IRRADIATED FILMS VIA NUCLEAR TECHNOLOGY FOR FOOD PACKAGING PURPOSES

NUR SARA SYUHADA BINTI BAHARUDIN

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Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

The application of radiation towards the polymer modification seems to be beneficial as polymers play an important role in our daily life. At this moment, there is about 200 million tonnes of plastics consumption globally, with an approximation growth of 5% per annum. The increasing amount of synthetic plastics packaging films has led to a serious ecological problem due to its non-biodegradability properties. Therefore, this research is to produce different formulations of biodegradable irradiated antimicrobial starch films with different amount of dosage, where several characteristics of the films were tested. The characterization includes 'Absorption Test', 'Gel Content Test', 'Conductivity Test', 'Soil Burial', and 'Scanning Electron Microscopy'. From the results obtained, the highest dosage of radiation seems to be the best condition in producing the biodegradable films. This is because, the highest dosage, which is at 30kGy, results in the lowest amount of water absorption (%), lowest amount of conductivity, as well as the highest amount of gel content (%). The application of radiation process on the production of biodegradable films seems to be a good potential solution in substituting the synthetic plastics for a better future.

ABSTRAK

Aplikasi radiasi terhadap pengubahsuaian struktur polimer dilihat amat berguna disebabkan oleh peranan polimer yang penting dalam kehidupan seharian manusia. Secara globalnya, sebanyak 200 juta tan plastik digunakan, di mana kadar kenaikan penggunaan plastik ialah sebanyak 5 % bagi setiap tahun. Khususnya, penggunaan plastik sintetik yang meningkat saban tahun mengakibatkan masalah serius terhadap ekologi disebabkan oleh sifat semulajadinya yang tidak boleh dikitar semula mahupun dilupuskan. Oleh hal yang demikian, kajian ini bertujuan untuk menghasilkan filem boleh-lupus beradiasi yang bersifat antibakteria, bersumberkan kanji, di mana karakteristik filem tersebut akan diuji. Ujian tersebut termasuklah ujian resapan, ujian kandungan gel, ujian konduktiviti, ujian penggemburan tanah, dan pengimbasan elektron mikroskop. Daripada kajian ini, didapati bahawa dos tertinggi yang digunakan (30 kGy) adalah yang terbaik kerana kadar resapan air dan konduktiviti yang terendah, selain kandungan gel yang tertinggi. Aplikasi radiasi terhadap proses penghasilan filem biodegradasi ini dilihat sebagai satu langkah yang baik dalam alternatif menggantikan plastik sintetik untuk masa depan yang lebih terjamin.

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α	Alpha
β	Beta
γ	Gamma
PVC	Polyvinyl Chloride
PET	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
PVOH	Polyvinyl Alcohol
RH	Relative Humidity

1 INTRODUCTION

1.1 Background

Nuclear technology is also can be understood as a development of nuclear in science, which are based on the reactions of radiation, namely as alpha, beta, gamma rays and other charged particles with nuclei (Fujii-e, 1995). Alpha ray, or denominated as 'α-ray', is the weakest radiation among the others, where its velocity is only about 5% from the speed of light, and has a low depth of penetration. It consists of two protons and neutrons that are bounded together to become a helium nucleus. It is an ionizing radiation where discovered by Ernest Rutherford at 1899-1900.

Beta irradiation, or sometimes being called as electron beam irradiation (β-ray), is a highly-speed electron emitted by certain type of radioactive nuclei such as Potassium-40. Beta radiation penetrates hundred times more than alpha particles. However, it can be stopped by a piece of aluminium (Bennett, 2012). On the other hand, gamma radiation, signified by the Greek letter γ, is the strongest ray between the other two rays mentioned before. It is an ionizing radiation, where it exhibits an extremely high frequency and energy while being emitted. A French chemist, named Paul Vilard, while he was studying the radiation emitted by radium nuclei, discovered gamma radiation. Since it is a strong energy, it only can be stopped by the shielding of lead. However, the shield needs to be thicker, in order to stop the radiation according to the amount of particles being transmitted. The diagram and table below shows a clear definition between the types of radiation discussed.

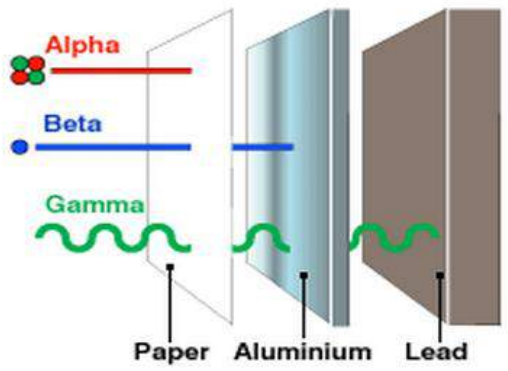

Figure 1.1 : Penetration depth for different types of radiation particles

Table 1.1 : Comparison between different types of radiation

Type of Radiation	Alpha particle	Beta particle	Gamma ray
Symbol	α or $^{4}_{2}\alpha$ or $^{4}_{2}He$	β or β^{-}	γ (can look different, depends on the font)
Mass *(atomic mass units)*	4	1/2000	0
Charge	+2	-1	0
Speed	slow	fast	very fast (speed of light)
Ionising ability	high	medium	0
Penetrating power	low	medium	high
Stopped by:	paper	aluminium	lead

Until Year 2013, there are more than two dozens of countries that have build the nuclear power plant, as reported by Cable News Network (CNN). The countries include Japan, United States of America, Russia, United Kingdom, France, China, India, and others. Although some countries are against the nuclear energy because of its usage is more on the production of firearms, it cannot be denied that nuclear energy is more efficient despite of its controversial issue. This is because, it is economically feasible and it generates more than 20% of electricity for the world's demand (Whitman, 2007).

Although nuclear energy seems to be a good alternative in supplying electricity for the future, it also can contribute in other applications. This includes wastewater treatment, pasteurization, sterilization of medical equipments, polymer modification, inhibition of sprouts for vegetables and fruits, treatment in cancer diseases, as well as gems stones colours' modification.

The application of radiation towards the polymer modification seems to be beneficial as polymers play an important role in our daily life. Furthermore, it is used as common packaging materials because of its features, which are soft, light, and transparent. Those packaging materials are polymer-based and most of them were added with several chemicals such as additives, stabilizers, colourants, and plasticizers.

At this moment, there is about 200 million tonnes of plastics consumption globally, with an approximation growth of 5% per annum. Currently, the petrochemical-based plastics such as polyvinyl chloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and others are largely used as packaging materials as its wide availability, low cost, besides of its good barrier to oxygen, heat ability, and so on (Sorrentino et al., 2007). This shows that those packaging films, or plastics, is the largest sector of application for crude oil (Siracusa et al., 2008). Nevertheless, it is needed to bear in mind, that the increasing of crude oil and natural gas price will as well affect the plastic market.

The plastic waste from petrochemical-based seems to be a serious scenario as most of the plastic packaging is non-biodegradable. Other alternatives have been taken in order to reduce the usage of these non-biodegradable plastics, including the substitution of plastic bags to paper bags and non-woven bags. However, those bags are not the best method in solving the problem, as the paper bags will torn in carrying heavier loads, and easy to get wet when it contacts with water, while the non-woven bag is costly.

1.2 Motivation & Problem Statement

Synthetic plastics that is made up from the petrochemical-based seems to be the best as they are light-weight, resistance to corrosion, and low temperature processing resulting in energy saving (Colwill et al., 2010). Although they are very good, they seem to face critical problems as they create pollutions to the environment. This is because; the increasing numbers of synthetic plastics packaging films has led to a serious ecological problem due to its non-biodegradability properties. Furthermore, Tang (2011) stated that its usage has been under attack since they lack of recycling facilities, non-recyclable, and non-renewable. In addition, it is easily are contaminated by foodstuff and biological substance and it is impracticable to recycle this materials, since it will contribute to a high cost of pyrolysis (Siracusa et al., 2008). Moreover, David and Song (2006) stated that recycling of plastics is difficult as it is not easy to identify the presence of other materials and additives inside it. Consequently, all of the plastics were dumped into the landfill sites, increasing the problem of municipal waste disposal (Kirwan & Strawbridge, 2003). However, if the waste poorly disposed, it may threats the wildlife when it enters the natural environment such as oceans or the rivers (Rao, 2010).

With the growing environmental concern, the substitution of conventional non-biodegradable synthetic materials to the biodegradable ones seems to be a great challenge. Although it does not promise a complete replacement with the eco-friendly packaging films, at least for specific applications like food packaging, the use of bioplastics should be the future. This is because, packaging films and containers made up of renewable sources have a relative short service life and end up in landfills (Jerez et al., 2007). Furthermore, it is a good research to pay attention at since it will reduce the dependence and consumption of petrochemical feedstock, as well as to diminish the environmental pollution issues (Rosentrater & Otieno, 2006). Other than that, it is designated to improve food safety or to maintain the quality of the packaged food.

Many studies on starch have been conducted for the past few years. Almost all of the past researches on the starch bioplastics involve chemicals, where the chemicals act as a cross-linker. However, in this research, a new approach is being introduced, where irradiation of the thermoplastic starch is using gamma ray (γ-ray), and it does not use any chemicals as the cross-linker. Instead of focusing on the production of thermoplastics starch itself, Parparita et al., (2010) suggested, the addition of an antimicrobial properties into the developed materials would be interesting.

The purpose of adding the antimicrobial properties towards the thermoplastic starch is to improve the food safety. It is such a good way to inhibit bacteria from growing in foods. For the antimicrobial properties, chitosan seems to be a suitable material for designing food coatings and packaging structures.

Therefore, this research is mainly about the production of irradiated antimicrobial starch films. Furthermore, several characteristics of different biodegradable films were investigated where different amount of irradiation dosages were injected towards the films.

1.3 Objective

The main objective of this research was to determine the effects of different dosage of γ-irradiation injected towards the films by certain characterization. The characterization includes 'Water Absorption Test', 'Gel Content Test', 'Conductivity Test', 'Soil Burial', and 'Scanning Electron Microscopy'.

1.4 Scope

In order to achieve the objective, different types of biodegradable films (Type I, II, III, & IV) were prepared with different types of ingredients. Starch solution, chitosan solution, and PVOH solution were prepared (2% w/v), with a ratio of 1:1:1 for each type of films. A small amount of glycerol solution (1% from total volume) was added into Type III & IV samples, while a small amount of metal solution (1% from total volume) was added into Type II & IV. Next, the samples were sent to Sinagama plant (Malaysian Nuclear Agency) to be irradiated using gamma ray at different dosages (10-30 kGy). The irradiated films were dried inside the vacuum oven with a temperature of $40^{o}C$ for 16 hours, before the characterization of biodegradable films were conducted.

The characterization includes ‘Water Absorption Test’, ‘Gel Content Test’, ‘Conductivity Test’, ‘Soil Burial’, and ‘Scanning Electron Microscopy’.

1.5 Organization of thesis

The structure of the reminder of the thesis is outlined as follows:

Chapter 2 provides the descriptions of each material that are used in the research. Other than that, this chapter is also discussing about the mechanism of cross-linking that occur during the radiation process that may cause modifications towards the polymer blends. Next, Chapter 3 is all about the methods involve during the research work. An overview of the methodology and the sample preparations is also presented. Findings and discussions are available in Chapter 4, where all of the results obtained from the characterization of films are presented in graphs and tables. Conclusions and recommendations for the research will be in the last chapter, which is in Chapter 5.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the experimental studies on the production of films from blends of starch-Polyvinyl alcohol (PVOH), and chitosan, where additives are added into it. Additives used are metal and glycerol. Since the natural polymers do not have a good mechanical strength, therefore, synthetic polymers sand additives are added in order to improve its strength. Generally, chemicals are used to ensure that the polymers cross-link each other, which resulting to a better mechanical properties. However, this research is using a different method of cross-linking, which is the irradiation process by using gamma ray.

2.2 Introduction

Food packaging has become an important role in food industries, where they are gaining more attention currently. Furthermore, there is also an increased awareness on sustainability. In terms of raw material, the renewable resources are used as a strategy to reduce the amount of carbon dioxide emissions besides of reducing the dependency on petrochemicals feedstock (Peelman et al., 2013). Moreover, according to the European Bioplastics organization, bioplastic is a plastic that made up of renewable resources where it consists of compostable properties. In this research, several characteristics of different biodegradable films made up of starch were investigated where different amount of irradiation dosages were injected towards the films.

2.3 Materials

2.3.1 Starch-based material

Among all of the natural biopolymers, starch is considered as one that has a bright future in producing bioplastics. Starch is a natural polymer that is mainly comprised of branched amylopectin and linear amylose where the amounts of the amylose and amylopectin varied according to the source and type of plants (Dean et al., 2008). Ray & Bousmina (2005) added, amylose molecules may consist of 200-20000 glucose units, where it occurs in the helix form, while amylopectin molecules may contain up to two million glucose units, since it is attached to every 20-30 glucose units along the chain. In some review, it mentioned that starch includes 30% of amylose and 70% of amylopectin (Zhai et al., 2002). Fazilah et al. (2011) stated that, amylose is relatively strong. Cross-linking in starch are mainly formed by amylose. In contrast, the branched amylopectin generally leads to brittleness in films, reducing the tensile strength.

Peelman et al. (2013), Averous et al. (2009), and Tang et al. (2011), agreed that starch is widely available and easy biodegradable natural resource. It can be used to form edible, as it is the major form of stored carbohydrates such as corn and wheat. Since the starch is widely available in nature, it is cheap and renewable. The problem with the starch is, it lacks in term of strength. Therefore, starch needs to be blended with other biodegradable synthetic polymer in order to overcome the drawback.

2.3.2 Starch-Polyvinyl Alcohol (PVOH) blends

Polyvinyl alcohol (PVOH) is a water-soluble synthetic polymer, which has good physical and chemical properties. It is not made up by the polymerization of vinyl alcohol. It is made by partial or completely hydrolysis of polyvinyl acetate to remove acetate groups (Tang & Alavi, 2011). Other than that, Bahrami et al. (2002) and Ibrahim et al. (2010) agreed that PVOH is non-toxic, and has the ability to form films. It has been used in many applications such as membrane preparation, recycling of polymers, and controlled drug delivery system besides of paper adhesives and paper coatings. PVOH is also acts as a water soluble polymer and oil resistance. Previous studies show that PVOH has the capabilities in forming gel, and it is very suitable to be used in medical applications such as haemodialysis, artificial pancreas, and implantable medical device. It is also exhibits the same properties of starch, where it is easy to degrade (Cascone et al., 2001)

PVOH depends much on humidity. In other words, the higher the humidity, the higher amount of water will be absorbed. The role of water is to act as plasticizer. Tensile strength will reduce if more water is being absorbed. However, the tear strength and its elongation will increase (Kuraray America, Inc., 2010). Since starch lacks the strength, PVOH seems to be a suitable choice to be blended with at any concentrations, in order to improve the mechanical properties of the material for variety applications.

The synthetic polymer is successfully become a biomaterial mainly due to its mechanical properties, other than its transformation processes that allow a variety of different shapes to be easily obtained besides of its low production costs. In contrast, biological polymers represent good biocompatibility but their mechanical properties are often poor, the necessity of preserving biological properties complicates their process ability and their production costs are very high. Therefore, it is favourable that intermolecular interaction exists between these polymer species.

From Zhai et al. (2002) previous study, a series of starch-PVOH blend was prepared and undergone the irradiation technique, by using the electron beam. As a result, after the blends were irradiated, the hydroxyl radicals could easily initiate both PVOH and starch. PVOH radicals will reacted easily with other PVOH molecules, forming the cross-linked networks between them. However, the reaction between starch and other starch was very low after the irradiation, where starch degraded obviously. In the overall view of the research, it shows that the blend of starch-PVOH showed an excellent elasticity and flexibility.

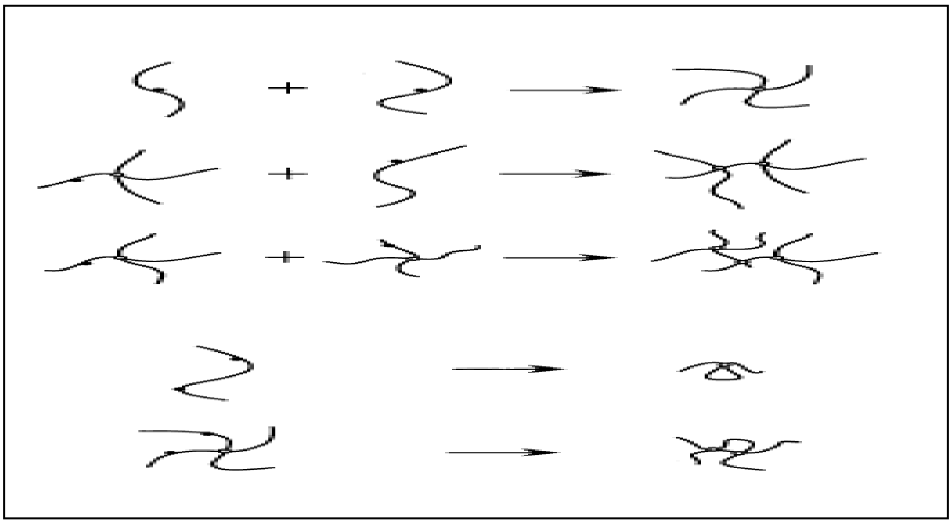

Figure 2.1 : Schematic representation of possible cross-linking reactions occur in PVOH solution during γ-irradiation

In other case, PVOH and chitosan were prepared by γ-irradiation (Yang et al., 2008). The swelling behaviour is an important parameter in practical uses of bioplastics. It should have low capacity in absorbing water content so that it will not expand. The swelling capacity decreases as the irradiation dose increases. This is because; the higher the irradiation dose will lead to a higher number of cross-linking. However, increasing the irradiation dose will lead to a higher degradation rate of the natural polymers. Therefore, a good plasticizer should be added into the bioplastics so that it will be practical to be used, as well as to enhance the properties.

Plasticizers such as glycerol, water, and sorbitol have been successfully employed (Liu et al., 1999; Park et al., 2005) in making the plastics. On top of that, glycerol seems to be more effective and powerful as compared to other plasticizers. The addition of glycerol towards the starch-PVOH blends help in preventing the development of surface cracks. This can be explained by the presence of hydroxyl groups (-OH) in their chemical structures. These highly polar hydroxyl groups tend to form hydrogen bonds which will improve the properties of the blends. The figure below shows a possible hydrogen bond formation between the starch and PVOH.

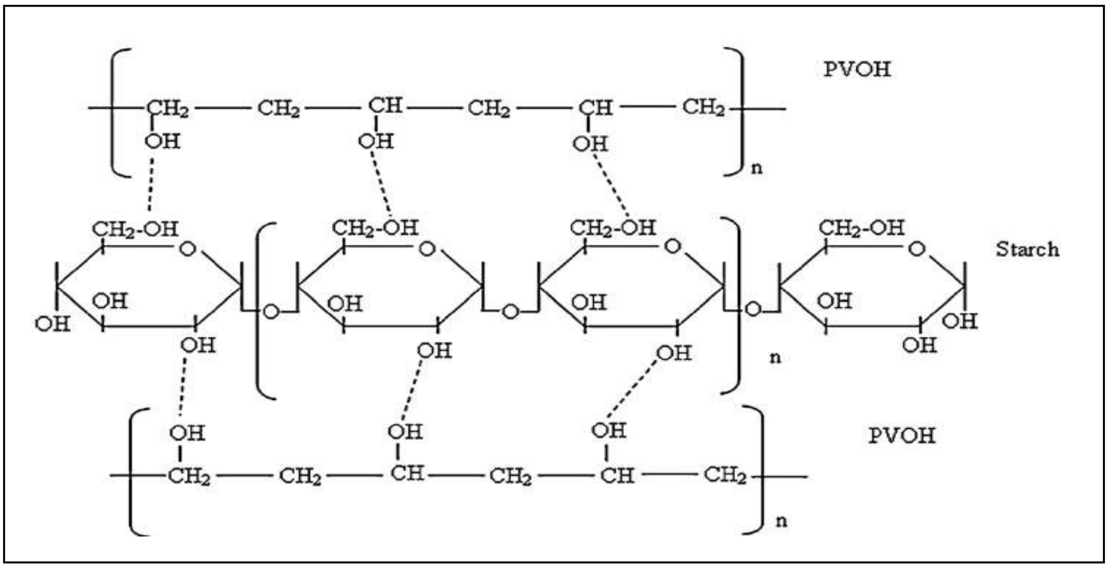

Figure 2.2 : Possible hydrogen bond formation between starch and PVOH

Another problem has arisen although the combination of starch-PVOH and glycerol seems to give a bright future in the food packaging industry where the blends are lacking in water barrier properties. Since they have a large number of hydroxyl groups, they exhibit hydrophilic nature. Mao et al. (2000) reported that starch–glycerol–PVOH formulations were very sensitive to relative humidity (RH) and tensile strength decreased significantly with increase of RH as stated earlier. Therefore, an alternative of improvements were taken by using the cross-linking reactions.

2.3.3 Chitosan

Chitin is first identified in 1884 and the second most abundant polysaccharide found in nature (Leceta et al., 2013). It is composed by the poly (β-(1-4)-N-acetyl-D-glucosamine). It is generally occurs in the exoskeleton of arthropods, crustaceans, or can be obtained in the cell walls of yeast and fungi. (Rinaudo, 2006; Tahtat et al., 2012). Table below shows some sources of chitin and chitosan.

Table 2.1 : Sources of chitin and chitosan

Sea animals	Insects	Microorganisms
Annelida	Scorpions	Green algae
Mollusca	Spiders	Yeast (β-type)
Coelenterata	Brachiopods	Fungi (cell walls)
Crustaceans:	Ants	Mycelia Penicillium
Lobster	Cockroaches	Brown algae
Crab	Beetles	Spores
Shrimp		Chytridiaceae
Prawn		Ascomydes
Krill		Blastocladiaceae

Source : J Chem Educ 1990; 67: 938–942.

Chitosan (Figure 4) is actually obtained by the deacetylation of chitin under alkaline conditions or by enzymatic hydrolysis in the presence of chitin deacetylase, where it is a waste product in crustacean processing. Commonly, those chitin and cell walls are functioning as a protective shield to the plants and animals respectively. At 50% degree of deacetylation, it becomes soluble in aqueous acidic media due to the presence of amino acid, and it does not dissolve in the universal solvent, such as water. When it dissolves in acidic media such as acetic acid, it results in a water-soluble cationic polyelectrolyte. Therefore, it is able to form electrostatic complexes under acidic conditions.

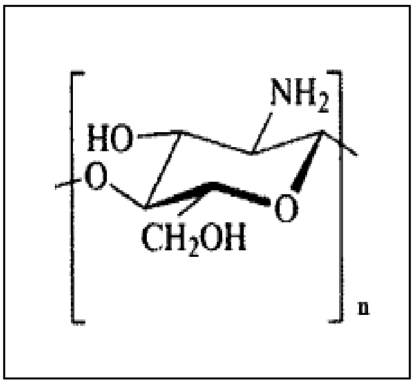

Figure 2.3 : Chemical structure of chitosan monomer unit (Rinaudo, 2006)

Chitosan, like other types of polysaccharides, is suddenly became a great attention in some industries such as cosmetics, agricultural, pharmaceuticals, and biomedical (Mourya & Inamdar, 2008) besides of being studied in the field of biomaterials. It is a good candidate as a support material as it exhibits antibacterial properties, antivirus and antiphage activities. This will retard the biological activities, where the growth of bacteria will be inhibited (Pospieszny et al., 1994). Table below shows the other properties of chitosan and its used in biomedical field. In addition, chitosan exhibits good oxygen barriers, besides of good in formation of films and membranes.

Table 2.2 : Properties of chitosan and its applications

Potential Biomedical applications	Principal characteristics
Surgical sutures	Biocompatible
Dental implants	Biodegradable
Artificial skin	Renewable
Rebuilding of bone	Film forming
Corneal contact lenses	Hydrating agent
Time release drugs for animals and humans	Nontoxic, biological tolerance
Encapsulating material	Hydrolyzed by lyzosyme
	Wound healing properties
	Efficient against bacteria, viruses, fungi

Source : Rinaudo, 2006

Blending of polymers seems to be a useful way to have new material with required properties and there have been great scientific and commercial progress in the area of polymer blends. This can be implemented more rapidly and economically than the development of new materials since new molecules are not always required to meet the need for new material (Cascone, 1997).

Although chitosan is impermeable towards the oxygen, however, chitosan seems to face the same problem with the starch-PVOH, where it has poor water barrier properties, since it consists of hydroxyl and amine group. Previously, chitosan has been cross-linked by chemical reagents such as epichlorohydrin and 1,4-butanediol diglycidyl ether in the presence of reducing agent (Welsh & Price, 2003). As a replace, irradiation process seems to be a good technique to cross-link the chitosan besides of degrading it (Tian et al., 2004). Although the chitosan undergoes degradation process, it still shows a good antibacterial activity.

2.4 Polymer Modification via Irradiation Process

Irradiation is a very convenient tool for the modification of polymer materials by using cross-linking, grafting, or degradation techniques (Lacroix et al., 2002). For gamma irradiation process, the source is mainly comes from Cobalt-60. However, Cobalt-60 is not found in nature. It acts as a synthetic radioactive isotope made by the neutron activation of Cobalt-59 (McKeen, 2012). Radiation processing is the most promising method, since the process is simple, and it is carried out at room temperature where no purification of the product is required after processing. Besides of its great application, the process does not need any initiators or cross-linkers, which may be harmful and difficult to remove (Yang et al., 2008). Most of polymers used being processed by the addition of initiators and other chemicals. As an example, the production of polystyrene involves the addition of initiators such as benzoyl peroxide. The initiator is oftenly used in order to generate free radicals, which is then, will lead to cross-linking process, where the cross-linking takes place through the covalent bonds or through the chemical bridges which connect the polymer molecules (Tamboli et al., 2004).

In addition, the irradiation process will promote the reduction of the mass of starch after being irradiated. In other words, the cross-linking reduces the melt index and elongation at break, while it helps in improving the strength besides of reducing the crack. As described by Tamboli et al. (2004), free radicals are generated via high energy of radiation. The high energy in radiation will abstract hydrogen from the backbone of polymer chain to produce free radicals as below.

$$\mathrm{PH} \xrightarrow{h\nu} \mathrm{H}^* + \mathrm{P}^*$$

After the free radicals have been generated, they will go through the process of cross-linking, as described by Peacock (2000). This will cause a dense network of polymer chains through chemical bonding. The phenomenon is also called as propagation. Instead of linear branch, it may lead to branching formation. Branching polymers are the reason for variation number of important physical properties such as hardness and