DURIAN SEED AS A POTENTIAL SUBSTRATE FOR BOLUS IN RADIOTHERAPY

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DURIAN SEED AS A POTENTIAL SUBSTRATE FOR BOLUS IN RADIOTHERAPY

By

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BIJI DURIAN SEBAGAI POTENSI BAHAN UNTUK BOLUS DALAM RADIOTERAPI

Oleh

FAIRUZDZAH BINTI AHMAD LOTHFY

Tesis yang diserahkan bagi memenuhi keperluan Sarjana Sains

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

A	Cross sectional area of the sample
B	N-Containing base
C	Carbon
CS	Corn Starch
CT	Computed Tomography
DDS	Dehulled Durian Seed
DP	Degree polymerization
dpi	Dots per inch
D_{max}	Dose at reference depth of maximum dose
D_s	Surface dose at beam entrance side
D_d	Dose at any depth
D_{ex}	Surface dose at the beam exit side
DNA	Deoxyribonucleic acid
E	Young's modulus
EB	Electron beam
F	Force
^oF	Fahrenheit
FDA	Food and Drug Administration
FSCF	Field size correction factor
G’	Elastic modulus
G’’	Viscous modulus
GR	Gamma ray
H	Hydrogen
HU	Hounsfield Unit
H_2O	Water
k	Number of groups
LLDPE	Linear low-density polyethylene
MU	Monitor unit
N	Nitrogen

O	Oxygen
OD	Optical density
P	Phosphorus
π	Pair production interaction
π/ρ	Mass attenuation of Pair production interaction
ρ	Physical density
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_z	Z- number of average molecular weight
N_A	Avogardo's number
MSE	Mean squares error
MSG	Mean squares group
n	Number of observation in the groups
ρ_e	Electron density
σ	Compton interaction
$\hat{\sigma}$	Standard deviation
σ/ρ	Mass attenuation of Compton interaction,
σ_{coh}/ρ	Mass attenuation of Coherent interaction
PV	Pixel value
$PV_{unirradiated}$	Mean pixel value for unirradiated film
$PV_{after\ irradiation}$	Mean pixel value of film after irradiation
PTV	Planning Target Volume
PVA	Polyvinyl alcohol
RPOP	Radiation Protection of Patients
R	Side chain
s_i	Standard deviation of the i_{th} group
S	Sulphur
Sp	Pooled estimate of the common population standard deviation
SE	Standard error
SID	Source Image Distance

SSE	Sum of square error
SSG	Sum of square group
TSP	Tamarind seed polysaccharide
τ	Photoelectric
τ/ρ	Mass attenuation of Photoelectric interaction
μ	Linear attenuation coefficient
μ_m	Mass absorption coefficient
(μ/ρ)	Total mass attenuation coefficient
WDS	Whole durian seed
Z_{eff}	Effective atomic number

BIJI DURIAN SEBAGAI POTENSI BAHAN UNTUK BOLUS DALAM RADIOTERAPI

ABSTRAK

Tiga jenis bolus telah dihasilkan dengan menggunakan tiga jenis komposisi dengan beza nisbah polivinil alkohol (PVA) terhadap gam biji durian. Nisbah PVA kepada gam biji durian untuk bolus jenis pertama ialah 1:9; 3:7 dan 5:5. Bolus yang dihasilkan diciri berdasarkan kepada sifat-sifat mekanikal seperti kekuatan ketegangan, terikan, dan kelenturan. Akhirnya, kesemua bolus yang dihasilkan mempunyai kekuatan ketegangan yang kecil. Kekuatan tegangan maksimum yang boleh dicapai untuk bolus 1:9 ialah 0.083 MPa, bolus 3:7 ialah 0.323 MPa dan bolus 5:5 ialah 0.786 MPa. Peratus terikan bagi setiap jenis bolus yang dihasilkan memenuhi keperluan minimum iaitu melebihi 50 %. Kesemua bolus yang dihasilkan mempunyai nilai Modulus Young yang rendah di mana memenuhi satu keperluan bagi bolus yang digunakan dalam radioterapi iaitu kurang daripada 100 MPa. Nilai ini penting untuk menghasilkan bolus dengan kelenturan yang baik. Bolus yang dihasilkan perlu mempunyai sifat kesetaraan tisu. Justeru, adalah satu keperluan untuk mengukur ketumpatan fizikal, ketumpatan elektron relatif dan faktor transmisi. Nilai ketumpatan fizikal untuk bolus 1:9 ialah 1.07 ± 0.01 g cm^{-3}, bolus 3:7 ialah 1.00 ± 0.01 g cm^{-3} dan bolus 5:5 ialah 1.00 ± 0.01 g cm^{-3}. Ketumpatan bolus 1:9 berbeza dengan ketumpatan air sebanyak 7 %. Bolus 3:7 dan bolus 5:5 tidak mempunyai beza ketara dengan ketumpatan air. Walau bagaimanapun, dengan membandingkan semua

ketumpatan bolus yang dihasilkan dengan senarai ketumpatan bolus komersial, nilai-nilai tidak menunjukkan beza ketara terhadap ketumpatan. Ketumpatan elektron relatif untuk bolus 1:9 ialah 1.028 ± 0.019, bolus 3:7 ialah 1.002 ± 0.003 dan bolus 5:5 ialah 1.002 ± 0.002. Dengan membandingkan ketumpatan elektron relatif bolus 1:9 dengan ketumpatan elektron relatif air ia menunjukkan perbezaan ketara manakala bolus 3:7 dan bolus 5:5 menunjukkan tiada beza ketara. Faktor transmisi diukur dengan mengira peratus kedalaman dos (PDD) pada kedalaman dos maksimum selepas menggunakan bolus. PDD pada kedalaman dos maksimum untuk bolus 1:9 ialah 85.63%, bolus 3:7 ialah 98.13%, dan bolus 5:5 ialah 98.88%. Perbandingan faktor transmisi bolus 3:7 dan bolus 5:5 dengan phantom air 2967 menunjukkan tiada perbezaan ketara dan faktor transmisi bolus 1:9 dan phantom air 2967 menunjukkan perbezaan ketara.

DURIAN SEED AS A POTENTIAL SUBSTRATE FOR BOLUS IN RADIOTHERAPY

ABSTRACT

Three types of bolus were fabricated using three types of composition with different ratios of polyvinyl alcohol (PVA) to durian seed gums. The ratio of PVA to durian seed gum were 1:9; 3:7 and 5:5. The fabricated bolus was characterized based on the mechanical properties such as tensile strength, strain, and flexibility. Eventually, all bolus composition that were prepared had low tensile strength. The maximum tensile strength for bolus 1:9 was 0.083 MPa, bolus 3:7 was 0.323 MPa and bolus 5:5 was 0.786 MPa. The strain of every type of fabricated bolus fulfilled the minimum requirement which was more than 50%. All types of bolus had less than 100 MPa value of Young's Modulus which fulfilled one of the requirements for bolus to be used in radiotherapy. This value was important to produce bolus with good flexibility. The fabricated bolus had tissue equivalent properties. Hence, physical density, relative electron density and transmission factor were measured. Physical densities for bolus 1:9 was 1.07 ± 0.01 g cm^{-3}, bolus 3:7 was 1.00 ± 0.01 g cm^{-3} and bolus 5:5 was 1.00 ± 0.01 g cm^{-3}. The density bolus 1:9 differed from water density by 7 %. However, density bolus 3:7 and bolus 5:5 had no significant difference with water density. All types of fabricated bolus density were compared with a list of commercial bolus density. The values did not show significant difference towards the density. Relative electron density for bolus 1:9 was 1.028 ± 0.019, bolus 3:7 was

1.002 ± 0.003 and bolus 5:5 was 1.002 ± 0.002. There was a significant difference in electron density between bolus 1:9 and water. However, bolus 3:7 and bolus 5:5 showed no significant differences. Transmission factor was measured by calculating the percentage depth dose (PDD) of the maximum depth dose.. PDD of the maximum depth dose for bolus 1:9 was 85.63%, bolus 3:7 was 98.13%, and bolus 5:5 was 98.88%. The comparison of transmission factor for bolus 3:7 and bolus 5:5 with water phantom type 2967 showed no significant difference, and transmission factor of with bolus 1:9 and water type 2967 showed significant difference.

CHAPTER 1

INTRODUCTION

1.1 Background

In radiotherapy, the correct amount of radiation is desired to extinguish the abnormal tissue, like cancer in head and neck, brain, breast, cervical, prostate and skin cancer. It is capable to devastate some benign diseases (Radiation Protection of Patients, 2013).

The radiotherapy treatment inadvertently to gives exposure to normal tissues. A case in point is patients may get the effect to damage of the normal tissue during the course of therapy at a few weeks, months or years after therapy. As an example, the salivary glands are often affected when radiotherapy is given for head and neck cancer. Rectums are often affected by pelvic irradiation for treatment of prostate and cervical, skin, mucosa, subcutaneous tissues, and bone cancer (Stone et al., 2003).

Megavoltage photon radiotherapy penetrates the skin to irradiate deep-seated tumors, with skin-sparing property. Consequently, one must be a layer on the skin to act as the skin surface as purpose to treat superficial lesions. Hence, bolus is used in order to deliver the full prescribed dose to the skin surface and underlying tissue (Vyas et al., 2013). Bolus is also applied to the surface of a patient to compensate irregular patient contour, negating skin sparing, and extra attenuating. Bolus is put in close contact with the human body to correct for the distribution of absorbed dose in radiotherapy.

The required properties for the bolus are Young's Modulus of less than 100 MPA, ability to withstand 50 % strain and the substance must have radiation properties equivalent to human body tissue. The standard bolus should not sag during treatment. Basically, bolus should have good plasticity, flexibility and adhesion to a living body besides free from air bubble (Cooney et al., 2006; U.S Patent no. 6,231,858 B1, 2001).

Durio zibethinus, commonly called as 'Durian' is favorable tropical fruit in some Asean countries. Fruit Crops Statistic Malaysia,(2012) written by Department of Agriculture, Malaysia states that the durian is the main fruit planted in Malaysia. Figure 1.1 shows that durian crop is most the abundant fruit in Malaysia among ten types of fruit crops. The production of durian is 347,704 metric tonne (Agriculture Department, 2012).

Pie chart : Fruit Heritage Malaysia, 2012)

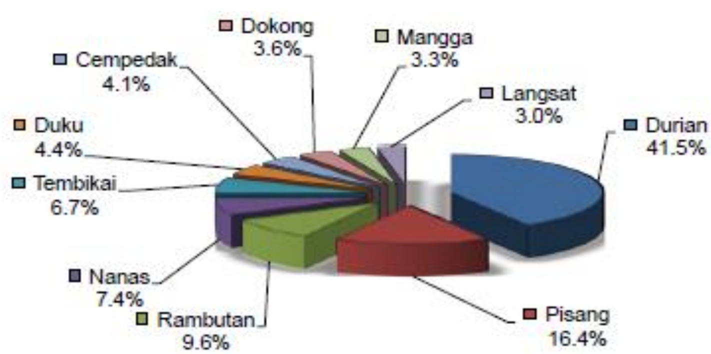


Figure 1.1. Pie chart of Fruit Heritage, Malaysia 2012. Adapted from Fruit Crop Statistic 2012 (p.7) by Agriculture Department, Malaysia.

Durian seed consists aproximately 20 % to 25% of the total fruit mass (Amid et al., 2012) and has 54.90 % moisture, 1.58 % ash, 3.40 % protein, 1.32 % fat and 18.92 % starch in durian seed (Srianta et al., 2012). The biopolymer from durian seed consists of a heteropolysaccharide-protein structure (Amid & Mirhosseini, 2012a). Natural biopolymer from plant sources provides variety of functional properties and has more advantages than synthetic polymer. It is due to its biocompatibility, non-toxicity, and inexpensive properties (Navaratne & Nawarathne, 2014). Chemical composition and molecular structure of the polymer induce the physiochemical and functional properties of natural plant-based biopolymer (Amid et al., 2012). The processes such as extraction, purification, drying and/or further modification significantly affects the chemical composition, molecular structure, rheological properties and viscoelastic behavior. As a consequence, it will involve the functional properties of biopolymers (Amid & Mirhosseini, 2012a; Amid & Mirhosseini, 2012b). Therefore, this modification allows the polysaccharide-protein biopolymer from *Durio zibethinus* seed to be a new substrate for bolus production. This study will focus on the fabrication of the bolus for radiotherapy by using a new substrate which is durian seed.

1.2 Scope of study

The scope of this study was to make the durian seed as a new substrate for bolus in radiotherapy. Bolus was fabricated by applying the the blended durian seed gum and polyvinyl alcohol (PVA). The best methods such as extraction, purification and drying of the seeds have to be selected to get it as an appropriate gum for producing the bolus. All of these methods can influence the chemical composition, molecular structure, rheological properties and viscoelastic behavior from the durian seed gum (Amid et al., 2012; Amid & Mirhosseini, 2012b, 2012c).

In general, the fabricated bolus must be equivalent to human body tissue, homogeneous, excellent plasticity, good form-compatibility and adhesive to the human body. Other criteria such as toxicity level are important due to direct contact of bolus on human skin surface during treatment. The fabricated bolus must fulfill all the aforementioned properties and conditions.

1.3 Problem Statement

Requirement of consumable materials that are disposed such as bolus was practiced as a way to prevent bacterial and viral infections in the hospital through medical apparatus and instruments. Although the price of conventional boluses using plastics, paraffin, silicone, or synthetic rubbers as their base material is very high, but they must be disposed as industrial waste. This is due to that, used boluses cannot be disposed effortlessly without treatment. It is impracticable to dispose the bolus after only one use due to high cost. If water is used as a bolus material, the container enclosing water is difficult to discard (U.S. Patent no. 6,231,858 B1, 2001).

Nowadays, many types of synthetic polymers are used to produce bolus such as elastometric polymer, synthetic rubber and paraffin (U.S. Patent no. US 6,231,858 B1, 2001). Most of these substances originate from petroleum and most of the conventional ones are regarded as non-renewable petroleum sources. Petroleum resources are limited and the use of non-degradable polymers causes environmental problems (Shafik et al., 2014).

Durio zibethinus is a commercial farming industry. Approximately 20 % of durian mostly thrown away after consumption (Amid et al., 2012). Natural polymers are suitable sources for their inherent biodegradability, accessibility, and relatively low cost. Thus, crop waste such as durian seed can be used to develop a new product.

1.4 Research Objectives

The objectives of this study are:

1. To fabricate a bolus for radiotherapy by using durian seed as a new substrate.
2. To ensure that the fabricated bolus satisfies the dosimetric properties, physical and mechanical characteristics needed.

1.5 Significant of Study

Natural organic polymers such as *Durio zibethinus* seeds, ordinarily be as crop waste after consumption. Hence, this crop waste can be a new resource of raw material which encourages development of value added product. The features of *Durio zibethinus* seeds make it appropriate as the bolus for radiotherapy.

In addition, by using the *Durio zibethinus* seed to replace the current material used as bolus, the cost for producing the bolus will be inexpensive. In addition, the natural organic polymers will preserve the petrochemical resources and reduce environmental impact.

CHAPTER 2

LITERATURE REVIEW

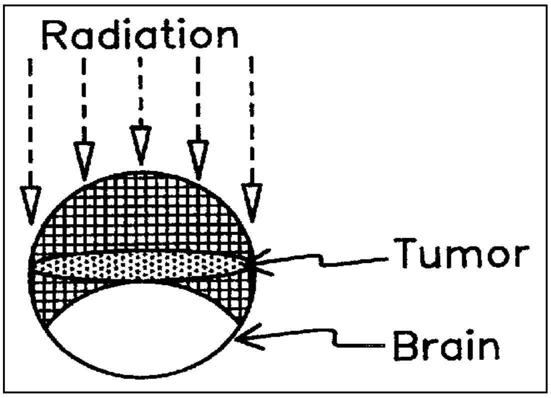
2.1 Importance of bolus in radiotherapy

Megavoltage photon, such as gamma-rays or x-rays causes deoxyribonucleic acid (DNA) devastation of cell in target area in radiotheraphy. The most familiar radiation treatment used is external radiation from the machine outside out of the patient's body such as a linear accelerator (U.S. Patent no. 2008/0123810 A1, 2008).

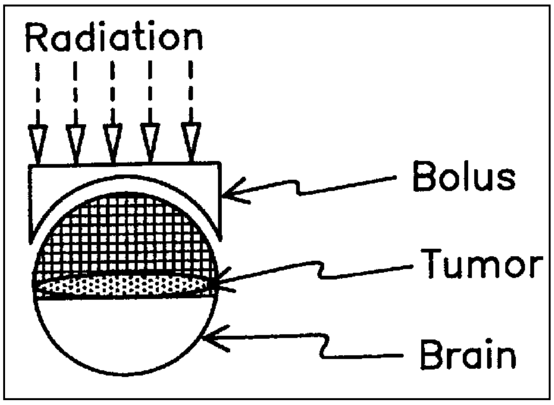
By destroying the genetic material that controls how the cells develop and divide, the radiation is able to trigger cell injury and devastation. By using the higher energy radiation, both healthy and malignant cells are destroyed (American Cancer Society, 2014).

Radiotherapy treats a target volume, which can be allocated at the breast or thoracic wall, the axillary region, the supraclavicular region, and the internal mammary chain. The presence of healthy organs in close proximity of the target to be treated can lead to side effect of radiation. It must be avoided especially the lungs, the heart, the brachial plexus, the cervical spinal cord, the larynx and the thyroid (U.S. Patent no. 2010/0070236 A1, 2010).

The main purpose of radiotherapy bolus is to equate the irregular patient contour and provide a flat surface for normal beam incidence. Hence the bolus consists of tissue equivalent material properties which is positioned directly on the skin surface. Theoretically, the use of bolus is useful in radiotherapy treatment (Podgorsak, 2005).



(a)



(b)

Figure 2.1: Radiation Distribution (a) without bolus (b) using bolus (U.S. Patent no. 6231,858 B1, 2001).

Figures 2.1 (a) and 2.1 (b) illustrated the difference in dose distribution of rays with or without a bolus in radiotherapy for head. The bolus controls dose dissemination of X-rays to irradiate the maximum absorbed dose to the focus target volume.

The second purpose of the bolus is to treat the lesions on or close to the skin surface. Bolus material is placed on top of the skin region undergoing radiation therapy to raise the radiation dosage at the skin surface. Hence, the aim to treat the lesions on or close to the skin surface can be achieved by increasing dose on or close the skin surface.

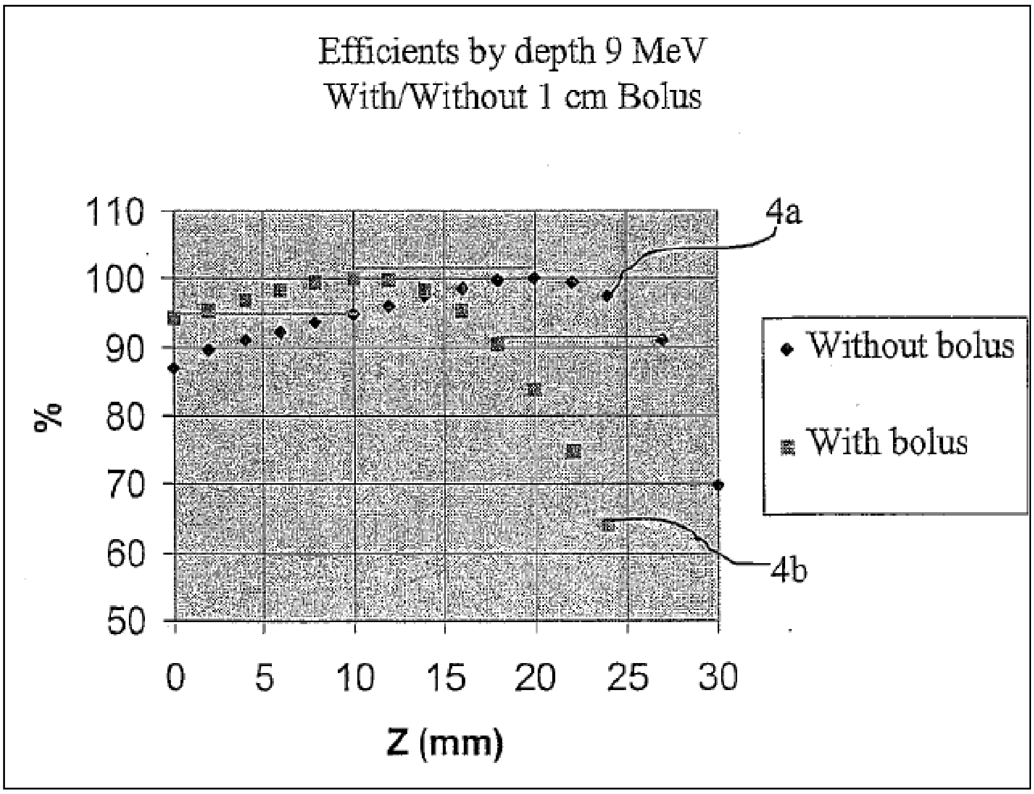
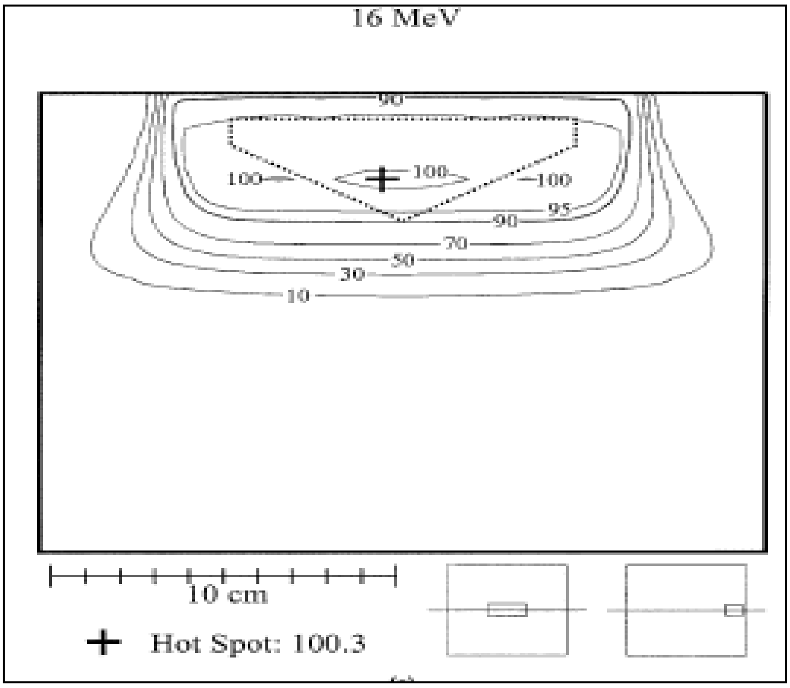
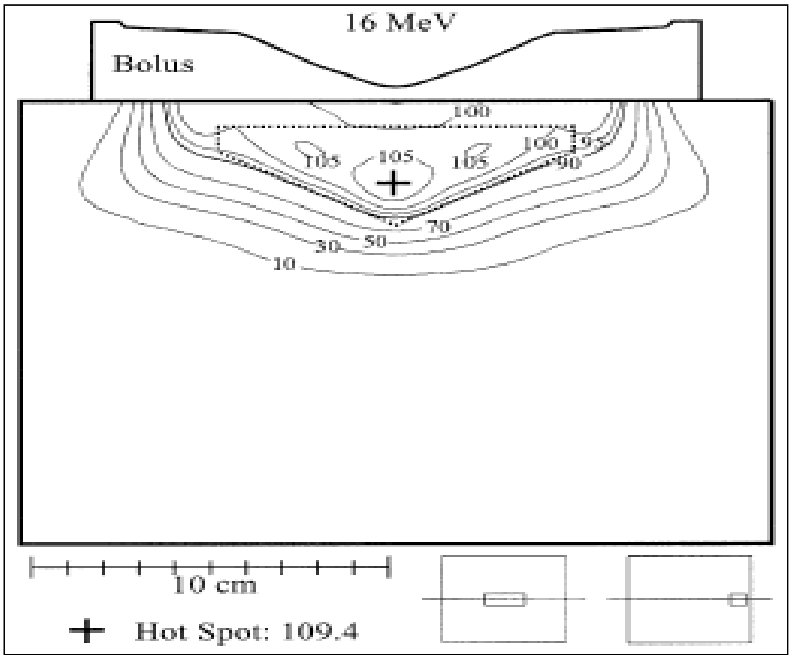


Figure 2.2: The efficiency of an electron beam dose as a function of distance of penetration into the human body, in the presence (4b) and in the absence (4a) of a bolus according to the present invention (U.S. Patent no. 2010/0070236 A1, 2010).

Figure 2.2 illustrated two efficiency curves 4a and 4b as a function of the depth of penetration of the electron beam for the source of 9 MeV electrons and for 1 cm bolus. A bolus with tissue equivalent properties of 1 cm bring about the maximum dose shifted about 1 cm. Thus, the maximum dose is achieved at the depth of 1 cm, then the curve decreases rapidly. Consequently, it allows the healthy organs close to the target is prevented from being damaged (U.S. Patent no. 2010/0070236 A1, 2010).



(a)



(b)

Figure 2.3: Dose distribution for hypothetical target volume case (a) without electron bolus, (b) with electron bolus (Kudchadker et al., 2002).

Figure 2.3 (a) illustrated that planning target volume (PTV) is covered by the 90 % isodose, and the dose variation is about 10 %. As a consequence of that, a significant volume of healthy tissue outside the PTV is being exposed to higher dose (> 90 %). Figure 2.3 (b), the 90 % isodose line now follows the distal boundary of PTV. As a result, it minimizes the potential of damage the healthy tissue outside the PTV (Kudchadker et al., 2002). However, tumors will receive needed doses in an actual situation for the patient without bolus, but normal tissue received overdoses. It is therefore essential to use electron bolus to compensate for above irregular. Hence, to make sure that the required dose is received by the patient, bolus with adequate thickness must be placed correctly. Bolus requirements must be clearly documented to ensure the delivered doses to patient are homogeneneous (Kudchadker et al., 2002).

2.2 Characteristics of bolus

Commonly the usable bolus must fulfill the following properties and conditions. For physical properties, the bolus should be homogenous, resilient, has excellent plasticity, form-compatibility and adhesiveness to a living body. In addition, the bolus materials are non- toxic, have even thickness and do not contain air (U.S. Patent no. 6,231,858 B1, 2001).

The mechanical properties of bolus such as Young's Modulus must be less than 100 MPa and ability to withstand over 50 % strain. Bolus materials must have stability between 40 ^{o}F and 125 ^{o}F. The bolus should be odorless, non- tacky, non-adherent, and its types of materials have been approved by Food and Drug Administration (FDA) for human skin contact (Cooney et al., 2006).

Boluses should have tissue-equivalent (within 2 %) dosimetric properties. The tissue equivalent properties need to comprise a density that is equal to water. Thus, the density of bolus material can be about 1 g cm^{-3}. Alternative ways need to be taken if the density value is not equal to 1 g cm^{-3} in order to achieve tissue equivalent properties. The thickness of the bolus material needs to be adjusted based on the ratio of thickness to obtain the desired tissue equivalent properties. For instance, a bolus material of an oil gel comprising mineral oil and suitable styrenic block copolymer have density between about 0.86 g cm^{-3} and 0.91 g cm^{-3}. This bolus material may achieve the desired tissue-equivalent dosimetric properties by adjusting the bolus thickness (U.S. Patent no 2008/0123810 A1, 2008).

Preferably, the bolus material should be checked by comparing the depth dose distribution in the bolus and the water. If scaling factor is needed, it should be documented and used in treatment planning while using the bolus (Khan & P.Gibbons, 2014).

2.3 Current bolus technology in radiotherapy

Commercial materials that are often used as bolus are such as paraffin wax, polystyrene, lucite, superstuff, and superflab. Superflab bolus is a good bolus. This material has fulfilled the requirement of the bolus for radiotherapy which are transparency, flexibility, and almost water equivalent (Khan & P. Gibbons, 2014).

All the bolus material must obtain Food Drug and Administration (FDA) approval for human contact. Bolus consists of pre-formed gel sheets that are draped over the target area and usually comes in form of ready made such as superflab and elasto-gel. Bolus also comes in form of powders and mix with water, then molded onto the target area where they solidify such as Super Stuff and Aquaplast RT (Cooney et al., 2006).

Superflab bolus (Figure A.1) is the most popular, best confirming, not expensive and non-sticking (Feaster, 2014). The composition of these bolus materials of gels are vinyl plastic w/di-isodecyl phthalate and water-based gels with acrylic polymer. It fulfills the requirements of producing bolus which are flexible, have uniform thickness, and conform to the skin. The density of Superflab bolus is 1.02 g cm^{-3}. Maximum strain for superflab bolus 1.6, tensile stress is 120 MPa, and Young's modulus 37 MPa at low strain to 97 MPa high strain (Cooney et al., 2006). Superflab bolus material can be washed with soap and water, followed by a talcum or corn starch that can be cut with scissors and approved for human contact. Superflab bolus material is provided in varying thicknesses as to provide maximum dose build-up for relevant photon energies. A superflab bolus needs to be handled with a full care due to synthetic oils that can damage plastic surface (Feaster, 2014).

Elasto-gel bolus (Figure A.2) has self-adhesive nature of gel material that provides excellent skin contact without air gaps and maybe layered together for different thicknesses (Radiation Products Design Inc., 2013). Elasto-gel bolus consists of non-toxic material and transparent and does not have any changes on the physical properties such as appearance and property of the elasto-gel pad after irradiating with high doses (Chang et al., 1992). Elasto-gel bolus is easy to use which can be easily cut into the desired size and shape, mildly adhesive, reusable on the same patient, and conforms exceptionally well to body contours (JRT

Associates, 2012). Elasto-gel bolus is prepared by mixing the water, glycerine, and acrylic polymer, which gels the whole mixture. Density elasto-gel bolus is 1.20 g cm^{-3} (Chang et al., 1992).

Aquaplast RT bolus (Figure A.3) is used for single patient use. This bolus is placed in hot water, then the material softens and can be molded to almost any area of the body without air pockets. Aquaplast RT bolus material has a density about 1.7 g cm^{-3} (JRT Associates, 2012).

2.4 Durian seed gum composition and properties

"Gum" is defined as a group of naturally occurring polysaccharides and / or proteins initiate from different sources such as animal, plant and microbial (Amid et al., 2012). Gums are substances contain of hydrophilic, long-chain, high molecular weight molecules, commonly with colloidal properties, that in water-based systems produce gels. It has highly viscous suspensions or solutions in low dry-substance content. Ordinarily, primary purpose of gum for thickening and/or gelatin (Hoefler, 2004). Natural plant gums are usually safe for oral consumption due to their safety (non-toxic), low cost and availability (Amid et al., 2012). pH value of the durian seed gum solution is 6.93 at room temperature, which are quite similar with guar gum. It is stable in condition of pH between 2.0 to 10.0 (Amin et al., 2007). The durian seed can be made up of 54.90 % moisture, 1.58 % ash, 3.40 % protein, 1.32 % fat and 18.92 % starch (Srianta et al., 2012). Amin et al (2007) studied the composition of durian seed gum for the whole durian seed (WDS) flour and dehulled durian seed (DDS) flour. This study found that WDS contains 6.5 % water, 6.0 % protein, 3.1 % ash, 0.4 % fat, 10.1 % crude fiber and 73.9 %

carbohydrate. For DDS, it contains 6.6 % moisture, 7.6 % protein, 3.8 % ash, 0.4 % fat, 4.8 % crude fiber and 76.8 % carbohydrate (Amin & Arshad, 2009).

The highest monosaccharide in the carbohydrate composition of durian seed gum are galactose (48.6-59.9 %), glucose (37.1-45.1 %), arabinose (0.58-3.41 %), and xylose (0.3-3.21 %) (Amid et al., 2012). The large fatty acid of the lipid fraction from the durian seed gum comprises palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid. The largest amino acids of durian seed gum consists of leucine (30.9-37.3 %), lysine (6.04-8.36 %), aspartic acid (6.10-7.19 %), glycine (6.07-7.42 %), alanine (5.24-6.14 %), glutamic acid (5.57-7.09 %), valine (4.5-5.50 %), proline (3.87-4.81 %), serine (4.39-5.18 %), threonine (3.44-6.50 %), isoleucine (3.30-4.07 %), and phenylalanine (3.11-9.04 %) (Amid et al., 2012).

Amin et al (2007) found that the main sugar of durian seed gum are rhamnose, D-galactose, and glucose in the ratio of 3:1:9. This study found that durian seed gum do not have galactomannan (Amin et al., 2007). The major element in forming of gum in durian seed is L-rhamnose, which is a C-5 polysaccharide (Amin et al., 2007). Polysaccharide can form the structure of arrest water molecules when rhamnose sugar contacts with water. As a result, a thick gel is formed after arresting water molecules by C-5 polysaccharide (Navaratne and Nawarathne, 2014).

The natural polymer from durian seed has more elasticity (gel- like behavior) than viscous (liquid-like) characteristic at a low frequency (Amid & Mirhosseini, 2012c). The natural heteropolysaccharide/protein polymer from durian seed gum has a relatively low solubility ranging from 9.1 % to 36.0 % (Amid & Mirhosseini, 2012c). It is caused by the presence of impurities, insoluble matter and large particles present in the chemical structure of the natural polymer from the durian seed gum. The viscosity of crude durian seed gum consists of diverse values from 3.3 mPa.s to 24.3 mPa.s reliant on the extraction condition. The protein content of crude durian seed gum ranges from 3.8 % to 9.3 %, and it depends on chemical extraction condition. Degree of elastic modulus (G') ranges between 1.48 Pa to 9.46 Pa and degree of viscous modulus (G'') varies from 0.28 Pa to 4.51 Pa (Amid & Mirhosseini, 2012c).

The functional characteristics of polysaccharide plant gums are governed by the chemical composition, molecular weight, sequence of monosaccharide, configuration of glycoside linkages, and the position of glicoside linkages in the backbone and side chain (Amid et al., 2012). The composition, molecular structure, rheological behavior and functional properties of durian seed depend on the method of extraction condition, purification and drying process(Amid et al., 2012; Amid & Mirhosseini, 2012a, 2012b, 2012c; Mirhosseini et al., 2013).

Chemically-extracted durian seed gum has a typical gel network and revealed gel like behavior at low concentration (0.5 % w/w) and low frequency (0.1 Hertz). Degree of gel-like or viscosity behavior depends on gum concentration. When elastic modulus is higher than the viscous modulus, the sample behaves more gel-like behavior and weak viscous behavior. Table 2.1 showed extraction condition effect extraction yield, viscosity, elastic modulus, viscous modulus, and solubility (Amid & Mirhosseini, 2012a).

Table 2.1: Independent and response variable effected by extraction condition. H;high , M;medium , L; low (Amid & Mirhosseini, 2012a).

Variable	Decoloring times (minutes)			Soaking times (hours)			Soaking temperatures (C^o)		
	60	**120**	**180**	**4**	**8**	**12**	**25**	**40**	**55**
Extraction yield	L	M	H	L	M	H	L	M	H
Viscosity	H	M	L	H	M	L	M	L	H
Protein content	$P \geq 0.05$			H	M	L	M	H	L
Elastic modulus	L	M	H	H	M	L	-		
Viscous modulus	-			H	M	L	H	M	L
Solubility	H	M	L	L	M	H	L	M	H

Based on a previous study, purified seed gum contains 17.9 % of moisture content and 29.8 % total ash content (Amin et al., 2007). Ash content of durian seed gum was higher compared to the others commercial gum and only 0.2 % of the ash as water soluble (Amin et al., 2007). The ash will lead the natural gum to less solubility. The effect of purification process to minimize the ash contents (Table 2.2) (Amid et al., 2012).

Table 2.2: Effect of different purification technique on moisture %, total ash % and lipid % content of durian seed gum. A; isopropanol and ethanol, B; isopropanol and acetone, C; saturated barium hydroxide, D; Fehling solution (Amid et al., 2012).

Test	Crude gum (Aqueous)	Crude gum (Chemical)	Purified gum A	Purified gum B	Purified gum C	Purified gum D
Moisture %	26.8 ± 1.09[a]	24.6 ±1.22[ab]	23.2 ± 1.03[b]	22.8 ± 0.79[bc]	20.5 ± 0.35[c]	21.7 ± 1.13[bc]
Total ash %	32.8 ± 1.57[a]	34.3 ± 1.78[a]	20.6 ± 0.89[b]	23.4 ± 1.34[b]	15.8 ± 1.13[c]	12.1 ± 0.94[d]
Soluble ash %	1.7 ± 0.03[a]	1.5 ± 0.01[a]	0.9 ± 0.00[b]	1.0 ± 0.14[b]	0.7 ± 0.03[c]	0.5 ± 0.06[d]
Lipid %	1.92 ± 0.07[a]	0.78 ± 0.11[b]	0.14 ± 0.04[c]	0.16 ± 0.02[c]	0.21 ± 0.06[d]	0.19 ± 0.03[d]

All drying methods lead to significantly lower the elasticity (G’) and viscous modulus (G”) of durian seed gum. The freeze-dried gum and oven-dried (105 ^{0}C) gum reveal the highest and lowest viscous modulus (G’). All drying techniques significantly ($p<0.05$) change the dynamic viscoelastic properties durian seed gum. All drying techniques show significant ($p<0.05$) reduction of both elastic (G’) and viscous modulus (G”) (Figure 2.4) (Amid & Mirhosseini, 2012c).

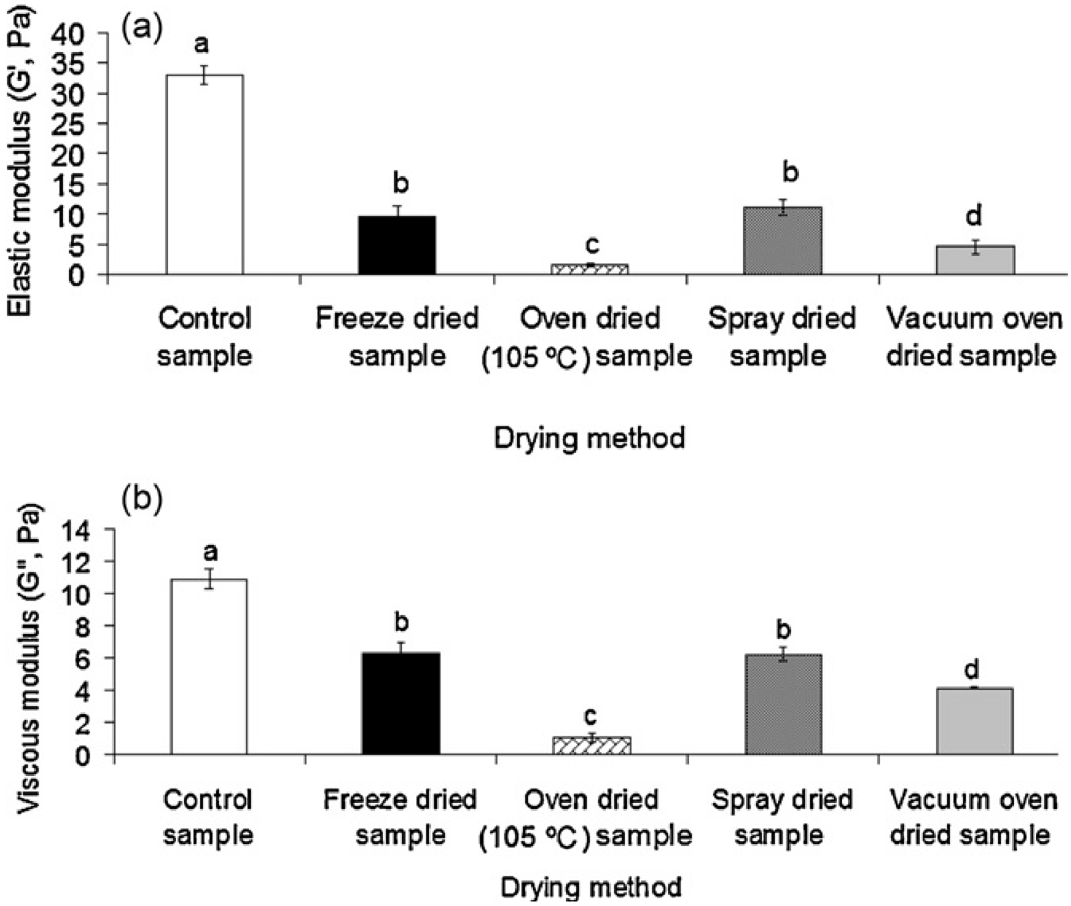


Figure 2.4: Effect of different drying technique techniques on the elastic modulus (G') and viscous modulus (G") of durian seed gum significant differences at 95 % confident level (Amid and Mirhosseini, 2012b).

2.5 Polyvinyl alcohol improve mechanical properties of natural polymer

Polyvinyl alcohol (PVA) is a synthetic biodegradable polymer and possesses excellent mechanical properties. PVA has physical properties such as adhesive strength, tensile strength and flexibility. For instance , pure PVA films have tensile modulus at 1.9 ± 0.2 GPa (Zhang et al., 2003). PVA has improved mechanical properties of natural biopolymer since natural biopolymer have poor mechanical properties.

Previous study on the different ratios of PVA to starch shows that it improves the dimensional stability and strength (Sadhu et al., 2014). By increasing the ratio of PVA to starch, the mechanical strength improves (Sadhu et al., 2014).

Shafik et al (2014) illustrated the variation of the tensile strength with blend ratio PVA/ corn starch (CS) blend film. As the percentage of the corn starch in the blends ratio increases, the tensile strength decreases. This study concludes that the amorphous nature of starch increases the brittleness (Figure 2.5) (Shafik et al., 2014).

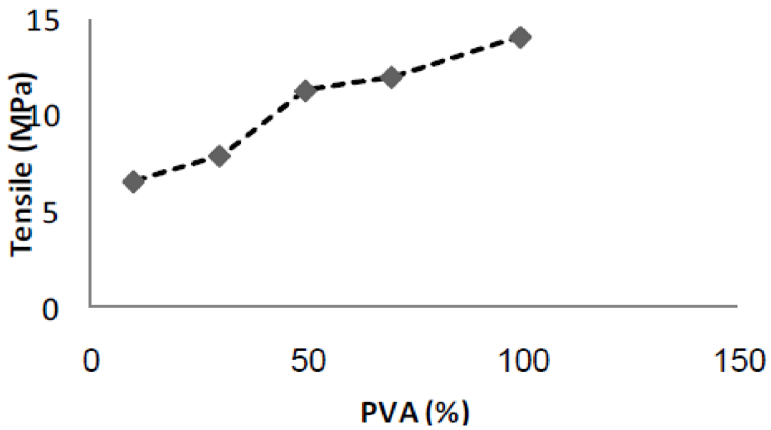


Figure 2.5: Effect of PVA/ corn starch (CS) ratio on tensile strength with (10 % formaldehyde) (Shafiq et al., 2014).

Research conducted by Parvin et al (2010) reveal that the tensile strength increases as percentage of PVA in starch increases. It is due to the decreased crystallization of the blend film. The researchers use micrograph analysis to observe the physical structure of the blend film. Figures 2.6 (a)-(c) illustrate the micrographs of 10 % to 30 % starch containing blend films. The micrographs also divulge that the phase structures in the starch/PVA blend films with different ratios of starch have significant differences. These figures show that by increasing the concentration of starch from 10 % to 30 %, starch micro domains reverse to be continued phase from disseminate phase, which implies that the amorphous starch is partially miscible with PVA (Parvin et al., 2010).

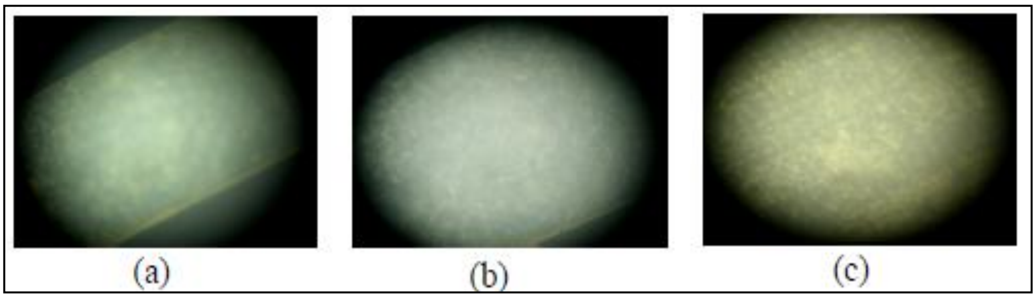


Figure 2.6: Stereo micrograph of starch/PVA blend film (Parvin et al., 2010).

Shafik et al (2014) found that the smallest PVA weight percent shows the lowest percentage of elongation at break for PVA/CS films. This is due to the amorphous nature of starch led to a lower elongation at break of the films (Figure 2.7) (Shafik et al., 2014).

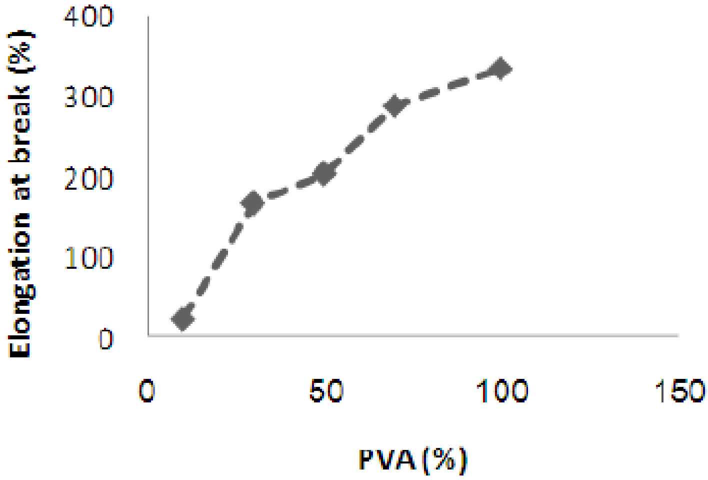


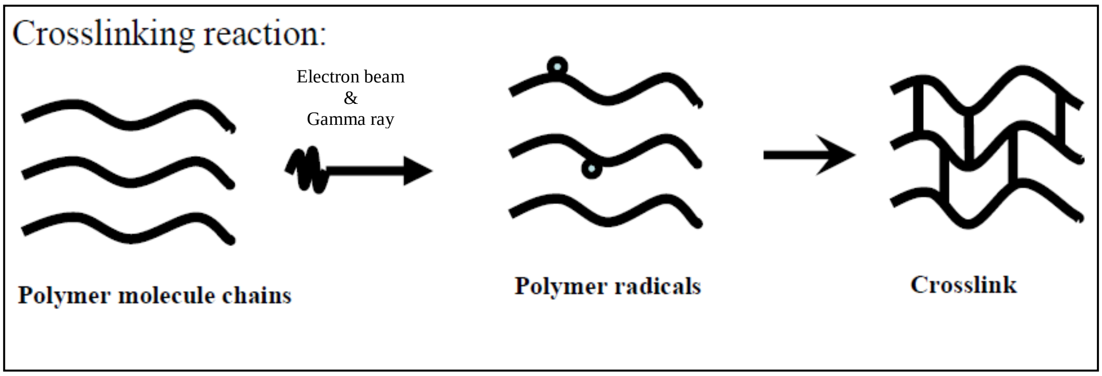
Figure 2.7: The effect of PVA/CS ratio on elongation at break (%) with 20 % formaldehyde (Shafiq et al., 2014).

2.6 Effect of electron beam on polymer

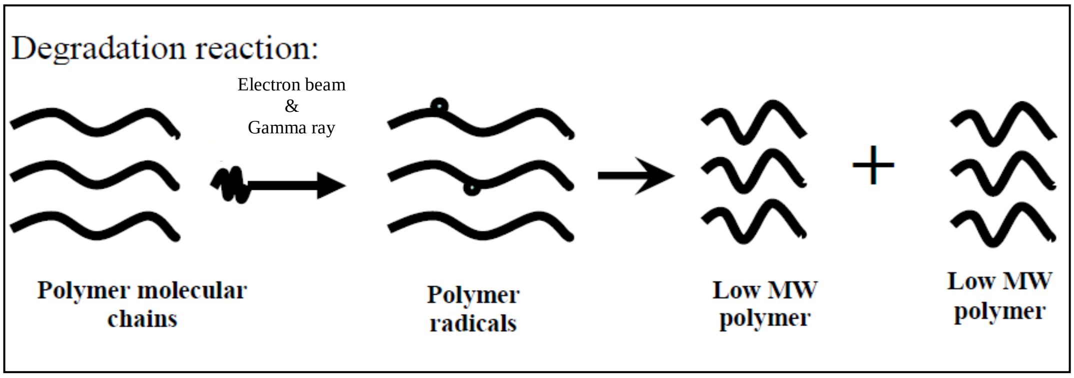
Electron beam is ionizing energy that is generally characterized by low penetration and high dose rate. The use of higher dose rate causes less exposure time and brought about reduction in potential degradation of polymers (Silindir & Ozer, 2010).

Electron beam treatment can modify the mechanical properties of the surfaces and interface of synthetic polymers and biopolymers (Schwars, 2010).

The effect of irradiation on the polymeric materials by electron beam irradiation may be due to (a) cross-linking (b) chain-scission (c) oxidation reaction. The cross-linking process brings about the formation of a covalent link between adjacent molecules which consists of three dimensional networks. Henceforth, the mechanical properties will increase (Deepalaxmi & Rajini, 2014). In addition, the net result of cross-linking is that the molecular weight of the polymer increases with increasing dose. The cross-linking process has continued until a three dimensional network is formed where each polymer chain is linked to one other chain on average. The process of cross-linking and degradation schematically can be illustrated as Figure 2.8 (a) and (b).



(a)



(b)

Figure 2.8: (a) The cross-linking process of polymer (b) The degradation reaction of polymer from high molecule weight to lower molecule weight (Darwis, 2010).

When scission of polymer molecule chains are in the majority in an irradiated polymer, the molecular weight decreases as dose increases. The final product might be a low molecular weight liquid in some cases (Darwis, 2010).

A method to modify the structure without introducing new chemical group could prove the benefit of the electron beam. For instance, novel cross-linking of arabic gum occurred without the need to any additive and only cross-link by irradiation by using high solute concentrations Gum arabic will degrade once irradiated with electron beam in aqueous solution at low concentration. Conversely, cross-linking occurs with minimal degradation in highly concentrated aqueous solution (Guven, 2012). Commonly, electron beam irradiation is a method to degrade polymers both in solid and liquid state. Radiation processing of polysaccharides is based on the generation of free radicals which are capable to induce molecular changes by decomposition of macromolecules and the creation of molecules with smaller chains. This method changes some physicochemical degradation rate of molecular weight fractions depending on the botanical source of starches (Nemtanu et al., 2010). Polysaccharides can be degraded due to a scission of glycoside bonds with irradiate by ionizing radiation (Yoshii, 2004). These intermediates can continue several reaction paths process which cause rearrangements and/or formation of new bonds. These reactions can be the formation of oxidized products, grafts, scission of main chain (degradation) or side chains or cross-linking (Guven, 2012).

The number of average molecular weight (M_n), weight of average molecular weight (M_w), and z number of average molecular weight (M_z) are determined for study samples in order to reveal the influence of the degradation and cross-linking polymer. It can be determined by electron beam treatment on molecular weights and distribution.

Table 2.3: Molecular weight distribution of starch sample (Nemtanu et al., 2010).

Irradiation dose [kGy]	M_n x 10^{-4} [g/mol]	M_w x 10^{-5} [g/mol]	M_z x 10^{-5} [g/mol]
		Corn starch	
0	**5.52 ± 0.45**	**3.07 ± 0.22**	**8.36 ± 0.31**
10	**4.19 ± 0.14**	**2.34 ± 0.02**	**6.43 ± 0.03**
20	**3.62 ± 0.37**	**1.78 ± 0.08**	**5.43 ± 0.02**
30	**3.42 ± 0.21**	**1.50 ± 0.03**	**4.75 ± 0.12**
40	**2.87 ± 0.03**	**1.16 ± 0.02**	**3.82 ± 0.10**
50	**2.84 ± 0.13**	**1.12 ± 0.05**	**3.48 ± 0.39**
		Potato starch	
0	**8.85 ± 0.04**	**4.41 ± 0.04**	**9.81 ± 0.06**
10	**6.72 ± 0.54**	**3.67 ± 0.23**	**9.38 ± 0.17**
20	**5.57 ± 0.44**	**2.98 ± 0.09**	**8.50 ± 0.28**
30	**4.16 ± 0.11**	**2.22 ± 0.01**	**7.60 ± 0.08**
40	**3.38 ± 0.15**	**1.83 ± 0.10**	**6.57 ± 0.07**
50	3.20 ± 0.14	1.73 ± 0.05	6.01 ± 0.23

Table 2.3 illustrates the molar mass distribution of samples treated with electron beam in comparison with control samples. An important point to note is that the decrease of molecular weights as the irradiation increase for both starches, indicating the degradation phenomenon of the macromolecules occurred effect by