INVESTIGATION OF TMPTMA ADDED ABS, LDPE, HDPE AND EVA WITH ELECTRON BEAM

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**A project report submitted in partial fulfilment of the
requirements for the award of the degree of
Bachelor (Hons.) of Chemical Engineering**

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April 2015

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"INVESTIGATION OF TMPTMA ADDED ABS, LDPE, HDPE AND EVA WITH ELECTRON BEAM"** was prepared by **CHEW WOON SIN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

The purpose of this research was to investigate the effect of increasing the loading levels of trimethylolpropane trimethylarcylate (TMPTMA) on the physical and mechanical properties of low density polyethylene (LDPE), high density polyethylene (HDPE), ethylene vinyl acetate (EVA) and acrylonitrile butadiene styrene (ABS) crosslinked via electron beam irradiation. Constant loading level of LDPE, HDPE, EVA and ABS (at 100 phr) was compounded with various loading levels of TMPTMA from 0 to 8 phr under electron beam irradiation dosages of 50 to 250 kGy. The gel content for all samples was found to increase significantly in the presence of TMPTMA upon subjection to electron beam irradiation due to the formation of three dimensional crosslinking networks in the polymer matrix. The formation of three dimensional crosslinking networks could enhance the tensile properties of LDPE, HDPE, EVA and ABS samples. However, the tensile properties of irradiated samples were found to deteriorate with higher loading level of TMPTMA due to the release of excessive amount of monomer free radicals. The excessive amount of monomer free radicals would pre-dominate the chain scissioning reaction over crosslinking reaction. Moreover, significant enhancement effect can be observed in the both mechanical and physical properties of all LDPE, HDPE, EVA and ABS samples with subjection to appropriate electron beam irradiation dosages due to the formation of irradiation-induced crosslinking. This irradiation-induced crosslinking could promotes greater three dimensional crosslinking networks that increase the tensile strength while decreasing the elongation of all LDPE, HDPE, EVA and ABS samples

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS / ABBREVIATIONS

H_m	Heat of enthalpy, J/g
T_c	Crystallinity temperature, ^{o}C
T_m	Melting temperature, ^{o}C
W_i	Initial weight of the sample before the extraction process (g)
W_f	Final weight of the remaining dried sample after the extraction process (g)

ABS	Acrylonitrile Butadiene Styrene
EVA	Ethylene Vinyl Acetate
FTIR	Fourier transform infrared spectroscopy
LDPE	Low Density Polyethylene
HDPE	High Density Polyethylene
MDSC	differential scanning calorimetry
PLA	Polylactic acid
SBR/NBRr	styrene butadiene rubber/ recycled acrylonitrile butadiene rubber
TGA	Thermogravimetric analyser
TMPTMA	Trimethylolpropane Trimethylarcylate
TMPTA	Trimethylolpropane triacrylate
TPGDA	Tripropylene glycol diarcylate
UHMWPE	Ultra-high molecular weight polyethylene

CHAPTER 1

INTRODUCTION

1.1 Background

Acrylonitrile butadiene styrene (ABS) is a family of thermoplastic called “terpolymers”. It involves the combination of three different monomers, which are acrylonitrile, butadiene and styrene to form a single polymer, which possesses the properties of all of the three monomers that made it up. The acrylonitrile contributes to the thermal and chemical resistance; the butadiene has rubberlike properties which act to increase the ductility and impact strength, while styrene provides the glossy surface to the material, as well as makes the ABS easier machinable and less expensive. However, different properties and grades of ABS can be achieved by adjusting the amount of monomers blend. ABS has a very wide range of application due to its toughness and good impact strength at low temperature with its ease of moulding and high quality surface finishing.

Low density polyethylene (LDPE) and high density polyethylene (HDPE) are both family of polyethylene which are obtained by polymerizing ethylene gas. LDPE has comparatively lower density than HDPE due to the presence of a small amount of branching in its chain which gives a more open structure, unlike HDPE, where the absence of branching results in a more closely packed structure, which gives its a higher density structure. HDPE also has a higher chemical resistance and strength, but lower flexibility compared to LDPE (United Plastic Components Inc, 2010).

Ethylene vinyl acetate (EVA) is the copolymer of ethylene and vinyl acetate, which has a soft and elastic yet excellent toughness, good barrier properties, stress-crack resistance, hot-melt adhesive waterproof properties, and good ultraviolet radiation resistance. However, EVA is sensitive to heat in handling & shipping (United Plastic Components Inc, 2010).

The mechanical properties of polymers (ABS, LDPE, HDPE and EVA) can be improved by inducing cross-linking in polymer matrices (Taylor & Francis Group, LLC, 2010). Generally, employment of irradiation techniques is an effective way to promote the formation cross-linking reaction in polymer matrices with the incorporation of chemical cross-linking agent. The types of high energy irradiations that are commonly used to improve the properties of polymers are: electron, gamma, and X-ray beam (Murray et al., 2013). The employment of high energy irradiation to polymers are able to generate high energy free radicals in the polymer matrix that could enhance the inter-chain interaction of polymer by forming carbon-carbon intermolecular bonds, which link two long molecular chain together. This reaction is also known as cross-linking reaction. However, during irradiation process, the polymers undergo mechanical and structural changes via two possible mechanisms, which are: cross-linking and chain scissioning reaction (Kumar et al., 2012). Both crosslinking and chain scissioning reactions occur simultaneously during irradiation process. However, the domination of either one of the reactions will caused different effect to polymer during irradiation process. The predomination of chain scissioning reaction over crosslinking reaction will reduce the molecular weight of polymer due to the unfavourable degradation process of the polymer. On the other hand, the molecular weight of polymer will increase when cross-linking reaction outweighs chain scissioning reaction due to the formation of irradiation induced crosslinking network in polymer matrices (Loo et al., 2004). Thus, the physical and mechanical properties of polymers can be greatly improved by cross-linking reaction via electron beam irradiation process (Rytlewski et al., 2010).

The addition of appropriate cross-linking agent also plays an important role in attaining a predomination of cross-linking reaction instead of chain scissioning upon polymer irradiation process (Rytlewski et al., 2010). During irradiation process, the cross-linking agent will produce additional monomer free radicals to react with the polymer free radicals to form a greater three dimensional crosslinked network in polymer matrix. The formation of greater three dimensional cross-linking networks in polymer matrixes can thus retard the chain scissioning reaction by protecting the polymer backbone chain from breaking (Phong, et al., 2010).

Four different types of base polymers were used in this research, which were acrylonitrile butadiene styrene (ABS), low density polyethylene (LDPE), high density polyethylene (HDPE) and ethylene vinyl acetate (EVA). Each of the polymers was then subjected to electron beam irradiation with the incorporation of trimethylopropane trimethylarcylate (TMPTMA) as the cross-linking agent. TMPTMA is a water insoluble and low viscosity tri-functional methacrylate promoter that was used as cross linker in this research. The structural formula of TMPTMA was shown in Figure 1.1.

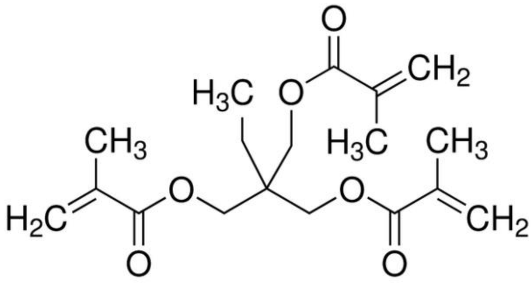


Figure 1.1 Trimethylolpropanetrimethacrylate, TMPTMA [CAS No: 3290-92-4, Molar mass: 338.4 g/mol] (Source: Sigma-Aldrich Co. LLC., 2014)

The aims of this project were to investigate the effect of increasing electron beam irradiation doses on the properties of pristine ABS, LDPE, HDPE and EVA, and also the effect of various loading levels of TMPTMA on the properties of electron beam irradiated ABS, LDPE, HDPE and EVA, respectively.

1.2 Problem Statements

In this project, the effect of various loading level of crosslinking agent (TMPTMA) on the properties of polymers (ABS, LDPE, HDPE and EVA) cross-linked via electron beam irradiation had been investigated. The problem statements for this project were shown as below:

1. What is the effect of increasing loading level of TMPTMA on mechanical and physical properties of polymers, ABS, LDPE, HDPE and EVA, respectively?
2. What is the effect of increasing electron beam irradiation doses on the mechanical and physical properties of pristine ABS, LDPE, HDPE and EVA, respectively?
3. What is the effect of increasing electron beam irradiation doses on the mechanical and physical properties of TMPTMA added ABS, LDPE, HDPE and EVA, respectively?

1.3 Objectives

The main objective of this project was to investigate the effect of increasing the loading level of TMPTMA on the properties of different types of polymers such as ABS, LDPE, HDPE and EVA when subjected to increasing electron beam irradiation dosages. The following sub-objectives were identified to achieve the objective:

1. To study the effect of increasing loading level of TMPTMA on mechanical and physical properties of ABS, LDPE, HDPE and EVA, respectively.
2. To investigate the effect of increasing electron beam irradiation doses on the mechanical and physical properties of pristine ABS, LDPE, HDPE and EVA, respectively.
3. To investigate the effect of increasing electron beam irradiation doses on the mechanical and physical properties of TMPTMA added ABS, LDPE, HDPE and EVA, respectively.

1.4 Scopes

This study was divided into two main scopes, which were samples preparation and samples characterization.

1.4.1 Samples Preparation

Firstly, Acrylonitrile butadiene styrene (ABS), low density polyethylene (LDPE), high density polyethylene (HDPE) and ethylene vinyl acetate (EVA) were compounded with TMPTMA by using Brabender mixer. The compounded samples were then pressed into sheet form by using compression molding. Lastly, the compression molded samples were subjected to electron beam irradiated with various dosages from 0 to 250 kGy, with 50 kGy per pass.

1.4.2 Samples Characterization

i. The mechanical properties of samples had been investigated by using tensile tester in accordance to ASTM D1822.
ii. The physical properties of samples had been investigated by conducting the gel content test, hot set test and scanning electron microscopy test.

CHAPTER 2

LITERATURE REVIEW

2.1 Acrylonitrile Butadiene Styrene (ABS)

Generally, Acrylonitrile Butadiene Styrene (ABS) is the copolymerization of Acrylonitrile, Butadiene, and Styrene monomers. It is a thermoplastic called as terpolymer, where the polymerization of ABS involves the combination properties of three different monomers to form a single material that draws from the properties of all three. Acrylonitrile-butadiene-styrene is produced by grafting the polybutadiene with a copolymer of styrene and acrylonitrile and embedded in the matrix. ABS can be processed by emulsion process, injection moulding or even extrusion technique. The general purpose ABS has a composition of 50% styrene with 25% butadiene and 25% acrylonitrile (UL LLC, 2014). However, variation grades of ABS could be obtained by changing composition of Acrylonitrile, Butadiene, and Styrene monomers.

The physical properties of ABS are intermediate between glass and rubber, while the mechanical properties, prone to be similar to glassy material than rubber with the exception of its impact toughness (Colborn, Buckley & Adams 1993). Basically, the function of acrylonitrile in ABS is to increase the surface hardness and chemical resistance, butadiene is used to increases the overall toughness and also the impact strength, whereas styrene contributes to the ease of processing characteristics (RTP Company, 2014). The combination of the strength of the acrylonitrile and toughness of the polybutadiene rubber with rigidity of styrene polymers give advantages to ABS. The general chemical structure of ABS is as shown in Figure 2.1 (Rutkowski and Levin, 1986).

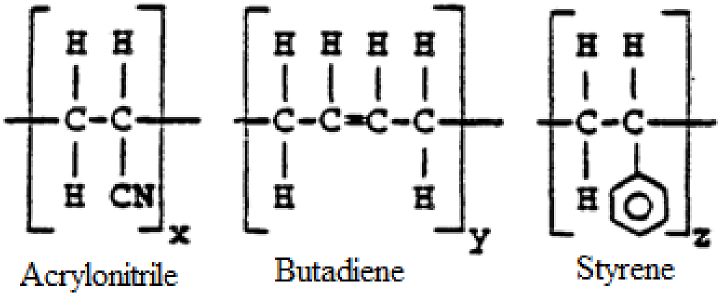


Figure 2.1 Acrylonitrile Butadiene Styrene (ABS) [CAS No: 9003-56-9] (Source: Joseph V. Rutkowski and Barbara C. Levin, 1986)

ABS was first introduced into the market in 1940’s due to the development of synthetic rubbers, then its demand increase start from 1950’s due to the variability of these copolymers and ease of processing in engineering polymers. ABS possesses advantages such as: dimensional stability, toughness, chemical resistance, creep resistant, very high impact and high tensile strength, excellent high and low temperature performance, resistant to many plasticizers, and also excellent ductility. The physical properties of ABS are shown in Table 2.1 below (Plastipedia, n.d.).

Table 2.1 Physical Properties of Acrylonitrile Butadiene Styrene

Tensile Strength	40-50	Mpa
Notched Impact Strength	10-20	kJ/ m^2
Thermal Coefficient of expansion	70-90	x 10^{-6}
Max Cont Use Temp	80-95	^{o}C
Denstiy	1.0-1.05	g/ cm^3

ABS is used in human’s everyday life applications such as: housings for vacuum cleaners, kitchen appliances, telephones casing and also toys (PlasticsEurope, n.d.). However, there are few disadvantages and limitation of ABS, which are its poor weathering resistance, poor solvent resistance, moderate heat and moisture ressitance, high smoke generation when burned and lastly is its relatively high cost of processing (UL LLC, 2014).

2.2 Polyethylene (PE)

Polyethylene is the largest commercial plastic in the world due to its simplest structure and wide range of uses. Polyethylene is a huge family of thermoplastics which are obtained by polymerization of ethylene gas. Figure 2.2 shows the general structure for a long chain of polyethylene from polymerization of ethylene gas, $H_2C=CH_2$ (Polymer Science Learning Center, 2005).

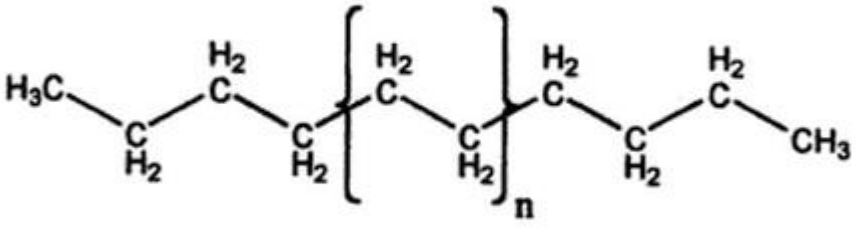


Figure 2.2 Chemical Structure for Pure Polyethylene (Source: Andrew Peacock, 2000)

Basically, there are four polymerization methods used to prepare polyethylene: high-pressure process, Ziegler process, Phillips process, and also the Standard Oil (Indiana) process.

The mechanical, chemical and thermal properties of different type of polyethylene depend on the thermoplastics processing methods used to produce it (UL LLC, 2014). Even small changes in the molecules are able to make a huge difference in the characteristic of polyethylene. Generally, there are two main types of polyethylene, which are: low density polyethylene (LDPE) and high density polyethylene (HDPE). Due to the differences in structure, HDPE is much stronger than LDPE.

Although there are different types of polyethylene, however, all of the types have the following properties:

- Strong and light weight.
- Chemically stable and inert as PE does not readily react with other chemicals.
- Can be used as insulator as it does not conduct electricity.

However, there are some disadvantages of polyethylene, such as:

- High thermal expansion
- Poor weathering resistance
- Subject to stress cracking
- Flammable
- Poor temperature capability
- Low strength and stiffness

2.2.1 Low Density Polyethylene (LDPE)

Low density polyethylene, LDPE is long chain of branched polyethylene, having a density of range 0.91 to 0.925 g/cm³ (UL LLC, 2014). LDPE have relatively long and numerous branches compared to other type of polyethylene structure. LDPE are polymerized at very high temperature and pressure. Figure 2.3 shows the example of structure for low density polyethylene (Andrew Peacock, 2000).

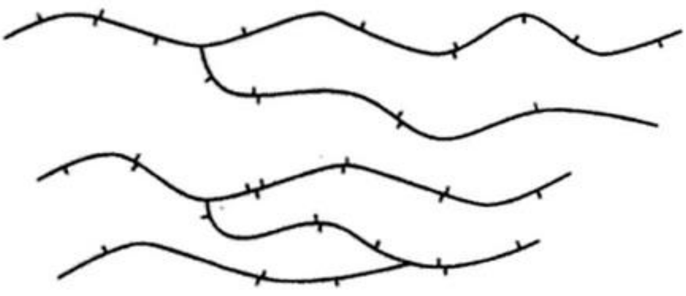


Figure 2.3 Structure of Low Density Polyethylene (Source: Andrew Peacock, 2000)

LDPE is a soft, waxy and flexible type of polyethylene, which have a shiny appearance and also smooth to touch. Due to these properties, LDPE are normally used to produce packaging material, sandwich and garbage bags, cling wrap and also squeezable bottles. Besides, LDPE are also applicable in screw caps and lids production due to its tough properties (Plastic Europe, n.d.).

2.2.2 High Density Polyethylene (HDPE)

High density polyethylene, LDPE is linear long chain of polyethylene, having a density of range 0.935 to 0.96 g/cm³ (UL LLC, 2014). HDPE is a more linear molecule compared to LDPE due to its lesser and shorter side chains. HDPE are polymerized at very relatively low temperature and pressure. Figure 2.4 shows the example of structure for high density polyethylene (Andrew Peacock, 2000).

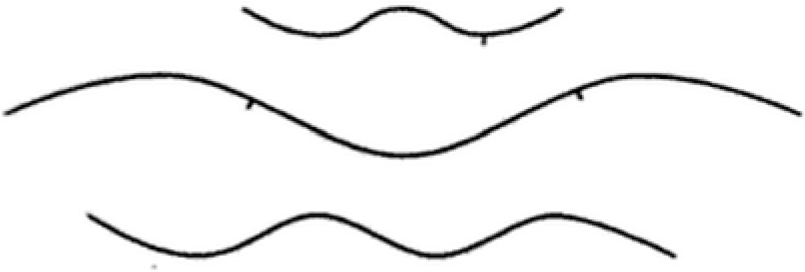


Figure 2.4 Structure of High Density Polyethylene (Source: Andrew Peacock, 2000).

HDPE is the most tough and flexible among all the type of polyethylene. Due to its tough properties, HDPE have a wide range of applications, such as clothes pegs and also bottles for domestic products. Other than that, it can be also used in the production of paper-thin foil, such as sandwich bags, pedal bin bags or packaging for vegetables, fruit or meats (Plastic Europe, n.d.).

2.3 Ethylene Vinyl Acetate (EVA)

Ethylene vinyl acetate, EVA is a copolymer produced by the copolymerization of ethylene and vinyl acetate. EVA polymer chains are comprised of the two monomer units, which are ethylene and vinyl acetate, connected via free-radical addition polymerization. Figure 2.6 below showing the structure of ethylene vinyl acetate copolymers (Harper & Petrie, 2003).

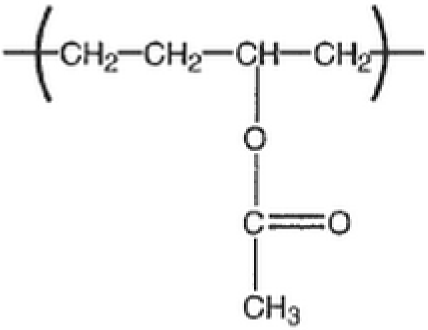


Figure 2.5 Structure of a random Ethylene Vinyl Acetate copolymers (EVA) [CAS NO: 24937-78-8] (Source: Charles A. Harper & Edward M. Petrie, 2003)

The degree of crystallization of EVA is influence by the composition of vinyl acetate in the polymer. When the composition of vinyl acetate increases, the crystallinity of the polymer decreases causing the EVA copolymer to become softer (Ken, 2012). This is because with the increasing composition of vinyl acetate, the polymer will change to rubber-like a product which is softer.

EVA has a range of properties such as:

- Soft and highly flexible yet tough
- High impact strength
- High cohesive strength and compatibility
- Highly resistant to rupture
- Ability to ensures excellent adhesion to a wide range of substrates
- Good clarity and gloss with no or little odor

EVA is commonly used in wire and cable insulation, sealants in meat and packaging structures and shoe sole foaming. Besides that, EVA is also used in hot melt, blow and compression molding, and also sheet and film extrusion.

2.4 Cross-linking Agent

A cross-linking agent is a substance that links the polymer chains together by promoting the intermolecular covalent bonding between the polymer chains to create a more rigid structure. Type of cross-linking agent used can have much influence in the cross-linking reaction for different type of polymers. It is very important to choose a suitable cross-linking agent for cross-linking reaction during irradiation process.

During the irradiation process of polymers, the addition of an appropriate cross-linking agent is essential to achieve a predomination of cross-linking reaction instead of chain scissioning reaction. The incorporation of appropriate cross-linking agent are able induce a greater three dimensional networks in polymer matrixes by promoting the release of additional free radicals to prevent the radiation- induced chain scissioning reaction from happening. The additional free radicals from cross-linking agent could protect the ester bonds of polymers chain by preventing the high energy of irradiation from breaking it (Quynh et al., 2007).

The main purpose of adding cross-linking agent in polymers is to decrease the possible venomous effect of high-energy ionizing irradiation on polymers, as the cross-linking reaction may not be absolutely predominant without the presence of a cross-linking agent (Rytlewski et al., 2010). The types of cross-linking agent that are commonly used are: trimethylolpropane trimethylarcylate (TMPTMA), trimethylolpropane triacrylate (TMPTA), tripropylene glycol diarcylate (TPGDA). However, only TMPTMA will be discussed further due to its wider usage in polymer application.

2.4.1 Trimethylolpropane Trimethylarcylate (TMPTMA)

Trimethylolpropane trimethylarcylate (TMPTMA) is one of the most common types of cross-linking agent used incorporation with radiation cross-linking reaction. TMPTMA is a trifunctional methacrylate monomer, having a molecular weight of 338.4 g/mol, which is used as cross-linker in various applications. TMPTMA has a boiling point >200 ^{o}C and a melting point of -25 ^{o}C with density of 1.06 g/mL (Chemical Book, 2010). The structural formula of TMPTMA is shown in Figure 2.7.

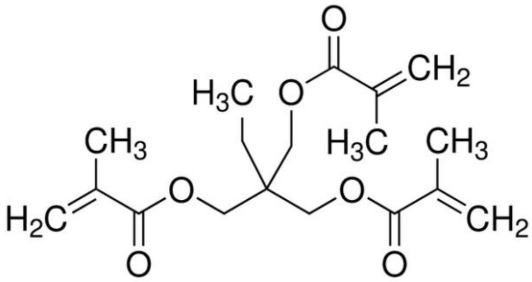


Figure 2.6 Trimethylolpropanetrimethacrylate, TMPTMA [CAS No: 3290-92-4, Molar mass: 338.4 g/mol] (Source: Sigma-Aldrich Co. LLC., 2014)

TMPTMA has a very low viscosity, 69mPa.s and it is relatively insoluble in water, with water solubility of 0.3% only at room temperature (Thames River Chemical, 2010). TMPTMA is also used as a useful diluent due to its high degree of functionality and low volatility, with vapour pressure of <0.01 mm Hg (Chemical Book, 2010).

The few applications of TMPTMA are:

- It is used as cross-linker in polymer
- It is a useful feedstock for chemical synthesis
- It is used in anaerobic adhesive
- It is used in formulation of wire, cable coatings and paints

Besides, the benefits of TMPTMA is that it can be used to increase the properties of polymers such as, chemical resistance, adhesion, heat resistance, weather resistance, hardness, high cross-linked density, abrasion resistance and strength of a polymer (BASF Group, 2011).

2.5 Cross-linking of Polymer

Cross-linking is a process of linking the long chains of polymers together to forms higher molecular mass of polymers.

2.5.1 Background of Cross-linking of Polymer

In 1839, Charles Goodyear, an American Chemist discovered the earliest example of cross-linking of polymer, that is the vulcanization of natural rubber. He found out that the process of heating natural rubber in the presence of sulfur could create the links between the latex molecules which made the rubber to become stronger by forming stronger interlocking mass in it. Figure 2.81 below shows the chemical process of vulcanization of natural rubber (Polymer Science Learning Center, 2005).

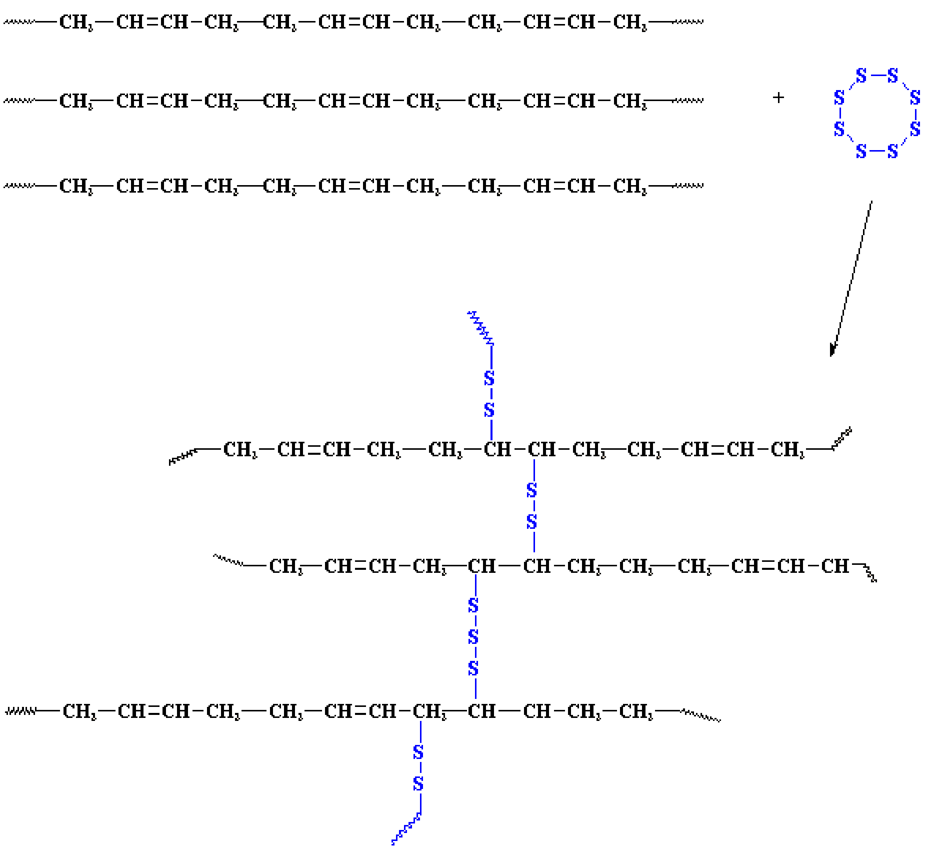


Figure 2.7 Process of vulcanization of Natural Rubber (Source: Polymer Science Learning Center, 2005).

These sulfur cross-links prevent the melting of rubber by tying the polymer chains together which limits the flow of rubber around each other when heat is applied. This increases the strength properties of vulcanized rubber over a range of temperature that could prevent it to get brittle during cooling.

However, the vulcanization of rubber does not in high demand before 19th Century. By the end of 19th Century, the demand of vulcanization of rubber increased due to the increasing popularity of bicycle. The vulcanization of rubber becomes more and more important when automotive industries started to growth during 20th Century (The Centre of Applied Research in Education, 1999). The discovery of vulcanization rubber has thus made the cross-linking reaction becomes important in polymer applications.

2.5.2 Uses of Cross-linking of Polymer

By introducing cross-linking bonds between adjacent molecular chains, the original properties of polymers can be improved as the entire polymer molecules are able to be tied together by the bridge formed between two long chains of molecules. Figure 2.9 and 2.10 showing the difference between uncross-linked polymer chain and cross-linked polymer chain (Polymer Science Learning Center, 2005).

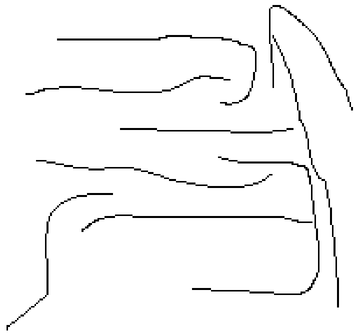


Figure 2.8 Uncross-linked Polymer Chains (Source: Polymer Science Learning Center, 2005).

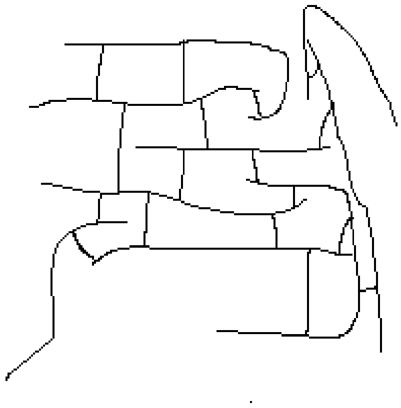


Figure 2.9 Cross-linked Networks in Polymer Chains (Source: Polymer Science Learning Center, 2005).

Cross-linking is used to improve properties of polymer such as:

- Improving mechanical properties, such as tensile strength and abrasion
- Better chemical resistance
- Better heat resistance
- Better stress cracking resistance
- Slightly better flame resistance
- Shape memory retention
- Reduced creep

Through cross-linking, the chemical structure of the polymer can be altered. Different techniques are used for cross-linking for different types of polymer (Parks, 2010).

2.5.3 Types of Cross-linking Reaction

Polymer cross-linking can be accomplished by using two ways, which are: chemical cross-linking and radiation cross-linking (Sterigenics Advanced Applications, 2005).

2.5.3.1 Chemical Cross-linking Reaction

Chemical cross-linking is one of the most commonly used way to cross-link amorphous thermoplastic at room temperature. Chemical reactions occurred during chemical cross-linking, where bonds will be formed between the polymer chains on the active sites generated. The two methods to carry out chemical cross-linking reaction are: peroxide and silanes methods.

Cross-linking by using peroxide need to be done in molten state. The peroxide will decompose to generate free radicals when exposed to high temperature.

The free radicals will then withdraw a hydrogen atom from the polymer chains to generate polymer radical. Cross-link bonds will then formed between two adjacent polymer radicals. The reaction stops when the temperature is decreased below the decomposition temperature of peroxide or when all peroxide is consumed (Makuuchi & Cheng, 2011). Cross-linking using peroxide is reliable and is it an easily understandable technique. Besides, this technique can be used to cross-link a reasonable range of polymers compared to silane technique. However, there are also few disadvantages of peroxide technique such as its relatively complicated compound design and also high energy consumption during cross-linking reaction (Parks, 2010).

For silanes method, three dimensional network of siloxanes linkage are formed when the polymers containing hydrolysable alkoxy groups react with adjacent molecule in the presence of moisture (Makuuchi & Cheng, 2011). Few advantages for silane method are its easily understandable technique and it ability to process small batches of material, while its disadvantages are that it is limited to few number of polymers only, the relatively complicated compound design, and the sensitivity in controlling the cross-linking. Moreover, the potential for undesirable residues to form in the product are very high, which caused a dirtier process (Parks, 2010).

In this chemical cross-linking technique, the processing step must be exposed to heat for peroxide cross-linking, and to moisture for the silane cross-linking.

2.5.3.2 Radiation Cross-linking Reaction

The cross-linking of polymer may be achieved using high-energy ionizing irradiation, such as electron beam, gamma or x-ray irradiation. High-energy ionizing irradiation technique has been widely used to improve and modify the properties of polymers. It is one of the alternative methods that aids in inducing cross-linking networks in polymer matrices besides using chemical cross-linking agent.

Upon irradiation, not only the matrix structure, but the mechanical properties of polymers also could be changed. Generally, two prominent effects might occur during polymer irradiation process, which are cross-linking and chain scissioning reactions. Both the cross-linking and chain scissioning reactions will occur at the same time throughout the irradiation process. However, the molecular weight of the cross-linked polymers will increase if the cross-linking reaction is more predominant than the chain scissioning reactions during irradiation process. On the other hand, if chain scissioning reaction is more predominant than cross-linking reaction, the molecular weight of polymer will decrease due to unfavourable degradation process of the polymer.

The degree of cross-linking and chain scissioning reaction that occurs during ionizing irradiation is much influenced by the amount of irradiation dosage (Oostenbrink & Gaymans, 1992). Different base polymers have different optimum amount of irradiation dosage. Thus, the amount of irradiation dosage must be controlled to achieve the domination of cross-linking reaction over chain scissioning reaction.

The advantages of using radiation cross-linking are its reliability and efficiency, and cleaner process compared to chemical cross-linking reaction. Moreover, radiation process are relatively simple to operate with a huge range of polymers can be processed by using this technique. Some of the disadvantages of radiation cross-linking are its high capital cost and require equipment expertise for operation (Parks, 2010).

2.5.3.2.1Electron Beam Irradiation

Electron beam irradiation is a type of ionizing energy irradiation reaction used in cross-linking. Generally, electron beam is characterized as an electromagnetic radiation with very short wave length and very high frequency. Due to short wave length and high frequency, electron beam have low penetration and high dosage rates.

During electron beam irradiation process, the high ionizing energy caused the bombardment of electron from the polymer molecule. Due to high energy of irradiation process, hydrogen atoms will be ejected from each of the polymers chains to form molecular hydrogen gas, and cross-link bonds will then forms on the vacant sites on the adjacent polymer chains. Figure 2.11 and 2.12 below illustrating two random polyethylene molecules being subject to irradiation.

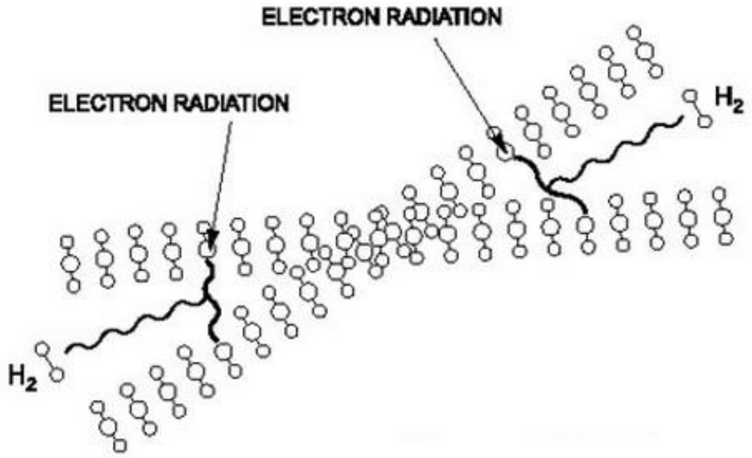


Figure 2.10 Two random polyethylene molecules being subject to irradiation (Source: RSCC Aerospace & Defense, 2014)

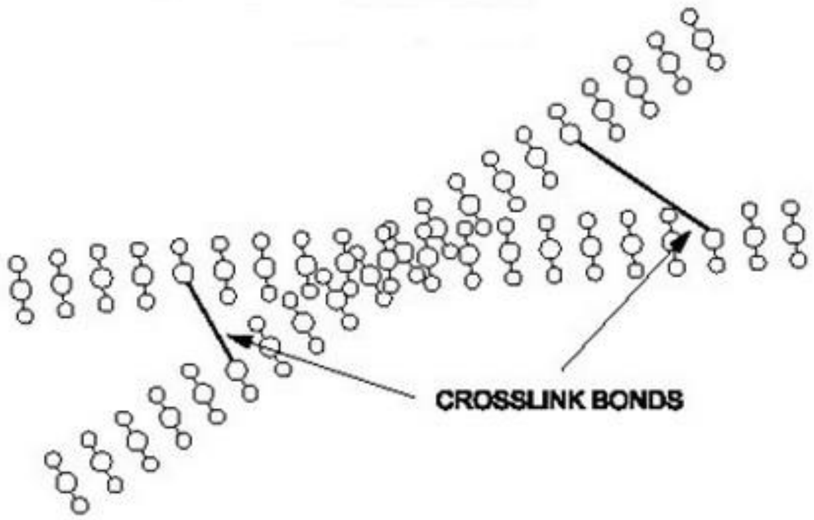


Figure 2.11 Two random polyethylene molecules after subjected to irradiation (Source: RSCC Aerospace & Defense, 2014)

Electron beam irradiation is more widely used in radiation processing as it is clean. Due to shorter exposure time of electron beam irradiation, the products usually have lesser oxidative effects. Besides that, electron beam can be controlled precisely and swift because when the power is turned off, the radiation stops. Moreover, electron beam irradiation is more friendly to plastic device and its packaging compared to gamma irradiation. However, electron beam irradiation is more suitable to be used in small batches of products.

2.5.3.2.2 Gamma-ray Irradiation

Gamma-ray irradiation is a high-energy irradiation that has high penetration and low dosage rate. Usage of gamma rays in irradiation is an alternative method that improves the properties of polymer by restraining the motion of macromolecule chains by forming three-dimensional networks in polymer. Gamma irradiation is sometimes used in increasing the properties in certain polymer that has been added filler into it.

Gamma-ray irradiation is also a clean process that does not leave any residue on the product. Furthermore, gamma-ray process is predictable and repeatable. However, when using gamma-ray, the material selection is an important criterion to be considered. Material that is brittle should be avoided.

2.5.3.2.3 X-rays Irradiation

X-rays irradiation is a high ionizing energy electromagnetic radiation that is suitable for processing of bulk materials. According to Cleland, X-ray has a dosage rate between the low dose rates of gamma ray sources and high dose rates of electron. Since X-ray has a medium dosage rate, thus it is suitable to be used for those applications that are more sensitive to the dose rate.

Although X-ray irradiation process is still considered as a relatively new irradiation method, but it has been used in various applications, such as its uses in the area of food safety and for the crosslinking of thick cross-sectioned materials and composites. The wide uses of X-ray irradiation process is due to its high penetration, which is beneficial in process such as preserving foods, curing composite structures and improving the properties of bulk materials. Besides that, X-ray irradiation is more energy saving than gamma ray, because just like electron beam generator, X-ray generator can be switched off when it is not needed in production.

2.5.3.3 Comparison of Cross-linking Methods of Polymers

For different cross-linking methods, there are different in technological aspects. Table 2.2 summarized the technological aspects of radiation, peroxide and silane cross-linking method.

Table 2.2 Technological Comparison of Cross-linking Methods of Polymers (Source: Makuuchi & Cheng, 2011)

Cross-linking method		Radiation (EB)	Peroxide	Silane
Major products		Wire & cable, tube, pipe, film, foam	Wire & cable, tube, pipe, foam	Wire & cable, pipe
Plastic	PE	√	√	√
	PP	√	√	Δ
	PVC	√	Δ	Δ
	Engineering plastics	√	X	X
	PTFE	√	X	X
	Fluoropolymer	√	√	Δ
Cost of compounding		Low	Medium	High
Shelf life of compound		long	Medium	Short
Product thickness restriction		< 10cm	> 0.3mm	> 0.3mm
Rate of cross-linking		High	Low	Low
Degree of cross-linking		Medium	High	Low

Notes: √ in practical use, Δ technically possible but no practical example, X hard to apply.

2.6 High Energy Electron Beam Induced Modification in Properties of Low Density Polyethylene

To examine how electron beam irradiation affects the properties and structure of low density polyethylene (LDPE), the LDPE samples were subjected to high energy electron beam irradiations, 10 MeV with different doses ranging from 25 to 400 kGy at room temperature to obtain the results from few characterization techniques. The characterization techniques include modulated differential scanning calorimetry, MDSC and fourier transform infrared spectroscopy, FTIR were conducted on both the irradiated and non-irradiated samples of LDPE. The non-irradiated LDPE samples served as the reference point to compare with the irradiated samples obtained from the characterization techniques.

The study done by Murray et al. had shown that the melting temperature of LDPE decreases slightly when the irradiation dose increased, according to results obtained from DSC thermograms as tabulated in Table 2.3. The decrease in melting temperature (T_m) was due to the preferential destruction of large crystal, where the thickness of the crystallites reduced as chain branches was formed with increasing irradiation. Besides that, the crystallinity temperature (T_c) also decreases with increasing of irradiation doses due to the cross-linking reaction that occurred during irradiation which prevents the macromolecular chains to crystallize and prevent the crystal growth of LDPE. These two finding are in agreement with Suarez et al. and Puig et al, where they found that the cross-linking and branching reactions caused by irradiation could changes the melting temperature due to the changes in macromolecules.

Table 2.3 Melting Temperature (T_m), Crystallinity (T_c) and crystallinity of LDPE before and after electron beam (Source: Murray et al., 2011)

Sample dosage (kGy)	H_m (J/g)	Onset T_m, ^oC	Peak T_m, ^oC	Onset T_c, ^oC	Peak T_c, ^oC	% crystallinity	Crystallinity degree variation (%)
0	83.40	105.50	113.01	106.74	102.84	28.83	0.00
25	81.38	103.90	113.12	106.39	102.40	28.13	2.42
50	82.04	103.81	112.72	106.40	101.99	28.36	1.63
75	82.43	102.53	112.59	106.09	101.63	28.49	1.16
100	82.77	102.45	112.37	105.66	100.58	28.61	0.76
150	76.59	100.95	111.67	105.52	100.41	26.47	8.17
200	78.24	100.41	111.32	105.06	99.40	27.04	6.19
400	79.08	97.87	109.24	103.99	96.94	27.33	5.18

According to results obtained by Murray et al. from FTIR, the concentration of trans-vinylene double bonds increased with the increasing irradiation dose to

LDPE. McGinnise (1986) reported that the release of hydrogen from the LDPE chain during irradiation cross-linking produced the trans-vinylene double bonds.

With the increasing of irradiation dose up to 150 kGy, the gel content of LDPE increased, according to Sharif et al., and this is also applied to the tensile strength of the LDPE. The further increased in electron beam irradiation doses decreased both the gel content and tensile strength due to the chain scissioning reaction at high dose. However, the elongation at break of LDPE decreased with increasing doses of irradiation due to the decrease in mobility of internal chain caused by cross-linking.

In a nutshell, the thermal, structural and mechanical properties of LDPE can be modified significantly by electron beam irradiation.

2.7 Electron Beam Induced Modification in Properties of High Density Polyethylene

The effects of electron beam irradiation on the properties and structure of high density polyethylene, HDPE had been studied by Kumar et al. in their research. The compression molded HDPE samples were exposed to electron beam irradiation over ranges of doses from 90 to 360 kGy to obtain the changes in structural and thermal properties of irradiated HDPE. The non-irradiated HDPE samples were also tested to serve as the baseline in the comparison with irradiated HDPE samples.

According to the results obtained from DSC thermograms by the research done by Kumar et al., the melting temperature of HDPE increased significantly with the increasing in irradiation dose. The melting temperature of HDPE irradiated with 360 kGY was the highest, whereas the melting temperature of non-irradiated HDPE remained the lowest. Moreover, the degree of crystallinity of HDPE also increases with increase in irradiation doses. The increasing in melting temperature and degree of crystallinity indicates that the cross-linking reaction was more predominant than chain scissioning reaction upon electron irradiation in HDPE. The results obtained were tabulated in Table 2.4 below.

Table 2.4 DSC Characterization of HDPE Irradiated to Different Dose of Electron Beam Irradiation (Source: Kumar et al., 2011)

Irradiation Dose (kGy)	Melting Peak (^oC)	Heat of enthalpy (J g^{-1})	Degree of Crystallinity (%)
0	128.85	183.83	~63
180	130.37	187.57	~65
360	133.43	192.56	~67

On the other hand, the results obtained by thermogravimetric analyser (TGA) also showed the increase in thermal stability for irradiated HDPE compared to non-irradiated HDPE. The decomposition rate for HDPE decreased with increasing of irradiation doses. This is due to the increasing of molecular weight and compactness of HDPE as a results of predomination of cross-linking, which allowed the HDPE to withstand the thermal strain that applied on it.

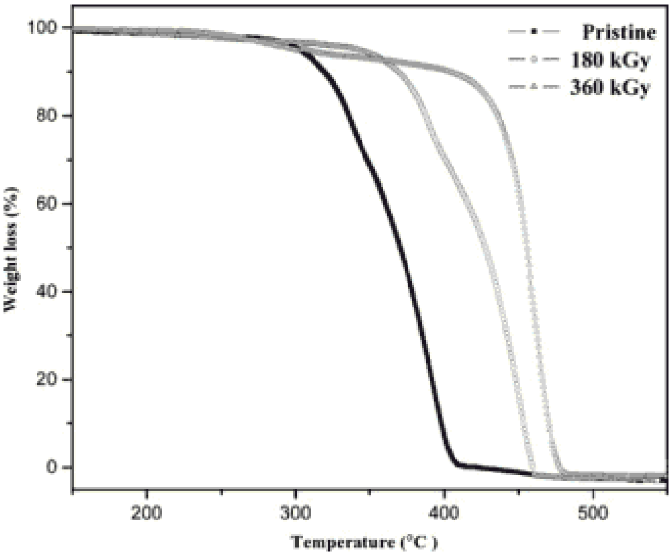


Figure 2.12 Thermogravimetric Analysis for Pristine and Irradiated HDPE at Doses of 180 and 360 kGy (Source: Kumar et al., 2011)

The FTIR results obtained by Kumar et al. had shown that the concentration of trans-vinylene bonds, carbonyl and hydroxyl groups increased slightly with increasing in irradiation of HDPE.

The mechanical properties of HDPE can also be improved with electron irradiation process. According to Gheysari (2000), the irradiated HDPE, up to 100 kGy has higher tensile strength than non-irradiated HDPE. Besides, the gel content of HDPE also increased with increasing irradiation doses. The increasing in tensile strength and gel content might due to the cross-linking reaction that taken place during the irradiation process. Thus, the properties of HDPE can be significantly modified by electron beam irradiation.

2.8 Electron Beam Induced Modification in Properties of Ethylene Vinyl Acetate

The effects of electron beam irradiation on the properties and structure of ethylene vinyl acetate, EVA were tested by Sabet et al. in their studies. The EVA samples were subjected to electron beam irradiation of 3 MeV with different irradiation doses ranging from 120 to 240 kGy at room temperature in the presence of air.

From the studies, it had been shown that the gel content of EVA increased significantly with the increasing of electron beam irradiation up to 150 kGy. The increasing in gel content was due to the higher cross-linking induced by the increasing of irradiation doses. The increased in gel content also indicates the predomination of cross-linking reaction over chain scissioning of irradiated EVA. A similar result was reported by Sujit et al. in their studies on pure EVA, where they also found that the gel fraction of EVA increased with increasing electron beam irradiation. The high amorphous phase in EVA contributes to its superior cross-linking ability when subjected to high-energy electron beam irradiation. According to Dadbin et al. (2005), the formation of free radicals that are necessary in cross-linking reaction are more likely to occur in the amorphous phase of a polymer, where the free radicals can subsequently react to initiate cross-linking reaction.

Also according to Sabet et al., increasing of irradiation doses decreased the melting temperature and thus the crystallinity of EVA. The decreased in crystallinity is probably caused by cross-linking and chain branching which disrupt the crystallinity region during the irradiation process (Dadbin et al., 2005).

The tensile strength of EVA also increased with increasing doses of irradiation up to 200 kGy, according to the research done by Sharif et al.. The further increase in electron beam irradiation doses however decreased the tensile strength of EVA due to the predominant of chain scissioning reaction at higher dose of irradiation. On the other hand, the elongation at break of EVA decreased with increasing electron beam irradiation doses. This might due to the increasing formation of three-dimensional structure of EVA caused by the cross-linking reactions which decrease the mobility of the chain and thus, decrease the elongation at break. However, the maximum irradiation dose should not go beyond 150 kGy in order to obtain the optimum mechanical properties of EVA, as reported by Burns (1979).

Therefore, the properties of EVA can be improved by subjecting it to electron beam irradiation.

2.9 Electron Beam Induced Modification in Properties of Styrene Butadiene Rubber/ Recycled Acrylonitrile Butadiene Rubber Blends

The mixture of styrene butadiene rubber/ recycled acrylonitrile butadiene rubber (SBR/NBRr) with ratio of 95/5, 85/15, 75/25, 65/35 and 50/50 in the presence of little amount of trimethylolpropane triacrylate (TMPTA) were prepared to determine their properties. Cross-linking agent, TMPTA was added to help in aligning the polymer chains through cross-linking. The samples prepared were then subjected with electron beam at 40 kGy of irradiation dose, with 20 kGy per pass. This research was done by Noriman and Ismail in 2011.

Their research had shown that the crystallization temperature of irradiated SBR/NBRr blends was higher than non-irradiated SBR/NBRr blends. This was due to the cross-linking that formed between the polymer blends when subjected to irradiation doses with the help of TMPTA.

Table 2.5 DSC Experimental Data of Non-irradiated and Irradiated SBR/NBRr for R05 and R50 blends (Source: Noriman and Ismail, 2011)

Blends	Crystallization Temperature (T_c)		
	T_{onset} (^oC)	T_c (^oC)	Delta H (J g^{-1})
Unirradiated SBR/NBRr ((R05)	33.9	36.7	-17.9
Irradiated SBR/NBRr (R05)	33.7	36.7	-18.8
Unirradiated SBR/NBRr (R50)	33.7	37.0	-13.8
Irradiated SBR/NBRr (R50)	33.5	38.6	-11.7

Notes: R05 = 95phr SBR with 5phr NBRr, R50 = 50phr SBR with 50phr NBRr

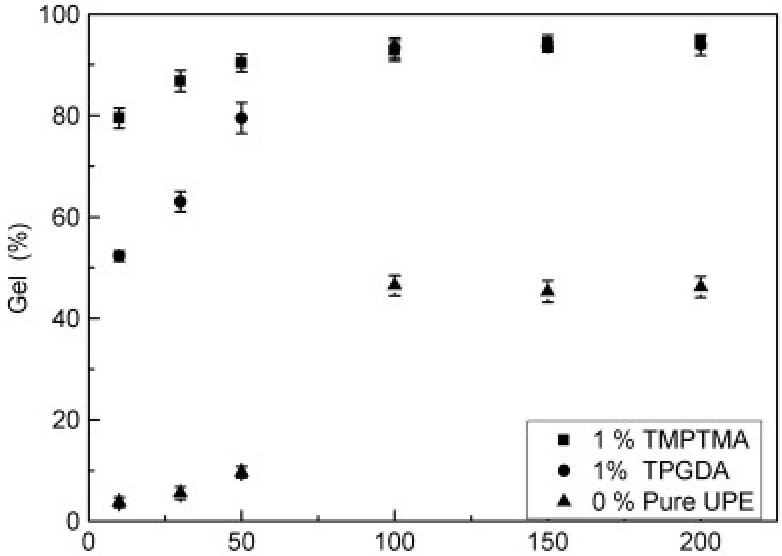
For non-irradiated and irradiated SBR/NBRr (R05) blends, although the melting temperature, T_c does not change, however the increment in heat enthalpy indicates that the polymer was aligning themselves more nicely to form semi-crystalline phase with the aids of irradiation. For non-irradiated and irradiated SBR/NBRr (R50) blends, an increase in melting temperature and heat enthalpy can be observed more clearly due to the higher compability of NBRr with TMPTA.

According to results obtained by Noriman and Ismail (2011), the irradiated SBR/NBRr blends showed a better tensile retention compared to non-irradiated SBR/NBRr blends. The increase in tensile strength is due to the cross-linking induced by irradiation in the presence of TMPTA. However, TMPTA acts as plasticizer which tends to reduce the tensile strength in the absence of irradiation.

2.10 Investigation of TMPTMA and TPGDA as Cross-linking Agent on Properties of Polymer with Electron Beam Irradiation

To examine how cross-linking agent affects the properties of polymers, ultra-high molecular weight polyethylene (UHMWPE) samples were added with 1 wt% of trimethylolpropane trimethylarcylate (TMPTMA) or tripropylene glycol diacrylate (TPGDA) and subjected to electron beam irradiations with different doses ranging from 10 to 200 kG, in the research done by Wu et al., 2012.

According to their results, the gel content of UHMWPE added with TMPTMA or TPGDA are much higher than pure UHMWPE. The gel content of TMPTMA and TPGDA with UHMWPE also observed to increase with increasing of irradiation doses up to 100 kGy. This result indicates that the cross-linking reaction of UHMWPE can be promoted with cross-linking agent with the aids of irradiation.



Note: UPE = UHMWPE

Figure 2.13 The Effect of Irradiation Dose on Gel Fraction of UHMWPE (Source: Wu et al., 2013)

The results also showed that the gel content for 1 wt% of TMPTMA in UHMWPE was higher than that of TPGDA, which shows that TMPTMA is more efficient cross-linking agent in aiding of cross-linking reaction compared to TPGDA.

This might due to the three pendant double bonds that presence in TMPTMA, whereas there are only two pendant double bonds in TPGDA. The higher number of pendant double bonds in TMPTMA provides higher chances of cross-linking reactions when exposed to irradiation doses.

On the other hand, the degree of crystallinity for irradiated was higher than that of non-irradiated for all of the samples. The degree of crystallinity also increased with the aids of cross-linking agent, TMPTMA or TPGDA. However, the results is same as what obtained in gel content, where the degree of crystallinity of UHMWPE added with TMPTMA was higher compared to TPGDA, which proved that TMPTMA is more efficient in crystal formation during irradiation process.

2.11 Effectiveness of Trimethylolpropane Trimethylarcylate (TMPTMA) in Cross-linking of Polymer Induced by Electron Beam Irradiation

Studies had been carried out to investigate the effect of TMPTMA on the properties of polymer, such as polylactic acid, PLA. Different loading level of TMPTMA, 3 and 5 wt%, were added into PLA were subjected to electron beam irradiation doses ranging from 25 to 250 kGy with 25 kGy per pass. Various characterization tests were then carried out to test the physical properties of TMPTMA added with PLA.

Study done by Ng et al. (2014) reported that the gel content of PLA increased significantly with the increase in both the TMPTMA loading level and electron beam irradiation dose, whereas pristine PLA has the lowest gel content, as shown in Figure 2.15. The increase in gel content is due to the formation of cross-linking network during irradiation process. Moreover, the addition of TMPTMA able to promotes cross-linking reaction through its existing tri-functional pendant group. However, when the irradiation doses increase to more than 200 kGy, the gel content decrease due to predomination of chain scissioning reaction over cross-linking reaction in high irradiation doses.

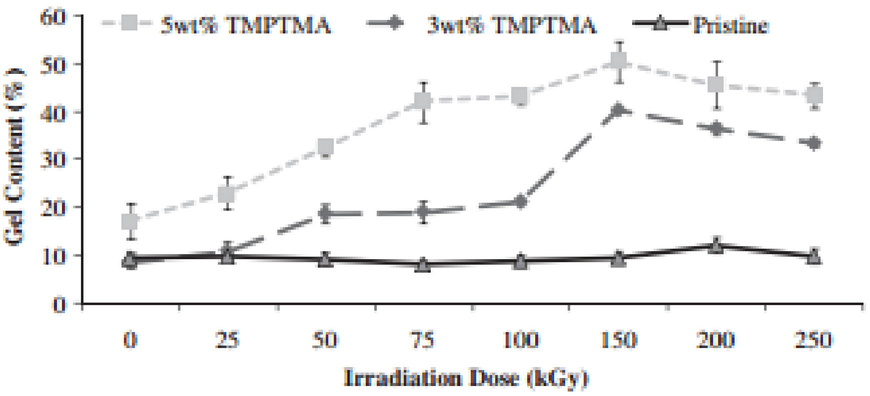


Figure 2.14 The Effect of Increasing Irradiation Dose of Various TMPTMA Loading Level on Gel Fraction of PLA (Source: Ng et al., 2014)

Beside gel content, the additions of TMPTMA and irradiation doses up to 100 kGy are able to increase the tensile strength of PLA compared to pristine PLA. Based on Figure 2.16, the tensile strength for PLA with 5 wt% of TPMTMA decrease more rapidly than that with 3 wt% of TMPTMA with increasing of irradiation doses. This might due to the chain scissioning reaction, where the excess unreacted TMPTMA gained the opportunity to attack the PLA backbone chain, causing the tensile strength of PLA to decrease. This also explains why the tensile strength of PLA with 5 wt% and 3 wt% of TMPTMA are lower than that of pristine PLA at 0 kGy irradiation dose.

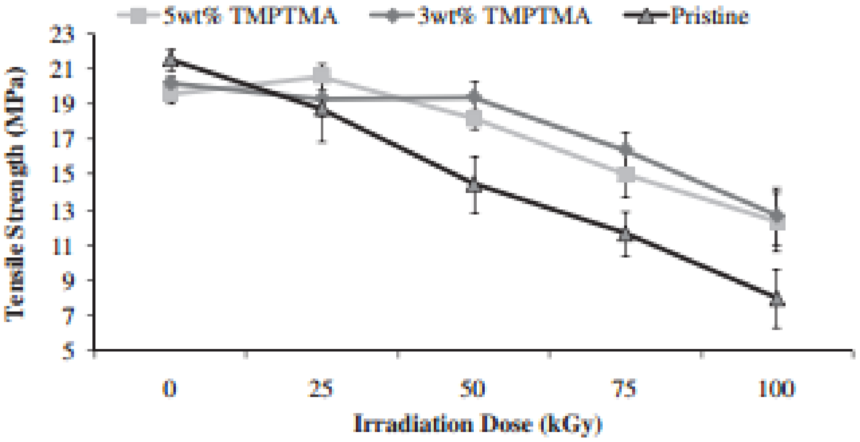


Figure 2.15 The Effect of Increasing Irradiation Dose of Various TMPTMA Loading Level on Tensile Strength of PLA (Source: Ng et al., 2014)

On the other hand, Young's modulus of PLA also increased with addition of TMPTMA, but decrease with increasing irradiation doses up to 25 kGy. However, the decreasing of Young's Modulus of PLA added with TMPTMA was not obvious as compared to pristine PLA due to the reason that the addition of TMPTMA are able to restricted the mobility of PLA chains by the formation of cross-linking network between TMPTMA and radiation-induced free radicals. The effect of TMPTMA and irradiation doses on Young's modulus is shown in Figure 2.17.

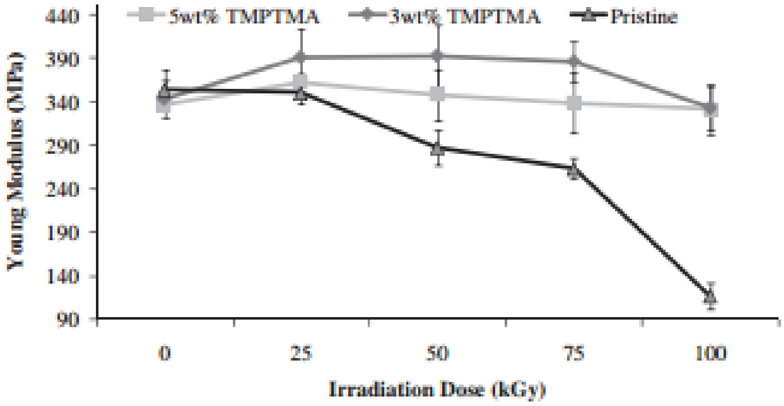


Figure 2.16 The Effect of Increasing Irradiation Dose of Various TMPTMA Loading Level on Young's Modulus of PLA (Source: Ng et al., 2014)

According to Figure 2.18, the elongation at break reduce with the addition of TMPTMA in PLA for non-irradiated samples due to the cross-linking network that formed during the compression molding process that decrease the mobility of polymer chain. When irradiation doses increase, the elongation at break of virgin PLA decreased because of the occurring of chain scissioning reaction. The elongation at break was observed to reduce the most for higher level of TMPTMA (5 wt%), due to the same reason as explained in tensile strength.

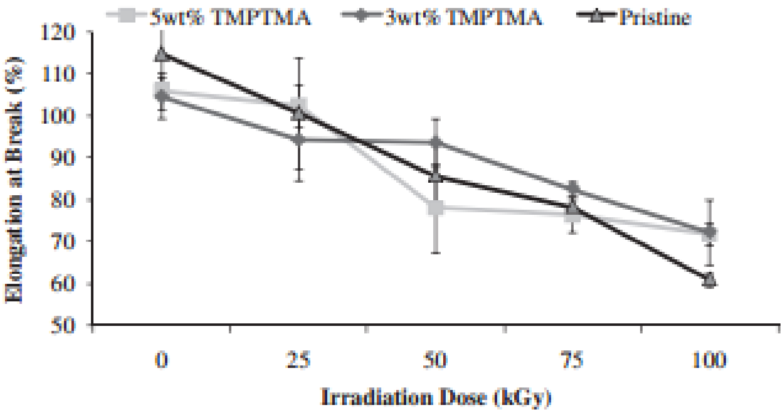


Figure 2.17 The Effect of Increasing Irradiation Dose of Various TMPTMA Loading Level on Elongation at Break of PLA (Source: Ng et al., 2014)

In X-ray Diffraction (XRD) study, the crystallinity of PLA was observed to increase with increasing loading level of TMPTMA and irradiation doses. The addition of TMPTMA aids in inducing the formation of cross-linking network which allowed the molecular chain to align in a more ordered structure upon electron beam irradiation. The crystallinity increase more significantly at higher irradiation doses due to high flexibility of polymer chain caused by chain scissioning reaction, which allowed the polymer chain to recrystallize into a more ordered structure.

All the results obtained indicated that the addition of cross-linking agent such as TMPTMA could improve and modified the original properties of polymers.

CHAPTER 3

METHODOLOGY

3.1 Materials

In this research, acrylonitrile butadiene styrene (ABS), low density polyethylene (LDPE), high density polyethylene (HDPE), and ethylene vinyl acetate (EVA) were used as polymer base in compounding process. ABS with industrial grade of 500 322 manufactured by Toray Plastic (m) Sdn. Bhd., Malaysia, while LDPE with industrial grade of Titanlene LDF200GG manufactured by Lotte Titan Chemicals Corporation Sdn. Bhd, Malaysia, HDPE with pellet name of Etilinas HD5301AA manufactured by Polyethylene Malaysia Sdn Bhd and EVA with the grade of UE 629 supplied by USI Corporation, Taiwan were used in this research. Industrial grade trimethylopropane trimethylarcylate (TMPTMA) manufactured by Sigma- Aldrich (M) Sdn. Bhd., Malaysia was used as a promoter to induce the formation of cross-linking network in polymer matrix.

3.2 Formulation

Varying loading level of trimethylopropane trimethylarcylate (TMPTMA) were added into a fixed loading level of polymer resins (ABS, LDPE, HDPE and EVA), respectively as shown in Table 3.1. The loading levels of TMPTMA were varied from 0 to 8 phr with a constant loading level of polymer resins of 100 phr.

Table 3.1 Formulation for the Addition of Varying Amount of Trimethylolpropane Trimethylarcylate (TMPTMA) into Acrylonitrile Butadiene Styrene (ABS), Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE) and Ethylene Vinyl Acetate (EVA)

Samples	Loading level, part per hundred resin (phr)	
	Polymer resins	TMPTMA
0 ABS	100	0
2 ABS	100	2
4 ABS	100	4
6 ABS	100	6
8 ABS	100	8
0 LDPE	100	0
2 LDPE	100	2
4 LDPE	100	4
6 LDPE	100	6
8LDPE	100	8
0 HDPE	100	0
2 HDPE	100	2
4 HDPE	100	4
6 HDPE	100	6
8 HDPE	100	8
0 EVA	100	0
2 EVA	100	2
4 EVA	100	4
6 EVA	100	6
8 EVA	100	8

3.3 Sample Preparation

The polymer resins (LDPE, HDPE, EVA and ABS) was compounded with TMPTMA by using Thermo Haake Rheomix Mixer at specific mixing temperature and a rotor speed of 50 rpm with mixing time 5 minutes.

The compounded polymer samples were hot pressed into 1 mm thickness sheet using hot press machine under specific temperature and pressure of 10 MPa, respectively for 10 minutes. Initially, the samples were pre-heated at heating temperature for 5 minutes. The preheated samples were then further pressed under pressure of 10 MPa at heating temperature for another 5 minutes. After that, the compression molded samples were cooled to room temperature using a cold press with a cooling rate of 15^{o}C/min for 2 minutes under a pressure of 10 MPa. The 1 mm thickness sheets were then cut into dumbbell shapes in accordance to ASTM D1822 by using dumbbell cutter. The temperature for compounding and hot pressing for each type of polymers were summarised in Table 3.2 below.

The dumbbell specimens were then subjected to electron beam irradiation at room temperature under an acceleration voltage of 175 kV. The irradiation dosages subjected to each samples were 0, 50, 100, 150, 200 and 250 kGy, with 50 kGy per pass.

Table 3.2 Temperautre used in Compounding and Hot Pressing of Acrylonitrile Butadiene Styrene (ABS), Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE) and Ethylene Vinyl Acetate (EVA)

Temperature used (^{o}C)	Type of polymer resins			
	LDPE	HDPE	EVA	ABS
Compounding	180	170	130	130
Hot press	170	180	145	145

3.4 Sample Testing and Charaterization

In this section, the testing methods and the characterization of the prepared samples will be discussed.

3.4.1 Gel Content Test

The gel content test was performed to investigate the degree of cross-linking networks formed in polymer matrix. The gel content test for LDPE, HDPE and EVA were conducted in accordance to ASTM D2765 standard by immersing the samples into xylene solvent. The samples were first weighted to determine the initial weight, W_i before the extraction process. Then the samples were heated at a temperature of 120°C in xylene solvent for 24 hours. After the 24 hours extraction process, the remaining samples were washed few times with clean methanol to remove the staining of soluble materials from the extracted samples, and the washed samples were allowed to settle for 30 min. Then, the samples were dried at a temperature of 30°C for 3 hours in a vacuum oven. The dried remaining samples will then be weighted again to obtain the final weight of the insoluble materials, W_f. The percentage of gel content of the samples will be calculated using Equation (3.1). For ABS, the gel content test was conducted by immersing the ABS samples into Methyl Ethyl Ketone (MEK) solvent with all other conditions remained the same.

$$\text{Gel Content Percentage (\%)} = \frac{W_f}{W_i} \times 100\% \tag{3.1}$$

where,

W_i= initial weight of the sample before the extraction process (g)

W_f= final weight of the remaining dried sample after the extraction process (g)

3.4.2 Hot Set Testing

Hot set test was another testing performed to investigate the degree of cross-linking networks formed in polymer matrix besides gel content testing. Besides, hot set testing was also used to measure if the samples have sufficient mechanical properties at elevated temperature. In this testing, dumbbell specimens in accordance to ASTM D1822 were used. Different samples were given different load according to Equation 3.2. Samples were then put in to oven Heraeus UT 6050 HS together with hanging load at a temperature of 200°C for 15 minutes. For samples that were broke within 15 minutes, time taken for the samples to break was recorded. On the other hand, for samples that do not break within 15 minutes, the elongation of the samples was recorded.

$$\text{Load} = \text{thickness x width x } 10.2 \qquad (3.2)$$

Where,
10.2 = static load (g/mm^2)
Thickness and width of dumbbell specimens were measure in unit of mm

3.4.3 Tensile Test

Tensile test was conducted to investigate the mechanical properties of the samples under loading. The tensile strength, Young’s modulus and elongation at break of the samples were evaluated by conducting the tensile test. Dumbbell specimens in accordance to ASTM D1822 were used in tensile test. The dumbbell specimens were tested using Instron Universal Testing Machine (Model 4302 Series IX) under crosshead speed of 50 mm/min. The gauge thicknesses of each dumbbell specimens were measured before the tensile testing. The tensile test was carried out at room temperature of 25°C using a load cell of 2 kN. The tensile strength, Young’s modulus and elongation to break of the sample were obtained as the average of five specimens.

3.4.4 Scanning Electron Microscopy (SEM) Analysis

SEM analysis was performed to obtain the surface morphologies of the fracture surface from tensile test. The fracture surface of samples were scanned and observed using a BS 340 TELSA Hitachi scanning electron microscope (SEM). The fracture surface of the samples was cut into smaller portion before the scanning process. The cut samples were then placed and mounted on copper stubs with the fracture surface facing upwards. Each of the cut samples were coated with a thin layer of gold samples by using EMITECH SC7620 Sputter Coater for the scanning purpose. The coated samples were scanned at an electron beam voltage of 15 kV under the magnifications of 1000, 8000 and 15000 for ABS, while for HDLE, LDPE and also EVA, the magnifications of 1000, 3000 and 8000 were used.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Physical Properties

In this research, two tests were conducted to investigate the physical properties of polymers, which were: gel content and hot set test.

4.1.1 Gel Content Test

The gel content test was performed to investigate the degree of crosslinking networks formed in polymer matrix. Figures 4.1 to 4.2 shows the relationship between TMPTMA loading level on the percentage of gel content for LDPE and HDPE samples with various electron beam irradiation dosages. From Figures 4.1 to 4.2, it is clearly seen that the percentage of gel content for non-irradiated pristine LDPE and HDPE as well as TMPTMA added LDPE and HDPE was zero, due to no cross-linking networks formed inside polymer matrix of all non-irradiated LDPE and HDPE samples. This also indicates that all non-irradiated LDPE and HDPE samples were fully dissolved in xylene solvent after 24 hours of extraction.

According to Figures 4.1 to 4.2, the gel content of pristine LDPE and HDPE was observed to gradually increase with increasing irradiation dosage from 0 kGy to 150 kGy. This inferred that the application of electron beam irradiation dosage on pristine LDPE and HDPE could slightly induce the formation of cross-linking network in polymer matrix of pristine LDPE and HDPE samples. The electron released by the electron beam accelerator would attack the LDPE and HDPE macromolecular chains to generate polymeric free radicals inside LDPE and HDPE matrix by releasing water vapour. Then, the polymeric free radicals formed would further react together to form the crosslinking networks inside LDPE and HDPE matrix (Bee et al., 2014). Thus, the formation of crosslinking networks inside LDPE and HDPE matrix could significantly reduce the solubility of LDPE matrix into hot xylene.

By referring to Figure 4.1, the gel content of all TMPTMA added LDPE samples was observed to increase up to more than 30% when irradiated up to (≤100 kGy). The gel content of all irradiated LDPE samples was observed to be higher than gel content of pristine LDPE at the same irradiation dosage. This indicate that the presence of TMPTMA in LDPE matrix would act as cross-linking agent plays by releasing more free radicals in LDPE matrix when exposed to irradiation energy (Ng et al., 2014). The increasing of free radicals amounts in LDPE matrix could promote the development of three dimensional crosslinking networks via the three pendent double bonds in its structure (Wu et al., 2012).

At higher irradiation dosages (≥ 100 kGy), the gel content of all TMPTMA added LDPE samples was increased up to more than 60%. Higher energy released during higher electron beam irradiation dosages could release and generate more monomer free radicals from TMPTMA. The released monomer free radicals could further react with polymer free radicals from LDPE to form three dimensional networks (Ng et al., 2014). However, it was observed that the increment of gel content become less significant at higher irradiation dosage (≥150 kGy). This might due to the cross-linking and chain scissioning reaction that occurred simultaneously in high irradiation dosage tended to reach a balancing effect, thus no significant results can be seen (Sujit et al., n.d.).

It also can be observed that the increasing loading level of TMPTMA has gradually increased the gel content of TMPTMA added LDPE samples. This might due to the released of additional monomer free radicals by higher loading level of TMPTMA would react with large amount of polymer free radicals of LDPE to form additional graft bridges (Bee et al., 2014). Thus, the formation of three dimensional cross-linking networks could significantly reduce the solubility of TMPTMA added LDPE samples in hot xylene solvent.

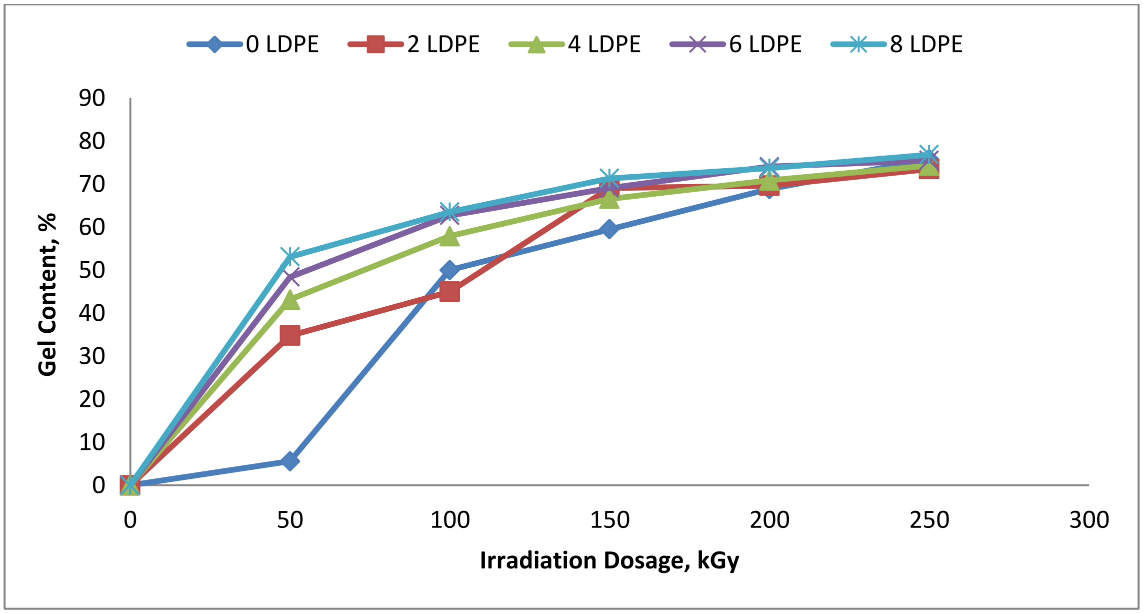


Figure 4.1 Effect of Increasing Loading level of TMPTMA on Gel Content of LDPE under Variation of Electron Beam Irradiation Dosages

From Figure 4.2, the percentage of gel content for TMPTMA added HDPE samples also seen to be increased with increasing irradiation dosage. This implied that the crosslinking reaction was able to take place more readily in the presence of TMPTMA with electron beam irradiation. As discussed above, the addition amount of three pendent double bonds in TMPTMA was the reason that aided in the formation of three dimensional cross-linked networks with the HDPE free radicals when exposed to electron beam irradiation (Wu et al., 2012).

The increasing loading level of TMPTMA up to 2 phr significantly increased the percentage of gel content in HDPE matrix. This might due to the released of monomer free radicals by TMPTMA to form three dimensional cross-linked networks with HDPE free radicals under electron beam irradiation (Ng et al., 2014). However, further increased of TMPTMA loading level (≥2 phr) and also high irradiation dosage (≥100 kGy) could not show a more significant effect in increasing the percentage of gel content for TMPTMA added HDPE samples. This inferred that the chain scissioning reaction tended to compete with crosslinking reaction for higher TMPTMA loading level and also higher irradiation dosages (Wu et al., 2012).

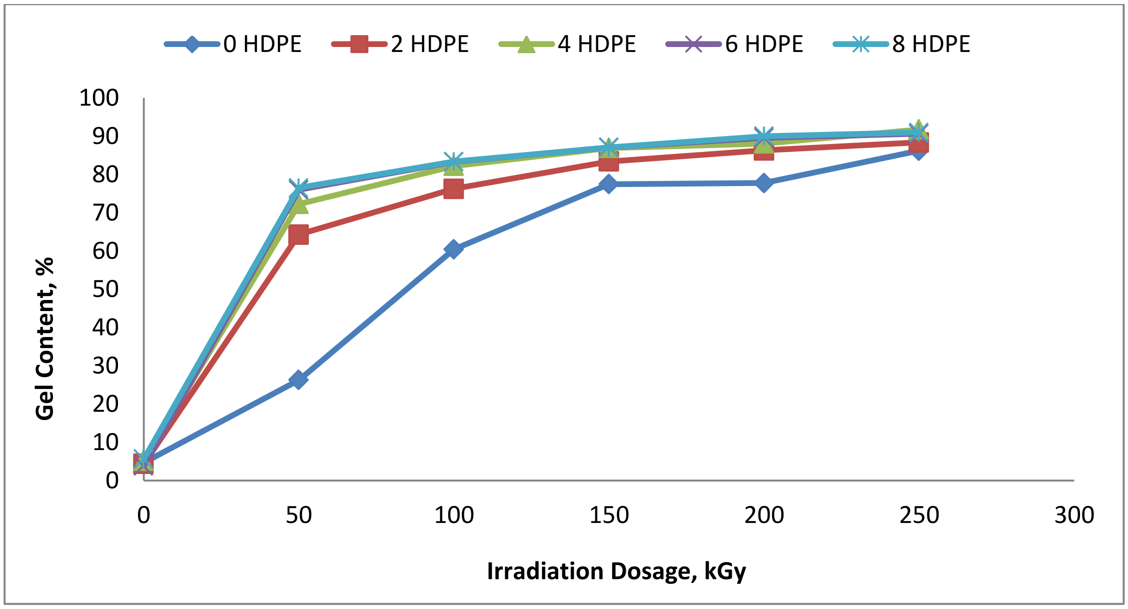


Figure 4.2 Effect of Increasing Loading level of TMPTMA on Gel Content of HDPE under Variation of Electron Beam Irradiation Dosages

Figure 4.3 shows the relationship between TMPTMA loading level on the percentage of gel content for EVA samples with various electron beam irradiation dosages. It was observed that the percentage of gel content for non-irradiated pristine EVA was zero and all the non-irradiated TMPTMA added EVA was the lowest among all samples, where the percentage for gel content almost approaching zero. The very low percentage of gel content found in non-irradiated TMPTMA added EVA samples was due to the presence of TMPTMA that have the tendency to mildly react with EVA radicals under elevated temperature conditions (Ng et al., 2014). Meanwhile, the nature structure of EVA also aided in contributing the tendency to form cross-link networks for non-irradiated TMPTMA added EVA samples, where crosslinking mechanism was more likely to occur with the free radical species in the increasing amorphous phase of EVA (Sujit et al., 1996).

The percentage of gel content for pristine EVA samples was observed to increase significantly to more than 58% with increasing irradiation dosage up to 50 kGy. This might due to the nature of EVA that is easily cross-linked when being exposed to high-energy electron beam irradiation (Sabet et al., 2010). The increasing amorphous phase in EVA compared to other polymer was the main reason of superior crosslink ability of EVA when exposed to electron beam irradiation (Burns, 1979), as radiation induced crosslink are more likely to occur within the amorphous phase of polymers due to the mobility of the chains in the amorphous regions (Dadbin et al., 2004).

As seen in Figure 4.3, the percentage of gel content for all TMPTMA added EVA samples was observed to increase significantly with irradiation dosage up to 50 kGy. This might due to formation irradiation induced crosslink networks with the incorporation of TMPTMA. The monomer free radicals from TMPTMA react with polymer free radicals in amorphous phase of EVA to form three dimensional cross-linked networks with the when subjected to electron beam irradiation (Sharif et al., 1999).

However, the percentage of gel content seemed to keep at a consistent value with further increasing of irradiation dosages (≥150 kGy) and further increasing of TMPTMA loading level (≥2 phr). This might due to the reason that crosslinking and chain scissioning reactions occur simultaneously and compete with each other to reach a balancing effect at higher loading level of TMPTMA and electron beam irradiation dosages, as discussed above (Wu et al., 2012).

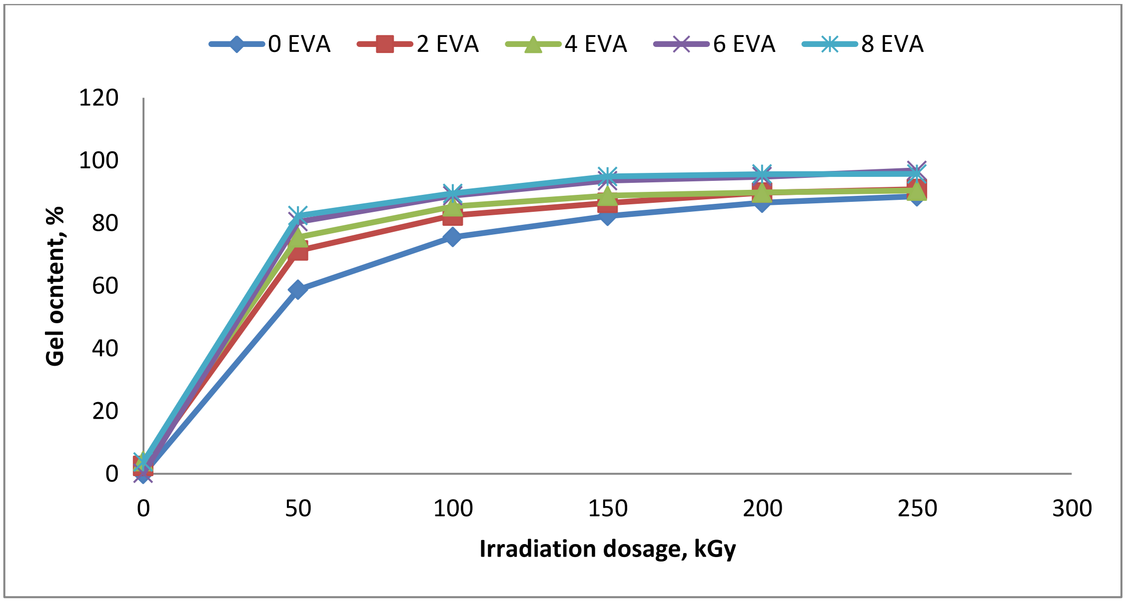


Figure 4.3 **Effect of Increasing Loading level of TMPTMA on Gel Content of EVA under Variation of Electron Beam Irradiation Dosages**

Figure 4.4 shows the relationship between TMPTMA loading level on the percentage of gel content for ABS samples with various electron beam irradiation dosages. As seen in Figure 4, the non-irradiated pristine ABS was observed to fully dissolve into hot solvent due to the absence of crosslinking networks in ABS matrix. However, all the irradiated pristine ABS samples were also found to be fully dissolve in hot solvent (MEK) after 24 hours of extraction process. This indicates that the application of electron beam irradiation did not provide any significant effect in inducing the formation of crosslinking networks in ABS matrix. This might due to the electron released from electron beam accelerator would attack the polymer chains inside ABS matrix to generate the polymeric free radicals inside ABS matrix. However, the generated polymeric free radicals would cause the crosslinking process and chain scissioning process to be occurred simultaneously when subjected to electron beam irradiation (Bee et al., 2014). Thus, the pristine ABS samples were fully dissolved in hot MEK solvent after the 24 hours extraction process.

From Figure 4.4, it was observed that the percentage of gel content for all non-irradiated TMPTMA added ABS increased with increasing loading level of TMPTMA. This inferred that the incorporation of TMPTMA into ABS matrix could promote the occurrence of crosslinknig reaction in ABS matrix even without the application of electron beam irradiation. This might due to the tendency of TMPTMA to midly release monomer free radicals at elevated temperature. The heat provided during the samples compounding and compression molding would break the three pendent double donds in TMPTMA to form free monomer radicals (Ng et al., 2014). The free mononer radicals then react with polymer free radicals to form three-dimensional crosslinking networks, which could reduce the solubility of TMPTMA added ABS samples in hot MEK solvent.

The percentage of gel content for irradiated ABS samples was found to increased sginificantly with the addition of TMPTMA (2 phr to 6 phr) upon electron beam irradiation dosage of 50 kGy. High loading level of TMPTMA could generate additional monomer free radcials to react with ABS free radicals forming a greater three dimensional crosslinked networks (Ng et al., 2014). The percentage of gel content showed continuous increase for all TMPTMA added ABS samples under electron beam irradiation dosages from 50 kGy to 150 kGy. This might due to the genearation of additional TMPTMA free radicals to react with additional ABS free radicals at higher irradiation dosages to formed larger three dimensional crosslinked networks structure (Pentimallia et al., 1999).

From Figure 4.4, it was observed that further increase in electron beam irradiation dosages (250 kGy) decreased the percentage of gel content at 4 phr of TMPTMA. This inferred the predominant of chain scissioning reactions over crosslinking reaction at higher irradiation dosages. The dissipation of excess energy from higher electron beam irradiation dosages causes chain scissioning of the bonds between the ABS backbone chains (Bee et al., 2014). A slight increase in the percentage of gel content was observed at higher loading level of TMPTMA (≥6 phr) with high irradiation dosage (≥200 kGy). This might due to the occurance of re-crosslinking reaction, where the short chain formed during chain scissioning recombined and rearranged to form three-dimensional crosslinked networks again.

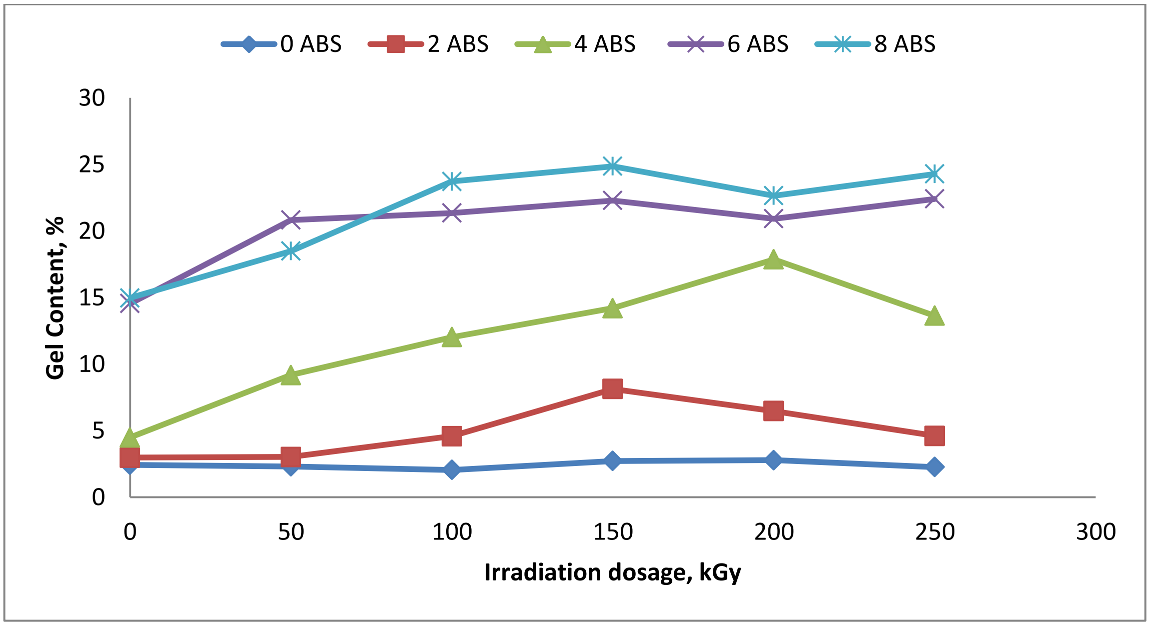


Figure 4.4 Effect of Increasing Loading level of TMPTMA on Gel Content of ABS under Variation of Electron Beam Irradiation Dosages

4.1.2 Hot Set test

Tables 4.1 to 4.3 show the results obtained from hot set testing for LDPE, HDPE and EVA samples under various electron beam irradiation dosages. By referring to Tables 4.1 to 4.3, all the non-irradiated LDPE, HDPE and EVA samples failed the test immediately under static load at elevated temperature of 200°C. This is due to the absence of crosslinking networks that could cause the non-irradiated samples to melted and deformed easily by the load under elevated temperature of 200°C (Sharif et al., 2007). These results were found to be consistent with the gel content test.

It can be observed that the application of electron beam irradiation dosages up to 150 kGy on pristine LDPE samples still failed the hot set test. However, the failure these

LDPE samples were observed to occur at a longer time when compared to non-irradiated samples. This might due to the low level of crosslinking, which was still unable to prevent the deformation of samples by load. However, the pristine LDPE samples were found to remain unbroken and elongated to a certain length until 15 minutes with further increment of irradiation dosages from 150 kGy to 250 kGy. This is because the increment of radiation-induced crosslinking networks in LDPE matrix could resist the failure of LDPE samples.

The samples were observed to fail the test at a longer time (>2 minutes) with incorporation of TMPTMA at low irradiation dosage of 50kGy. This inferred that the presence of TMPTMA could delay the failing time of LDPE samples due to the reactions of monomer free radicals from TMPTMA with polymers free radicals to form crosslinking networks in LDPE matrix. By referring to Table 4.1, the polymer matrix of LDPE samples added with higher loading level of TMPTMA (≥ 4 phr) under higher irradiation dosages (≥ 100 kGy) was found able to resist from failure for more than 15 min. At higher irradiation dosages (≥ 100 kGy), the increasing of TMPTMA loading level was observed to reduce the creep elongation of LDPE samples. This could be attributed to the higher degree of crosslinking networks formed at higher loading level of TMPTMA under higher irradiation dosages rate (Dadbin et al., 2001).

Pristine HDPE and EVA samples, the samples were found to fail the test at lower irradiation dosage (50 kGy) in comparison to LDPE which failed the test at higher irradiation dosages (150 kGy). As reported by Weisner (1991), different specific numbers of crosslinking are required by different polymer structure for certain reduction deformation caused by the load in hot set test. Further increment of irradiation dosages (100 kGy and above) was observed to reduce the creep elongation of both HDPE and EVA samples due to formation of adequate crosslinking network as evident by gel content results in section 4.1.1. Moreover, the nature structure of EVA which easily crosslink when exposed to irradiation is one of the reason for the improvement in performances of EVA samples (Sharif et al., 1999).

The performances for both HDPE and EVA samples were found to improve with incorporation of TMPTMA and increasing irradiation dosages. This is due to the more crosslinking networks structure formed which caused the samples to become strong enough to pass through the hot set test. This is because the three pendent double bonds of TMPTMA tended to break and react with polymer free radicals to promoter crosslinking reaction in both HDPE and EVA samples.

Table 4.4 show the results obtained from hot set testing for ABS samples under various electron beam irradiation dosages. As observed in Table 4.4, all of the samples were found to fail immediately under elevated temperature of 200^{o}C. This might due to the inferior crosslink ability of ABS structure to promote crosslinking networks in ABS matrix that resist the deformation caused by the load in hot set test. This was proven in the gel content test, where lower crosslinking densities were observed for ABS samples in comparison to LDPE, HDPE and also EVA samples.

Table 4.1 Hot Set Results of LDPE with TMPTMA under Various Irradiation Dosages

Irradiation dose, kGy	Loading level of TMPTMA, phr				
	0	2	4	6	8
0	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately
50	Fail at 1-2 min	Fail at 2-3 min	Fail at 13-15 min	Fail at 3-6 min	Fail at 2-3 min
100	Fail at 2-3 min	Fail at 5-6 min	25.9mm ± 0.4	19.5mm ± 0.2	19.5mm ± 0.8
150	Fail at 4-5 min	Fail at 14-15 min	16.9mm ± 0.7	15.9mm ± 0.2	14.6mm ± 0.5
200	17.6mm ± 0.9	18.7mm ± 1.2	15.9mm ± 0.4	15.2mm ± 0.1	14.5mm ± 0.5
250	18.4mm ± 0.7	14.9mm ± 0	14.4mm ± 0.1	14.4mm ± 0.2	13.1mm ± 0.6

Table 4.2 Hot Set Results of HDPE with TMPTMA under Various Irradiation Dosages

Irradiation dose, kGy	Loading level of TMPTMA, phr				
	0	2	4	6	8
0	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately
50	Fail at 10-11 min	16.6mm ± 0.8	13.9mm ± 0.3	13.0mm ± 0.2	12.8mm ± 0.8
100	16.9mm ± 0.2	14.1mm ± 0.1	14.0mm ± 0.5	13.2mm ± 0.5	13.4mm ± 0.5
150	16.1mm ± 0.2	13.4mm ± 0.1	13.2mm ± 0.2	12.6mm ± 0.6	12.5mm ± 0.5
200	13.6mm ± 0.8	12.6mm ± 0.5	13.1mm ± 0.7	12.6mm ± 0.4	12.5mm ± 0.4
250	13.0mm ± 0.7	12.9mm ± 0.3	12.6mm ± 0.8	12.3mm ± 0.6	12.9mm ± 0.4

Table 4.3 Hot Set Results of EVA with TMPTMA under Various Irradiation Dosages

Irradiation dose, kGy	Loading level of TMPTMA, phr				
	0	2	4	6	8
0	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately
50	Fail at 12-13 min	35.0mm ± 1.4	18.4mm ± 0.2	16.3mm ± 0.5	14.3mm ± 1.0
100	21.1mm ± 2.8	14.7mm ± 0.4	13.9mm ± 0.7	12.8mm ± 0.4	13.1mm ± 0.3
150	15.0mm ± 1.2	13.3mm ± 1.3	12.5mm ± 0.2	12.5mm ± 0.2	11.8mm ± 0.6
200	14.3mm ± 0.3	13.6mm ± 0.2	13.1mm ± 0.5	12.9mm ± 0.3	12.7mm ± 1.8
250	13.0mm ± 0.1	12.9mm ± 1.2	12.6mm ± 0.7	12.3mm ± 0.3	12.9mm ± 0.5

Table 4.4 Hot Set Results of ABS with TMPTMA under Various Irradiation Dosages

Irradiation dose, kGy	Loading level of TMPTMA, phr				
	0	2	4	6	8
0	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately
50	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately
100	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately
150	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately
200	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately
250	Fail immediately	Fail immediately	Fail immediately	Fail immediately	Fail immediately

4.2 Mechanical Properties

The mechanical properties of polymers were tested by using tensile test. Through tensile test, parameters such as tensile strength, Young's Modulus and elongation at break were obtained.

4.2.1 Tensile Strength

Tensile strength measures the maximum tensile stress throughout the tensile elongation of a polymer. Figure 4.5 shows the relationship of tensile strength of LDPE samples with different loading level of TMPTMA under various irradiation dosages. In Figure 4.5, it was observed that non-irradiated pristine LDPE and all TMPTMA added LDPE samples posed the lowest tensile strength in comparison with samples that were subjected to electron beam irradiation. This low tensile strength was due to the lack of formation of crosslinking networks in all non-irradiated LDPE samples. Moreover, the high degree of long and short chain branching in LDPE structure also resulted in lower tensile strength due to weaker crystanillity and intermolecular forces between LDPE chains.

The tensile strength of all pristine LDPE samples showed significant improvement with the introduction of electron beam irradiation. This inferred the formation of three dimensional crosslinking networks with subjection of irradiation energy (Ziaie et al., 2007). The formation of crosslinking networks was able to increase the tensile strength of pristine LDPE samples due to the increment of intermolecular forces that prevent the LDPE chains from sliding past each other when forces was applied during stretching.

TMPTMA plays an important role in this research, where it acts as a crosslinking agent to promote crosslinking reactions in polymer matrix by the generation of monomer free radical to react with polymer free radicals through the breaking of three pendent double bonds via electron beam irradiation. Both molecular weight and also intermolecular bonding of polymers could be increased by the formation of crosslink. As shown in Figure 4.5, the tensile strength of LDPE samples improved significantly with incorporation of TMPTMA (up to 4 phr) upon electron beam irradiation of 50kGy. This indicates that the addition of crosslinking agent, TMPTMA was able to promote the formation of crosslinking networks efficiently in LDPE matrix via the breaking of the three pendent double bonds in TMPTMA (Wu et al., 2012). However, further increment in loading level of TMPTMA (≥4 phr) tended to decrease the tensile strength of LDPE samples. This could be due to the predominant of chain scissioning reactions over crosslinking reactions, where the excessive monomer free radicals generated by higher loading level of TMPTMA started to attack the LDPE backbone chain caused the backbone chain to break into shorter chains. Thus, the molecular weight as well as the tensile strength of LDPE samples decreased.

Without subjection to electron beam irradiation (0 kGy), the incorporation of TMPTMA could decrease the tensile strength of LDPE samples, as shown in Figure 4.5. The lower tensile strength could be attributed to the unreacted TMPTMA that enter into the macromolecular chain of LDPE matrix to weaken the intermolecular forces between the LDPE chains (Ng et al., 2014). Moreover, TMPTMA has the ability to act like plasticizer, which prevents the polymer molecules from coming closer to each other, thus reducing the intermolecular forces and also the strength of LDPE samples.

The tensile strength of all TMPTMA added LDPE samples were observed to decrease at high electron beam irradiation dosages (≥150 kGy). This might due to the chain scissioning reactions which are more predominant than crosslinking reactions, where LDPE tended to release excessive amount of polymer free radicals that might attack the backbone chain of LDPE matrix at higher irradiation dosages (Bee et al., 2014). The sudden increment of tensile strength with high loading level of TMPTMA (>2 phr) at higher electron beam irradiation dosages (250 kGy) was due to recombination of the shorter chains that previously caused by chain scissioning reactions to react with monomer free radicals from TMPTMA to form crosslinking networks again.

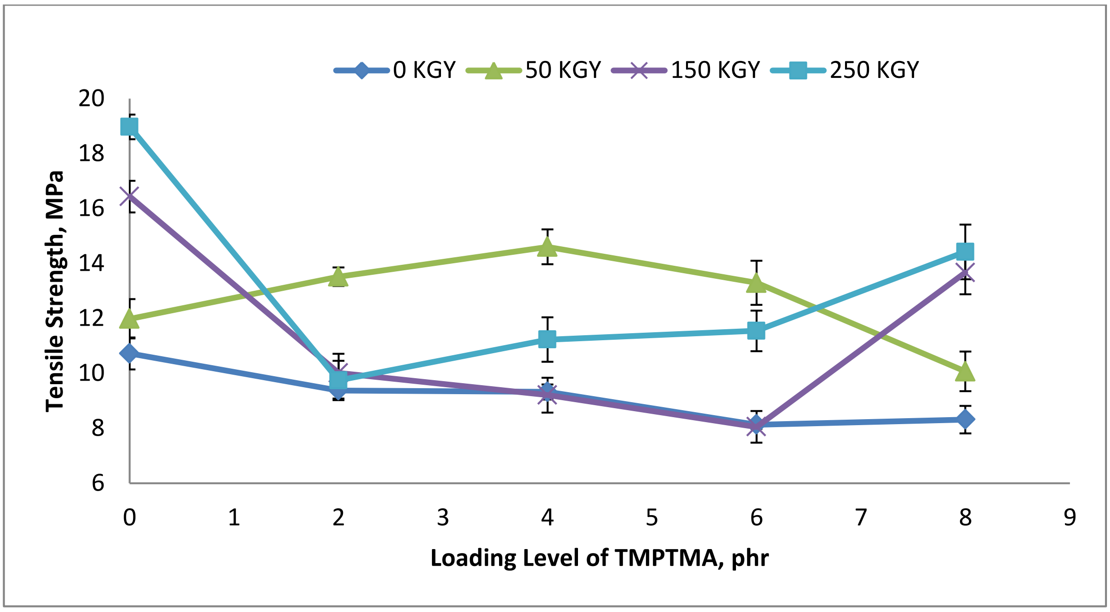


Figure 4.5 Effect of Loading Level of TMPTMA on Tensile Strength of LDPE Samples under Various Electron Beam Irradiation Dosages

Figure 4.6 showed the effect on tensile strength of HDPE samples with different loading level of TMPTMA upon electron beam irradiation dosages. As shown in Figure 4.6, the all the non-irradiated pristine HDPE and TMPTMA added HDPE samples posed the highest tensile strength among all HDPE samples. This is because HDPE originally have strong intermolecular forces and tensile strength due to its almost linear chain with very low degree of branching (Brennan, n.d.). Thus, introduction of electron beam irradiation dosages could not show any significant improvement in the tensile strength of HDPE although it does provide formation of crosslinking networks in HDPE matrix, as proved by gel content in section 4.1.1. The crosslinking network formed in HDPE matrix was unable to show any effect in enhancing the mechanical properties of HDPE samples.

The tensile strength of all pristine HDPE and TMPTMA added HDPE samples were observed to decrease more significantly at higher irradiation dosages (≥50 kGy). This might due to the predominant of chain scissioning reaction, where the HDPE backbone chain break into shorter chains when exposed to high energy of electron beam irradiation (Dadbin et al., 2001).

However, the incorporation of TMPTMA into HDPE does show some effect in tensile strength of HDPE samples. As seen in Figure 4.6, the addition of small amount of TMPTMA (2 phr) could gradually increase the tensile strength of HDPE samples for 50 kGy and 150 kGy when compared to pristine HDPE at the same irradiation dosages. This inferred that TMPTMA has the ability to induced significant crosslinking reactions in HDPE matrix that restrict the movement of chains to slide pass each other (Ng et al., 2014). Further increment of TMPTMA (>2 phr) was observed to decrease the tensile strength of HDPE samples due to generation of excessive monomer free radicals, which caused the domination of chain scissioning reaction over crosslinking reaction. The sudden increment in tensile strength of TMPTMA added HDPE samples at loading level of 6 phr at 250 kGy irradiation dosage was due to the occurrence of re-crosslinking reaction, as discussed earlier.

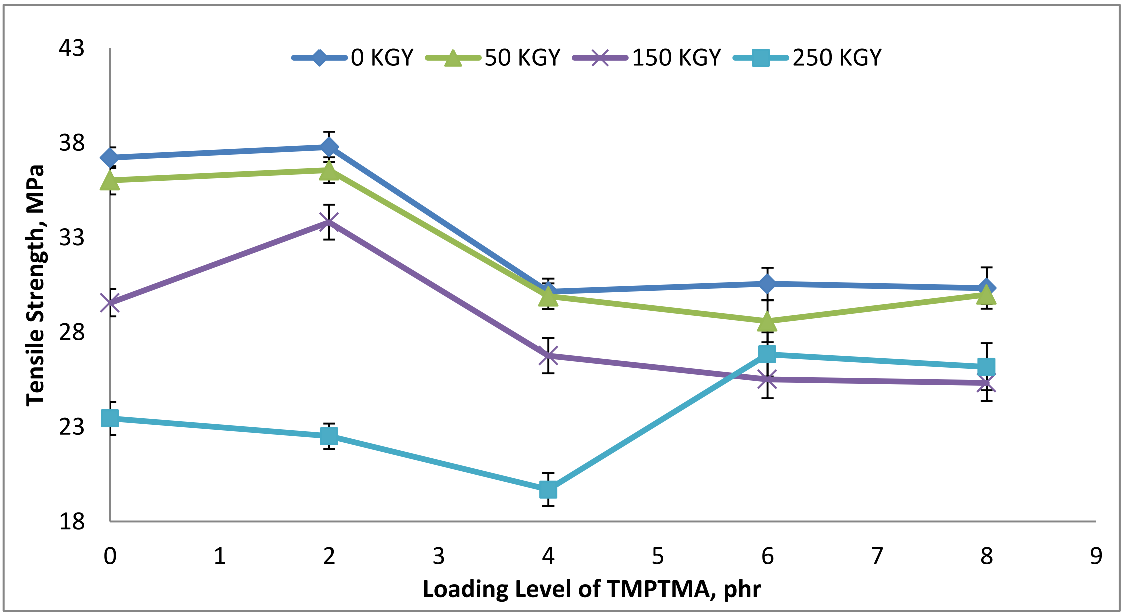


Figure 4.6 Effect of Loading Level of TMPTMA on Tensile Strength of HDPE Samples under Various Electron Beam Irradiation Dosages

Figure 4.7 demonstrates the effect of loading level of TMPTMA on tensile strength of EVA samples with various electron beam irradiation dosages**.** From Figure 4.7, it was observed that the tensile strength for all non-irradiated pristine EVA samples were the lowest due to the absence in crosslinking reaction in EVA matrix. Significant improvement can be seen in the tensile strength of all pristine EVA samples with the introduction of electron beam irradiation due to irradiation induced crosslinking reactions, as discussed earlier in the tensile strength for LDPE. Besides, the amorphous phase in the nature structure of EVA matrix is also one of the reasons for superior crosslink ability of EVA when subjected to electron beam irradiation (Burns et al., 1979).

Moreover, the tensile strength for all TMPTMA added EVA samples also showed continuously improvement with increasing electron beam irradiation dosages. This indicates the formation of greater crosslinking network due to the reaction of monomer free radicals from TMPTMA with polymer free radicals in the amorphous phase of EVA, as EVA is readily crosslink when subjected to electron beam irradiation due to the increasing amorphous phase in its matrix. According to Latwon et al., radiation crosslinking occurs mainly within the amorphous phase of a polymer.

As shown in Figure 4.7, the incorporation of TMPTMA at 2 phr was able to aid in the increment of tensile strength for EVA. Further increment of TMPTMA loading level (>2 phr) tended to decrease the tensile strength of EVA samples. All these were due to the same reasons as discussed earlier for LDPE and also HDPE.

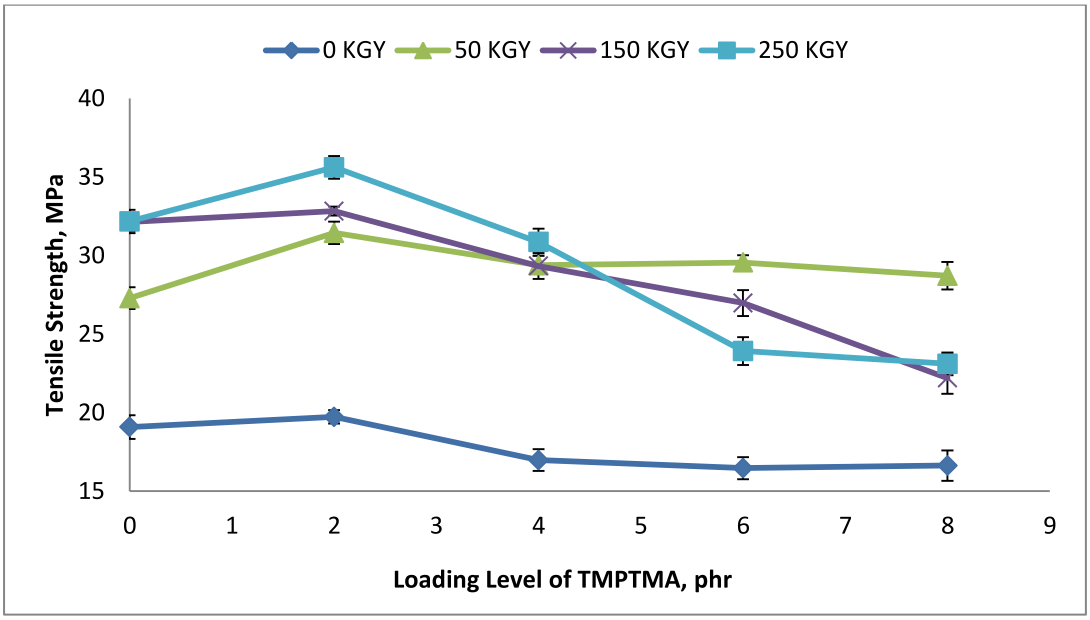


Figure 4.7 Effect of Loading Level of TMPTMA on Tensile Strength of EVA Samples under Various Electron Beam Irradiation Dosages

As shown in Figure 4.8, it was noticed that the tensile strength of all non-irradiated pristine ABS and TMPTMA added ABS samples were the lowest compared to irradiated samples. This is because without irradiation, breakage of double bond in TMPTMA couldn’t occur, thus no monomer free radical was generated to react with polymer free radicals and no cross-linking was formed (Ng et al., 2014). However, significant improvement in tensile strength can be seen in all pristine ABS samples as irradiation dosages increase. This is because high energy dissipated from higher irradiation dosage is needed to induce formation of crosslinking networks in pristine ABS samples due to the presence of strong benzene ring in the ABS structure (Rutkowski & Levin, 1986).

Moreover, tensile strength of TMPTMA added ABS (up to 4 phr) was observed to improve significantly with irradiation dosages up to 150 kGy. This indicates that greater crosslinking networks were formed with the addition of TMPTMA in ABS matrix due to the release of monomer free radicals from the three pendent double bonds of TMPTMA to reacts with ABS polymer free radicals (Wu et al., 2012). As seen in Figure 4.8, the tensile strength of ABS samples at 50 kGy and 150 kGy was observed to decrease with the addition of higher loading level of

TMPTMA (>4 phr). This might due to the excessive monomer free radicals generated by higher loading level of TMPTMA tended to attack the macromolecular chain of ABS and break the chain into shorter chains that decreased the tensile strength of polymers (Ng et al., 2014).

However, it can be seen that the tensile strength of ABS samples at high irradiation dosage of 250 kGy decrease initially with the addition of 2 phr of TMPTMA. This might due to the predominant of chain scissioning reaction over crosslinking reaction as chain scissioning tended to compete with crosslinking reaction at high irradiation dosage (Munusamy et al., 2009). However, the sudden increment of the tensile strength of TMPTMA added ABS samples at higher loading level of TMPTMA (≥4 phr) with irradiation dosage of 250 kGy was most probably due to the re-crosslinking reaction, where the shorter chains from chain scissioning reactions re-combined to from crosslinking networks again.

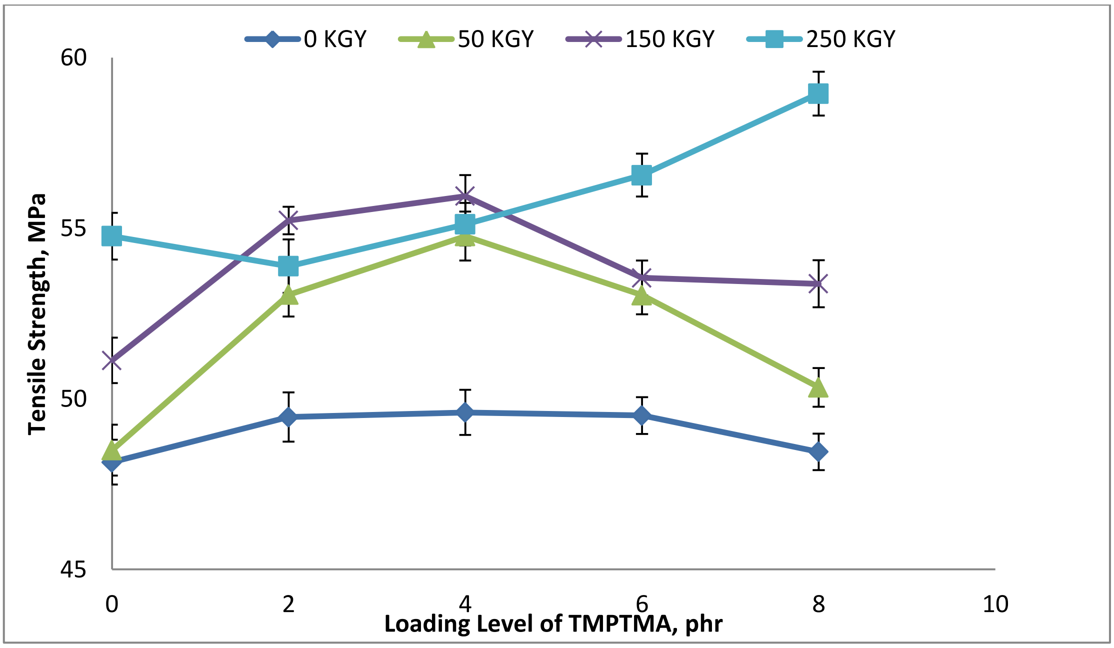


Figure 4.8 Effect of Loading Level of TMPTMA on Tensile Strength of ABS Samples under Various Electron Beam Irradiation Dosages

4.2.2 Elongation at Break

Figures 4.9 to 4.11 show the effect of loading level of TMPTMA on elongation at break of LDPE, HDPE and also EVA samples with various electron beam irradiation dosages. Generally, increasing electron beam irradiation dosages was observed to reduce the elongation at break for all pristine LDPE, HDPE and EVA samples. This obviously showed that the presence of electron beam irradiation could promote the formation of crosslinking networks in polymer matrix to restrict the slippage of the chain during straining (Sharif et al., 1999). Among all the non-irradiated samples, pristine LDPE, HDPE and EVA samples was observed to have highest elongation at break compared to all TMPTMA added LDPE, HDPE and EVA samples. This might due to the absence of TMPTMA to assist in the formation of three-dimensional crosslinking networks in pristine LDPE, HDPE and EVA matirx (Wu et al., 2012). The formation of low degree of crosslinking networks in polymer matrix of all non-irradiated TMPTMA added LDPE, HDPE and EVA samples was able to slightly reduced the flexibility of the molecular chains, as TMPTMA have a tendency to react under elevated temperature (Ng et al., 2014). These results were found consistent with the results obtained in gel content test.

From Figure 4.9, no significant reduction in the elongation at break could be seen for pristine LDPE and also low TMPTMA added LDPE (2 phr) samples for irradiation dosages up to 150 kGy. This is because lower degree of crosslinking networks can be formed by low loading level of TMPMTA (≤2 phr), as lower amount of monomer free radicals were generated to react with polymer free radicals of LDPE. Thus, the restriction effect on the mobility of LDPE chains was less signifcant. However, further increment of TMPTMA loading level (≥2 phr) with the application of electron beam irradiation dosages could significantly reduce the elongation at break of LDPE samples. At higher loading level of TMPTMA (4 phr to 8 phr), additional monomer free radicals were generated by the three pendent double bonds of TMPTMA to react with LDPE free radicals to form a greater three dimensional crosslinking network in LDPE matrix (Wu et al., 2012), as an evident by gel content. The higher degree of crosslinking in LDPE matrix could restrict the mobility of LDPE chains under straining stress, thus reduce the elongation at break of higher loading level TMPTMA added LDPE samples.

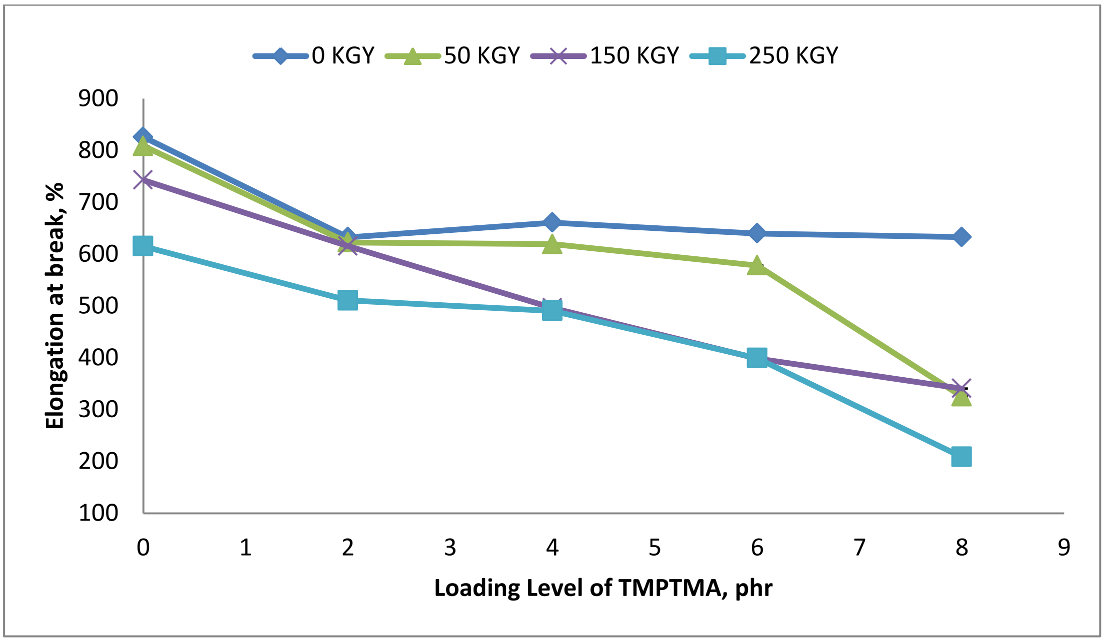


Figure 4.9 Effect of Loading Level of TMPTMA on Elongation at Break of LDPE Samples under Various Electron Beam Irradiation Dosages

As shown in Figure 4.10, significant reduction in elongation at break was observed in all HDPE samples with the incorporation of TMPTMA (up to 8 phr) and also electron beam irradiation (up to 250 kGy), except for sample with loading level of TMPTMA at 8 phr and 50 kGy. The significant reduction in all irradiated TMPTMA added HDPE samples (except 8 phr and 50 kGy) was due to the reason that greater three dimensional crosslinking networks that formed, as discussed above. Whereas, the sudden increment on elongation at break for loading level of TMPTMA at 8 phr with irradiation dosage of 50 kGy might due to the reason that the amount of HDPE free radicals generated by low electron beam irradiation dosages (50 kGy) was not enough to react with the excessive amount of monomer free radicals were generated by high loading level of TMPTMA (8 phr). Thus, the unreacted TMPTMA could acts as small molecules that enter into the backbone chain of HDPE to promote that chain flexibility (Ng et al., 2014).

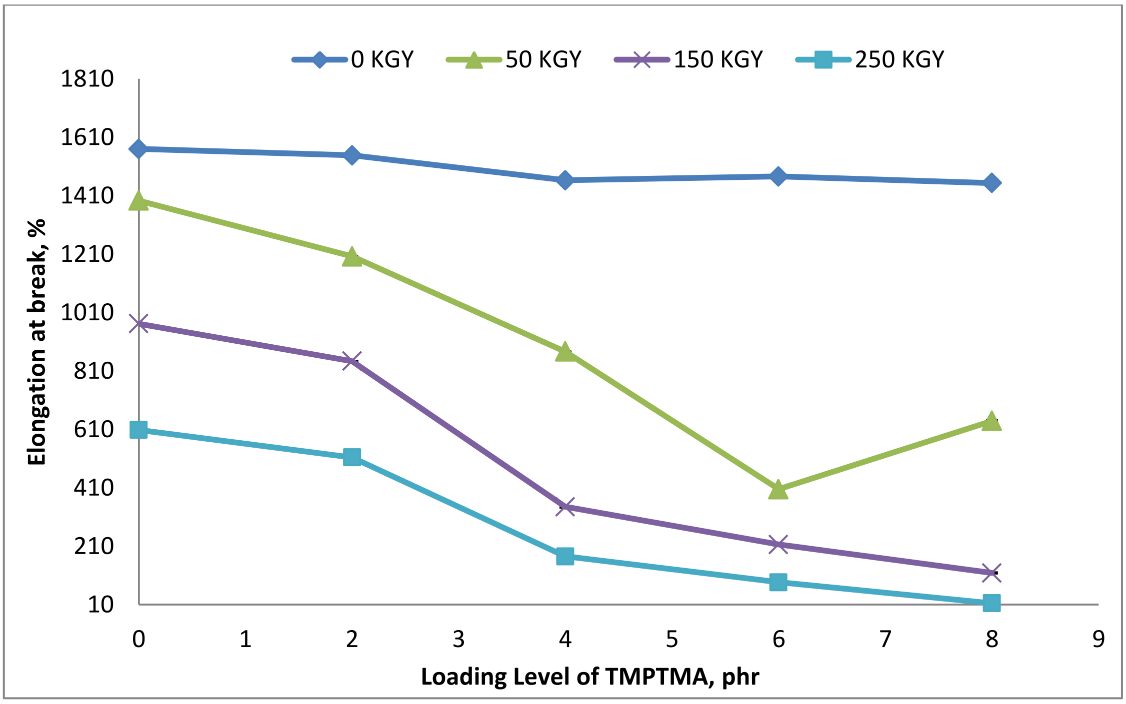


Figure 4.10 Effect of Loading Level of TMPTMA on Elongation at Break of HDPE Samples under Various Electron Beam Irradiation Dosages

Based on Figure 4.11, the elongation at break was observed to reduce significantly at lower loading level of TMPTMA (2 phr) for both irradiated and non-irradiated EVA samples. This might due to the increasing amorphous phase in EVA matrix that promotes its superior crosslinking ability to form crosslinking networks with the addition of TMPTMA (Sharif et al., 1999). However, the elongation at break was seen to be reduced gradually at higher loading level of TMPTMA (> 2 phr) due to the balancing effect between the crosslinking and chain scissioning reaction. The chain sicssioning reaction tended to compete with crosslinking reaction when there are excessive monomer free radicals generated by higher loading level of TMPTMA (Wu et al., 2012).

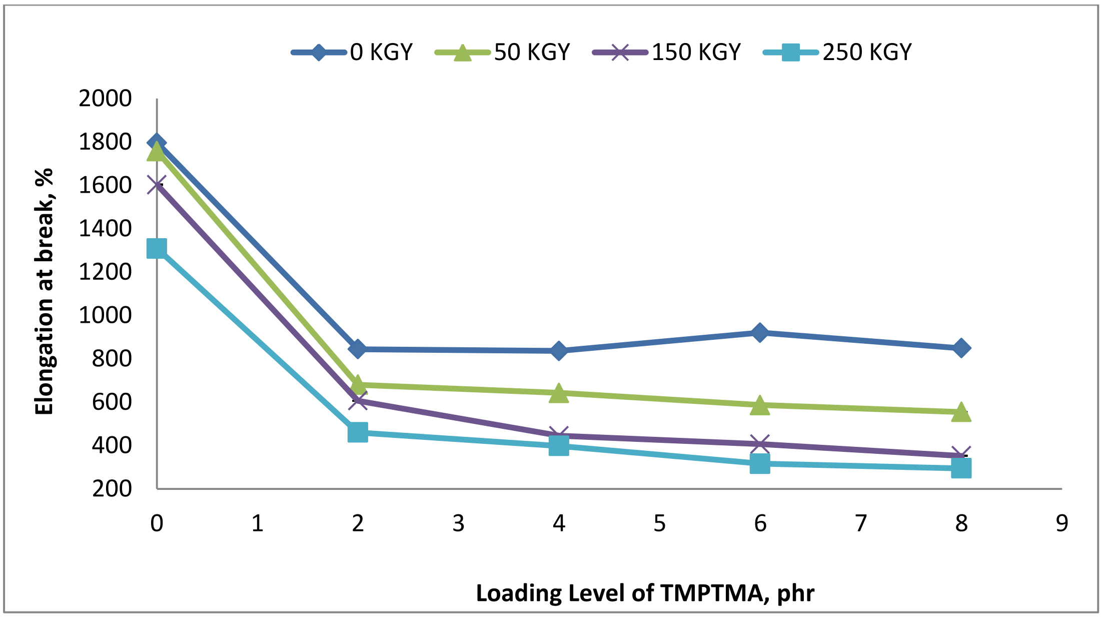


Figure 4.11 Effect of Loading Level of TMPTMA on Elongation at Break of EVA Samples under Various Electron Beam Irradiation Dosages

Figure 4.12 shows the effect of loading level of TMPTMA on elongation at break of ABS samples with various electron beam irradiation dosages. Significant reduction in elongation at break can be observed for pristine ABS and all TMTPTMA added ABS for electron beam when subjected to electron beam irradiation dosages up to 50 kGy. This might due to the predomination of crosslinking reaction over chain scissioning at low irradiation dosage (50 kGy) in ABS matrix, where reduce the flexibility in the movement of ABS chains during stretching (Sabet et al., 2010). Higher elongation at break was observed for pristine ABS and TMPTMA added ABS at higher dosages of electron beam irradiation (150 kGy and above) than all non-irradiated ABS samples. This inferred the predominant of chain scissioning reactions over crosslinking reaction at higher irradiation dosages. The dissipation of excess energy from higher electron beam irradiation dosages causes chain scissioning of the bonds between the ABS backbone chains (Bee et al., 2014).

Elongation at break of TMPTMA added ABS samples was observed to increase at high loading level of TMPTMA (4 phr) when irradiated up to 50 kGy. This might due to the excessive amount of unreacted TMPTMA that acts a plalsticizer to weaken the bonds between ABS matrix at low electron beam irradiation dosage (Ng et al., 2014). Moreover, increasing loading level of TMPTMA was also observed to continuosly increase the elongation at break of all TMPTMA added ABS samples for irradiation dosages of 150 kGy and above, indicating the predominant of chain scissioning reactions over crosslinking reaction in ABS matrix.

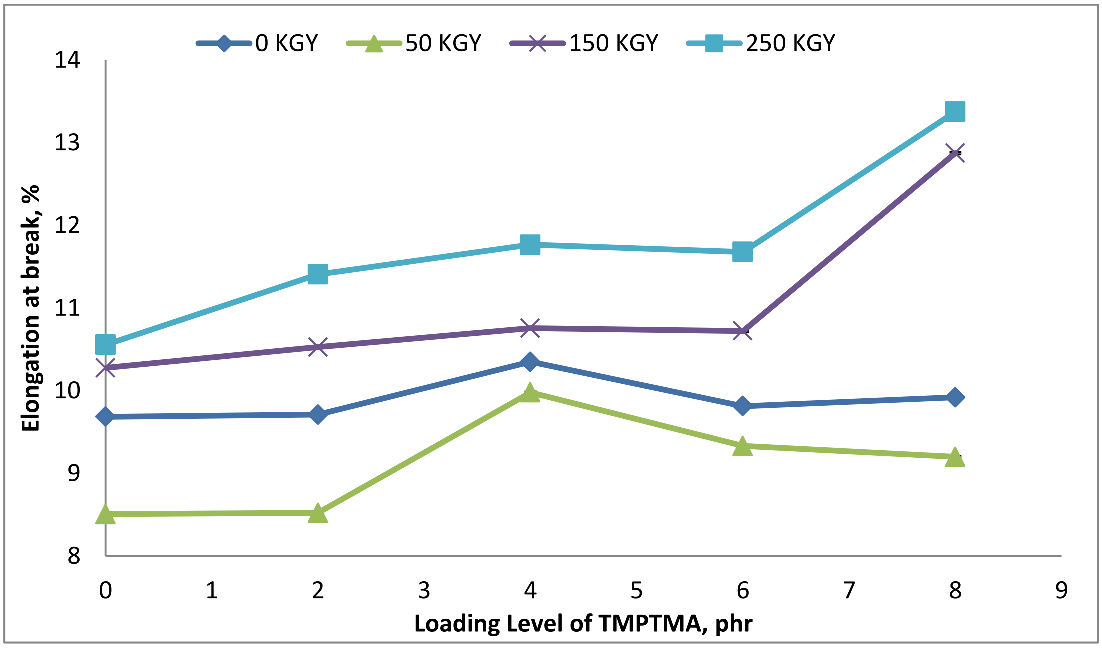


Figure 4.12 Effect of Loading Level of TMPTMA on Elongation at Break of ABS Samples under Various Electron Beam Irradiation Dosages

4.2.3 Young’s Modulus

Figure 4.13 show the effect of loading level of TMPTMA on young’s modulus of LDPE samples with various electron beam irradiation dosages. Based on Figure 4.13, the young’s modulus for pristine LDPE when irradiated up to 250 kGy was observed to be higher in comparing to the young modulus of all non-irradiated LDPE samples. This might due to the introduction of irradiation could promote the formation of three dimensional crosslinking networks in LDPE networks that increase the stiffness of the samples.

The incorporation of small amount TMPTMA into LDPE samples (2 phr) was observed to increase the young’s modulus of LDPE samples at 0 kGy and also 50 kGy electron beam irradiation dosages. This is because the monomer free radicals generated from TMPTMA could react with polymer free radicals to form three dimensional crosslinking networks that increase the strength and rigidity of LDPE samples in the presence of irradiation. Moreover, TMPTMA also have the tendency to react under elevated temperature during compounding and compression molding process. However, the young’s modulus was observed to reduce with further increment in loading level of TMPTMA for non-irradiated and low irradiated samples (50 kGy). This might due to the excessive amount of unreacted TMPTMA that acts as small molecules and enter into the LDPE chains to weaken the bonds between LDPE matrix at low electron beam irradiation dosage (Ng et al., 2014).

The young’s modulus of LDPE samples was observed to drop with addition of low loading level of TMPTMA (2 phr) at higher irradiation dosages (≥150 kGy). This might due to the insufficient amount of monomer free radicals released from low loading level of TMPTMA to react with vast amount of polymers free radicals at higher lelectron beam irradiation dosages. Higher loading level of TMPTMA (≥6 phr for irradiation dosage of 150 kGy and ≥4 phr for irradiation dosage of 250 kGy) was observed to sudden increased the young’s modulus LDPE samples. This is because greater crosslinking networks were formed by adidtional amount of monomer free radicals from TMPTMA to react with the vast amount of polymer free radicals at higher irradiation dosages (≥150 kGy).

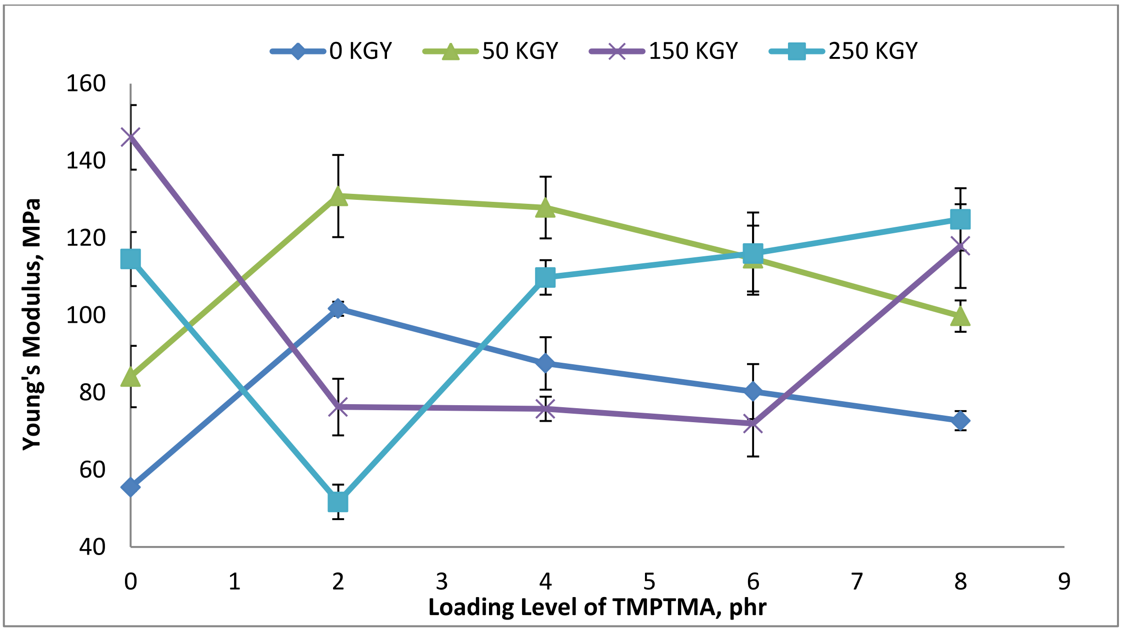


Figure 4.13 Effect of Loading Level of TMPTMA on Young's Modulus of LDPE Samples under Various Electron Beam Irradiation Dosages

As shown in Figure 4.14, all non-irradiated HDPE samples were observed to have the lowest young's modulus compared to all irradiated samples. This might due to the absence of crosslinking reaction that reduces the stiffness of HDPE samples at non-irradiation conditions. The young's modulus of all HDPE samples was observed to increase with the incorporation of electron beam irradiation dosages due to the formation of three dimensional crosslinking networks, as discussed above. Besides, the occurrence of TMPTMA in HDPE matrix also would act as plasticizer in improving the flexibility effect of HDPE samples and thus decrease the rigidity of HDPE samples. However, the decrease in the young's modulus of pristine HDPE at 250 kGy compared to irradiation dosages of 50 and 150 kGy was due to the predominant of chain scissioning reaction over crosslinking reaction, which promotes the formation of shorter chains at high irradiation dosage (Bee et al., 2014).

The young's modulus was observed to decrease continuously with the incorporation of TMPTMA in HDPE samples (except for 6 phr and 8 phr at 250 kGy). This might due to the reason that although there is formation of crosslinking networks by TMPTMA in HDPE samples, however the crosslinking networks could not show any significant improvement to increase the stiffness and rigidity of HDPE samples, as evident by gel content and also tensile test. The decrease in young's modulus of TMPTMA added HDPE (<6 phr) was more significant at higher irradiation dosages (≥250 kGy). This might due to the predominant of chain scissioning reaction, where the HDPE backbone chain break into shorter chains when exposed to high energy of electron beam irradiation (Ng et al., 2014). The sudden increment in young's modulus with TMPTMA loading level of 6 phr and 8 phr at 250 kGy might due to the occurrence of re-crosslinking reaction, where the sorter chains re-combined to form cross-linking networks again.

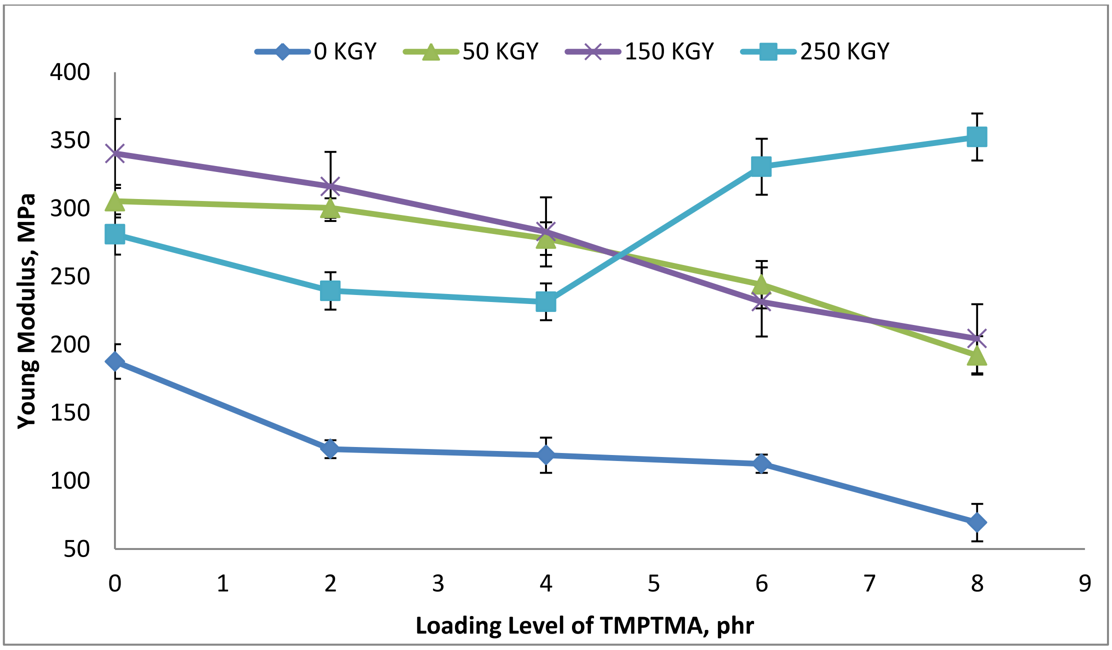


Figure 4.14 Effect of Loading Level of TMPTMA on Young's Modulus of HDPE Samples under Various Electron Beam Irradiation Dosages

As shown in Figure 4.15, all non-irradiated EVA samples were observed to have the lowest young's modulus compared to all irradiated samples due to the absence of crosslinking reaction, as discussed above. Further increment of irradiation dosages (up to 250 kGy) was observed to gradually increase the young's modulus of all EVA samples. This might due to the presence of electron beam irradiation could promote the formation of three dimensional crosslinking networks in EVA matrix (Sabet et al., 2010). As seen on Figure 4.14, the addition of TMPTMA was able to increase the young’s modulus of all EVA samples, except for TMPTMA loading level of 6 phr and 8 phr at 0 kGy and 50 kGy. This is because the monomer free radicals generated by TMPTMA could react with polymer free radicals in the amorphous phase of EVA matrix to form greater crosslinking networks that resists the deformation of EVA samples during stretching (Ng et al., 2014). The slight decrement in the young’s modulus for TMPTMA loading level of 6 phr and 8 phr at 0 kGy and 50 kGy was due to the excessive amount of unreacted TMPTMA that acts as small molecules and enter into the LDPE chains to weaken the bonds between LDPE matrix at low electron beam irradiation dosage, as discussed earlier.

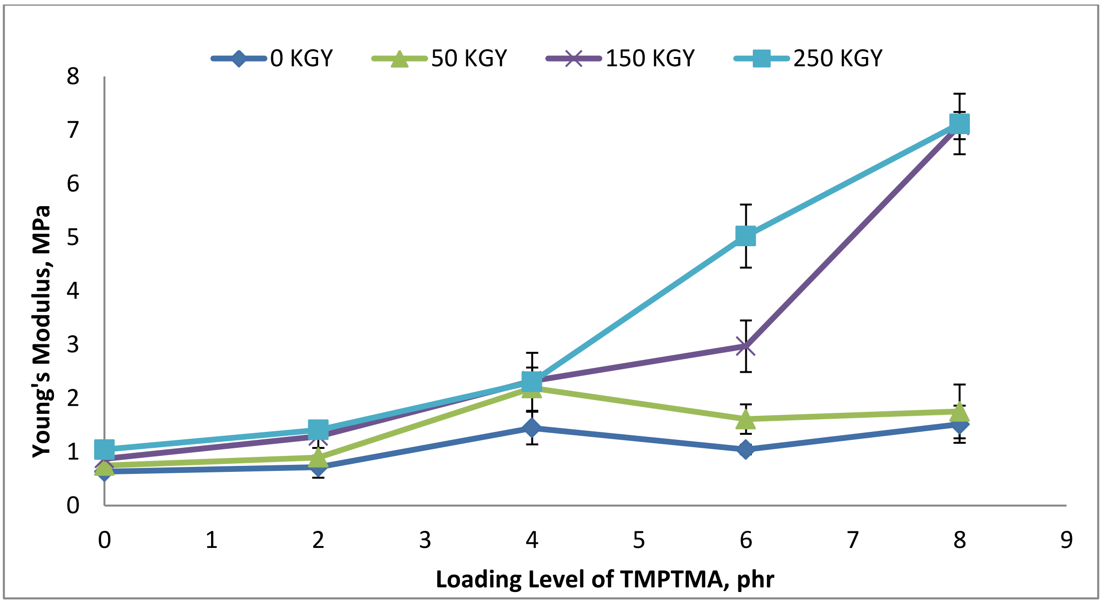


Figure 4.15 Effect of Loading Level of TMPTMA on Young’s Modulus of EVA Samples under Various Electron Beam Irradiation Dosages

Based on Figure 4.16, the young’s modulus for all ABS samples was observed to increase with increasing electron beam irradiation dosages (except for 250 kGy) compared to non-irradiated ABS samples. This is due to the introduction of electron beam irradiation could promote the crosslinking reactions in ABS matrix. At higher irradiation dosage, the young’s modulus for pristine ABS and TMTPMA added ABS (2 phr) was found to decrease due to the predominant of chain scissioning reaction over crosslinking reaction at high irradiation dosage (Bee et al., 2014).

The incorporation of TMPTMA in ABS samples was observed to decrease the young's modulus for all non-irradiated and irradiated samples up to 150 kGy irradiation dosages. This might due to the presence of strong benzene ring in ABS structure that caused the inferior crosslinking ability in ABS matrix to form crosslinking networks with monomer free radicals from TMPTMA. However, increasing in young's modulus was seen at higher irradiation dosages (250 kGy) with high loading level of TMPTMA (≥4 phr). This might due to the high energy dissipated by higher irradiation dosages to generate additional ABS free radicals to react with additional TMPTMA monomer free radicals, thus larger three dimensional crosslinked networks structure could be formed (Pentimallia et al., 1999).

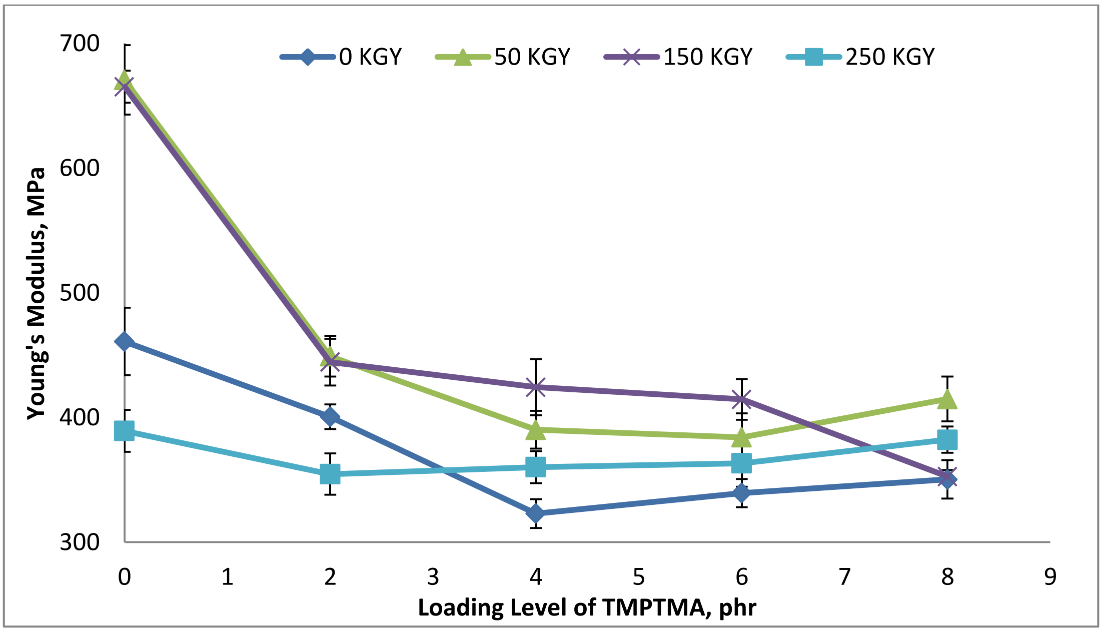


Figure 4.16 Effect of Loading Level of TMPTMA on Young's Modulus of ABS Samples under Various Electron Beam Irradiation Dosages

4.3 Morphology Structure

Figures 4.17 (a) to (d) illustrate the fracture surface observation for all non-irradiated LDPE, HDPE, EVA and also ABS samples. According to Figure 4.17 (a), formation of long fibrils was observed on the fracture surface on pristine LDPE. This inferred that the pristine LDPE posed high resistance to plastic deformation under the straining stress. Shorter and thinner fibrils was observed in Figure 14.7 (b), which shows that the straining effect could cause the tearing of pristine HDPE into short discontinues phase before break. Figure 14.7 (c) show good extendibility of pristine EVA, which indicate the high flexibility of EVA due to the increase amorphous phase in its structure. No fibrils can be found in Figure 14.7 (d), which inferred the immediate break of pristine ABS sample to the applied strain due to its poor elongation ability and brittle structure.

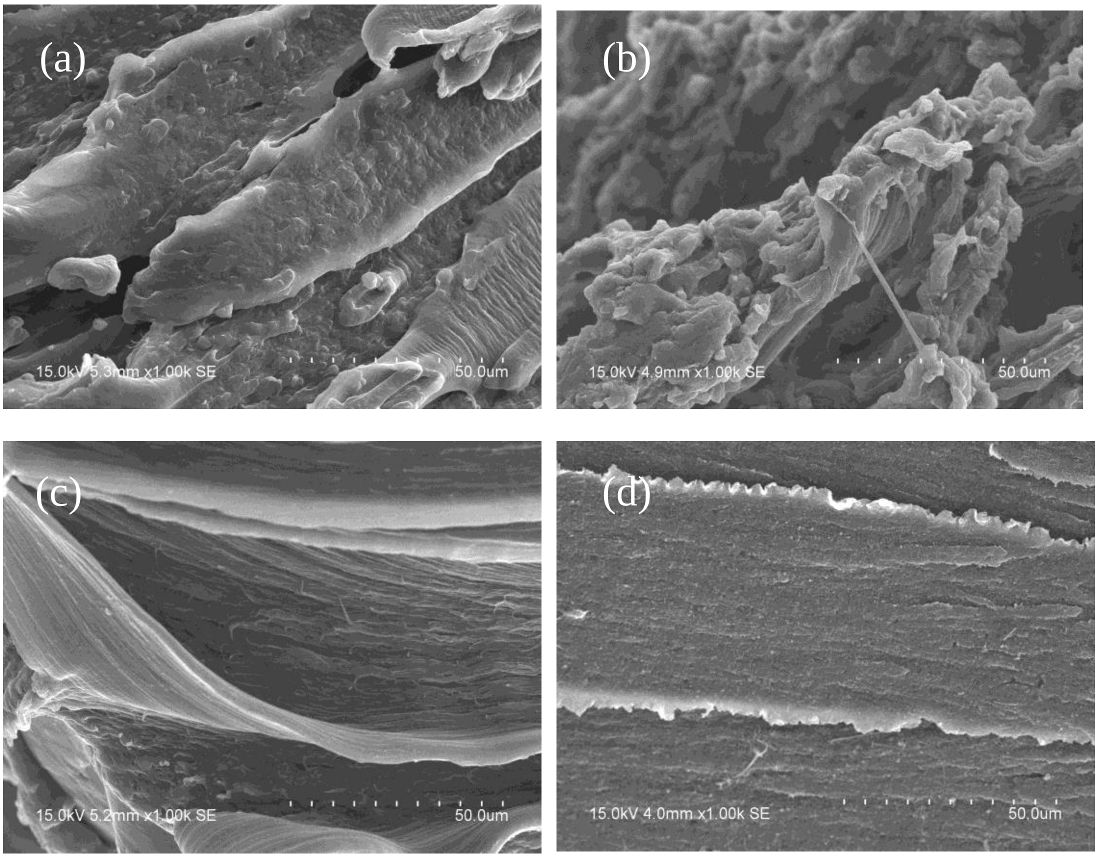


Figure 4.17 SEM Photograph (a) Non-irradiated Pristine LDPE (b) Non-irradiated Pristine HDPE (c) Non-irradiated Pristine EVA (d) Non-irradiated Pristine ABS under Magnification of 1000x

Figures 4.18 (a) to (f) illustrates the fracture surface observation for all pristine LDPE and TMPTMA added LDPE (2 phr and 8 phr) under irradiation dosages of 50 kGy and 250 kGy. As seen from Figure 4.17 (a) and (d), it was observed that the tearing effect of pristine LDPE become severe with increasing irradiation up to 250 kGy. Formation of long and continuous fibrils in Figure 4.17 (a) show better polymer continuity in the elongation, which indicates the formation of crosslinking networks via electron beam irradiation at 50 kGy (Bee et al., 2014). The short and weak fibrils as shown in Figure 4.17 (d) indicate the discontinuous phase in pristine LDPE matrix which caused detraction effect in plastic deformation when subjected to high electron beam irradiation dosages (250 kGy).

The addition of TMPTMA into LDPE samples was observed to promote the formation of crosslinknig networks when being subjected to electron beam irradiation. Based on Figure 14.7 (b), the formation of long continuity fibril can be observed with addition of 2 phr TMPTMA at irradiation dosage of 50 kGy. This results was attributed by the formation of greater crosslinking network due to the reaction of monomer free radicals from TMPTMA with LDPE polymer free radicals, as evident by gel cotent test (Ng et al., 2014). However, further increment in loading level of TMPTMA (8 phr) does not show any enchancement in plastic deformation as shown in Figure 14.7 (c), where vast number of short and thin fibrils was observed. Greater amount of shorter and weaker fibrils can be observed with higher loading level of TMPTMA (8 phr) and also higher irradiation dosages (250 kGy), as seen in Figure 14.7 (f). This showed that high loading level of TMPTMA (8 phr) and high irradiation dosages (250 kGy) could promote chain scissioning reaction due to excessive amount of monomer free radicals generated by TMPTMA and higher dissipated energy by irradiation.

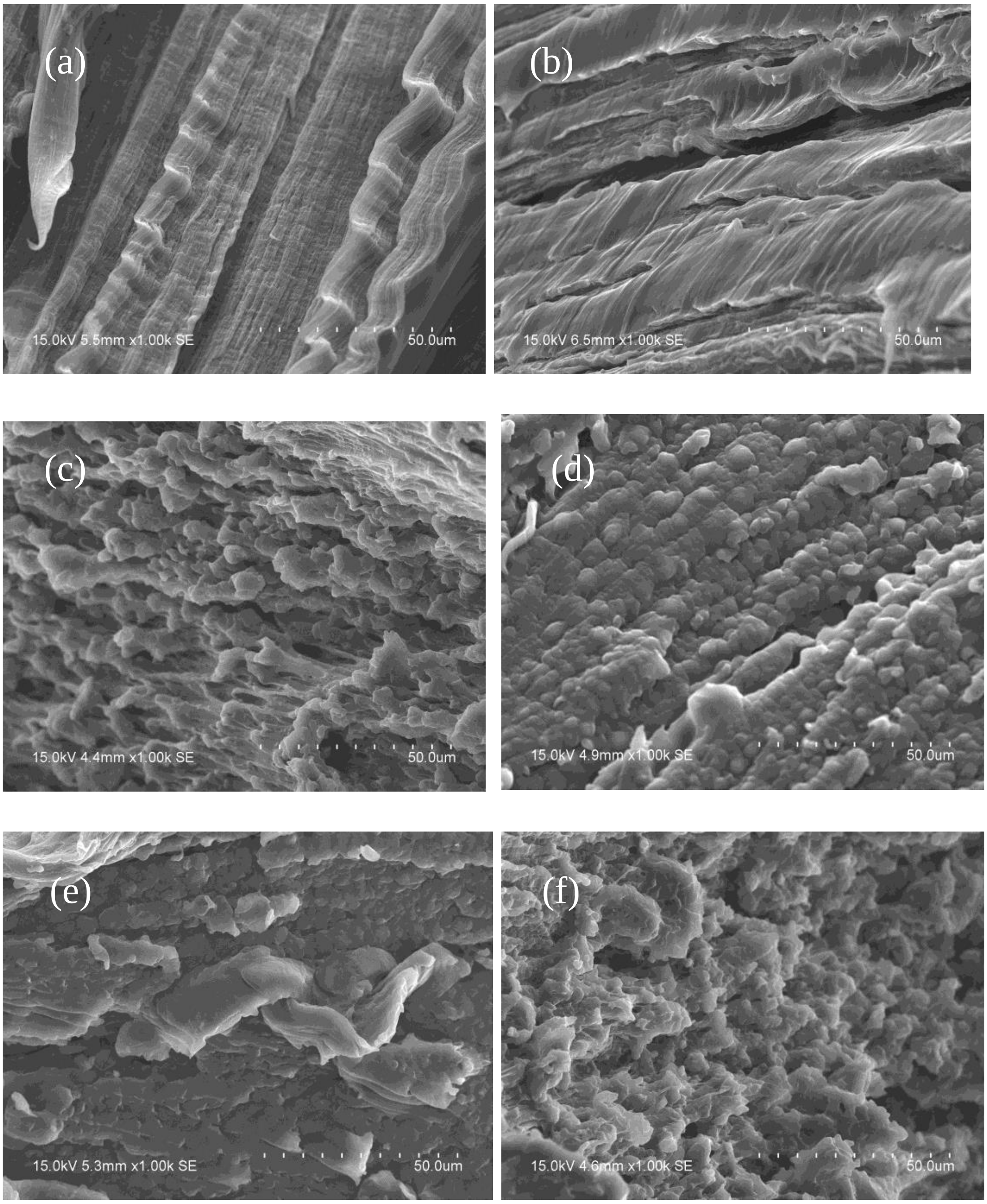


Figure 4.18 SEM Photograph (a) Pristine LDPE (b) LDPE added with 2 phr TMPTMA (c) LDPE added with 8 phr TMPTMA Irradiated at 50 kGy, and (d) Pristine LDPE (e) LDPE added with 2 phr TMPTMA (f) LDPE added with 8 phr TMPTMA Irradiated at 250 kGy under Magnification of 1000x

Figures 4.19 (a) to (f) illustrate the fracture surface observation for all pristine HDPE and TMPTMA added HDPE (2 phr and 8 phr) under irradiation dosages of 50 kGy and 250 kGy. It was observed that the incorporation of low loading level of TMTPMA (2 phr), can significantly enhance the plastic deformation in HDPE matrix upon subjection of electron beam irradiation dosages. As seen from Figure 14.8 (b) and (e), long and continuous fibrils indicates formation of crosslinking promoted by crosslinking agent, TMPTMA under irradiation dosages (Wu et al., 2012). However, addition of high loading level of TMPTMA (8 phr) at low irradiation dosage (50 kGy) was observed to form slight amount of cavitites as shown in Figure 14.8 (c). This might due to the excess unreacted TMPTMA that act as small molecules to enter and break the main HDPE chain, which caused the release of volatiles trapped in the polymer matrix of HDPE samples (Ng et al., 2014).

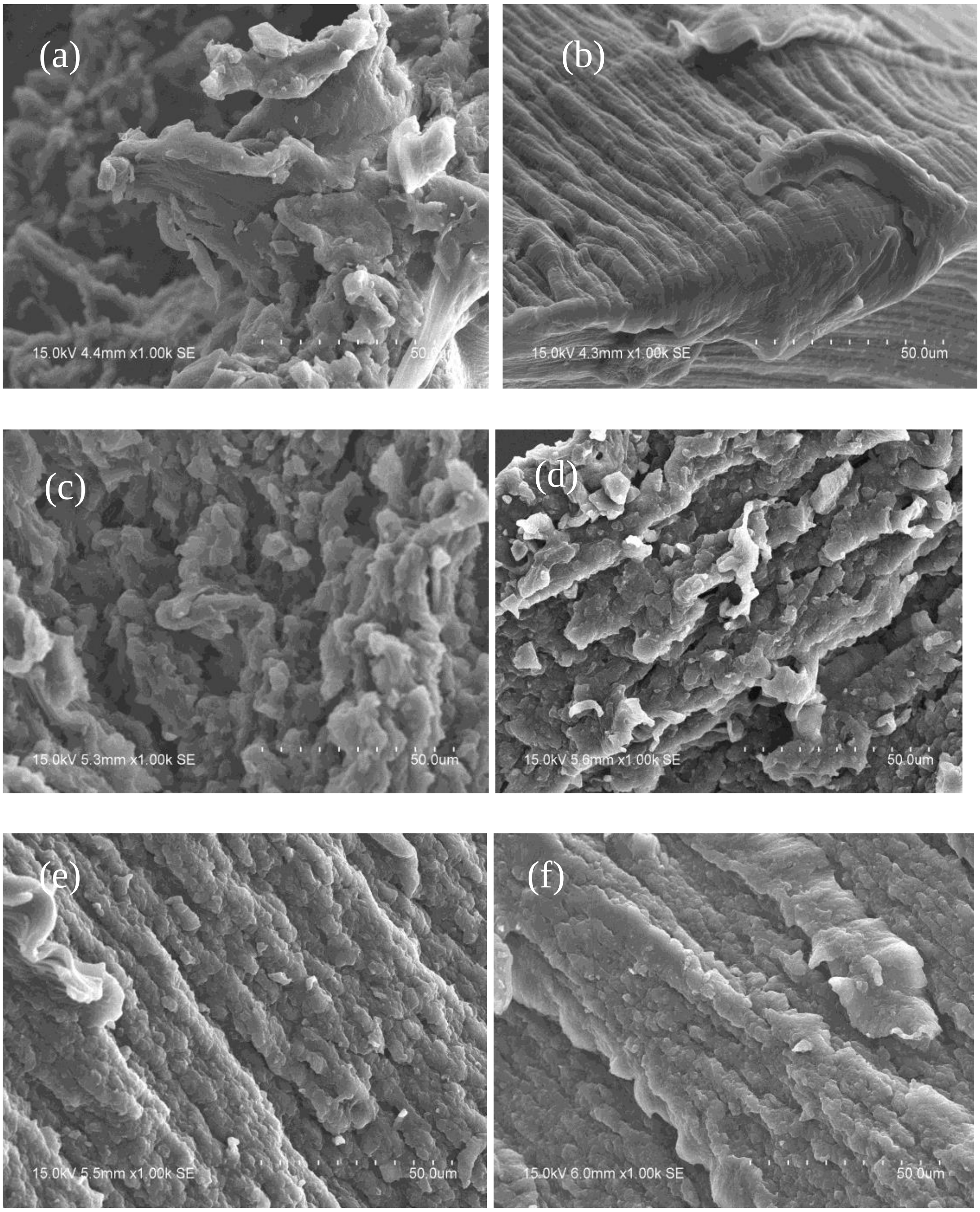


Figure 4.19 SEM Photograph (a) Pristine HDPE (b) HDPE added with 2 phr TMPTMA (c) HDPE added with 8 phr TMPTMA Irradiated at 50 kGy, and (d) Pristine HDPE (e) HDPE added with 2 phr TMPTMA (f) HDPE added with 8 phr TMPTMA Irradiated at 250 kGy under Magnification of 1000x

Figures 4.20 (a) to (f) illustrate the fracture surface observation for all pristine EVA and TMPTMA added EVA (2 phr and 8 phr) under irradiation dosages of 50 kGy and 250 kGy. As seen from Figure 4.19 (a) and (d), it was observed that the morphology structure of pristine EVA become more continuous at when subjected to higher irradiation dosage (250 kGy). This was due to the nature of EVA that can be easily crosslinked when subjected to irradiation. The increment in amorphous phase was the main reason of superior crosslink ability of EVA (Sharif et al., 1999). Addition of TMPTMA upon subjection to irradiation also able to aid in promoting the crosslink networks of EVA. As observed in Figure 14.9 (b, c and f), continuous matrix structure indicate formation of greater crosslink by the reaction of monomer free radicals from TMPTMA with polymer free radicals in the amorphous phase of EVA. However, severe tearing effect at 2 phr of TMPTMA upon irradiation dosages of 250 kGy can be seen in Figure 14.9 (e). This might due to the insufficient amount of monomer free radicals generated by low loading level of TMPTMA (2 phr) to react with excess amount of amount of HDPE free radicals generated by high electron beam irradiation dosages (250 kGy).

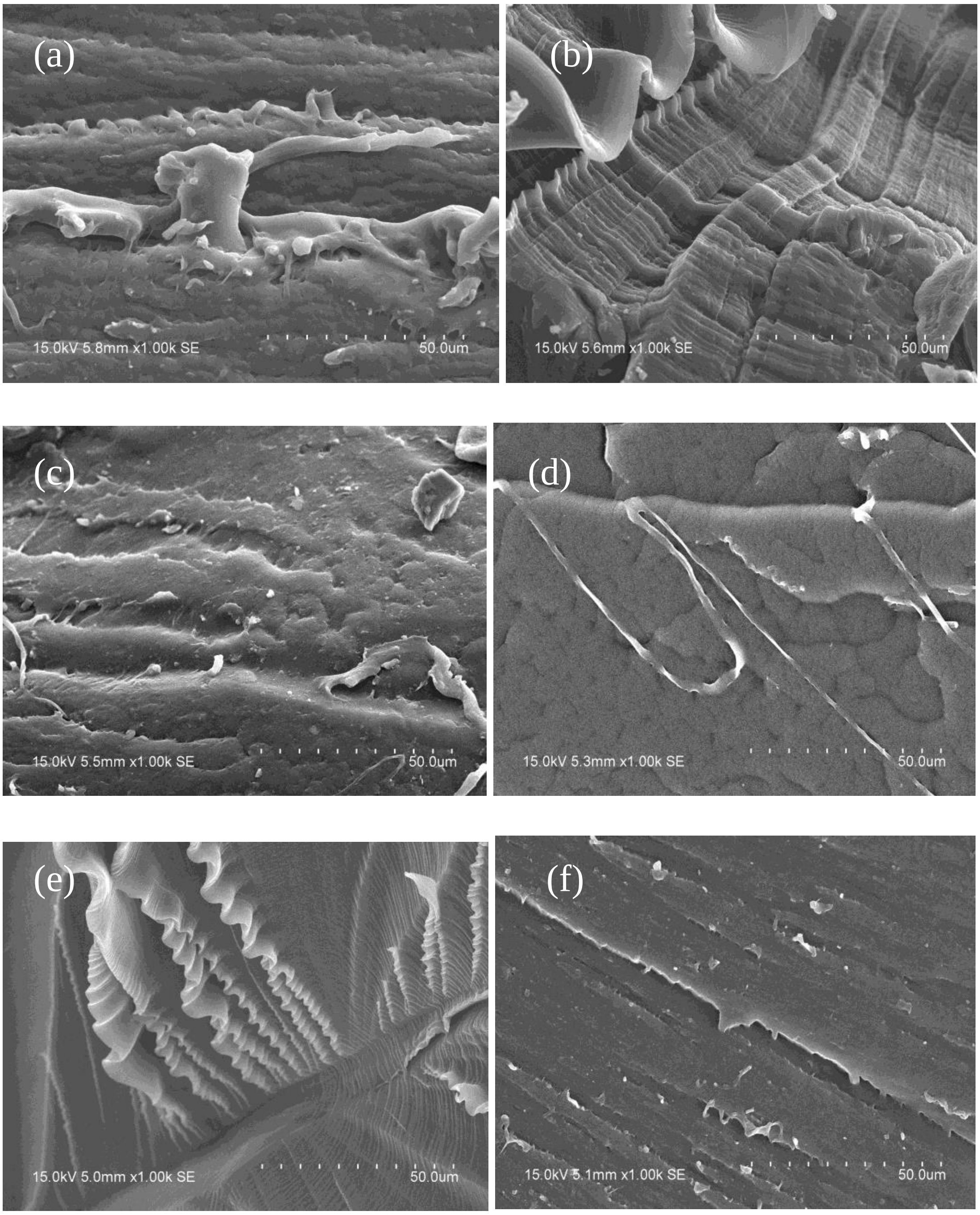


Figure 4.20 SEM Photograph (a) Pristine EVA (b) EVA added with 2 phr TMPTMA (c) EVA added with 8 phr TMPTMA Irradiated at 50 kGy, and (d) Pristine EVA (e) EVA added with 2 phr TMPTMA (f) EVA added with 8 phr TMPTMA Irradiated at 250 kGy under Magnification of 1000x

Figures 4.21 (a) to (f) illustrate the fracture surface observation for all pristine EVA and TMPTMA added EVA (2 phr and 8 phr) under irradiation dosages of 50 kGy and 250 kGy. As shown in Figure 4.20 (a) to (f), formation of voids was observed to become more severe with increasing loading level of TMPTMA and increasing electron beam irradiation dosages. As seen in Figure 4.20 (a), the formation of fibrils with small formation of cavities can be observed for pristine ABS samples when subjected to low irradiation dosage (50 kGy). However, larger and greater amount of cavities can be observed for high electron beam irradiation dosages (250 kGy). This inferred the predominant of chain scissioning reactions over crosslinking reaction at higher irradiation dosages. The dissipation of excess energy from higher electron beam irradiation dosages causes chain scissioning of the bonds between the ABS backbone chains (Bee et al., 2014).

Based on Figure 4.20 (b), formation of larger fibrils with higher amount of cavities was observed with the incorporation of TMPTMA (2 phr) at low irradiation dosages (50 kGy) than pristine ABS at the same irradaition dosage. The formation of larger fibrils indicating the occurrence of crossliniking reaction when subjected to electron beam irradiation. However, the formation of cavities also observed to occur in pristine ABS matrix where this indicating the presence of chain scissioning reaction. Thus no significant crosslinking networks can be obtained, as evident by gel content test. Severe voids was observed in Figure 4.20 (f) at high level of loading level (8 phr) with high electron beam irradiation (250 kGy) due to the excessive amount of TMPTMA and high dissipitation energy that leads the predominant of chain scissioning reactions over crosslinking reactions.

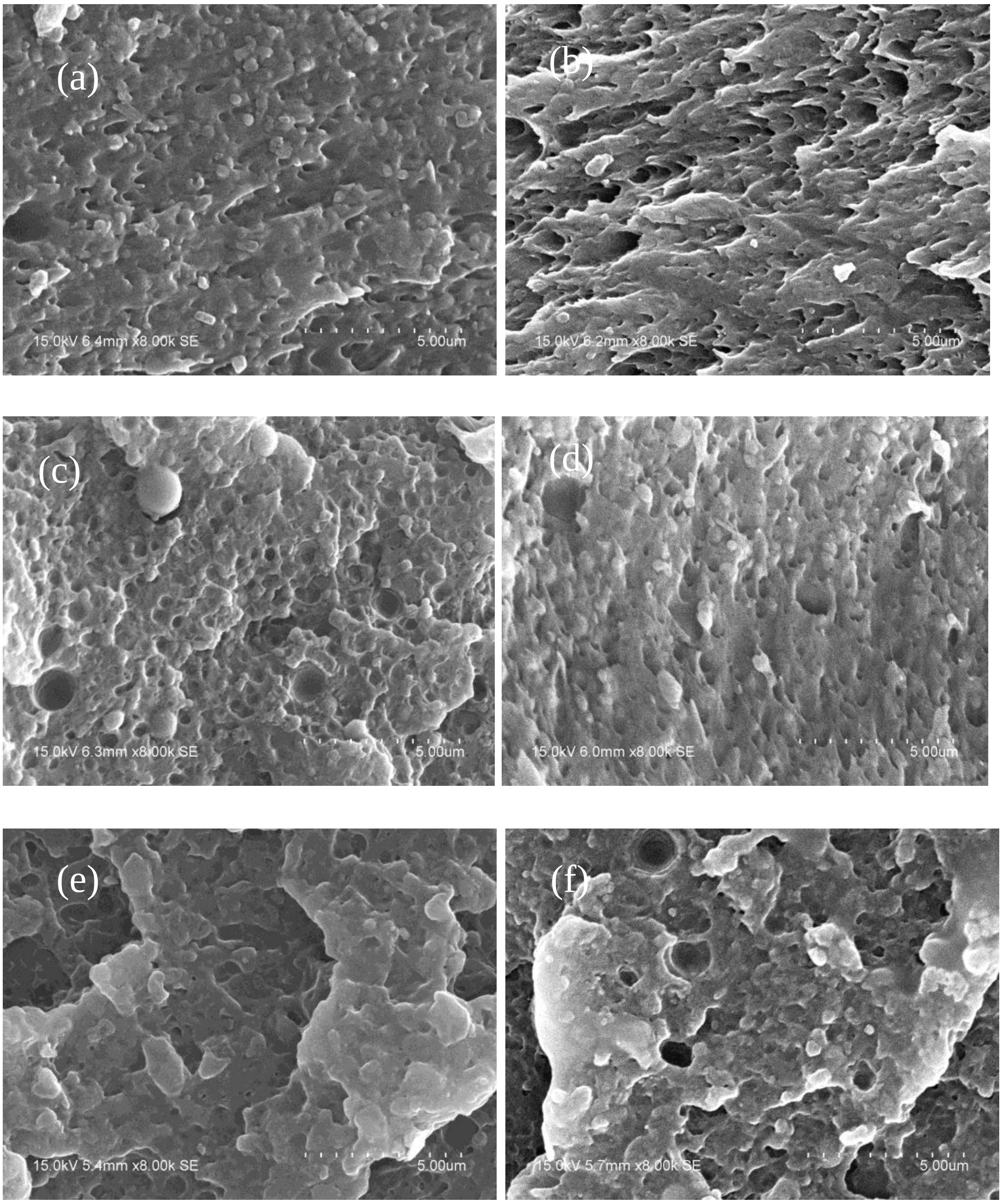


Figure 4.21 SEM Photograph (a) Pristine ABS (b) ABS added with 2 phr TMPTMA (c) ABS added with 8 phr TMPTMA Irradiated at 50 kGy, and (d) Pristine ABS (e) ABS added with 2 phr TMPTMA (f) ABS added with 8 phr TMPTMA Irradiated at 250 kGy under Magnification of 8000x

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, the gel content for LDPE, HDPE, EVA and also ABS was significantly increased by increasing the loading level of TMPTMA and increasing electron beam irradiation dosages. However, the gel content of all ABS samples was observed to be lower than the gel content of LDPE, HDPE and EVA samples, whereas the gel content for EVA was observed to be the highest among all samples. This indicates that the increasing of TMPTMA loading level could help in inducing the formation of three dimensional crosslinking networks when subjected to electron beam irradiation dosages (Ng et al., 2014).

The results from hot set testing showed that the enhancement in plastic deformation could be achieved for LDPE, HDPE and EVA samples with addition of TMPTMA upon electron beam irradiation dosages. This might due to the formation of crosslinking networks that restrict the mobility of polymer chains inside the polymer matrix of LDPE, HDPE and EVA samples under static load and high temperature. The increasing of electron beam irradiation dosages also could induce the degree of crosslinking in polymer matrix and the crosslinking networks could significantly help in restricting the polymer chains mobility. Thus, the creep elongation also reduced with increasing of electron beam irradiation dosages. All ABS samples were found to fail the test immediately due to its inferior crosslink ability.

The tensile strength of LDPE, EVA and ABS were found to increase significantly with incorporation of lower loading level of TMPTMA (2 phr to 4 phr) and also lower electron beam irradiation dosages (50 kGy). Less significant improvement was observed in tensile strength of all polymer samples for higher loading level of TMPTMA (>4 phr) and higher electron beam irradiation dosages (≥ 150 kGy). This is because crosslinking and chain scissioning reactions tended to compete with each other to reach a balancing effect, thus less significant increment can be observed (Wu et al., 2012). On the other hand, the introduction of electron beam irradiation dosages showed an insignificant improvement effect on the tensile strength of HDPE due to the nature structure of HDPE which poses strong intermolecular forces and tensile strength.

The elongation at break for LDPE, HDPE, EVA and ABS samples were found to generally decrease with addition of TMPTMA upon electron beam irradiation dosages. This might due to the formation of greater crosslinking networks that prevent the slippage between chains of polymers. Whereas, young modulus for LDPE, HDPE, EVA and ABS samples were found generally increase with addition of TMPTMA upon electron beam irradiation dosages. This indicates higher strength and rigidity of samples due to formation of form three dimensional crosslinking networks. However, higher electron beam irradiation dosages was found to decrease the mechanical properties (tensile strength, elongation at break and Young's modulus) of all samples due to dissipation of excessive energy from electron beam irradiation which show negative effect on mechanical properties of all samples. Moreover, higher loading level of TMPTMA was also found to decrease the mechanical properties of all samples due to excessive monomer free radicals generated by TMPTMA that promotes the predomination of chain scissioning reactions over crosslinking reactions.

5.2 Recommendations

Further investigation on physical and mechanical properties of TMPTMA added LDPE, HDPE, EVA and ABS can be carried out by conducting impact test and hardness. X-ray crystallography (XRD) is also recommended to be carried to investigate the crystallinity and crystalline size of samples. By obtaining both crystallinity and crystalline size of samples, the strength of samples could be determined more easily. Furthermore, testing such as thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) should be carried out to determine the thermal properties for all samples. With these tests, the thermal stability for all samples can be obtained. This could aid in the comparison of results between irradiated and non-irradiated samples. Moreover, fourier transform infrared spectroscopy (FTIR) should be carried out to investigate the bonding in all samples so that degree of crosslinking in each sample could be determine more precisely.

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