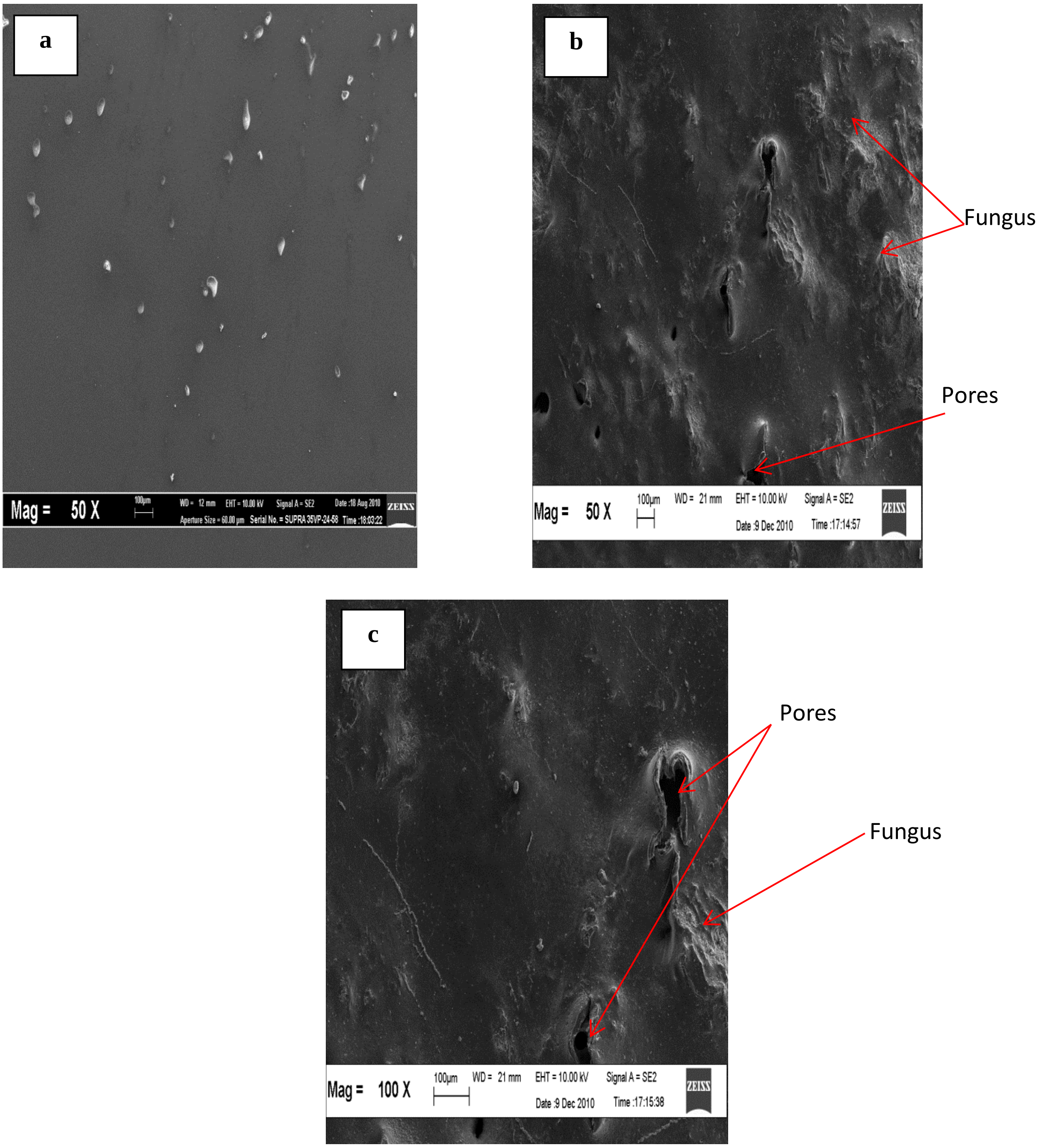

Figure 4.22: SEM images scanned from the surface of crosslinked PVA/SBF40 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 100x magnification after 3 months burial in natural soil conditions.

4.2.6 Natural Weathering

The unfilled PVA and PVA/SBF blend films with and without crosslinking agent were exposed to natural weathering and the ability to with stand the environment effects such as rain fall, sunlight, dew, wind and etc was determined by evaluating the weight loss of the films after subjected to natural weathering test. Based on the experimental results shown in Figure 4.23, the weight loss for non-crosslinked and crosslinked unfilled PVA and PVA/SBF blend films upon subjected to natural weathering tend to increase significantly and further deteriorated with the longer time of exposure.

According to Yew et al. (2009), the natural weathering usually involves the combined effect of two or more degradation phenomenon. This will results in the deterioration of the polymer's mechanical properties and leading to embrittlement and catastrophic failure to the polymer's product. Lower strength of the PVA/SBF blend films with higher SBF content previously discussed under tensile properties show that this blend films could not withstand the environmental effect such as rainfall and winds that act as external forces to deteriorate the weak PVA/SBF blend films with higher SBF content. This could explain the increment of weight loss of crosslinked and non-crosslinked PVA/SBF blend films with higher SBF content after exposure to natural weathering as shown in Figure 4.23. The reduced weight may be attributed to the surface cracking and degradation as result of chain scission. This was an agreement with the morphology observation on the exposed surface in which showed the formation of cracks and pore in Figure 4.24 and 4.25.

Recall that PVA and SBF are hydrophilic and containing plenty of hydroxyl groups, whereas HMTA linkages could be hydrolyzed under acidic conditions, pH 5.6 – 6.5 (Blank *et al.*, 1997). Thus, raining was caused the crosslinked and non crosslinked blend films tend to absorb the rain water and resulting in hydrolysis depolymerisation process. Again, as mentioned previously, the crosslinked and non-crosslinked blend films will undergo *thermal cycles effect* (swell during rains and shrink under sunlight), thus the surface cracking occurred and leading in reduction in weight for both crosslinked and non-crosslinked blend films. In short, addition of HMTA crosslinking agent did not significantly affect the weatherability of for both PVA and PVA/SBF blend films when exposed to weathering as compared to the non-crosslinked films.

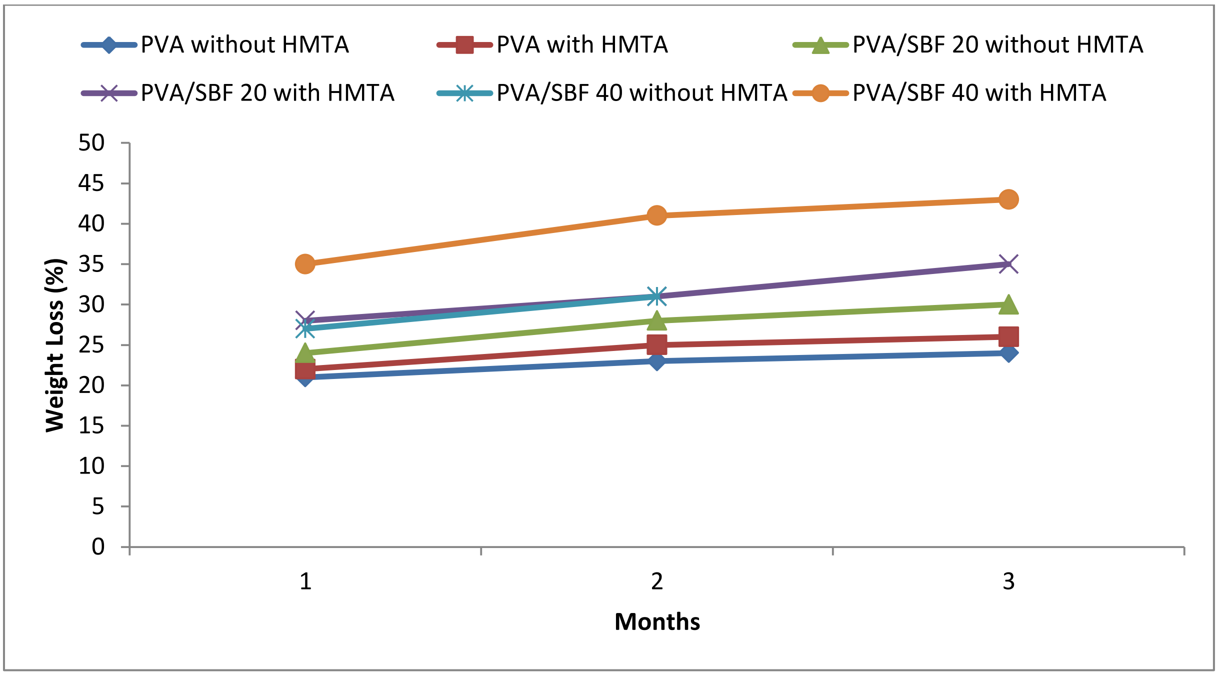

Figure 4.23: The weight loss of PVA and PVA/SBF blend film with and without HMTA crosslinking agent after exposure to natural weathering.

In order to examine the surface degradation on the PVA/SBF blend films in the presence of HMTA crosslinking agent after being subjected to natural weathering, the SEM micrographs were taken from weathered specimen surface of non-crosslinked and crosslinked PVA/SBF 40 blend films were shown in Figure 4.24 and 4.25, respectively. It could be clearly seen that severe surface deterioration occurred on all weathered PVA/SBF blend films. Interestingly, the microorganisms, surface cracks, and holes were observed by SEM. According to Yew *et al*. (2009), variety of microorganism tends to attack and grow on the biodegradable plastic product, especially in the warm humid climate and causing the degradation of tensile properties and product failure.

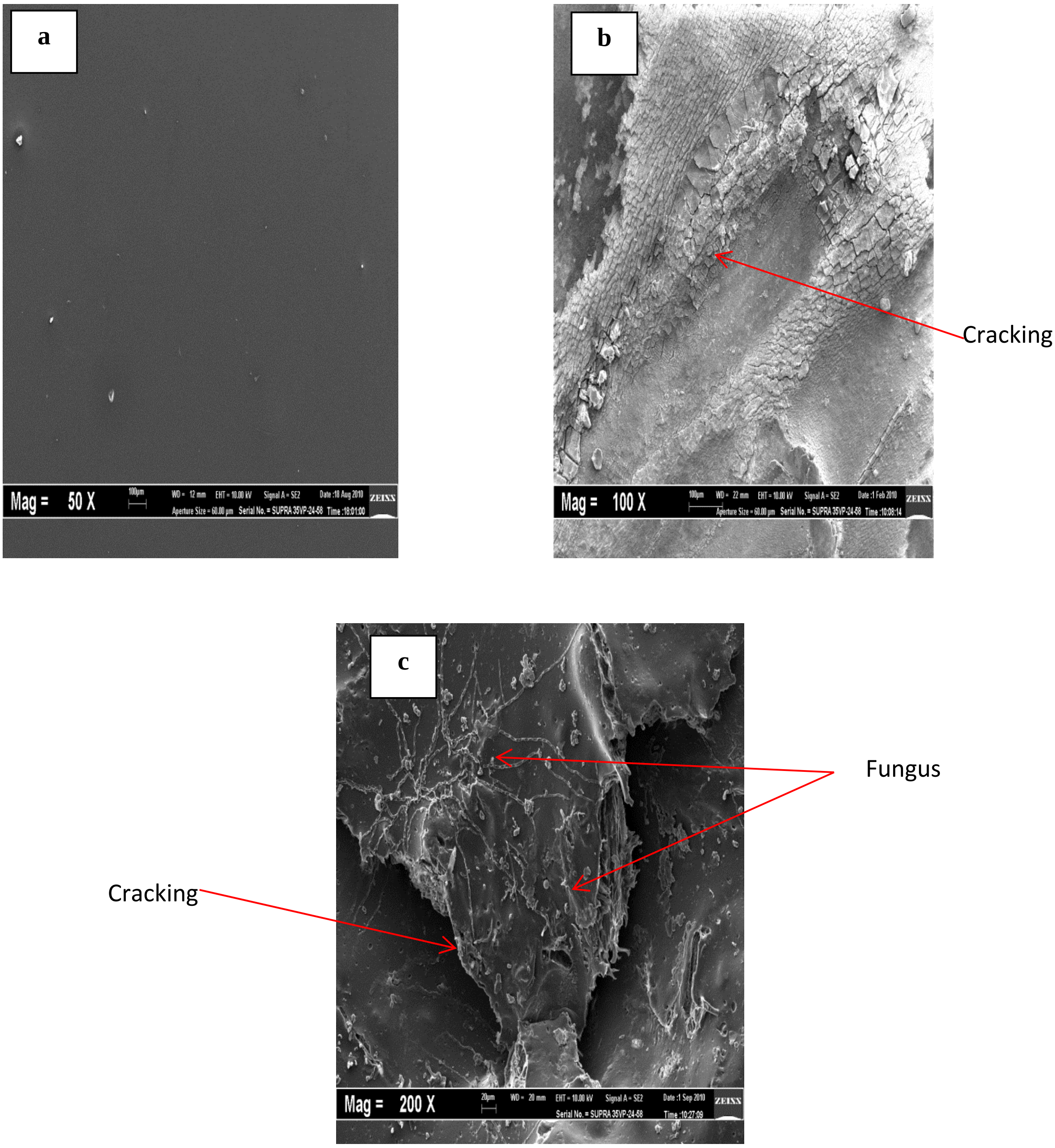

Figure 4.24: SEM images scanned from the surface of non-crosslinked PVA/SBF40 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 200x magnification after 3 months subjected to natural weathering.

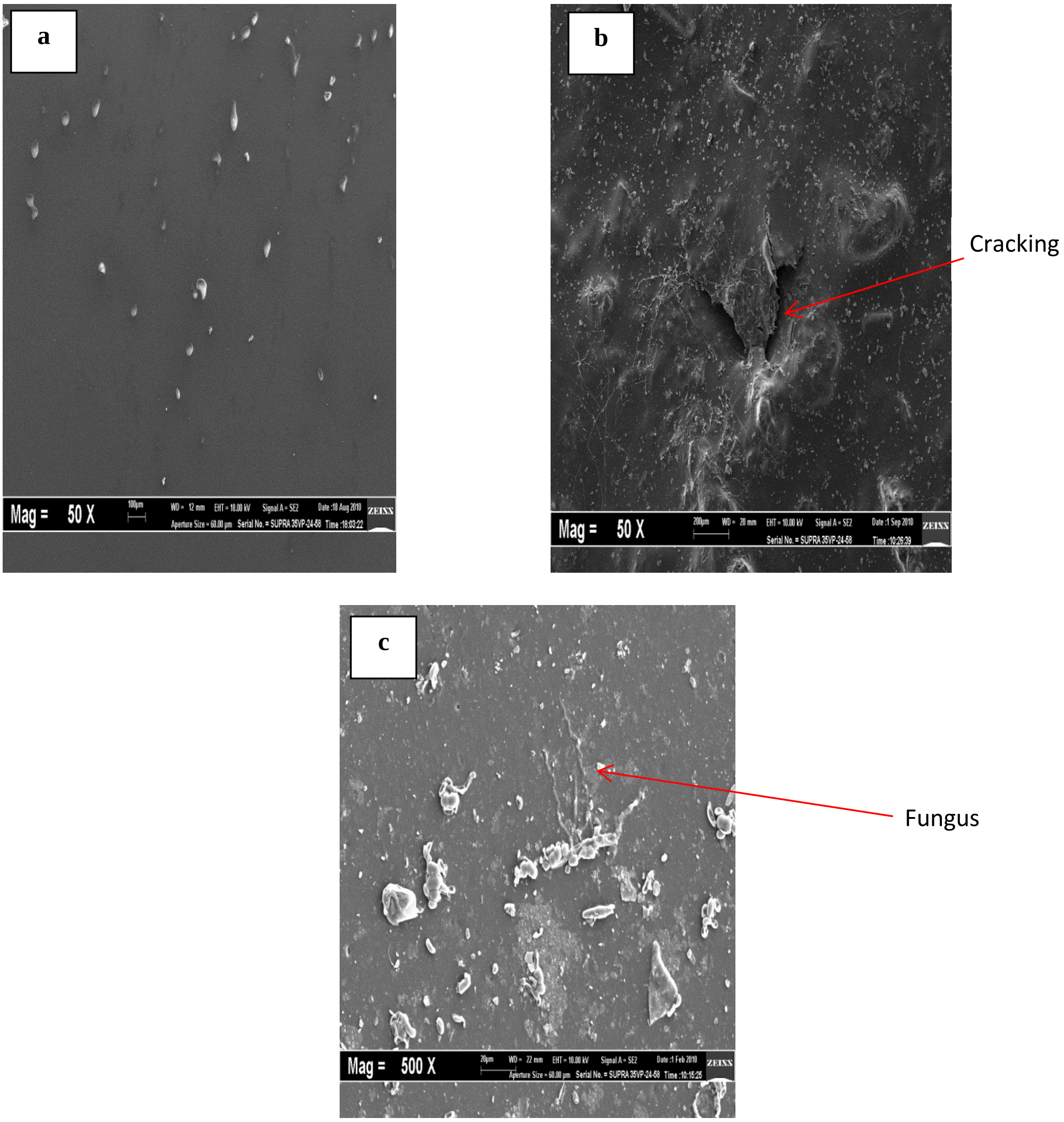

Figure 4.25: SEM images scanned from the surface of crosslinked PVA/SBF40 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 200x magnification after 3 months subjected to natural weathering.

4.3 Effect on Banana Frond Flour and Halloysite Nanotube Content on the Properties of Polyvinyl Alcohol/Soya Bean Flour Blend

Recently, ternary composite systems have attracted many researchers attention because of their potential to enhance the present of the composite system. The system can be developed either by polymer blend plus filler or hybrid of filler with polymer matrix. In this research, two different types of filler were added to PVA/SBF blend to form ternary blend films. The effect of banana frond flour (BFF) and halloysite nanotube (HNT) content on tensile properties, water absorption, water vapour transmission, Fourier transform infrared, soil burial, natural weathering and morphology analysis were investigated. The results showed the PVA/SBF/HNT blend films are better mechanical properties compared to the unfilled PVA/SBF blend films and PVA/SBF/BFF blend films.

4.3.1 Tensile Properties

Figures 4.26 – 4.28 illustrate the tensile properties of PVA/SBF/BFF and PVA/SBF/HNT blend films at different filler loading. In Figure 4.26, the tensile strength of PVA/BFF/SBF blends decreased from 22.95 MPa to 18.83 MPa as the increasing of the BFF content. The reduction of the tensile strength was due to the coarsely dispersed of BFF granules in the blend system (intramolecular forces will cause poor dispersion of BFF in PVA/SBF matrix) particularly in higher BFF content. This may also because of the poor compatibility between PVA/SBF and BFF.

Figure 4.26 shows that PVA/SBF blends reinforced with HNT had higher tensile strength than those reinforced with BFF. For PVA/SBF/HNT blends, the tensile strength of the blend films increase at low filler content of 5 phr and 10 phr, but started to decrease with the addition of 15 phr of filler as shown in Figure 4.26. The increase of tensile strength was due to the physical interaction between PVA/SBF matrix and the HNT filler. Hydroxyl group on the surface of the matrix and the HNT filler were able to form hydrogen bonding together. The PVA/SBF/HNT blend films showed higher tensile strength due to the higher L/D ratios of HNT. Thus, more interaction sites between filler and matrix were provided and more load was required to break the film (Khoo *et al.*, 2013). After addition of 15 phr of HNT, the tensile strength was reduced due to the filler agglomeration in the blends. The agglomerations will act as stress concentrators and resulting in early failure of the films. Furthermore, stress applied to the films was unable to transfer from matrix to the filler.

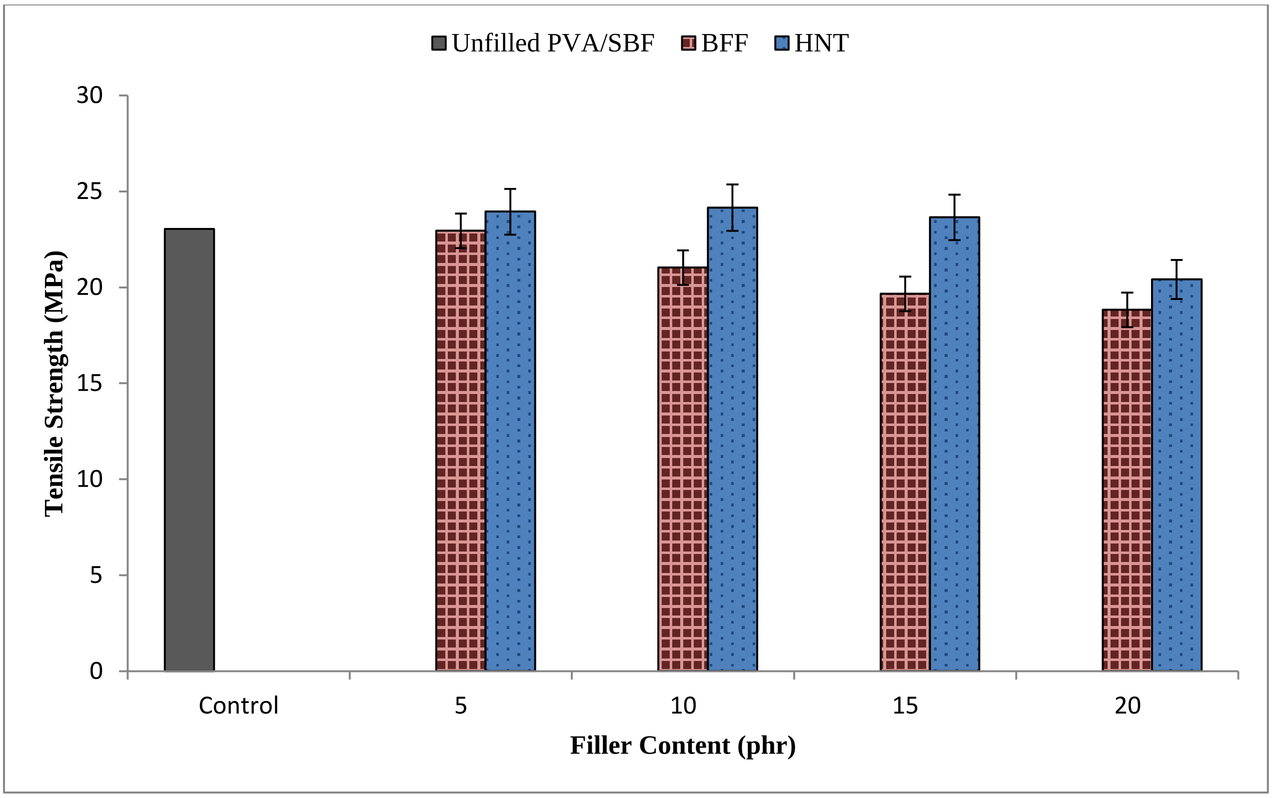

Figure 4.26: Effect of different filler on the tensile strength of PVA/SBF blend films at different filler content.

From Figure 4.27, elongation at break of PVA/SBF/HNT blend films value increase up to 10 phr of filler content. Again, the increment was due to physical interaction between filler and matrix. When load was applied to the films, HNT bare the excess load, thus resulting increase in elongation at break. At higher filler content of 15 phr and 20 phr resulted in a decrease of elongation at break of the PVA/SBF/HNT blend films. This may also have been due to the agglomeration in the blend films that act as a stress concentrator.

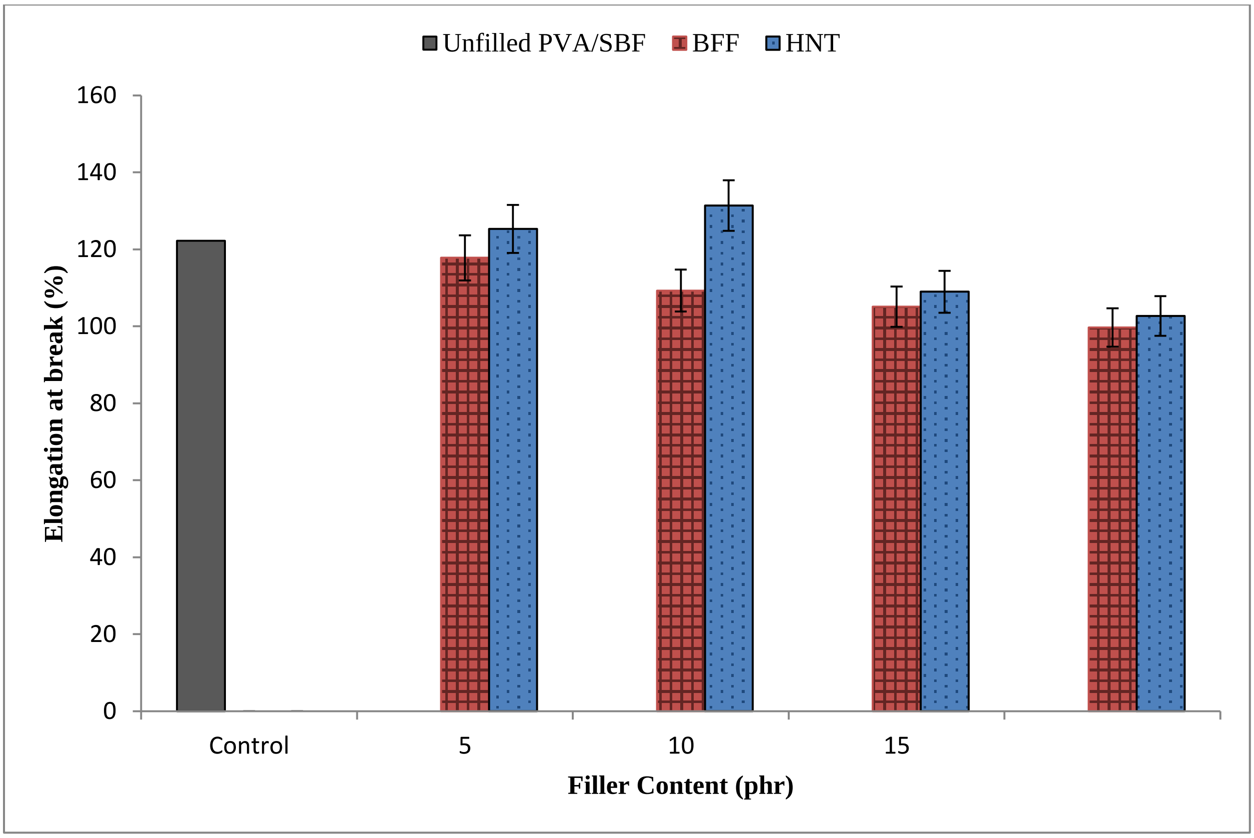

Figure 4.27: Effect of different filler on the elongation at break of PVA/SBF blend films at different filler content.

In Figure 4.28, tensile modulus shows an increasing trend as increase in the HNT and BFF content. This result show that the addition of both fillers enhanced the stiffness of the film as filler will disrupt the mobility of polymer chain. Ismail and Shaari (2010) stated that the strong interaction will reduce the elasticity and restrict the movement of the chains, so resulted in a more tough and rigid composites. Additionally, PVA/SBF/HNT blend films always show higher tensile modulus than PVA/SBF/BFF blend films. Qiu and Naravali (2013), Kumar *et al.* (2010) and He *et al.* (2012) agreed that this phenomenon is commonly observed for most polymers loaded with inorganic nanoparticles due to the increased tortuosity of the polymer molecules significantly harder nanoparticles, and increased nanoparticle-polymer interface.

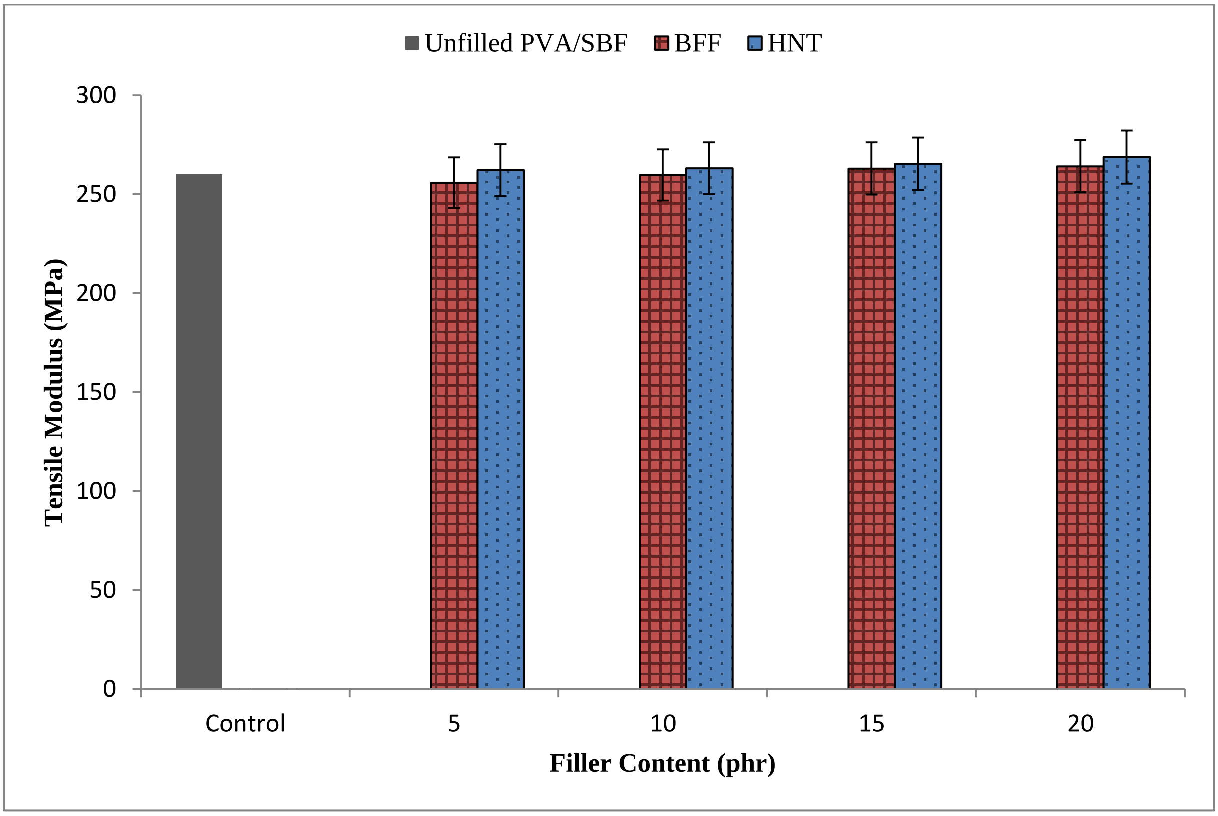

Figure 4.28: Effect of different filler on the tensile modulus of PVA/SBF blend films at different filler content.

In comparison, tensile modulus for PVA/SBF/HNT blend films was better compared to the PVA/SBF/BFF blend films. Again, this trend resulted from better distribution and interaction of HNT in the blend films as compared to those of BFF. The HNT have higher aspect ratio compared to BFF. Hence, they are able to accept the load more efficiently from the matrix and this is critical to the polymer binding process (Liu *et al*., 2007). Another reason might cause is the different size of both filler, BFF are in micron and have larger particle size compare to the HNT. Leong *et al*. (2003) has stated that larger particle has greater tendency to agglomerate and provide site for micro crack initiate, thus raising the possibility of the film to fracture at early stage.

4.3.2 Water Absorption

Figure 4.29 show that addition of BFF and HNT affects the water absorption of the film. Presence of small amount of fillers in the blend films will significantly increase the ability of the film to absorb water compared to PVA/SBF blend film. Film with the highest of filler content shows the highest percentage of water absorption compare to others. This is because of the HNT nature that has more hydroxyl groups on the surface of the tubes.

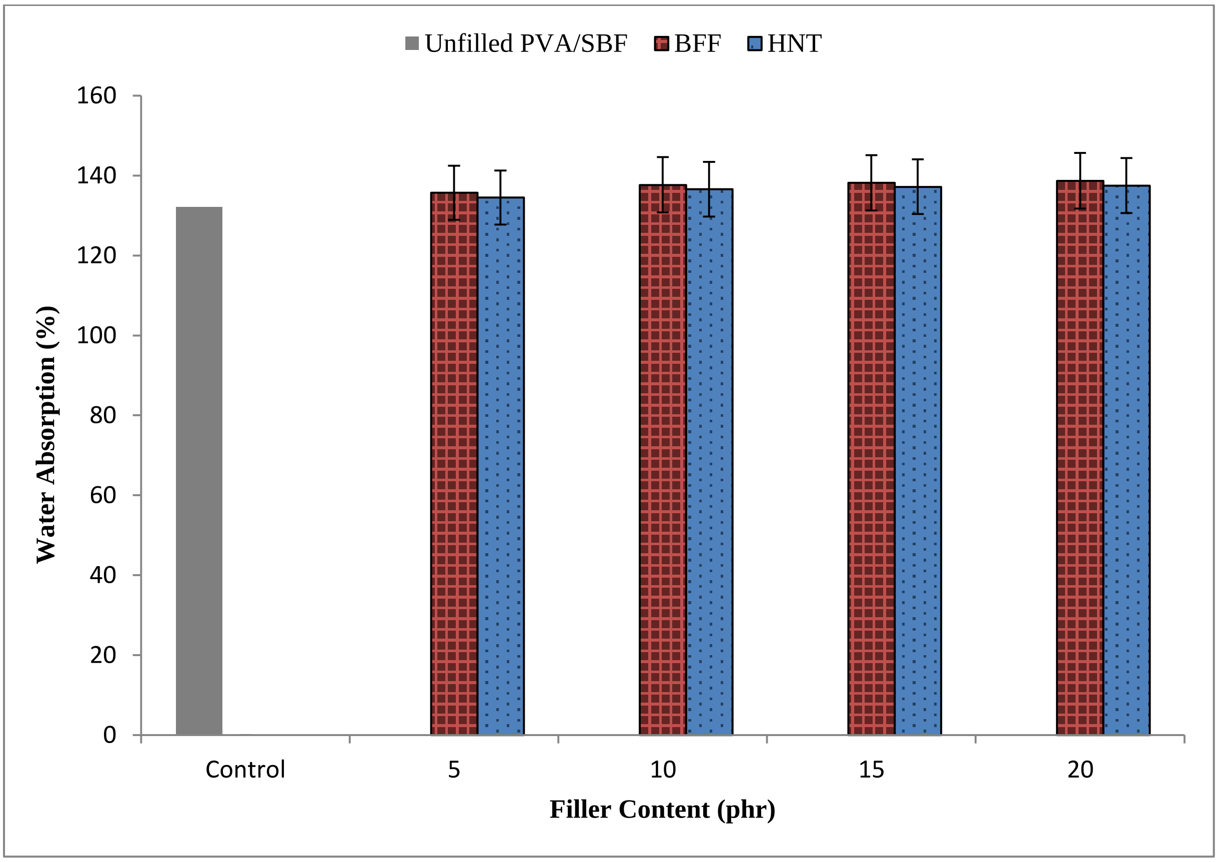

Figure 4.29: Effect of various types of filler on the water absorption of the PVA/SBF film at different filler content.

As reported by Liu *et al*. (2007), the inner and outer surfaces of tubules are covered by OH groups and oxygen atoms, respectively. The presence of OH groups from HNT attributed to the ability of the blend films to absorb more water or moisture as more hydrogen bond formed. But, according to Elizondo *et al.* (2009), better compatibility between PVA, BSF and HNT compare to PVA and BSF only will reduce the water absorption because of the strong interaction between the two polymers and homogenization of the blends.

4.3.3 Water Vapour Transmission

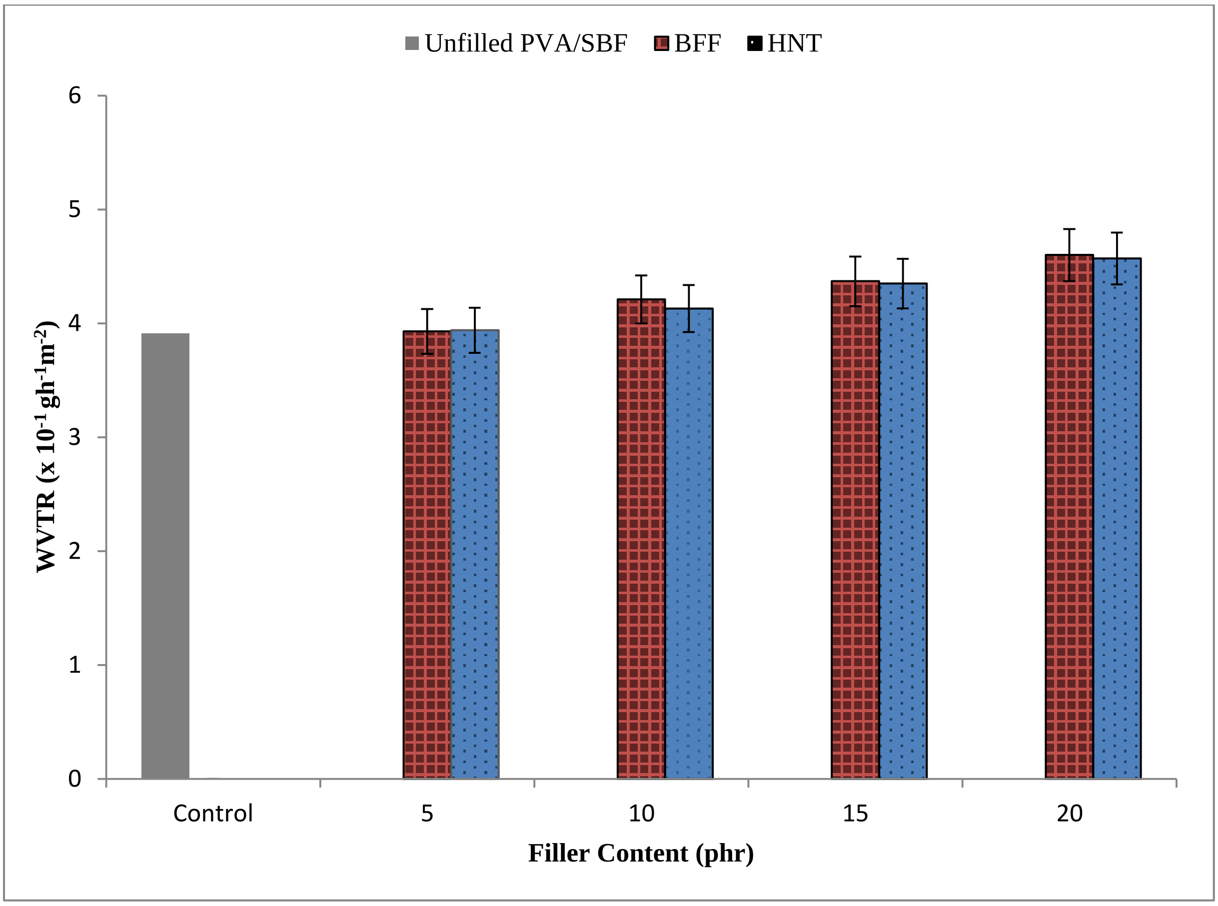

Figure 4.30: Effect of various types of filler on the water vapour transmission rate (WVTR) of the PVA/SBF film at different filler content.

The ability of water or moisture to penetrate and pass through the blend film was investigated. Figure 4.30 shows the rate of WVTR of the PVA/SBF/BFF and PVA/SBF/HNT blend films. Based on the results, the WVTR of both blend films increase slightly compared to the unfilled PVA/SBF blend film and the value increased as the filler content increasing. However, the PVA/SBF/HNT blend films show lower value of WVTR compared to the PVA/SBF/BFF blend films. This result deviated from the theory. According to Ooi *et al.* (2011), poor compatibility blend system will show higher rate of WVT because it will leads to an increase in the interchain spacing, which will allow more water molecules to diffuse through the films. Thus, PVA/SBF/HNT blend films which are more compatible blend should show lower rate of WVT compare to PVA/SBF/BFF blend film since less water molecules are allowed to diffuse through the film.

4.3.4 Fourier Transform Infrared

Figure 4.31 shows the FTIR spectra for PVA/SBF, PVA/SBF/BFF and PVA/SBF/HNT blend films. Similar peak characteristic were observed for BFF and HNT filled blend films.

For PVA/SBF/BFF blend film, the broad stretching vibration peak of hydroxyl groups appear 3260 cm$^{-1,}$ whereas the weak stretching peak of C-H appeared around 2940 cm^{-1}. The sharp vibration peak of C-O bond in associating with hydroxyl group and C-O-C group appeared around 1180 cm$^{-1,}$ 1110 cm^{-1} and 1020 cm^{-1}. In comparison of Figure 4.31 (a) and Figure 4.31 (b), the absorption peak of PVA/SBF/BFF was obviously changed and shifted. For instance, the stretching of vibration peak of hydroxyl group changed from 3250 cm^{-1} to 3262 cm^{-1}.

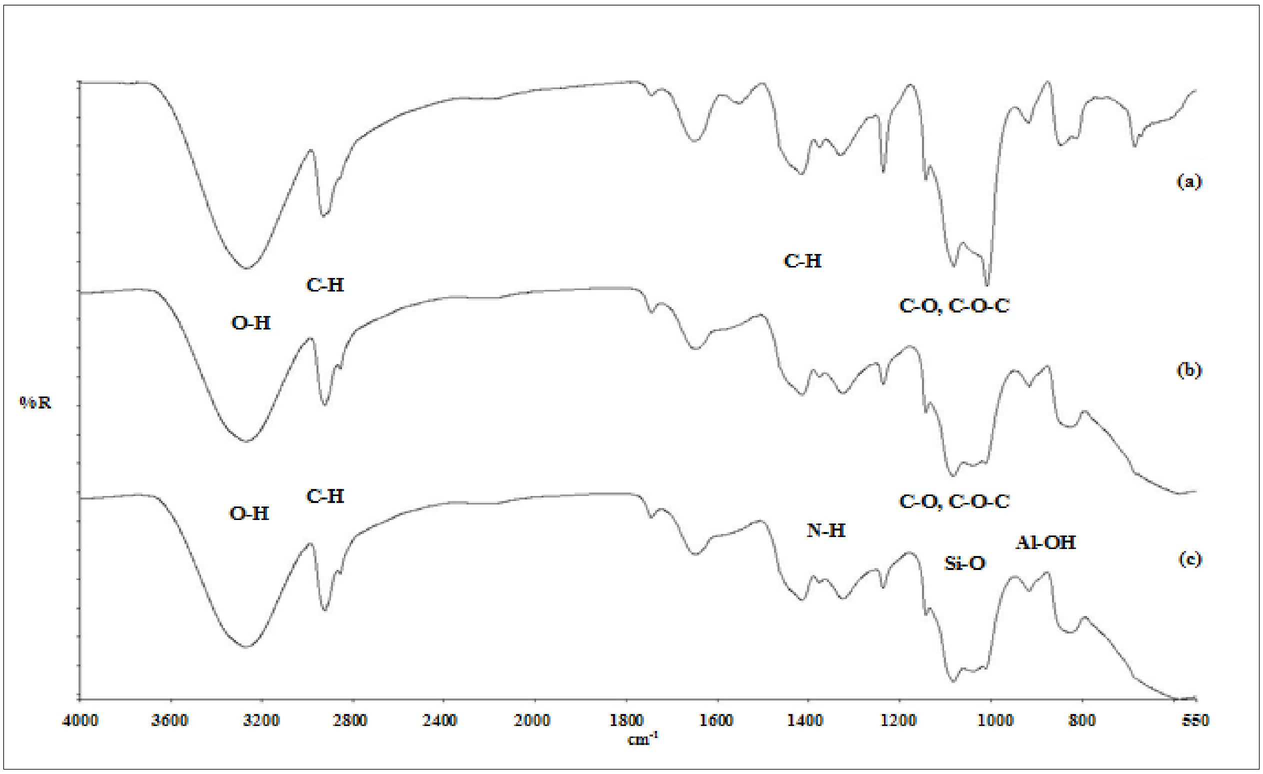

Figure 4.31**:** FTIR spectra of (a) PVA/SBF blend film, (b) PVA/SBF/BFF blend film and (c) PVA/SBF/HNT blend film.

For PVA/SBF/HNT blend films, C-H stretching indicates the alkyl groups in backbone of the polymers were detected at 2940 cm^{-1}. Stretching vibration and vibrations of hydroxyl bonds appears around 3280 cm^{-1} and 910 cm-^{1}, respectively. At 1553 cm^{-1} and 1350 cm^{-1}, the stretching vibration bands of the amide and N-H groups appears. The C-O groups of the film appear around 1121 cm^{-1} and 1070 cm^{-1}. The physical interactions and the formation of hydrogen bond in the blend can be proven by peak shift between Figure 4.31 (a) and Figure 4.31 (c). For example, O-H stretching was shifts from 3250 cm^{-1} to 3280 cm^{-1} after addition of HNTs. Meanwhile, Si-O bond peak shift from 1032 cm^{-1} to 1029 cm^{-1}. Further, the peak of Al-OH vibration shift from 920 cm^{-1} to 911 cm^{-1}.

4.3.5 Soil Burial Degradation

The results of the weight loss of PVA/SBF blend film in the presence of BFF and HNT during the experiment are shown in Figure 4.32. The weight loss of PVA/SBF blend film, as a control was also determined. As expected, PVA/SBF/BFF blend films were more rapidly biodegraded compared to PVA/SBF/HNT blend films. From Figure 4.32, the increase in weight loss percentage of all films especially the films with 20 phr of filler content were observed. This is proven in water absorption result, where film with 20 phr of BFF has the highest water uptake compare to others. This phenomenon might be due to the depletion of energy source from the carbohydrate content in BFF that required for microbes to growth and utilize the film (Goheen and Wool, 1991).

The process of biological degradation of polymer samples should be affected by the different condition of degradation media. This is because the temperature, pH and humidity have a significant effect on development of living microorganism which will cause the biodegradation process to occur. During the buried time, both type of blend films show comparable weight loss, especially compared to the control film. This results show that addition filler in the blend system had increased the degradability of the films due to water absorption capacity influenced by the presence of BFF and HNT. This was mainly because of the hydrophilic properties of both fillers that tend to absorb water. This moist environment enables more microorganisms to growth, survive and thus break down the film (Khachatourians and Qazi, 2008).

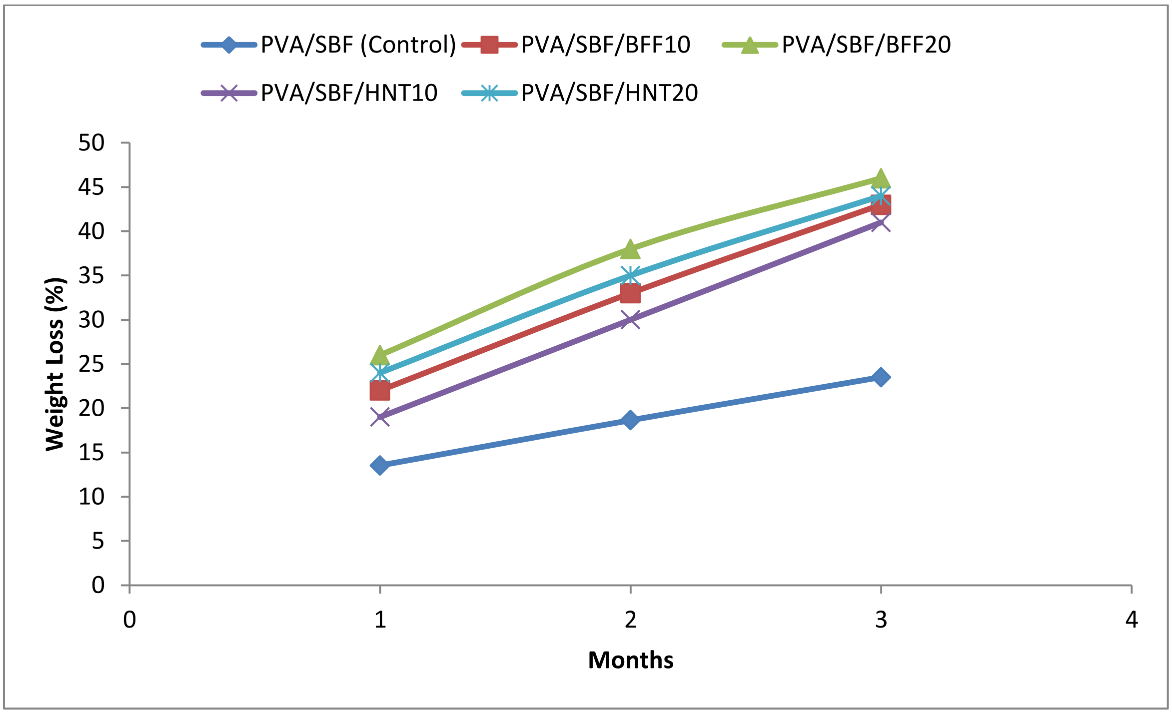

Figure 4.32: The weight loss of PVA/SBF, PVA/SBF/BFF and PVA/SBF/HNT blend films during biodegradation in natural soil burial test.

The SEM micrographs on the surface degradation of PVA/SBF/BFF and PVA/SBF/HNT blend films were shown in Figs 4.33 and 4.34, respectively. Trace of soil could be observed on the buried PVA/SBF blend films due to tendency of humid soil attach to the surface and additionally the microorganism might be removed during sanitizing purpose. The surface cracks, holes could be observed on the surface of all buried PVA/SBF/BFF and PVA/SBF/HNT blend films. It was due to the soil environment effect that caused the films to swell and shrink. However, the surface of the PVA/SBF/BFF blend films was deteriorated more than PVA/SBF/HNT blend films. As can be seen from Figure 4.33 (c), the cracks and hole were bigger than PVA/SBF/HNT blend films. Therefore, the weight loss of PVA/SBF/BFF blend films was highest.

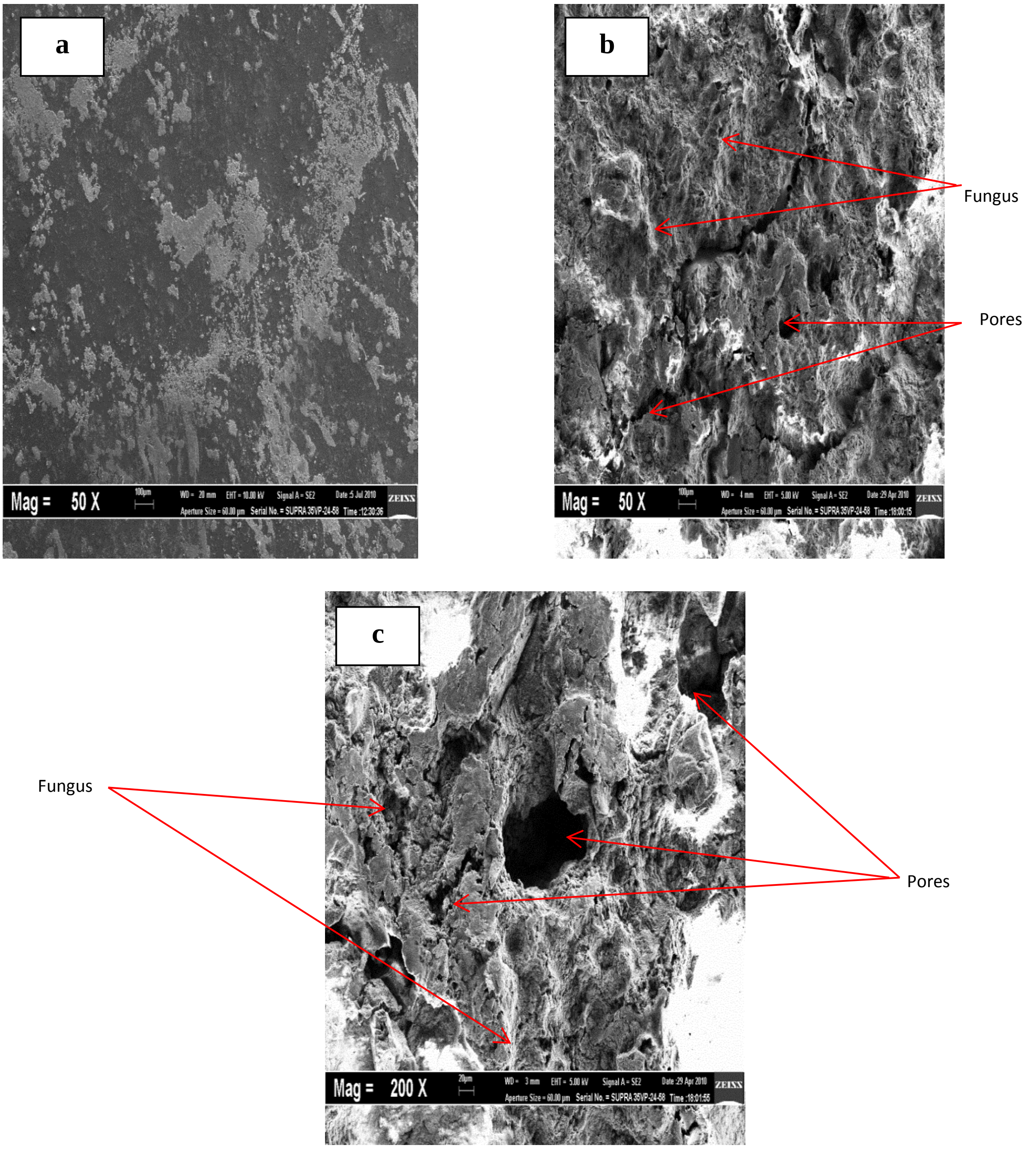

Figure 4.33: SEM images scanned from the surface of PVA/SBF/BFF20 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 200x magnification after 3 months burial in natural soil conditions.

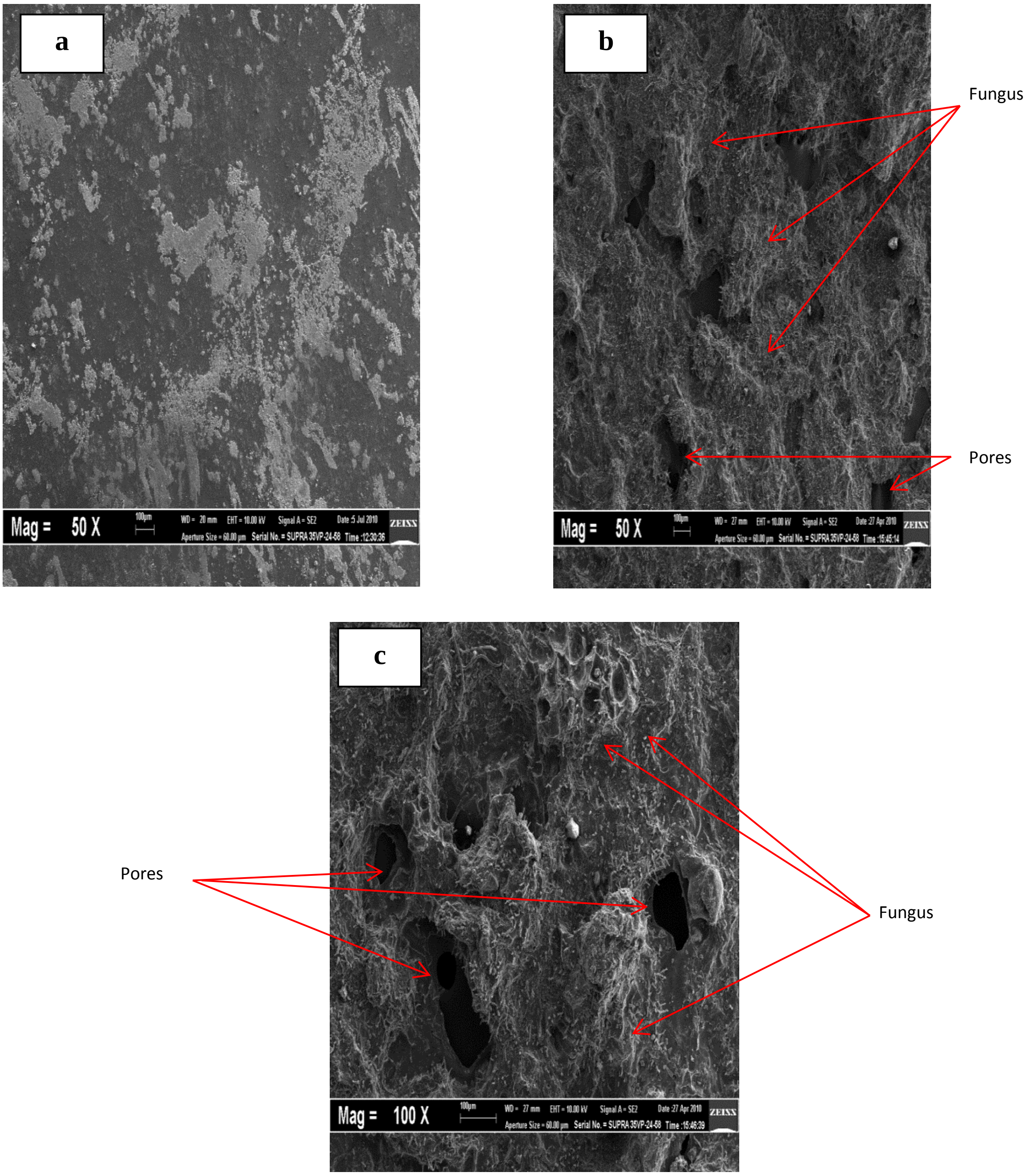

Figure 4.34: SEM images scanned from the surface of PVA/SBF/HNT20 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 100x magnification after 3 months burial in natural soil conditions.

4.3.6 Natural Weathering

Figure 4.35 shows the evaluation of the weight loss of PVA/SBF/BFF and PVA/SBF/HNT blend films after 3 months exposed to natural weathering. The weight loss of all weathered PVA/SBF/BFF and PVA/SBF/HNT blend films increased as the increasing of filler content and particularly with the longer time of exposure. Interestingly noted that, the weight loss for all blend films was slow and almost similar to each other at 1 month of exposure time. Natural weathering was done by exposing all the blend films to environmental effect such sunlight, dew, rainfall, wind and etc. From Figure 4.35, the weatherability between BFF and HNT blend films did not very significantly differ to each other. Recall that, the PVA/SBF/BFF blend films absorb more water than PVA/SBF/HNT blend films. Thus, it lead to the higher rain water absorption resulting in hydrolysis depolymerisation process. Besides, surface deterioration (cracking) due to the annealing effect caused by combination effects of swelling and shrinkage, as reported by Yew *et al.* (2009) on PLA/rice starch composites, also contributed to the weight loss of PVA/SBF/BFF and PVA/SBF/HNT blend films.

Further evidence on the surface degradation of weathered PVA/SBF/BFF and PVA/SBF/HNT blend films are shown in Figs 4.36 and 4.37. It is interesting to noted that the microorganism could be observed on the surface of PVA/SBF/BFF blend films. Hence, it was believed that microorganisms tend to grow on the surface of PVA/SBF/BFF blend films. Meanwhile, addition both filler in the blend system would enhance the degradability of PVA/SBF/BFF and PVA/SBF/HNT blend films, which can be proceed by the rough surface and severe deterioration like cracks and holes that observed on the surface of both blend films (Figs 4.36 and 4.37).

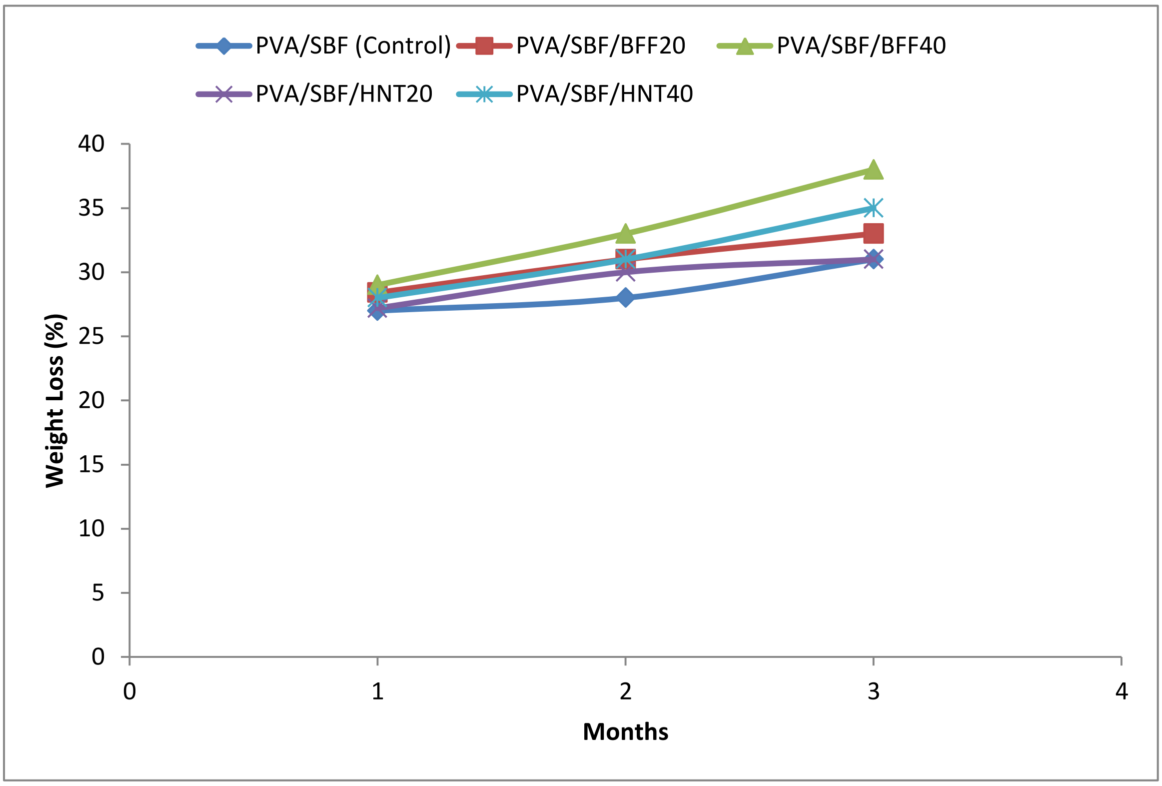

Figure 4.35: The weight loss of PVA/SBF, PVA/SBF/BFF and PVA/SBF/HNT blend films after exposure to natural weathering.

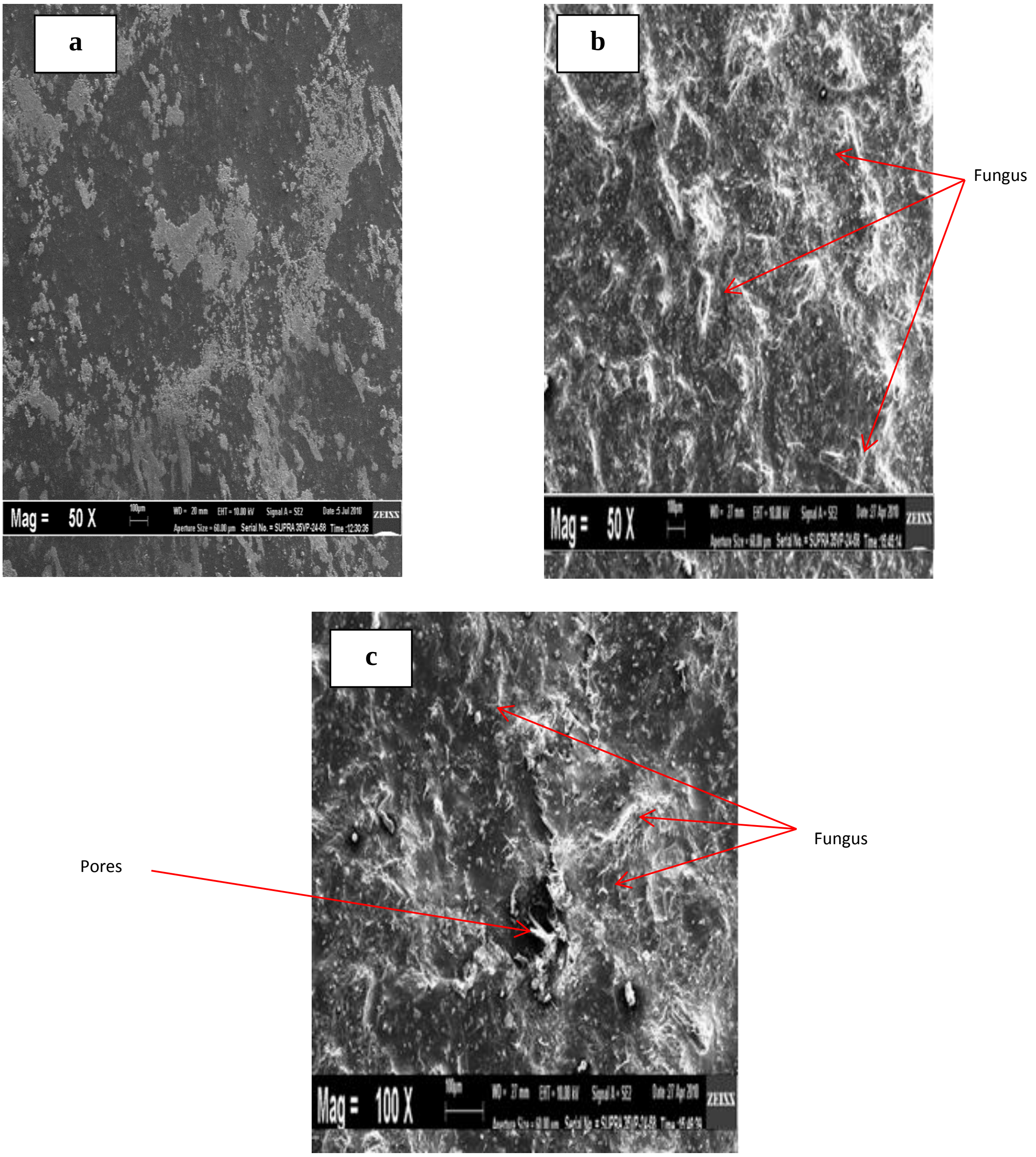

Figure 4.36: SEM images scanned from the surface of PVA/SBF/BFF20 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 100x magnification after 3 months exposure to natural weathering.

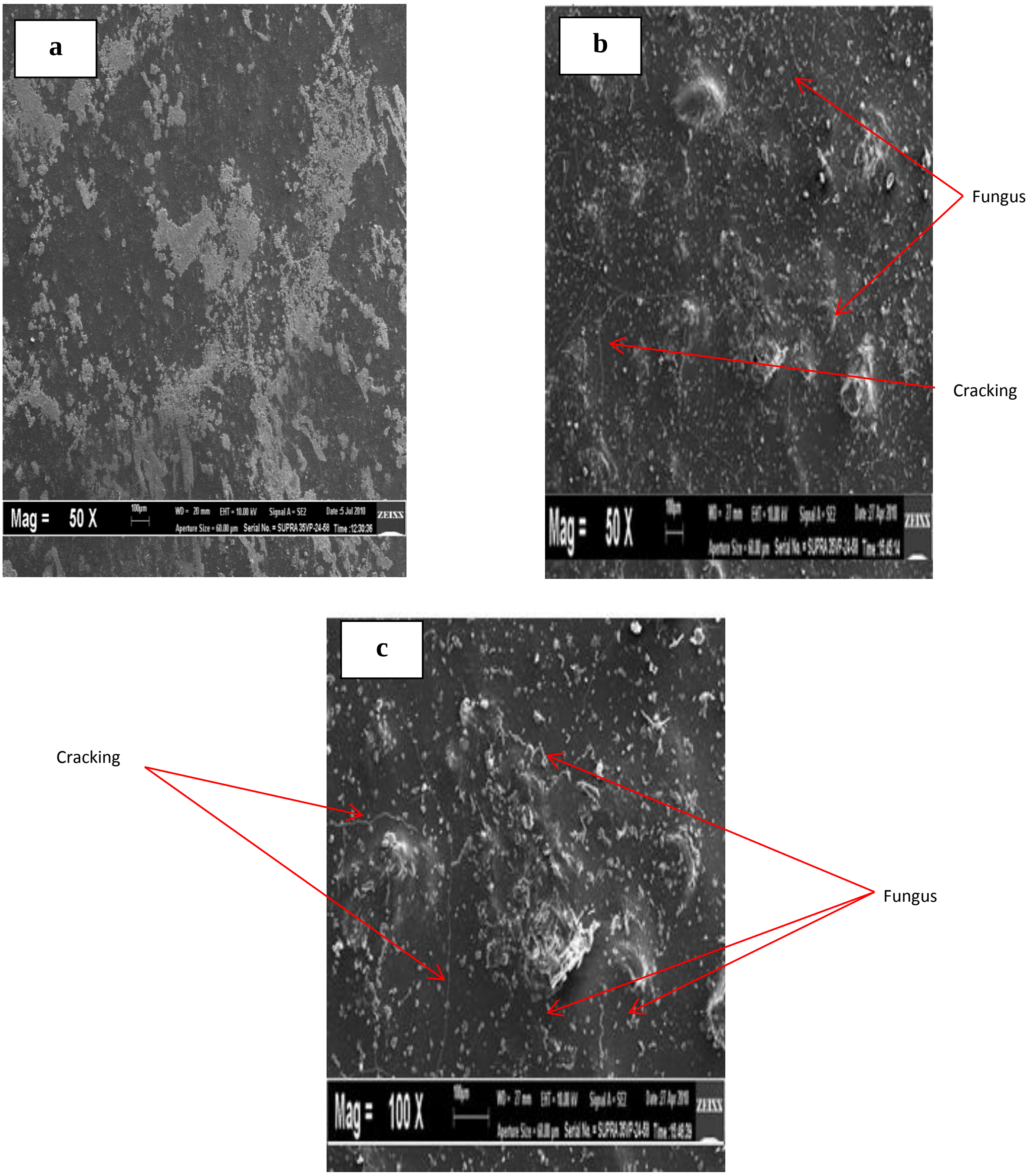

Figure 4.38: SEM images scanned from the surface of PVA/SBF/HNT20 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 100x magnification after 3 months exposure to natural weathering.

4.4 Effect on Modified Banana Frond Flour Content on the Properties of Polyvinyl Alcohol/Soya Bean Flour Blend Films

Alkaline treatment is one of the most used treatments of natural fillers. Alkaline treatment's main purpose is to disrupt hydrogen bonding in the network structure and remove some hemicellulose, lignin, and wax, thereby increasing surface roughness and reducing its hydrophilic nature. In this study, the sodium hydroxide was chosen because of its low cost and effectiveness. In this series, the effect of treated banana frond flour (BFF) were investigated in term of tensile properties, water absorption, water vapour transmission, Fourier transform infrared, soil burial, natural weathering and morphology analysis. The results showed an improvement in tensile properties and water resistance of the treated BFF film as compared to the untreated BFF films.

4.4.1 Tensile Properties

Figure 4.38 shows the comparison of tensile strength between untreated and treated BFF of PVA/SBF/BFF blend films at different BFF content. It can be seen that the tensile strength is continuously decreased with increasing of the BFF content. As shown in Figure 4.38, tensile strength for untreated PVA/SBF/BFF blend films decreased from 22.95 MPa to 18.83 MPa while for the treated PVA/SBF/BFF blend films, it decreased from 23.07 MPa to 19.53 MPa. Based on the result, it could be seen that at same amount of BFF content, the tensile strength of treated PVA/SBF films was higher than untreated PVA/SBF blend films. The increment in tensile strength by treated PVA/SBF/BFF blend films, indicating that treated BFF have better compatibility and interaction with PVA than untreated BFF. Similar result was reported by Guohua et al. (2006) on the methylated corn starch/PVA blend films and Yun et al. (2008) in their finding on the chemically modified starch/PVA blend films.

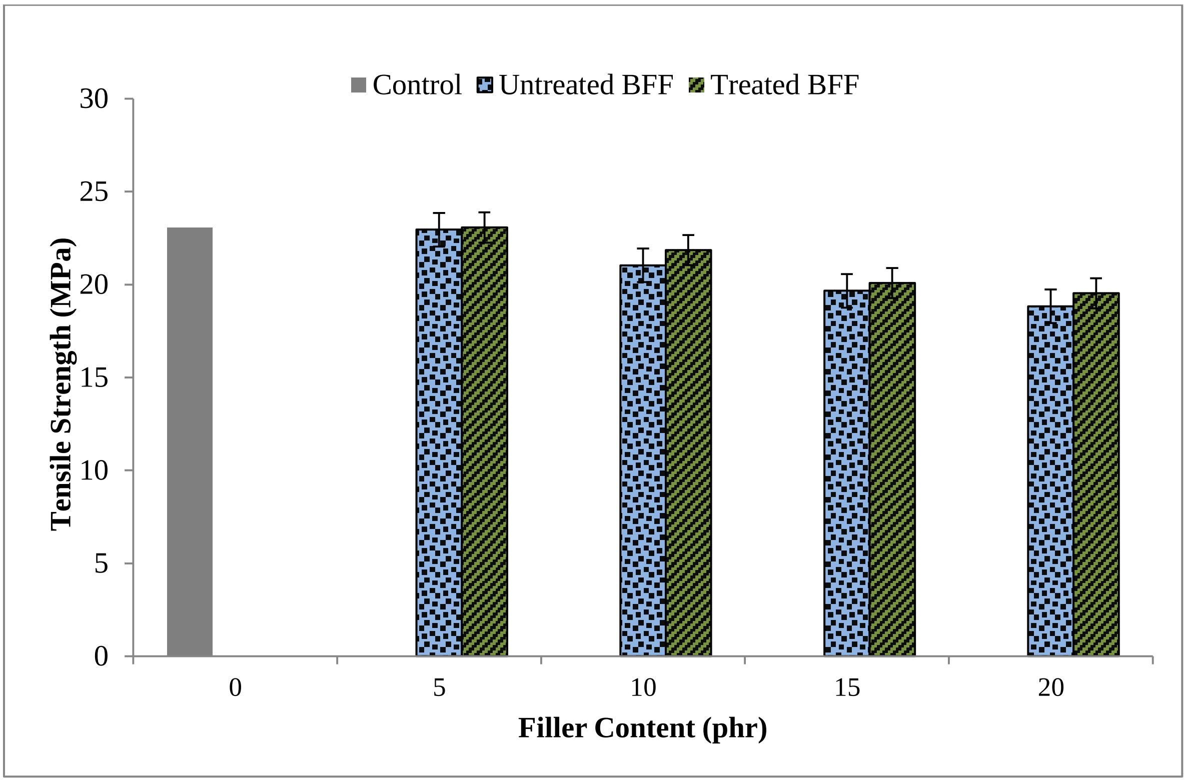

Figure 4.38: Effect of untreated and treated BFF on the tensile strength of PVA/SBF/BFF blend film at different BFF content.

The comparison of elongation at break between untreated and treated BFF of PVA/SBF/BFF blend films at different BFF content is shown in Figure 4.39. For the treated PVA/SBF/BFF blend films, the elongation at break of films decreased from 117.4 % to 100.5 % as increasing BFF content, and was slightly higher than the untreated PVA/SBF/BFF blend films (117.8 % to 99.7 %). The improvement in elongation at break by the treated BFF films, indicate that the treated BFF have better compatibility and interaction with PVA than the untreated BFF. Thus, the treatment of the BFF play the leading role in increasing the elongation at break value compared to the untreated PVA/SBF/BFF blend films. This similar finding was reported by Guohua *et al.* (2006).

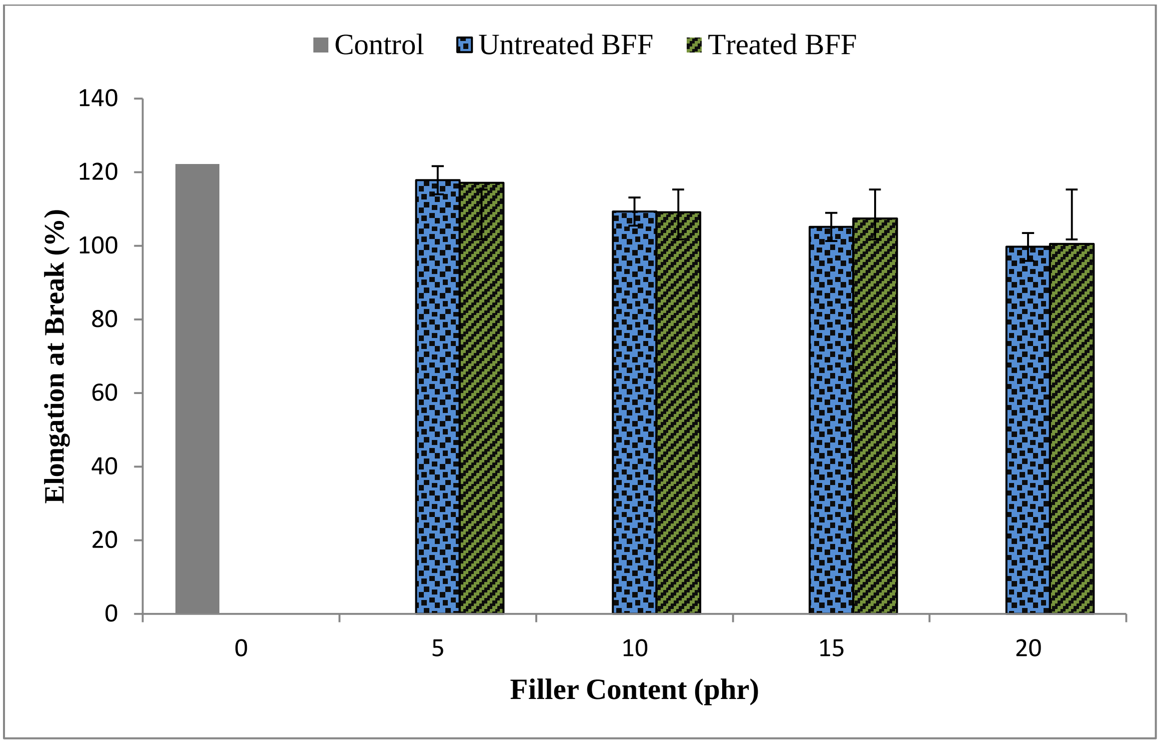

Figure 4.39: Effect of untreated and treated BFF on the elongation at break of PVA/SBF/BFF blend films at different BFF content.

The tensile modulus of the untreated and treated PVA/SBF/BFF blend films as a function of BFF content is presented in Figure 4.40. The experimental results show that the tensile modulus for treated PVA/SBF/BFF blend films were lower compared to the untreated PVA/SBFF/BFF blend films. In this work, the treatment might reduce the stiffness of the fiber. Ramadevi *et al*. (2012) had mentioned that alkaline treatment may be considered to be the most economical technique among other methods in improving the adhesion of fiber and matrix, but have the main disadvantage of the deterioration in the fiber strength during treatment. Theoretically, the treated blend films should show significant improvement in the tensile modulus. This could be related to better adhesion between the fiber and the matrix through an alkaline treatment reaction, because the NaOH reduced incompatibility between the fibers and the matrix. Therefore, it increased their interfacial adhesion and led to more restriction of the of the matrix and increased modulus (Zainal and Ismail, 2011).

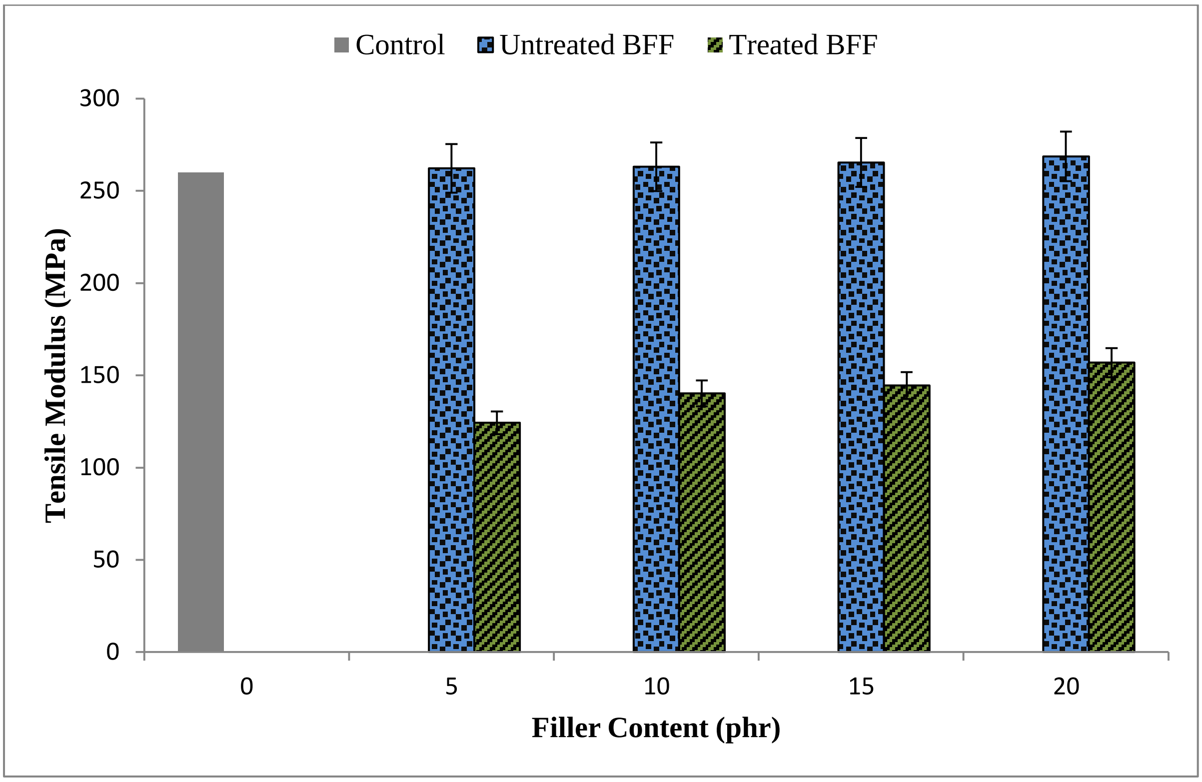

Figure 4.40: Effect of untreated and treated BFF on the tensile modulus of PVA/SBF/BFF blend films at different BFF content.

4.4.2. Water Absorption

The water absorption capacity and the degradability are the most important properties for biodegradable materials (Arajuo *et al*., 2004). The PVA/SBF blend films were degraded by surface absorption of moisture and microorganisms. Thus, the water absorbed on the films allowed the microorganisms to grow and utilize the films as an energy source (Zhao *et al*., 2006).

Figure 4.41 shows the effect of untreated and treated BFF on water absorption of PVA/SBF/BFF blend films. It was observed that water absorption of treated BFF film was reduced drastically compared to untreated BFF upon alkaline treatment. This agrees with previous reports by Bismarck *et al.* (2002) and Jimenez and Bismarck (2007). Reduction in water absorption may be due to removal of lignin and hemicellulose component of BFF by alkali treatment (Jannah *et al*., 2009, Srinivisa *et al*., 2010, Dhanalakshmini *et al*., 2012). As lignocellulosic material, BFF have a high concentration of hydroxyl groups, and they are very hydrophilic. Thus, the hydrophilic nature of BFF had changed into more hydrophobic nature by alkaline treatment.

As can be seen from Figure 4.41, presence of treated BFF has decrease the water resistance of the blend film compared to the untreated PVA/SBF/BFF blend films. The reduction of the water uptake capacity of the films was attributed by the alkaline treatment process that reduces the hydroxyl group in the cell wall of BFF molecules, thus reduce the water absorption of the films. However, as the BFF content increase from 5 phr to 20 phr, the percentage of water absorption for both treated and untreated PVA/SBF/BFF blend films increase. Similar finding were reported by Guohua *et al.* (2006) and Yun *et al*. (2008) on the studies of methylated cornstarch/PVA blend film and chemically modified starch/PVA blend films, respectively.

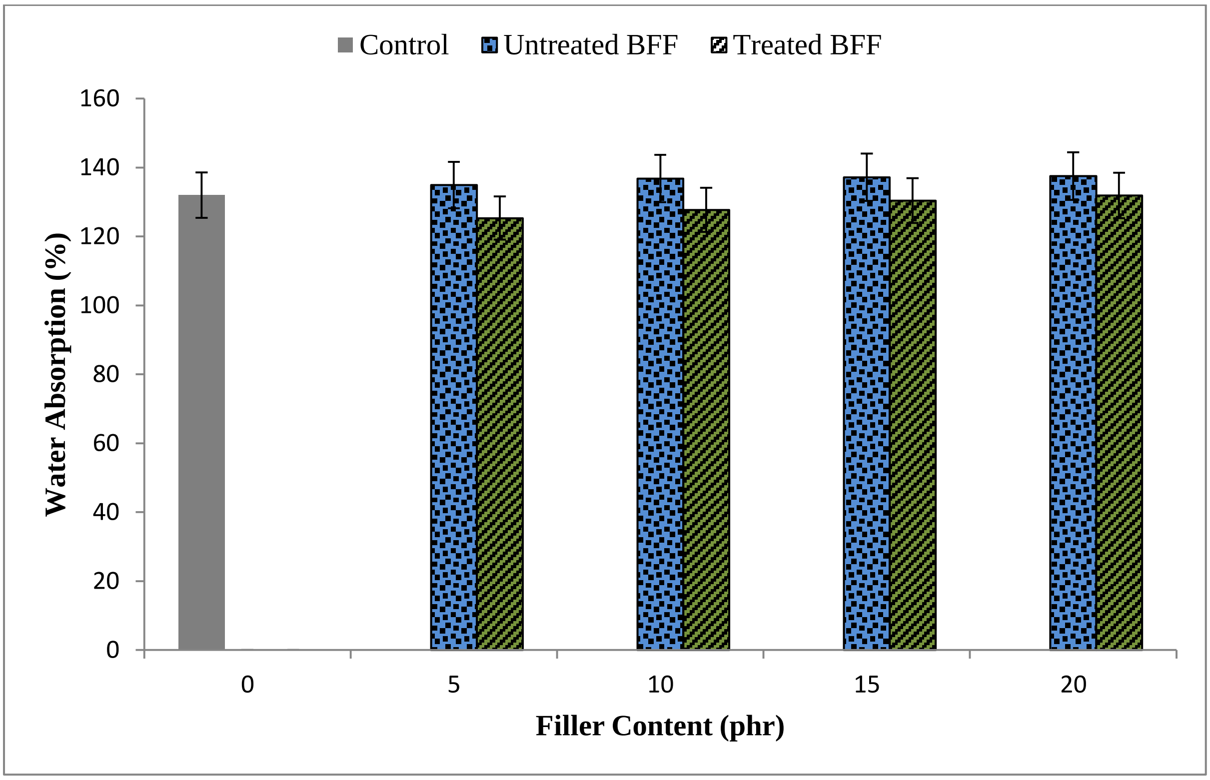

Figure 4.41: Effect of untreated and treated BFF on the water absorption of the PVA/SBF blend films at different BFF content.

4.4.3 Water Vapour Transmission Rate (WVTR)

The water vapour transmission rate (WVTR) of untreated and treated BFF of PVA/SBF blend films were calculated and shown in Figure 4.42. As the amount of BFF increased, the water vapor transmission of both blend films increase. This was due to the high water sensitivity of PVA/SBF/BFF blend films for absorbing the moisture. Nagaraja et al. (2012) had reported that the water vapour transmission rate depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. Thus, the hydrophilic nature of PVA and the water sensitivity of SBF and BFF lead to the absorption of water molecules and resulted in an increase of the WVTR of the PVA/SBF/BFF films.

As shown in Figure 4.42, the treated PVA/SBF/BFF blend films result shows a similar trend to water absorption results but lower compared to untreated blend films. The lower WVTR of treated PVA/SBF/BFF blend films was contributed to the increase in the hydrophobicity of the blend films with removal of lignin and hemicellulose component of BFF by alkaline treatment. This phenomenon could be related to the significant hydrogen bonding interaction with water. This was similar with Guohua *et al*. (2006) research studies where the presence of methyl group had replaced the hydroxyl group in the starch molecules. Thus, increase the hydrophobicity of the methylated corn starch/PVA films.

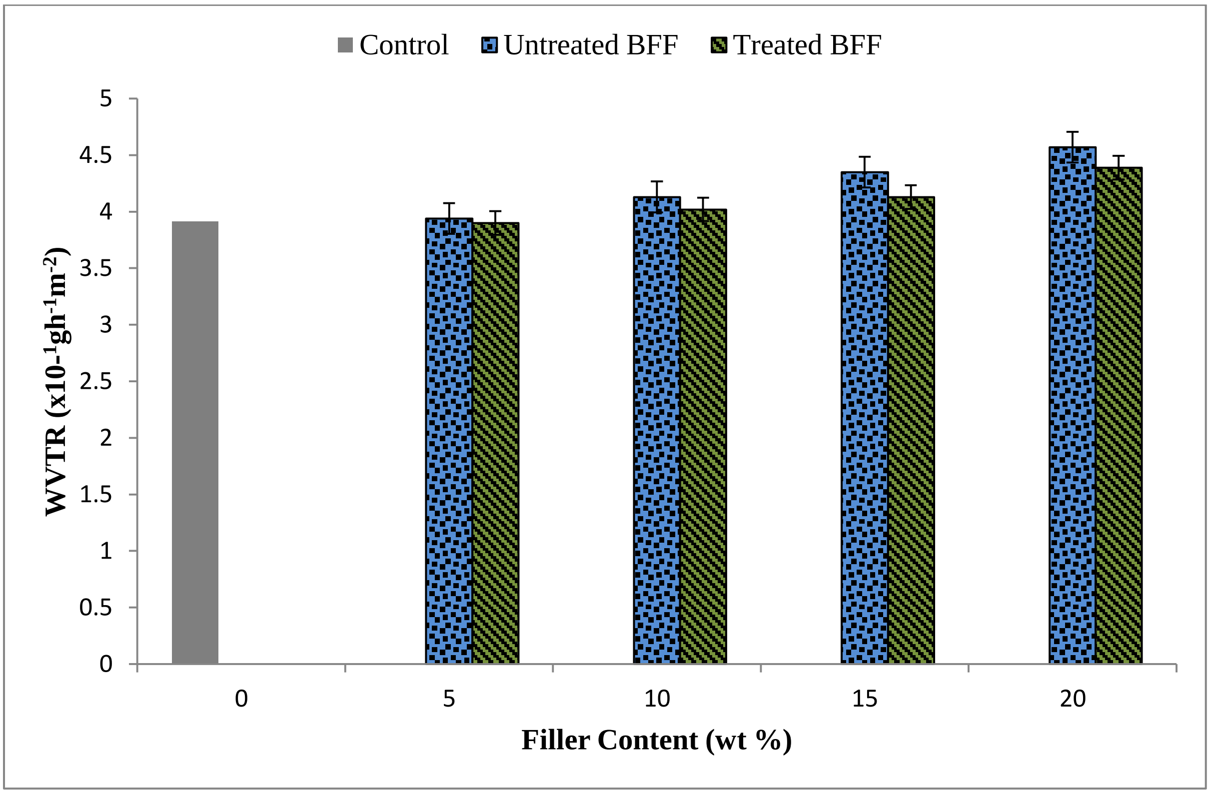

Figure 4.42: Effect of untreated and treated BFF on the water vapour transmission rate (WVTR) of the PVA/SBF film at different BFF content.

4.4.4 Fourier Transform Infrared

The infrared spectra for both untreated and treated BFF of PVA/SBF blend films were obtained by using an FTIR spectrometer as shown in Figure 4.43. Alkaline treatment of BFF resulted on significant differences in the infrared spectra for the blend film.

A large band at 3200-3600 cm^{-1} is mainly related to the hydroxyl groups and the bonded O-H stretching vibration present in carbohydrate (cellulose and hemicellulose) (Roger, 1997). As for treated BFF film, the 3435 cm^{-1} band assigned to the alcohol group was reduced. This was due to the removal of the hemicellulose component. Another peak due to the alcohol group of cellulose OH deformation that appeared at 1300 cm^{-1} was reduced by alkaline treatment.

The untreated BFF show the absorption band of carbonyl stretching at 1730 cm^{-1}, corresponding to hemicellulose. But, there can no longer be observed on treated BFF (Herrera-Franco and Valdez-Gonzales 2005). The large peak at 1593 cm^{-1} shown in untreated BFF could be due to the presence of lignin and they seem to be removed in treated BFF after alkaline treatment process. It is observed that the peak at 1245cm^{-1} disappears for treated BFF films due to alkali treatment that removes waxy epidermal tissue, adhesive pectins and hemicellulose that bind the BFF to each other (Jannah *et al*., 2009). The C-O-C symmetric glycosidic stretch at 1050 cm^{-1} arose from the polysaccharide components that was largely cellulose appeared in both untreated and treated BFF film.

It can be summarized that the alkaline treatment had removed most of the lignin and hemicellulose components. Thus, it helped to improve the mechanical properties of the treated BFF films by increasing the compatibility of both matrix and filler (Li *et al.*, 2005).

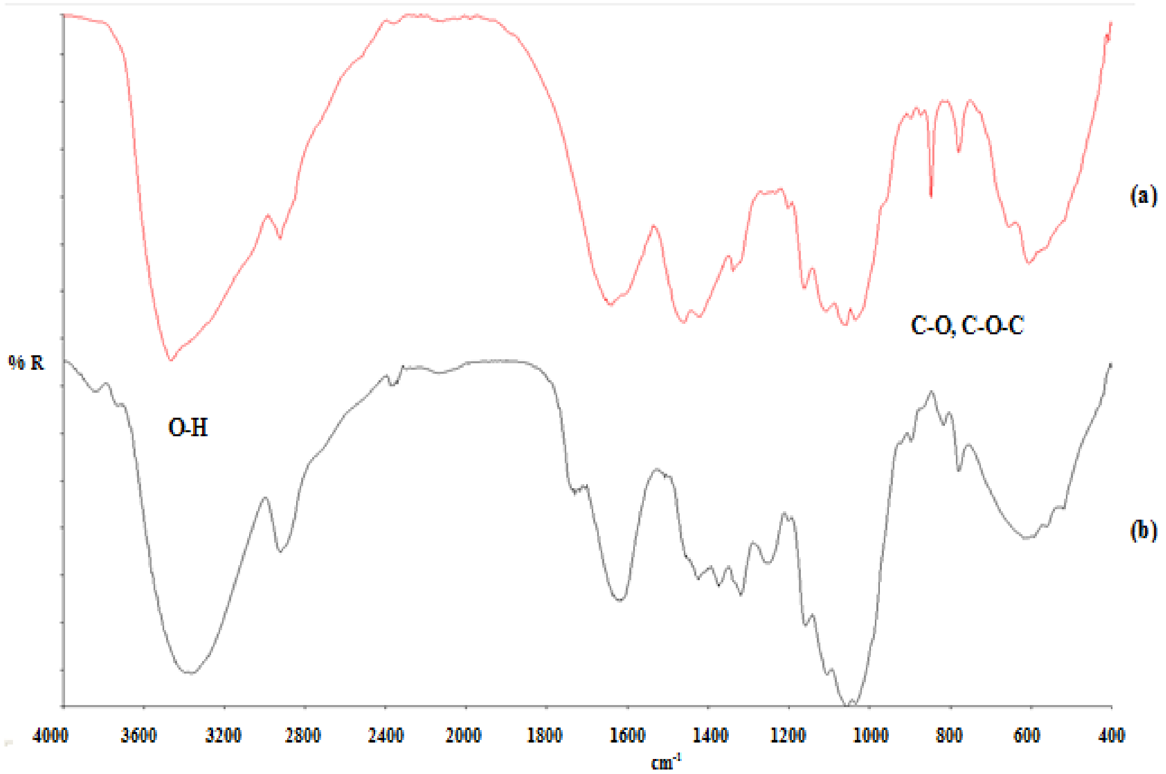

Figure 4.43: FTIR spectra of (a) treated PVA/SBF/BFF blend film and (b) untreated PVA/SBF/BFF blend film.

4.4.5 Soil Burial Degradation

As mentioned in water absorption and WVTR results, the modification of BFF with alkaline treatment has increased the hydrophobicity of the films. This was due to removal of lignin and hemicellulose component of BFF (Jannah *et al*., 2009; Srinivisa *et al*., 2010; Dhanalakshmini *et al*., 2012). Therefore, the water absorption of treated film decreased, thus reduce the degradation of the film. This is important because the penetration of microorganisms and enzymes is impossible without water absorption. (Dalev *et al*., 2000).

The results of the weight loss of the untreated and treated PVA/SBF/BFF blend films during this degradation test are shown in Figure 4.44. Knowing that BFF was more rapidly biodegraded compared to PVA, Figure 4.44 shows the decreases in the weights of all buried especially the PVA/SBF/BFF blend films with 20 phr of BFF content. Treated PVA/SBF/BFF blend films showed lower percentage of weight loss after 3 months in natural soil conditions. This finding was in agreement with the water absorption results in previous discussion. This proven that alkaline treatment had increased the film resistance towards water/moisture due to increase the hydrophobicity of the blend films with removal of lignin and hemicellulose component of BFF.

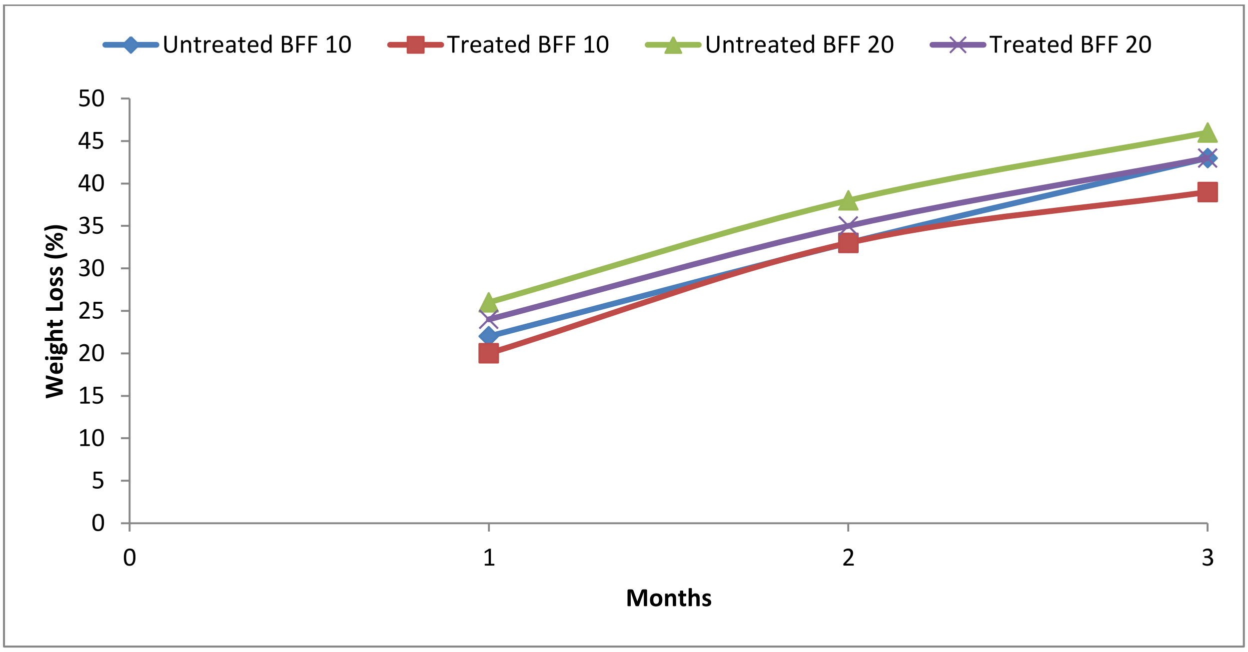

Figure 4.44: The weight loss of untreated and treated PVA/SBF/BFF blend films during biodegradation in natural soil burial test.

The changes in the surface microstructure of the untreated and treated PVA/SBF/BFF blend films were examined using SEM. Surface morphologies of treated PVA/SBF/BFF under SEM observation before and after 3 months subjected under soil burial are shown in Figure 4.33 and 4.45. Surface cracks and holes could be observed on the surface of the buried blend films. This was due to natural soil environmental effects, which caused the blend films swell and shrink. However, the surface degradation occurring on the untreated BFF blend film was greater than treated BFF blend films for both 10 phr and 20 phr. The cracks and holes of Figure 4.33(c) were bigger than in the treated BFF blend film (Figure 4.45(c)). Therefore, the weight losses of untreated PVA/SBF/BFF are higher than treated PVA/SBF/BFF blend films.

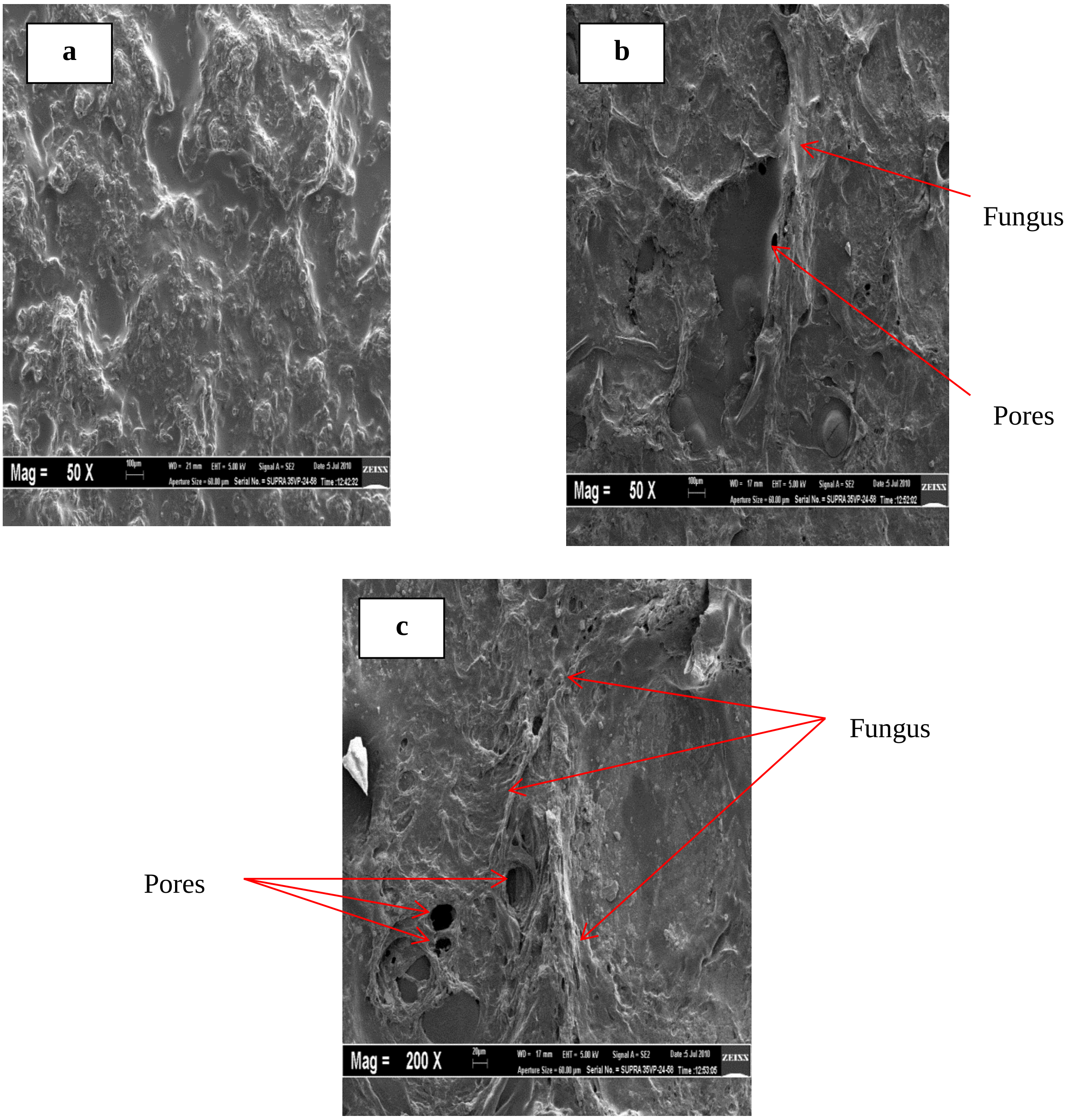

Figure 4.45: SEM images scanned from the surface of treated PVA/SBF/BFF20 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 200x magnification after 3 months burial in natural soil conditions.

4.4.6 Natural Weathering

In order to examine the surface degradation on the untreated and treated PVA/SBF/BFF blend films, SEM micrographs were taken from the specimen surface of untreated BFF and treated BFF at 20 phr BFF before and after exposure to natural weathering are shown in Figures 4.36 and 4.47, respectively. Severe surface deterioration can be observed for both weathered PVA/SBF/BFF blend films. A variety of microorganisms tended to attack and thus grow on the PVA/SBF/BFF blend films, especially in the warm humid climate like Malaysia. Then, it will cause the degradation of the films indicated by the weight loss of the films. Moreover, the large cracks appeared on the surface of both blend films were caused by the annealing effect. This similar observation was reported by Danjaji *et al*. (2002) in their studies of degradation for the surface of linear low-density polyethylene/sago starch films.

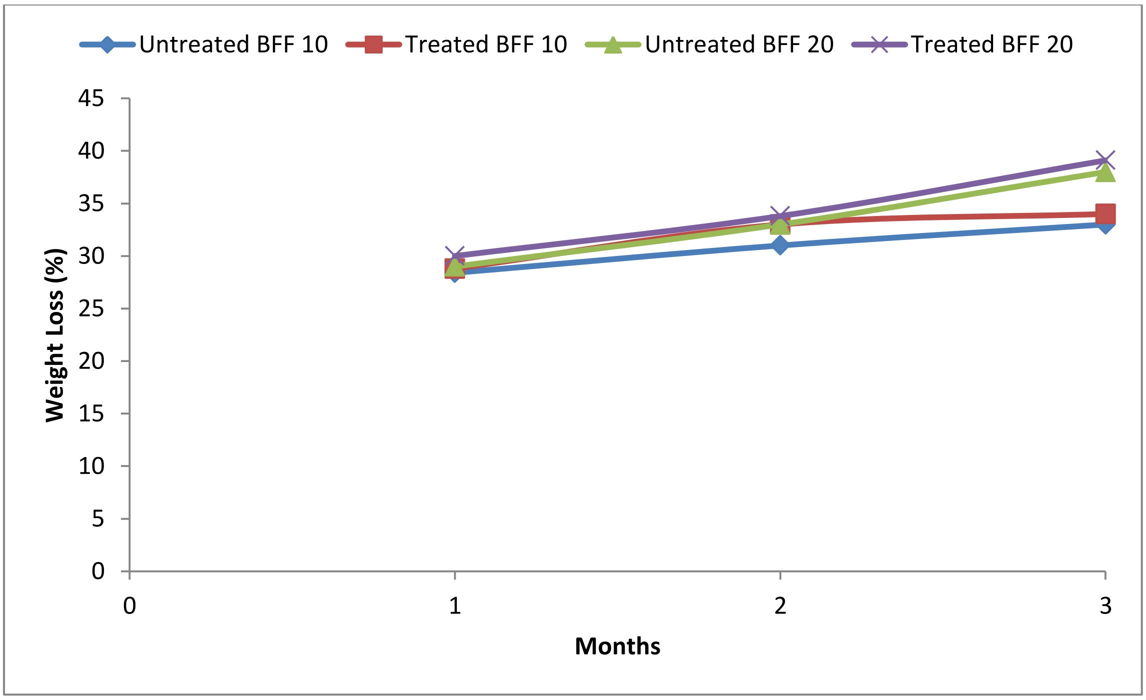

Figure 4.46: The weight loss of untreated and treated PVA/SBF/BFF blend films after exposure to natural weathering.

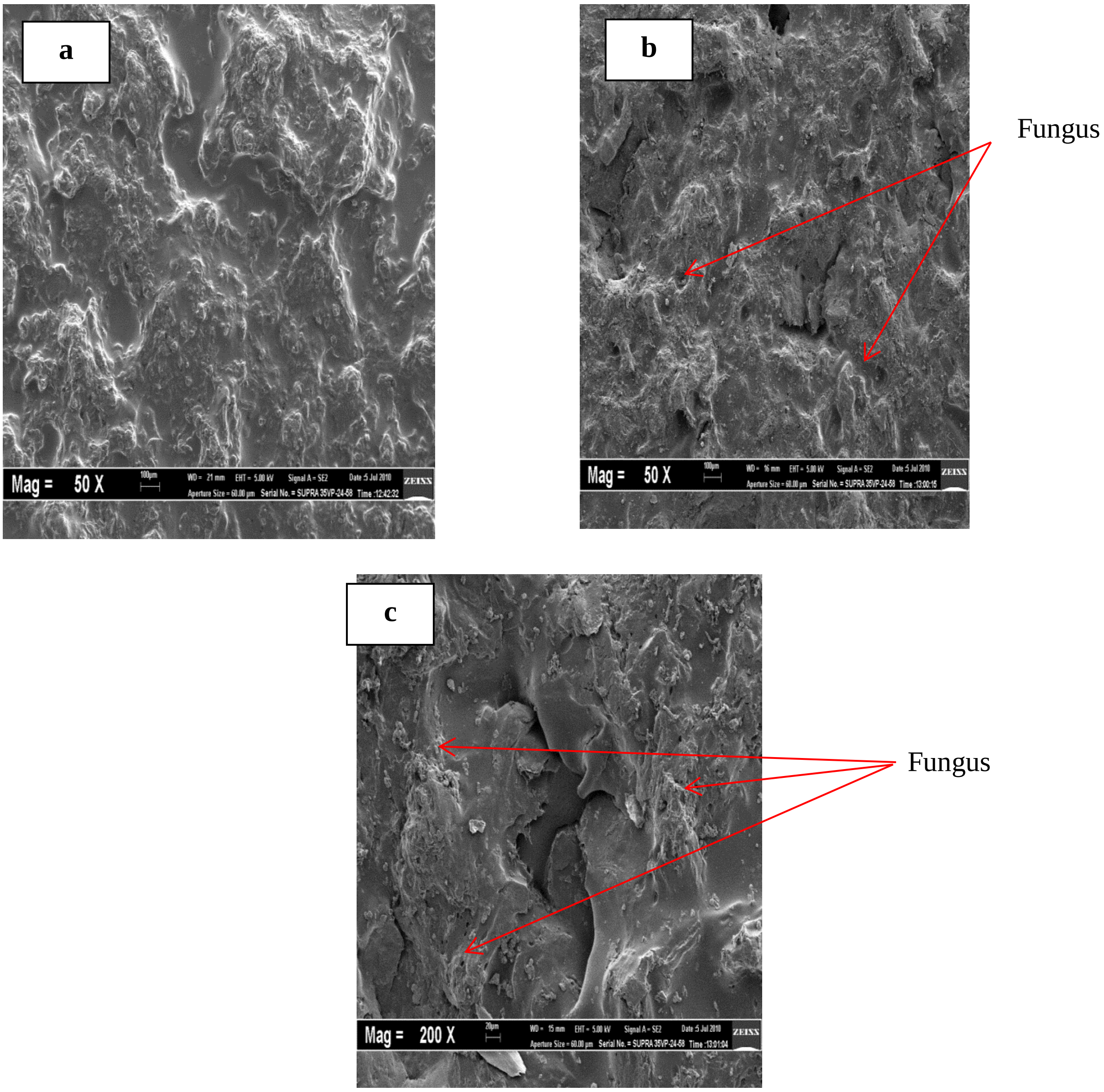

Figure 4.47: SEM images scanned from the surface of treated PVA/SBF/BFF40 blend films (a) before, (b) after 3 months, and (c) detailed micrograph at 100x magnification after 3 months exposure to natural weathering.

CHAPTER 5

CONCLUSION & SUGGESTIONS FOR FUTURE WORK

5.1 Conclusions

The ultimate goal of this research was to develop environmental friendly and low cost blend film for packaging application by using renewable materials. Polyvinyl alcohol/soya bean flour (PVA/SBF) blend films were developed by using solution casting method. The focus has been on selection and effect of the blend ratio, crosslinking agent, different types of filler and some modification on banana frond. From the results and discussion, the following conclusions can be drawn:

1. It was found that, the addition of soya bean flour (SBF) to polyvinyl alcohol (PVA) leads to decrease in tensile strength and elongation at break but the tensile modulus and water uptake increased with increasing of SBF content. Both natural weathering and soil burial test revealed that all unfilled PVA and PVA/SBF blend films exhibit loss in weight with longer period of degradation time.

2. The crosslinked PVA/SBF blend films show good improvement in tensile properties and exhibited good water resistance and low water vapour transmission rate. Soil burial test revealed that the non-crosslinked blend films show more weight loss than of the crosslinked blend films. However, natural weathering test revealed that addition of HMTA did not significantly affect the weatherability of the PVA/SBF blend films.

3. Both PVA/SBF/BFF and PVA/SBF/HNT blend films showed that the tensile strength and elongation at break decreased but the tensile modulus and water barrier properties increased with increasing filler content. PVA/SBF/HNT blend films exhibit higher tensile properties but lower water barrier properties compared to the PVA/SBF/BFF blend films. Regarding the degradation properties of both blend films the percentage of degradation increased as filler content increased.

4. Tensile properties of treated PVA/SBF/BFF blend films was higher in tensile strength and elongation at break but lower in tensile modulus compared to untreated PVA/SBF/BFF blend films. Besides, the water absorption and water vapour transmission of the treated PVA/SBF/BFF blend films are lower compared to untreated PVA/SBF/BFF blend films. Weatherability of the PVA/SBF/BFF blend films for treated BFF are not significantly affected, but for soil burial test, the treated BFF films degrade more than the untreated BFF blend films based on the weight loss result.

5.2 Suggestion for Future Work

A lot of time and work have been done to fulfill the various objectives of this research. However, there are still much more to be studied in order to improve the properties of soya bean flour filled polyvinyl alcohol blends. Below are some recommendations for the future works:

- A further study on suitable crosslinking agents (glutaraldehyde), plasticizing agents (glycerol, sorbitol) and other additives on the formulation used in this research are needed to enhance the properties of soya bean flour filled polyvinyl alcohol blends as well as mechanical properties and water barrier properties.

- Soya bean flour used in this research was directly added during solution blending process. The modification on soya bean flour through either chemical or physical treatments was suggested to enhance the properties of soya bean flour filled polyvinyl alcohol blends.

- Other type of filler should be considered for future studies to discover more properties of the hybrid system in soya bean flour filled polyvinyl alcohol blends especially filler from waste.

- Another type of degradation study like accelerated natural weathering and enzymatic test should be done in order to get more accurate results and clearly understand the degradation of those biodegradable films.

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