

**INVESTIGATION OF FLAME RETARDED ACRYLONITRILE-  
BUTADIENE-STYRENE AND POLYCARBONATE  
NANOCOMPOSITES**

By

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## **ABSTRACT**

### **INVESTIGATION OF FLAME RETARDED ACRYLONITRILE- BUTADIENE-STYRENE AND POLYCARBONATE NANOCOMPOSITES**

**Lim Kien Sin**

In this work, the effects of increasing APP and MMT loading levels on non-irradiated and irradiated PC/ABS blends were investigated. Furthermore, the effect of increasing electron beam irradiation dosage on the PC/ABS blends under various APP and MMT loading levels was examined as well. During blending process, resins of PC and ABS were compounded with various loading levels of APP and MMT using brabender mixer. The compounded PC/ABS blends were compression moulded into sheets and electron beam irradiated to different irradiation dosages. It is shown that appropriate addition of APP into PC/ABS blends could help in enhancing the flame retardancy as witnessed in the LOI testing. However, the loading level of APP has to be chosen carefully to prevent the deterioration of mechanical properties in PC/ABS blends. It is found that incorporation of suitable MMT into PC/ABS blends could enhance the flame retardancy, mechanical and physical properties through the intercalation of PC/ABS polymer matrix into the MMT interlayer. Besides that, cross-linking network in PC/ABS blends can be formed with proper application of irradiation under suitable dosage. It is concluded that 25 phr APP and 2 phr MMT added into the PC/ABS blends at

50 kGy irradiation is the optimum formulation of blend. Addition of 25 phr APP into the PC/ABS blend has improved the flame retardancy and increased the LOI while MMT loading level of 2 phr has strengthened the polymer structure through intercalation effect. Application of electron beam irradiation at 50 kGy has shown to be effective in cross-linking formation of PC/ABS blends that gives higher gel content value without further degrading the polymer chains.

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**SUBMISSION OF DISSERTATION**

It is hereby certified that *Lim Kien Sin* (ID No: *14UEM07887*) has completed this dissertation entitled “Investigation of Flame Retarded Acrylonitrile-butadiene-styrene and Polycarbonate Nanocomposites” under the supervision of Dr. Bee Soo Tuen (Supervisor) from the Department of Chemical Engineering, Faculty of Engineering & Science, Ir. Dr. Lee Tin Sin (Co-Supervisor) from the Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering & Science and Dr. Chantara Theyv A/P Ratnam (Co-Supervisor) from the Division of Radiation Processing Technology, Malaysian Institute for Nuclear Technology Research (MINT).

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## APPROVAL SHEET

This dissertation/thesis entitled “**INVESTIGATION OF FLAME RETARDED ACRYLONITRILE-BUTADIENE-STYRENE AND POLYCARBONATE NANOCOMPOSITES**” was prepared by LIM KIEN SIN and submitted as partial fulfillment of the requirements for the degree of Master of Engineering Science at Universiti Tunku Abdul Rahman.

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## DECLARATION

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

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## LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERMS

NBR	Acrylonitrile butadiene rubber
ABS	Acrylonitrile-butadiene-styrene
ATH	Aluminium trihydrate
APP	Ammonium polyphosphate
EVA	Ethylene vinyl acetate
HDPE	High density polyethylene
HIPS	High impact polystyrene
IFR	Intumescent flame retardant
LDH	Layered double hydroxide
LOI	Limiting oxygen index
LDPE	Low density polyethylene
MEK	Methyl ethyl ketone
MMT	Montmorillonite
PER	Pentaerythritol
PET	Poly(ethylene terephthalate)
PMMA	Poly(methyl methacrylate)
PVOH	Poly(vinyl alcohol)
PC	Polycarbonate
PLA	Poly(lactic acid)
PP	Polypropylene
PS	Polystyrene
SEM	Scanning electron microscopy
SBR	Styrene-butadiene rubber

TEM

Transmission electron microscopy

XRD

X-ray diffraction



## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

Recently, blending of two or more polymers has become a popular trend in the polymer processing industry. This technique plays an important role in reducing the cost of polymers, improving the processing of high temperature and heat sensitive thermoplastics, and enhancing the mechanical properties of the polymer without causing significant change in the polymer structure (Deanin and Chu, 1986; Jin, et al., 1998). Due to its distinct properties and characteristics, blends of polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) have been existed for several years owing to its few advantages such as the high toughness and ease of processing at low cost (Lombardo, Keskkula and Paul, 1994). PC/ABS blends can be used in a wide range of industrial applications such as in the automotive sector (used in structural components and pillars) and electronics segment (used in keypads, television frames and mobile phone bodies).

Although PC/ABS blend can be applied in most of the industries, it has a rather poor flame retardancy and thus the application of PC/ABS blends in high temperature condition could limit the use of the blends. The poor flame resistance of PC/ABS blends is mainly attributed to their hydrocarbon origin.

Hence, to improve the flame retardancy of PC/ABS blends, suitable amount of flame retardant such as ammonium polyphosphate (APP) can be incorporated. Generally, APP is synthesized from inorganic salt of polyphosphoric acid and ammonia. It is known to be preferred over the other flame retardants due to its smaller loadings at lower cost and excellent processability. Most importantly, APP is a halogen-free flame retardant and thus it does not generate additional amount of smokes, making it to be environmentally useful compared to other halogen-containing flame retardants (Levchik, et al., 1996).

It is important to note that excessive loading of flame retardant is shown to deteriorate the mechanical properties of the PC/ABS blends. To mitigate the loss of mechanical properties in PC/ABS blends, small amount of reinforcing filler such as montmorillonite (MMT) can be added together with the APP flame retardant. The addition of nanoclay based additives have gained increasing popularity due to its relatively low cost, improvement of intercalation between the polymer layers, and high cost-performance ratio of the polymer blends (Meri, et al., 2015). Besides that, the poor mechanical properties of high amount of flame retardant added PC/ABS polymer blends can be enhanced by introducing irradiation with high energy such as the electron beam, X-ray or gamma ray to modify the structure of the blends. However, the irradiation dosage must be kept at an optimum level to prevent excessive cross-linking in the polymer blends.

In this report, polymer blends of PC and ABS was prepared by melt blending of the two polymers. APP was chosen as the flame retardant to

investigate its flame resistance effect on the PC/ABS blends. In addition, secondary reinforcement factors such as the incorporation of MMT and electron beam irradiation were examined as well. The overall properties of the PC/ABS blends such as the flame retardancy, mechanical and physical properties were obtained in order to determine the optimum formulation of flame retarded PC/ABS blends reinforced with MMT at suitable irradiation dosage.

## **1.2 Problem Statements**

Based on the scenario stated in the introduction, some of the problem statements were identified as below:

1. How do the flame retardancy, mechanical and physical properties of PC/ABS blend behave after it was melt blended with increasing loading level of APP flame retardant?
2. What are the effects of increasing MMT loading level on the flame retardancy, physical and mechanical properties of PC/ABS blends?
3. What are the effects of increasing electron beam irradiation dosage on the properties of PC/ABS blends filled with APP and MMT?
4. What is the optimum formulation of flame retarded PC/ABS blends reinforced with MMT at suitable irradiation dosage?

### **1.3 Objectives**

The main objective of this project was to determine the optimum formulation of flame retarded PC/ABS blends with excellent flame retardancy, mechanical and physical properties. In order to achieve the main objective, the following sub-objectives were identified:

1. To investigate the effects of increasing APP loading level on the flame retardancy, mechanical and physical properties of PC/ABS blends under various electron beam irradiation dosages.
2. To investigate the effects of increasing MMT loading level on the flame retardancy, mechanical and physical properties of PC/ABS blends under various electron beam irradiation dosages.
3. To examine the effects of increasing electron beam irradiation on the flame retardancy, mechanical and physical properties of PC/ABS blends under various APP and MMT loading levels.

### **1.4 Scopes**

In this project, the following scopes were identified:

1. Sample preparations:
  - PC/ABS blends with different compositions were prepared by plastigraph brabender mixer. Suitable amount of APP flame retardant and MMT fillers were added. The blends were then pressed into

desirable shape by compression moulding before being cut into even smaller dumbbell shapes and notched sample bars for testing purposes.

- All the specimens were electron beam irradiated from 0 kGy to 250 kGy with dosage of 50 kGy per pass.

## 2. Testing and characterization:

- The flame retardancy of PC/ABS blends was examined by conducting limiting oxygen index (LOI) test.
- Mechanical properties of the blends such as the tensile strength, elongation at break and Izod impact strength were obtained by tensile and impact test.
- The gel content of the PC/ASB blends was assessed through gel content test.
- Scanning electron microscopy (SEM) was conducted to examine the morphology of the PC/ABS blends.
- X-ray diffraction (XRD) was performed to investigate the dispersion and intercalation state of MMT in the PC/ABS blends.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Blending of Polymers and Flame Retardants

Generally, polymer blends are the blending of two or more chemically distinct substances, polymers and/or copolymers (Utracki, 1982). In the last few years, blending of polymers has become more and more important in the polymer industry as it tends to have better processability and product uniformity, besides than the benefits of higher performance at reasonable price. In addition, the ability of the blends to be modified by changing the compositions of polymer constituents in the blends makes them to be extremely useful in the application of polymer industry. Lastly, blending of polymers has been shown to impart certain recyclability in the blends which are now gaining the attention of the world for the needs of sustainable development (Mohanty, Misra and Drzal, 2002; Azapagic, Emsley and Hamerton, 2003). Therefore, the challenges lied in four main criteria: 1) to offer polymer blends with a set of desired properties at reasonable or lowest price; 2) to enhance the resins performance of the polymer blends; 3) to improve the properties of the blends in terms of physical, chemical, mechanical, flow (or rheological) and thermal aspects; 4) to provide and propose a number of ways to handle and recycle the polymer wastes.

Blending of polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) has gained intensive interest among the researchers due to its high toughness and ease of processing at lowest possible cost. Besides that, PC/ASB blends are widely used in different industrial applications such as in automotive, construction and electronics industries. However, the application of PC/ABS blends can be limited by their high flammability or weak flame retardancy. In another word, application of PC/ABS blends in high temperature condition could reduce the properties as the polymer blends could not withstand the high temperature. To increase the flame retardancy of PC/ABS blends, suitable amount of flame retardants can be incorporated. Nowadays, incorporation of flame retardant in polymer system is very important. Flame retardants are essential in delaying the production and spreading of flames or fires. According to the conference proceeding held in Stamford, Connecticut on 19 May 2014 to 21 May 2014, the global consumption of flame retardants was about 4 billion pounds in year 2013. It was predicted that the market for flame retardant will reach 5.2 billion pounds in 2018, accounted for a compounded annual growth rate of about 5 %. With such a strong and healthy growth, research and development will definitely continued to keep up together with the demand in flame retardant market.

There are many different types of flame retardants available in the industry and market with aluminium trihydrate (ATH) or aluminium hydroxide being the most widely used (Beyer, 2001; Sain, et al., 2004). Basically, flame retardants can be either reactive or additive. They can be further categorized into several classes which includes minerals (ATH and

magnesium hydroxide), organohalogen compounds (organochlorines and organobromines), and organophosphorus compounds (organophosphates, phosphonates and phosphinates). In addition, flame retardants can be categorized into phosphorus-containing, halogen-containing, silicon-containing or any other chemical-containing flame retardants based on the chemical type in their structure instead of grouping them according to classes. For instance, both decabromodiphenyl oxide and tris(tribromoneopentyl) phosphate can be classified as halogen-containing flame retardants (Georlette, Simons and Costa, 2000). Among the chemical-containing flame retardants, ammonium polyphosphate (APP) which is synthesized from inorganic salt of polyphosphoric acid and ammonia is currently getting the attention among the industries. It is known to be preferred over the other flame retardants due to its lower loadings at lower cost and excellent processability. Most importantly, APP is a halogen-free flame retardant and thus it does not generate additional amount of smokes, making it to be environmentally useful compared to other halogen-containing flame retardants (Levchik, et al., 1996).

APP is able to function as flame retardant in the condensed or polymer phase through intumescence. During intumescence, a material swells when it is exposed to heat or fire to form a porous carbonaceous foam which acts as a barrier to prevent heat, air and pyrolysis product from entering the surface of the material (Camino, Costa and Luda, 1993; Le Bras, Bourbigot and Revel, 1999). When polymeric materials which contain APP are subjected to fire, APP will first decompose into polyphosphoric acid and ammonia. The polyphosphoric acid would then react with hydroxyl group or other groups of



synergists such as hydroxyethylcyanurates or cyclic urea-formaldehyde resins to form a non-stable phosphate ester (Cullis, Hirschler and Tao, 1991; Lewin, 1999). Upon dehydration of phosphate ester, charring would occur which involves the formation of a carbon foam above the surface of the polymeric materials to against the heat source. Furthermore, other than forming carbon foam, a viscous molten layer or surface glass can also be obtained on the polymeric surface which protects the polymeric materials from heat and oxygen (Green, 1992). Theoretically, three main components are needed in an intumescent flame retardant (IFR): 1) an acid source such as inorganic acid, acid salt or other acids that elevates the dehydration of carbonizing agent; 2) a carbonizing agent which is a carbohydrate that will be dehydrated by the acid source to become a char; 3) a blowing agent that will be decomposed to release gas resulting in the increase of polymer's volume and the formation of a swollen multi-cellular layer (Laoutid, et al., 2009). In order to achieve an optimum performance, APP needs to be properly dispersed into the polymer system and compatible with the polymer matrix. Besides that, it is better for APP to be insoluble in water to ensure a good weathering performance (Jimenez, Duquesne and Bourbigot, 2006).

There have been numerous literature published which focus on the flame retardancy and intumescence of APP on thermoset polymers or thermosetting resins. Over the decades, many improvements have been done by past researchers such as microencapsulation to enhance the performance of APP on thermoset polymers (Liu, et al., 2011). Hence, the next few sections will focus and discuss the application of APP as IFR in thermoplastics and

their composites. Mechanical properties (such as the tensile strength and elongation at break) and physical properties (such as surface morphology) are discussed here. Also, the thermal behaviour and intumescence are analyzed in order to understand the mechanism and effects of APP on thermoplastics and thermoplastics composites.

## **2.2 Commodity Thermoplastics and Their Composites**

### **2.2.1 Polyethylene**

Basfar, et al. (2008) have examined the mechanical and thermal properties of low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) blends cross-linked by both dicumyl peroxide and ionizing radiation. Besides that, they have performed a study to find out the effect of APP content on the mechanical properties of the chemically cross-linked 60/40 LDPE/EVA blends coupled with grafted polyethylene and maleic anhydride. Based on the results in Table 2.1, it was inferred that the retention of mechanical properties were independent to the amount of APP as both the retention of tensile strength and elongation at break was still remain in the range of about 100 %. However, addition of 35 phr caused a slight decrease in the tensile strength of the 60/40 LDPE/EVA blend although its elongation at break experienced a small increment. The result was in agreement with the findings by Stark, et al. (2010) as APP was assumed to have negative effect on the mechanical properties of wood flour-polyethylene composites. In fact, as shown by Basfar and other researchers, a minimum amount of 35 phr APP is needed to achieve

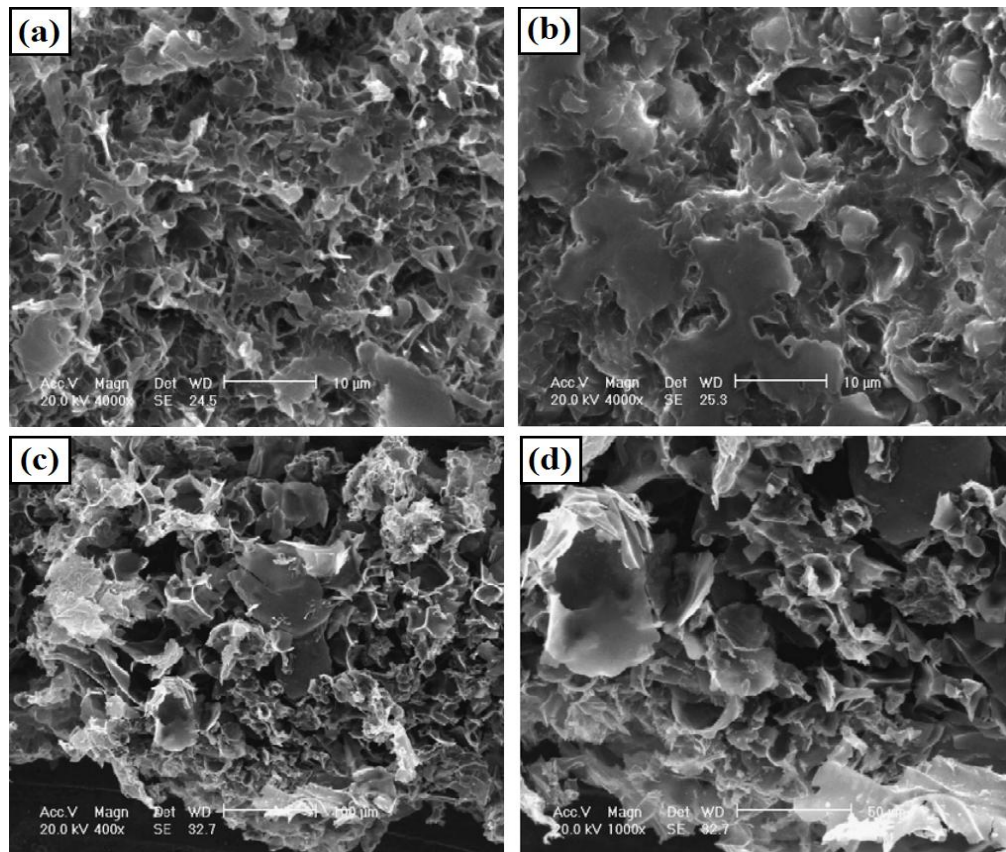
the required fire resistivity of the IFR compounds. In order to enhance the tensile strength of the LDPE/EVA without reducing the amount of APP, small amounts of inorganic additives such as talc can be incorporated. As shown in Table 2.1, addition of 1 phr talc showed a remarkable increase in terms of tensile strength for the LDPE/EVA blends cross-linked by dicumyl peroxide. Not only this, the elongation at break was found to be increased as well compared to its previous blends added with 30 phr APP. Both the retention of tensile strength and elongation at break was maintained in an acceptable range of 93 to 97 %.

**Table 2.1 Effect of APP and talc on the mechanical properties of 60/40 LDPE/EVA blends cross-linked by 3 phr dicumyl peroxide and coupled with 3 phr grafted polyethylene and maleic anhydride (Basfar, et al., 2008)**

<b>Property</b>	<b>30 phr APP</b>	<b>35 phr APP</b>	<b>35 phr APP + 1 phr talc</b>
<b>Tensile strength (MPa)</b>	13.0 ± 0.9	11.9 ± 0.3	15.2 ± 0.8
<b>Elongation at break (%)</b>	453 ± 23	487 ± 18	481 ± 10
<b>Retention of tensile strength (%)</b>	113	104	93
<b>Retention of elongation at break (%)</b>	97	99	97

In terms of surface morphologies, Cai, et al. (2006) have synthesized some shape stabilized phase change nanocomposites materials via the blending of high density polyethylene (HDPE), EVA, organophilic montmorillonite (MMT), paraffin and IFR compounds which include APP and pentaerythritol (PER). The samples were then observed under scanning

electron microscopy (SEM) to obtain the surface morphology images for both the shape stabilized and the char residue of the samples. From SEM micrographs illustrated in Figure 2.1(a) and 2.1(b), it can be observed that a compact network structure was formed via the entrapment of paraffin and flame retardant by the HDPE-EVA composites. Well dispersion of flame retardant in the composite and paraffin have achieved for the shape stabilized materials. On the other hand, when the sample added with APP-PER was burned in a muffle furnace under 800 °C to form a multicellular char residue, loose surface morphology was found to be present as shown in Figure 2.1(c). Under high magnification, the char residue displayed a rather non-homogeneous microstructure as compared to other samples added with organophilic MMT (Cai, et al., 2006). Hence, it can be concluded that incorporation of IFR compounds (APP and PER) has little or no effect on the network structure of the nanocomposites materials.



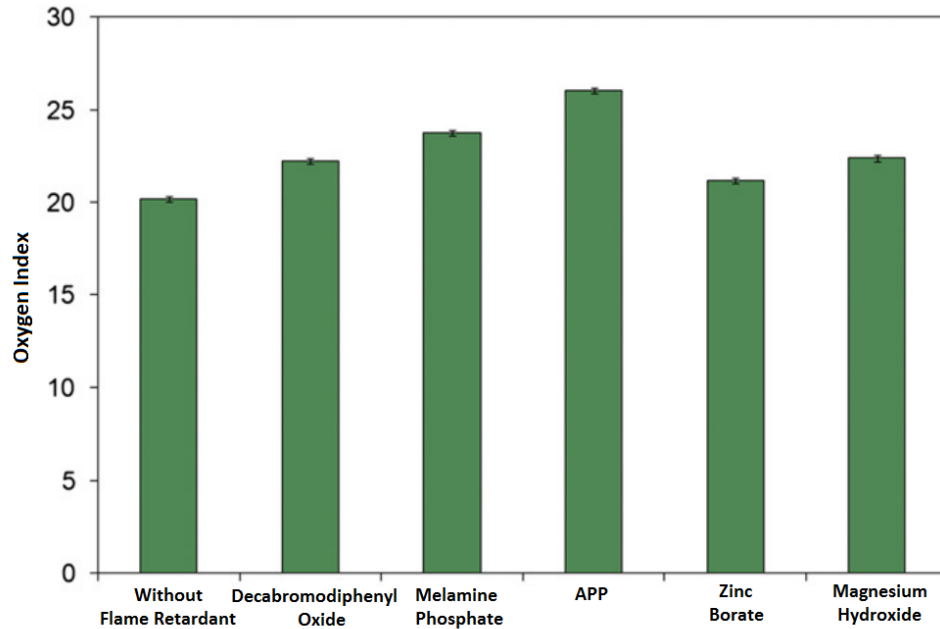
**Figure 2.1 SEM micrograph of the phase change nanocomposite materials: (a) shape stabilized 60 wt% paraffin + 40 wt% HDPE-EVA, (b) shape stabilized 60 wt% paraffin + 20 wt% HDPE-EVA + 20 wt% APP-PER, (c) char residue of 60 wt% paraffin + 20 wt% HDPE-EVA + 20 wt% APP-PER, (d) char residue of 60 wt% paraffin + 20 wt% HDPE-EVA + 20 wt% APP-PER under high magnification (Cai, et al., 2006)**

The effect of halogen-free flame retardant towards the phase change materials from paraffin/HDPE composites have been studied extensively by several authors. Cai, et al. (2008) have performed SEM on the paraffin/HDPE composites mixed with IFR composed of expandable graphite, APP and zinc borate. It was established that the flame retardants were evenly distributed in a three-dimensional net structure of paraffin and HDPE. Graphite sheets in round-like lamellar structure having an average size of 300  $\mu\text{m}$  were noticed to be embedded into the phase change materials. After combustion of the materials to produce char residues, worm-like structure of the expanded

graphite was found, and the addition of APP seems to result in a tighter and denser morphology than the materials added with only expandable graphite. In year 2009, it has been further proved that the paraffin/HDPE composites with APP produce a form-stable composites which appeared to be uniform with no agglomeration (Cai, et al., 2009). In order to enhance the dispersions of the paraffin and flame retardant within HDPE, suitable amount of expandable graphite can be supplemented which would cause partial absorption of paraffin into the porous structure of expandable graphite during the extrusion process (Zhang and Fang, 2006; Sarı and Karaipekli, 2007).

For thermal behaviour and properties, Stark, et al. (2010) have conducted a research to find out the fire performance and effectiveness of five different flame retardant systems (i.e. decabromodiphenyl oxide, magnesium hydroxide, zinc borate, melamine phosphate and APP) in the wood flour-polyethylene composites. The composites without flame retardant were first prepared via the blending of 35 wt% polyethylene, 60 wt% wood flour and 5 wt% lubricant to ensure a good composite surface characteristics. Then, five different flame retardants were added individually to the composites by replacing 10 % of the wood flour. For instance, APP added composite was made up of 35 wt% polyethylene, 50 wt% wood flour, 10 wt% APP and 5 wt% lubricant. Based on Figure 2.2 which depicts the limiting oxygen index (LOI) for different composites, it was suggested that each of the flame retardant systems increased the LOI of the wood flour-polyethylene composites with APP possessed the highest increment of about 29 % as compared to its composite without flame retardant. Thus, it was concluded by the authors that

APP functioned effectively as a flame retardant in the wood flour-polyethylene composites with the exception that it would cause a decline in mechanical properties (Li and He, 2004). On the other hand, it was showed by several literatures that enhancement of the protective effect in the APP associated with PER could be done through the combination of zeolites and conventional heat insulating materials (Bourbigot, et al., 1996). By applying these components, fire-proofing properties could be imparted into the polymer systems such as polyethylene and ethylenic copolymers. For example, the usage of 4A type zeolite in the flame retardant systems consist of APP and PER led to a synergistic effect for the formulations involving polyethylene. The LOI values have increased by 35 % with respect to the conventional APP-PER retardant system when 1.5 wt% of 4A type zeolite was added. However, it was noted that high zeolite content of more than 5 wt% would result in a dramatic decline of the fire performance.



**Figure 2.2 LOI for wood flour-polyethylene composites (35 wt% polyethylene, 50 wt% wood flour and 5 wt% lubricant) added with 10 wt% flame retardant (Stark, et al., 2010)**

### 2.2.2 Polypropylene

The mechanical properties of polypropylene (PP) involving APP have been studied and published by past few literatures. According to the research done by Schacker and Wanzke (2002), PP compounds added with APP would have Charpy impact strength in between 20 to 80 kJ/m<sup>2</sup>, Young's modulus of about 1300 to 2200 MPa, elongation at break of 15 to 350 % and melt flow index around 5 to 20 g per 10 minutes. In order to prevent the APP flame retardant from decomposition prior to processing stage, polymer compounding can be performed by twin screw extruder with a soft screw configuration which used the lowest possible melt temperature that gives a high output rate at low screw speed. Apart from that, sharper screw was recommended to be used during the compounding of PP and APP to produce an excellent flame



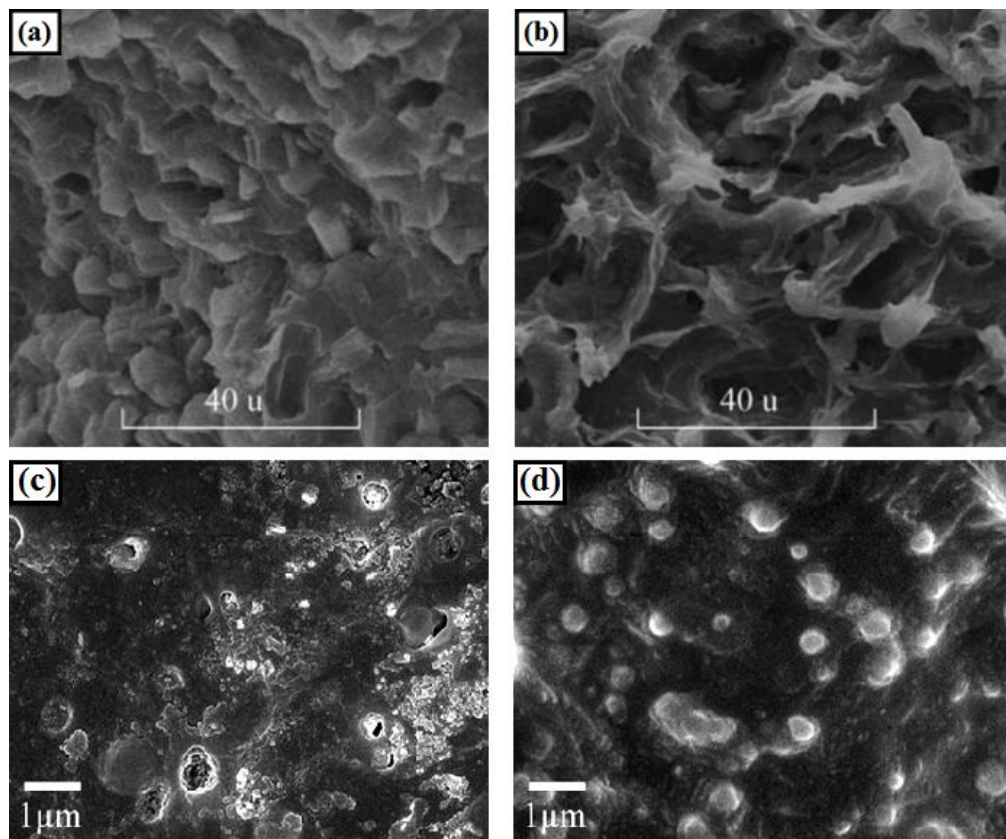
retarded polymer with slower rate of decomposition. Chiu and Wang (1998) have conducted an experiment to study the dynamic flammability properties of an intumescent fire retarded PP filled with APP, PER and melamine. From Table 2.2, it can be seen that increasing the amount of APP results in the decline of tensile strength. The inherent superior tensile strength of PP was found to be severely affected by the incorporation of APP in the composites due to the reducing crystallinity in the composites (Quynn, et al., 1959). This was proved later by Li, et al. (2011) when the graph of PP's crystallinity in PP/PS blends against the side chain length of PP-g-PS copolymer revealed that additives, PS and PP-g-PS copolymer would restrain the PP chain from folding into a growing crystal lamellae, thus reducing the crystallinity of PP in the blends. Throughout the whole experiment, it was concluded that pure PP has poor flame properties. In order to enhance the flammability of original PP and its composites or blends, APP, PER and melamine can be employed which function as intumescent flame retardant. However, it is important to note that excessive amount of APP added into the composites would cause a rather low tensile strength which limits their applications. Lin, et al. (2011) have showed that incorporation of silane coupling agent KH-550 improved the mechanical properties of PP and APP to a certain extent. The tensile strength, impact strength and elongation were found to be increased by 24 %, 25 % and 14 % respectively compared to its original blend without coupling agent.

**Table 2.2 Tensile strength of PP composites added with different amount of additives (Chiu and Wang, 1998)**

<b>PP (phr)</b>	<b>APP (phr)</b>	<b>PER (phr)</b>	<b>Melamine (phr)</b>	<b>Tensile strength (MPa)</b>
100	-	-	-	20.91
100	7	14	13	16.23
100	15	14	13	14.37
100	23	14	13	13.98
100	30	14	13	13.49

Figure 2.3 shows the SEM micrograph of PP composites mixed with APP flame retardant. From Figure 2.3 (a), it can be observed that most of the APP particles are distributed in the PP matrix and are exposed to the external surface due to its poor compatibility with the PP polymer matrix (Wu, et al., 2008; Wu, et al., 2009). Besides that, it was reported by Wu, et al. (2008) that the relatively higher polarity of APP was responsible for the exposure of APP particles to the fractured surface of PP/APP composites. When 70/30 PP/APP composites were treated in hot water medium at 50 °C for 24 hours, almost all APP particles have been eluted, causing some defects or voids on the fracture surface as displayed in Figure 2.3 (b). It was suggested that the water molecules have been absorbed onto the surface of the composites which lead to the dissolution of APP in the water to leave some defects on the surface (Lewin and Endo, 2003). For reduced APP amount in 80/20 PP/APP shown in Figure 2.3 (c), it was found that aggregation of APP occurred in the PP matrix which generated cracks and even holes between the components suggesting a poor dispersion and compatibility. The condition becomes even worse when the mechanical properties of 80/20 PP/APP composite were found to decrease

drastically due to the poor interfacial adhesion and accumulated microcracks at the PP and APP interface. In order to improve the surface morphology, suitable amount of coupling agent can be incorporated in the PP/APP composite. As shown by Lin, et al. (2011), 80/20 PP/APP modified with silane coupling agent gave a rather uniform dispersion of APP in the PP matrix with little or no agglomeration and cracks. This improvement would reduce the adverse effects of inorganic additives on the mechanical properties of thermoplastic composites.



**Figure 2.3 SEM micrograph of PP composites added with APP: (a) 70/30 PP/APP, (b) 70/30 PP/APP treated with 50 °C water for 24 hours, (c) 80/20 PP/APP, (d) 80/20 PP/APP modified with KH-550 coupling agent (Wu, Wang and Liang, 2008)**

The flammability and flame properties of PP composites mixed with APP flame retardant and other additives such as PER and melamine have been investigated by Chiu and Wang (1998). From their study, it was first stated that pure PP without APP flame retardant and additives is highly combustible as it has a low LOI of only 17.8 % given in Table 2.3. Through the addition of APP, PER and melamine in the PP, the LOI of the PP composites increased gradually to a maximum value of 38.4 %. Since the amount of additives remained constant in the composites, it can be said that APP exhibits a good fire protection to PP composites as it functions as IFR that interrupts the burning process in the condensed phase. In addition, it was confirmed by Lewin and Endo (2003) that addition of small amount of heavy metal salts such as zinc acetate, zinc borate, manganese acetate and manganese sulphate to APP-PER-PP composites appeared to elevate the flame retardant performance of APP in the PP matrix. Anion type of heavy metal was discovered to impose a lesser impact when compared to the cation heavy metal which increased the LOI of the PP composites by 4 to 5 units (Lv, et al., 2005). On the other hand, it was established by Lin, et al. (2011) that PP/APP composites modified with silane coupling agent KH-550 reduced the water solubility effectively and improved the interface compatibility between the APP and PP matrix. When increasing APP content in the composites modified with coupling agent, the LOI increased as well. This implied that a much higher oxygen concentration is needed to initiate and sustain the continuous combustion of the PP composites via the incorporation of APP. Besides that, APP has been proven to be effective in eliminating the dripping phenomenon

and self-extinguished when a certain compound is subjected to fire (Du, et al., 2009).

**Table 2.3 LOI of PP composites added with different amount of APP (Chiu and Wang, 1998)**

PP (phr)	APP (phr)	PER (phr)	Melamine (phr)	LOI (%)
100	-	-	-	17.8
100	7	14	13	27.0
100	15	14	13	31.9
100	23	14	13	34.5
100	30	14	13	38.4

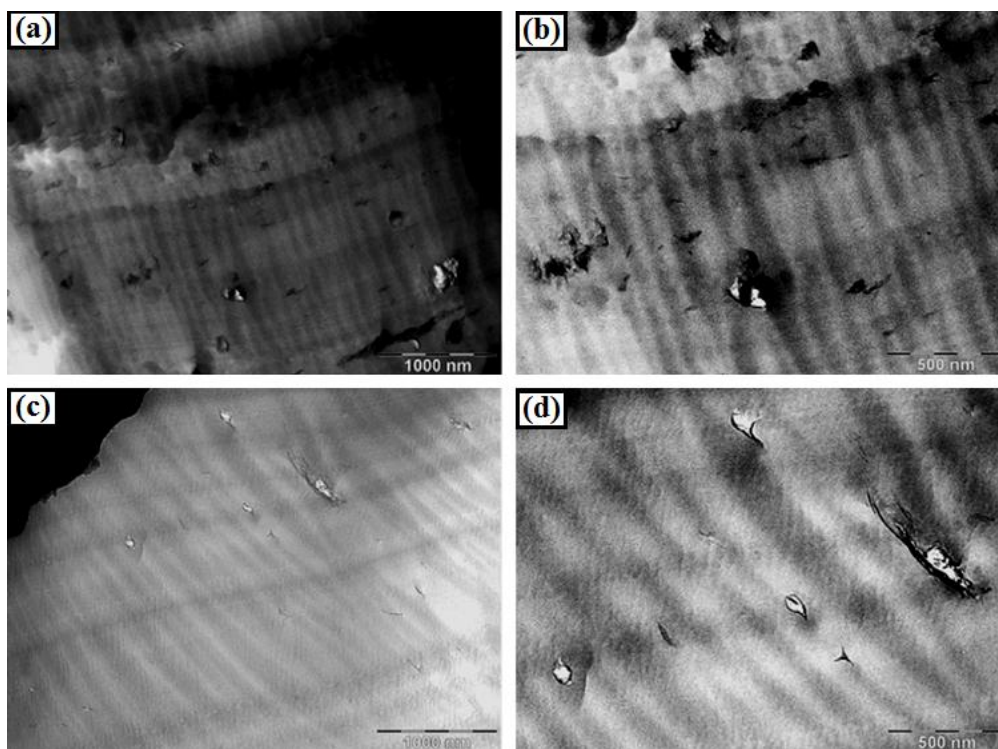
Generally, there are five major crystalline forms of APP. Crystalline form I is produced by the heating of equimolar ammonium orthophosphate and urea under the ammonia at 280 °C whereas the crystalline form II with orthorhombic symmetry ( $a = 4.256 \text{ \AA}$ ;  $b = 6.475 \text{ \AA}$ ;  $c = 12.04 \text{ \AA}$ ) is obtained by heating the crystalline form I under high temperature of 200 to 375 °C (Bourbigot, et al., 1995). During the transition of crystalline form I to form II, it was revealed that APP crystalline form III presents as an intermediate state. On the other hand, crystalline form IV shows a monoclinic structure while its form V is orthorhombic. Currently, it is known that only APP crystalline form I and II are commercially available in the market. Samyn, et al. (2007) have examined the crystallinity and crystal structure of APP coated with nitrogenous and carbonaceous species at different heat treatment temperature via the X-ray diffraction (XRD) analysis. It was stated that the powdered APP

at 20 °C has the same spectrum with the residue of treatment at 260 °C, both displaying the characteristic of APP crystalline form II. After thermal treatment of the APP sample at 415 °C, the residue showed a charred structure and a broad distribution of spectrum can be observed at  $2\theta$  between 22° to 23°. This suggests that an amorphous product has been formed as a result of thermal treatment which contains pregraphitic carbon (Drevelle, et al., 2004; Yi, et al., 2008). Lin, et al. (2011) have investigated the XRD patterns of PP, APP and PP/APP composites modified by silane coupling agent. For PP, it was reported that diffraction peaks at  $2\theta$  of about 14.2°, 17.1°, 18.6° and 21.2° were clearly noticed which correspond to the crystal planes of (110), (040), (130) and (131) that exhibits a  $\alpha$ -crystal form. However, the addition of APP into the PP composites has shifted the diffraction curves and a new peak was generated at  $2\theta$  around 16°. It was predicted that the peak might represent the crystal plane of (300) which corresponds to the  $\beta$ -crystal form (Cho, et al., 2002). Hence, it can be concluded that both  $\alpha$  and  $\beta$ -crystal forms were coexist in the PP/APP composites. Incorporation of APP was expected to trigger crystal transformation of PP and gave a  $\beta$ -crystal form of PP which is believed to be a relatively better crystal structure (Zhang, Horrocks and Hall, 1994).

### **2.2.3 Polystyrene**

Nyambo, et al. (2008) have conducted an experiment to explore the chemical interactions between APP and MgAl layered double hydroxide (LDH) on the polystyrene (PS) composites. During their research, magnesium and aluminium type of LDHs were selected as they appear to be similar to the

commonly used magnesium hydroxide and aluminium trihydrate fire retardants (Qiu, Chen and Qu, 2005). Transmission electron microscopy (TEM) was employed as a way to assess the presence of intercalated or exfoliated phases of layered inorganic materials within the PS matrix whereby low magnification gives some details about the degree of dispersion while high magnification provides certain information about the morphology, extoliation and intercalation of the materials. Based on Figure 2.4 which illustrates the TEM micrograph of 95 wt% PS added with different quantity of MgAl LDH and APP, it can be seen that some improvement in the overall additive dispersion happened when 2.5 wt% of APP was imparted to replace some MgAl LDH. There was a small number of tactoids exist in the PS composites with average length of 0.5  $\mu\text{m}$  as given in Figure 2.4 (d) under high magnification. It was suspected that the presence of tactoids in the composites might be due to the agglomeration of APP instead of the poor dispersion of LDH (Ding and Qu, 2005). Furthermore, it was anticipated by the authors that despite the improvement in dispersion, flammability and thermal stability of PS composites, incorporation of APP into the PS and MgAl LDH composites would cause a severe effect on the mechanical properties.



**Figure 2.4 TEM micrograph of 95 wt% PS added with (a) 5 wt% MgAl LDH under low magnification, (b) 5 wt% MgAl LDH under high magnification, (c) 2.5 wt% MgAl LDH and 2.5 wt% APP under low magnification, (d) 2.5 wt% MgAl LDH and 2.5 wt% APP under high magnification (Nyambo, et al., 2008)**

Back in 1970s, thermally stable phosphonium salts such as Cyagard RF-1 {ethylene-bis[tris(2-cyanoethyl)]phosphonium bromide} combined with APP have been proven to be useful flame retardants which function in the condensed phase of thermoplastics such as PP and high impact polystyrene (HIPS) (Savides, Granzow and Cannelongo, 1979; Granzow and Savides, 1980). From the literatures, it was discovered that the LOI of HIPS composites increased proportionately with the content of APP although the flame retardant efficiency of APP in HIPS was found to be lower than in PP by a factor of around 2.5. For the phosphonium salt, the flame retardant efficiency was said to increase non-linearly for both PP and HIPS and they tend to remain constant at high APP content. The difference in linearity of the APP and



Cyagard RF-1 was believed to be due to different mechanisms operated in its respective PP and HIPS. APP has been reported to be a halogen-free flame retardant used mainly in the condensed phase of polymers whereas Cyagard RF-1 is mostly likely to perform better in the gas phase. Meanwhile, the synergistic effect between oxide nanoparticles and APP on flame behaviour of PS has been published by Cinausero, et al. (2011). It was established that the LOI of pure PS has been elevated from 18.5 % to 20.5 % when 15 wt% of APP was mixed with PS to give 85/15 PS/APP composite. Through the substitution of 5 wt% hydrophilic and hydrophobic type of alumina and silica into the APP, the LOI was found to be maintained in the range of 19.5 to 20.5 %. However, with 5 wt% APP replaced with hydrophobic silica, the LOI of the composite was able to achieve a highest value of 23.0 %. This can be attributed to the specific silicon metaphosphate ( $\text{SiP}_2\text{O}_7$ ) crystalline phase which contributes to the improved charring and enhanced protective properties of the PS composite (Zanetti, Lomakin and Camino, 2000).

#### **2.2.4 Poly(methyl methacrylate)**

Poly(methyl methacrylate) (PMMA) has been widely applied in several areas owing to its good optical properties, excellent mechanical performance, high thermal stability and superior electrical properties (Jia, et al., 1999; Jin, et al., 2001). Although PMMA was employed in the form of sheets for making shatter resistant panels in building windows, bullet proof security barriers, furniture, skylights, signs and displays, it has a fatal disadvantage of being highly combustible (Lamonte and McNally, 2001).

Thus, flame retardants would need to be added to improve its flame behaviour so that the application of PMMA can be sustained. The morphology and mechanical properties of PMMA added with APP and other constituents have been reported by several authors. For instance, Friederich, et al. (2012) have discussed the ternary system of APP, melamine polyphosphate and titanium dioxide in PMMA from the views of thermal and fire resistance properties, morphology and other chemical properties. It was implied that if titanium dioxide was added individually into PMMA, it was hard to distinguish the phosphorated additives from titanium oxide particles although it was said that the presence of titanium oxide did not bring any negative effects to the dispersion of titanium dioxide (Song, et al., 2009). Friederich, et al. (2012) have concluded that replacement of a small amount of metal oxide with APP flame retardant containing phosphorus led to the enhancement in the flame behaviour and thermal properties of PMMA. In particular, 85 wt% of PMMA added with 7.5 wt% of APP and 7.5 wt% of titanium dioxide was suggested to be the best formulation among the ternary system since it exhibits the greatest thermal stability increase. Meanwhile, comparison was done by the same author based on two metal oxides (alumina and boehmite) in the mixture of APP and melamine polyphosphate with PMMA as the polymer matrix (Friederich, et al., 2012). From the SEM micrographs, it was supposed that residues with boehmite were more compact and gave a rather better morphology with fewer voids compared to the residues with alumina. The appearance of voids in the residues was believed to be the result of thermal degradation and it is undesirable for its ability to obstruct the efficiency of barrier effect. Hence, it was deduced that boehmite based ternary system

especially nanocomposites of 85 wt% of PMMA, 7.5 wt% APP and 7.5 wt% boehmite, displayed a better flammability than the system consist of alumina.

### **2.2.5 Poly(ethylene terephthalate)**

Poly(ethylene terephthalate) (PET) is a thermoplastic resin from the polyester family which has been commonly used as synthetic fibres. The excellence of its properties such as superior tensile and impact strength, clarity, good processability, high chemical resistance and reasonable thermal stability make it to be extremely useful in a wide variety of applications (MacDonald, 2002; Awaja and Pavel, 2005). Zhu, et al. (2010) have conducted an experiment to explore the effects of APP and coal on the flame retardancy, thermal degradation, char formation and mechanical properties of the PET composites. In particular, the tensile and flexural strength of the composites were measured with a Zwick multi-purpose tester following ISO 527 and GB 9341-2000. From Table 2.4, it was stated that the mechanical properties of the PET composites added with APP and coal were deteriorated. This can be attributed to the degradation of polyester and the poor interfacial adhesion between the PET and the additives. During the compounding of the composites, it was emphasized that APP and coal could promote the chain scission of polyester through hydrothermal and catalytic degradations (Balabanovich, 2003). The degradations can be traced back to the adsorption of water and polyacid by coal and APP respectively. Therefore, selection of suitable loading of APP and coal is vital to produce the PET composites with optimum properties. Besides that, pre-treatments of both APP and coal such as

the intensive balling and surface coating of interfacial compatibilizer could also be applied before mixing them into the PET.

**Table 2.4 Tensile and flexural strength of PET composites added with APP and coal in the ratio of 2 to 1 (Zhu, et al., 2010)**

	<b>Tensile strength (MPa)</b>	<b>Flexural strength (MPa)</b>
<b>Pure PET</b>	56.5	96.5
<b>95/5 PET/APP and coal</b>	39.9	74.8
<b>90/10 PET/APP and coal</b>	19.0	31.7

In terms of morphologies, Zhu, et al. (2010) have found out that addition of APP alone into PET would result in a featureless melting surface since both APP and PET would be in molten state by then, and APP was predicted to promote thermal degradation and thus melting of PET. On the other hand, APP and poly(acrylic acid) were chosen by Alongi, Carosio and Malucelli (2012) in the construction of a complex, four-layered (quadlayered) hybrid organic-inorganic structure via the layer by layer assembly method. The structure was said to be crucial in the formation of an aromatic and stable carbonaceous structure or char. Besides that, it was able to thermally protect PET, cotton and PET/cotton blends. From the SEM micrographs, it was supposed that the layer by layer film formed on the PET surface depends on the quadlayer number. For 5 quadlayers, the PET fibres were not entirely covered unless the high voltage beam employed was able to penetrate beyond any thin film formation and render any such film invisible (Podsiadlo, et al., 2009). As confirmed by the authors, increasing the quadlayer number would cause the coverage of the fibres to become even more homogeneous.

Furthermore, SEM micrographs showed that the structure and morphology of the deposited coating has greatly enhanced the thermal and thermo-oxidative stability of the PET, cotton and their blends. Favourable conditions were believed to be achieved for the formation of a stable char and thus increasing the final residues at high temperatures and preserving the polymer textures.

Table 2.5 shows the LOI of PET composites added with APP and coal at different loading level (Zhu, et al., 2010). From the table, it is obvious that the LOI values increase gradually with the amount of APP in the composites. This is in agreement with the findings by and Brauman (1980) and Balabanovich (2003). The LOI for coal powder was found to be 34.5 % while the composites of PET and coal exhibited slightly larger LOI values than the mere coal powder but smaller than the PET/APP composites. It was anticipated that coal is able to facilitate the degradation of PET and cause the chain scission of PET chains which were able to be ignited at ease (Chen, et al., 2005). Next, the trends of PET/APP/coal composites with different ratio of APP to coal were quite similar although they displayed different values of LOI. This was the result of accelerative degradation at low concentrations and blanketing at high concentrations of APP. Lastly, it was deduced that substitution of APP by coal did not exert much difference to the flame retardancy when the combined additive loading level was beyond 30 wt%.

**Table 2.5 LOI of PET composites added with APP and coal at different loading level (Zhu, et al., 2010)**

<b>Loading level (wt%)</b>	<b>10</b>	<b>25</b>	<b>30</b>	<b>40</b>	<b>50</b>
<b>APP</b>	49.0	57.0	62.0	76.0	>80
<b>Coal</b>	35.0	40.0	37.0	36.5	37.5
<b>APP : coal (2 : 1)</b>	47.0	52.0	61.0	>80	>80
<b>APP : coal (1 : 1)</b>	50.0	54.5	61.0	75.0	>80

## **2.3 Engineering Thermoplastics and Their Composites**

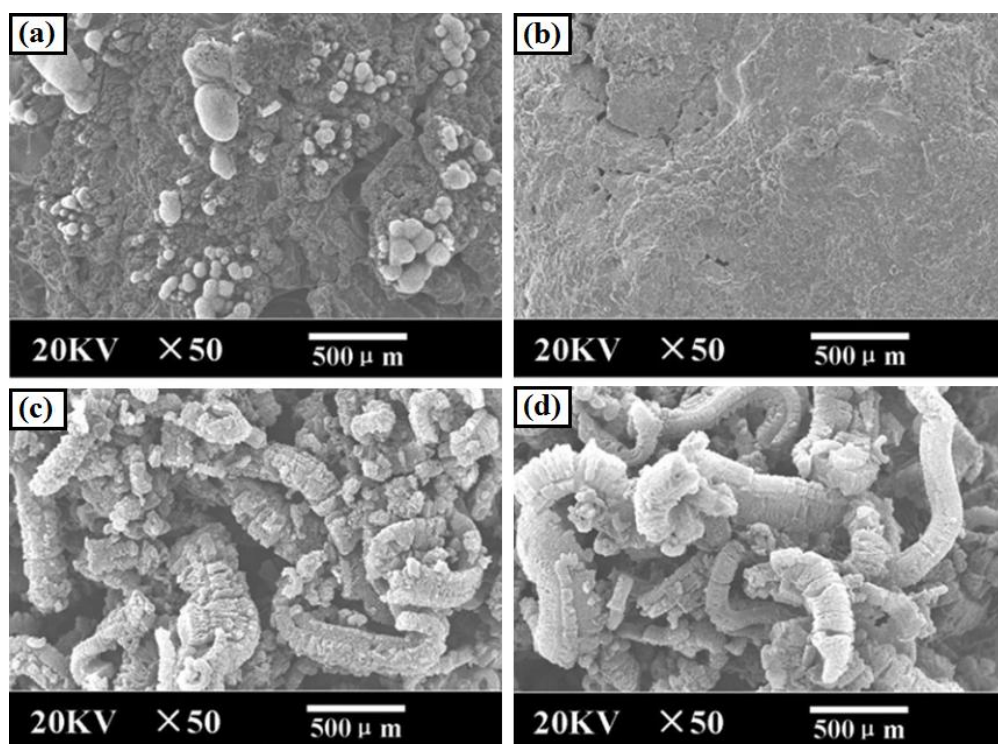
### **2.3.1 Acrylonitrile-butadiene-styrene**

Acrylonitrile-butadiene-styrene (ABS) is considered to be one of the vital and prominent type of engineering thermoplastics owing to its superior mechanical properties, good chemical resistance and rather easy processability (Majumdar, Keskkula and Paul, 1994; Arostegui, et al., 2006). It has been widely applied in several fields such as the electrical industries, medical areas, automotive production and even for households usage. Although ABS possesses overall excellent properties, it shows unsatisfying flame and thermal behaviour as it has a low LOI of only about 18 % (Wang, et al., 2004; Zhang, Chen and Fang, 2013). In particular, numerous amount of dense smoke and toxic gas will be liberated during the burning of ABS and its composites, and thus many literatures have now been focusing on how to increase the flame retardancy of ABS and its composites through the use of flame retardants and IFR. It has been proposed by several papers that application of APP in ABS composites would results in positive effect with the compensation of the

inherent properties of ABS. For instance, as shown by Zhang, Chen and Fang (2013), the storage modulus of ABS blended with 24 wt% APP and 6 wt% poly(diphenolic phenyl phosphate) was lower than the original ABS when the testing temperature exceeds 105 °C. This can be attributed to the plasticization effect of APP and poly(diphenolic phenyl phosphate). In order to mitigate the plasticization effect and enhance the interfacial adhesion between the flame retardants and the polymer matrix, appropriate amount of expandable graphite can be added.

Figure 2.5 shows the SEM micrograph of char residues for ABS composites added with APP and expandable graphite. For pure ABS alone, there were a number of big holes and cracks present in the residue due to the insufficient char formation or formation of a rather less condensed char during the combustion process (Ge, et al., 2012). For the case of 85/15 ABS/APP, it can be observed that a smooth thin film-like glassy coating was formed on the surface of the residue as a consequence of the decomposition of APP which generated viscous phosphoric or polyphosphoric acid. Nevertheless, this formation of coating or char was found to be ineffective in preventing the degradation of ABS. On the other hand, as seen in Figure 2.5 (c) and 2.5 (d), unique worm-like structures of carbon layer was developed which is different from the pure ABS and ABS/APP composites. It was believed to be the expandable graphite in the composites which tend to expand and spread in the ABS polymer matrix. However, the char residue of 85/15 ABS/expandable graphite seems to be brittle and susceptible to collapse whereas the char residue of ABS added with 15 wt% of expandable graphite and APP in the

ratio of 3:1 was found to be more compact, thick and tight with a larger expansion of volume. This char structure was suggested to be more able to inhibit the heat and mass transfer, thus protecting the ABS matrix from heat for a longer time at higher temperature and retarding the degradation of the underlying material (Xia, et al., 2007). Hence, it can be concluded that combination of both APP and expandable graphite in a suitable manner could enhance the ABS polymer with excellent flame retardancy.



**Figure 2.5 SEM micrograph of char residues from ABS composites (a) pure ABS, (b) 85/15 ABS/APP, (c) 85/15 ABS/expandable graphite, (d) 85/11.25/3.75 ABS/expandable graphite/APP (Xia, et al., 2007)**

Xia, et al. (2007) have investigated the synergistic effects of organic MMT and IFR made up of APP and PER on the flame retardancy of ABS. Besides that, they have examined the influence of IFR content (with the ratio of APP to PER being 3:1) towards the LOI and UL-94 rating of ABS



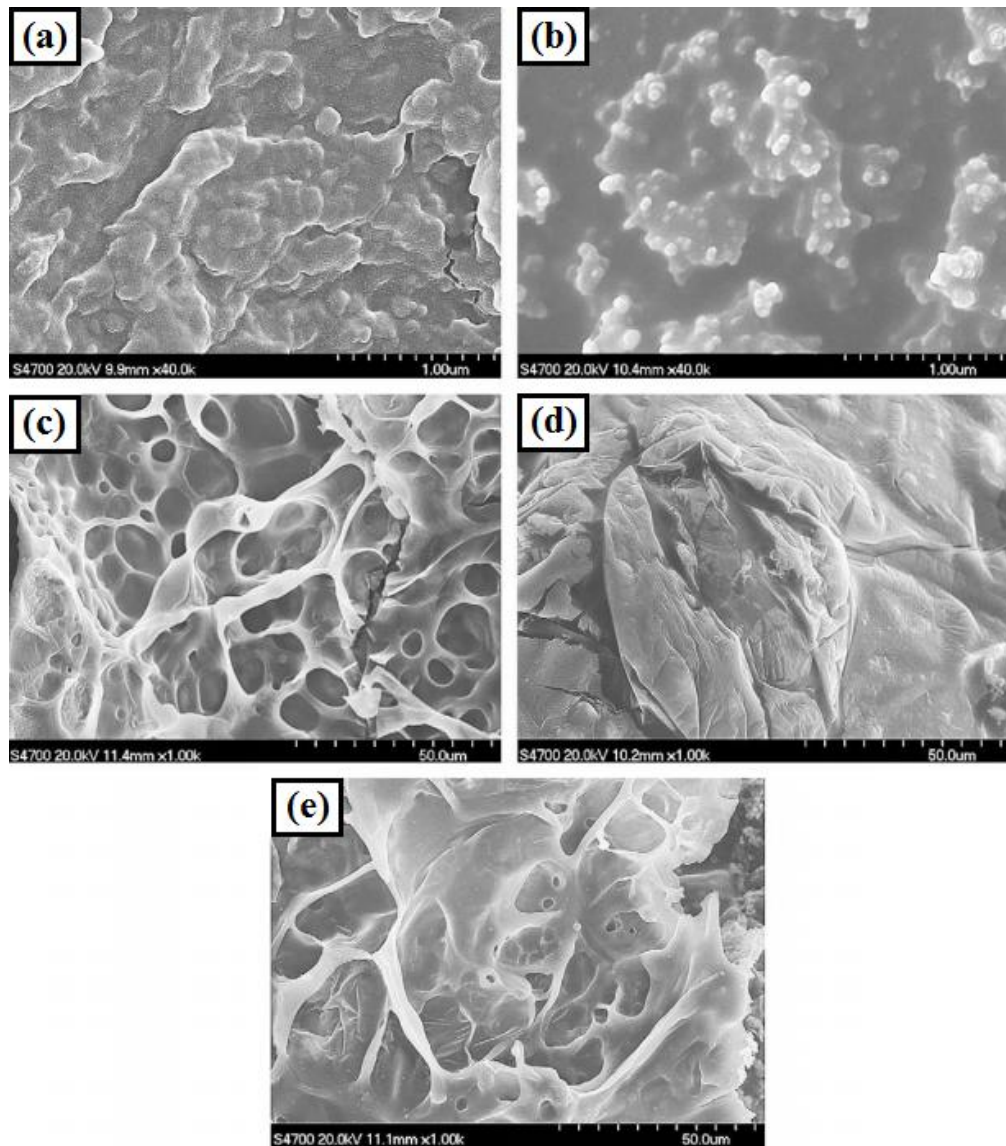
composites. From their findings, it was inferred that the LOI values were increasing continuously with the increasing amount of IFR. However, it must be noted that only addition of at least 30 wt% of IFR into the ABS would result in LOI of higher than 27 % with V-0 rating (burning ceased within 10 seconds after two applications of flame with 10 seconds each on the test specimen followed by no flaming drips). Although further addition of IFR into the ABS can further increase the LOI, other properties such as the mechanical strength and processability of the ABS composites would need to be sacrificed. Meanwhile, the effect of APP and expandable graphite on the flame retardancy of ABS was studied by Ge, et al. (2012). From the LOI test, it was confirmed that pure ABS is an easily flammable polymer with LOI of only 19 %. The LOI values of ABS added with 15 wt% APP alone and 15 wt% expandable graphite alone were shown to be 21.5 % and 26.0 % respectively, indicating that expandable graphite is more efficient in improving the LOI of ABS. Through the combination of APP and expandable graphite into the ABS, the LOI values have been increased remarkably above 26.0 % with a maximum of 31.0 % achieved when the ratio of APP to expandable graphite was 1:3. In spite of that, it was established that further increase of the APP content would worsen the LOI of the ABS composites.

### **2.3.2 Polyamide**

Polyamide, or generally known as nylon, is a long chain fiber-forming substance with recurring amide groups. It is often applied in monofilaments and yarns in the form of fibers. Over the years, polyamide was chosen as the

material of construction in the textile, transportation and automotive industries due to its excellent mechanical properties at high temperatures, good chemical resistance, low permeability to gases and high wear and abrasion resistance (Yang, Ou and Yu, 1998; Wu, et al., 2001). Until now, there have been a number of commercially available types of polyamide such as nylon-4,6, nylon-6,10, nylon-6,12 and nylon-11 with nylon-6 and nylon-6,6 being the most widely used (Chavarria and Paul, 2004; Hedicke, et al., 2006). Li, et al. (2009) have conducted tensile test on the nylon-6,6 fabric treated with IFR system made up of APP, melamine and PER. From their study, it was confirmed that the tensile strength of untreated nylon-6,6 fabric was 190.1 MPa with elongation at break of 26 %. When treated with IFR system containing APP, the tensile strength was found to reduce to only 149.5 MPa although the elongation at break increased to 28.3 %. This can be attributed to the breaking of fibers in nylon-6,6 when the fabric was dipped into the flame retardant solution and passed through the padder with two dips and nips. Furthermore, the high temperature of 135 °C employed during the preparation of the treated nylon-6,6 was believed to be another factor contributing to the decrease in tensile strength of the final polymer (Ou, Han and Zhao, 2006). In fact, as proved by Levchik, et al. (1995), the loading of halogen-free flame retardants need to be limited as they would cause unfavourable decrease in the mechanical properties of the polyamide materials. Other than mechanical properties, the microstructures of the untreated and treated nylon-6,6 was also characterized by Li, et al. (2009) and given in Figure 2.6. From the SEM micrograph, untreated nylon-6,6 gives a rather flat and smooth surface compared with other treated nylon-6,6 samples. For the case of nylon-6,6

treated with APP, the char residue showed some micro-convexities on its surface because of the formation of char promoted by the APP. On the other hand, nylon-6,6 treated with APP and melamine displayed a frothy structure contributed by the decomposition of melamine that released gas, whereas nylon-6,6 treated with APP and PER exhibited a continuous and thick structure of char residue due to the char formation effect with PER as the char source. Lastly, when nylon-6,6 was treated with APP, melamine and PER, a typical intumescent char structure was generated which is fairly frothy and swollen. The char formed on the surface was said to be effective in preventing the nylon-6,6 from contacting the flame and controlling the release of fuel gas (Aiyong, 2001; Horrocks and Zhang, 2004). Besides that, the intumescent char layer was able to support the melted nylon-6,6 so as to avoid dripping phenomenon during combustion process.



**Figure 2.6 SEM micrograph of char residues for (a) untreated nylon-6,6, (b) nylon-6,6 treated with APP, (c) nylon-6,6 treated with APP and melamine, (d) nylon-6,6 treated with APP and PER, (e) nylon-6,6 treated with APP, melamine and PER (Li, et al., 2009)**

The LOI of polyamide 6 or nylon-6 added with APP and other additives have been studied by different researchers in the past few decades. For instance, Levchik, Costa and Camino (1992) have discovered that an increase in LOI was observed when the APP content was over 30 wt%. Nevertheless, intumescent char layer could still form on the surface of the nylon-6 composites even in the presence of APP as little as 10 wt%. However,

the char layer with lower APP content was predicted to be not continuous and susceptible to flow and drip. This finding was later confirmed again by the same author when they found out that the intumescent char layer was produced only at the edges of the top specimen surface with higher tendency to flow and exposing the underlying nylon-6 polymer to the flame (Levchik, et al., 1995). By increasing the APP content to the range of 40 and 50 wt%, the LOI of the composites has been elevated tremendously to a maximum of about 50 %. In addition, it was suggested that progressive replacement of APP with fillers such as talc would results in an initial improvement of the fire retardancy of nylon-6 (Horrocks and Zhang, 2004). The improvement can be related to the formation of a protective viscous char which tends to stick to the surface of the polymeric material rather than flowing away as in the case of nylon-6/APP composites without the addition of filler. Furthermore, it was emphasized that substitution of as low as 1.8 wt% of APP with manganese dioxide in the nylon-6 composite would prevent the flowing of intumescent char and increased the LOI from 25% to 37% (Levchik, et al., 1996). The optimum synergistic effect was achieved when the mixtures of APP and manganese dioxide was used in the ratio of 6:1.

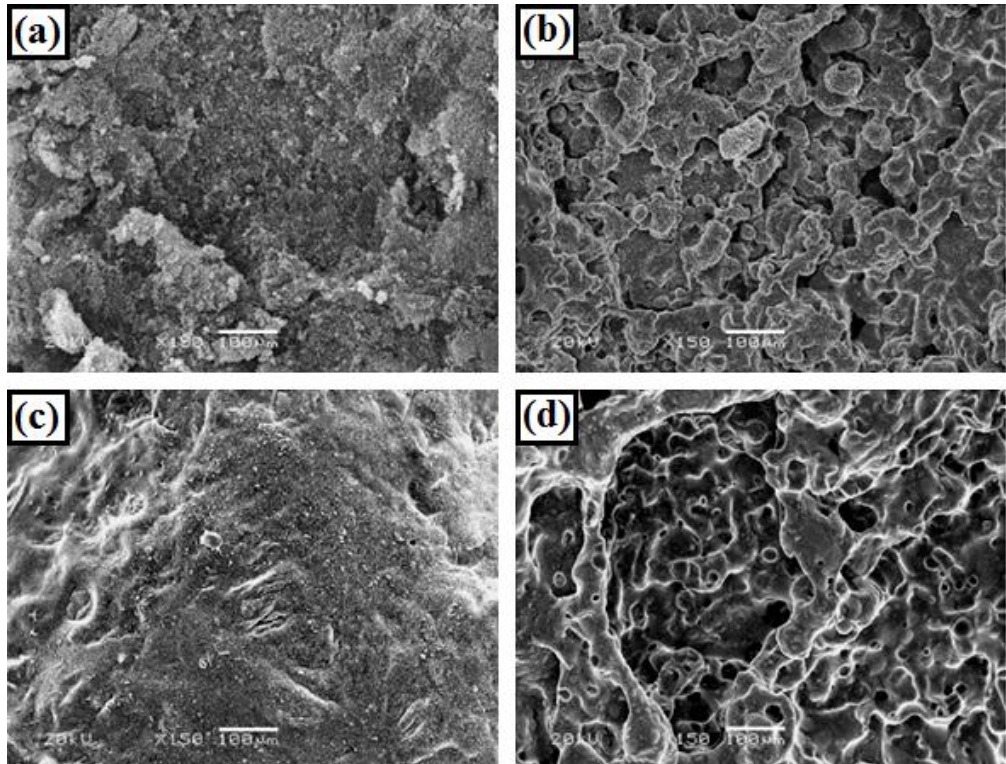
### **2.3.3 Poly(vinyl alcohol)**

Poly(vinyl alcohol) (PVOH) is a type of unique synthetic polymer as it cannot be prepared though the conventional polymerization of the corresponding vinyl alcohol monomers. Instead, it is prepared by first polymerizing vinyl acetate followed by the subsequent conversion of the

polyvinyl acetate into PVOH (Li, Wang and Wu, 2001; Pardoe, et al., 2001). Generally, PVOH possesses high tensile strength and flexibility that rely on the humidity. In another words, higher humidity is resulted when more water is being absorbed into the PVOH and this would cause the reduction in tensile strength (Lankveld and Lyklema, 1972; Kobayashi, Toguchida and Oka, 2003). With the advantage of being highly resistant to oil, grease and solvents, PVOH is mostly applied in textiles, paper making and coating industries. Not long ago, Zhao, et al. (2008) have verified the mechanical properties of PVOH mixed with flame retardant system consist of APP and 0.3 wt% of LDH. The types of LDH used were mainly composed of different combinations of metals such as zinc, aluminium, nickel and iron. From their research, it was revealed that addition of APP alone resulted in the decline of the mechanical properties in terms of tensile strength, elongation at break and tensile modulus. In particular, significant decrease was observed in the tensile strength as it decreased from 75.0 MPa to a remaining value of 33.0 MPa when 15 wt% of APP was added. In order to enhance the mechanical properties of PVOH without abandoning the APP (since it is crucial in increasing the flame retardancy of PVOH), suitable amount of LDH can be incorporated. As shown by the authors, overall mechanical performance of the PVOH composites has been increased when 0.3 wt% of LDH was added. Combination of nickel and aluminium in LDH was found to be the most effective in enhancing the mechanical properties of PVOH/APP composites. It was predicted that there exist a physical cross-linking network composed of layered particles, APP molecules and PVOH polymer chains in the composites. This physical cross-linking effect was believed to improve the mechanical properties and delay the

thermal decomposition of organic-additive/polymer or neat polymer (Qin, et al., 2005; Qiu, Chen and Qu, 2006).

From the perspective of surface morphologies, Zhao, et al. (2008) have performed SEM analysis on the char residue of PVOH/APP composites and PVOH/APP added with different types of LDH. Based on Figure 2.7, it can be seen that the outer surface of PVOH/APP char showed a fluffy and puffy morphology while the inner surface showed a rather restricted expansion. For the case of PVOH/APP added with nickel-aluminium type of LDH, continuous and compact outer surface was seen together with the swollen inner structure. This morphology was demonstrated to be able to hinder the heat and mass transfer besides than the ability to obstruct flammable gases from entering the surface of composite during fire. As quoted from Liang, Shi and Gong (2005), the outer surface of the charred layer ought to be compact enough to prevent the penetration of gases and to cut off the oxygen from the degraded volatiles more efficiently. Thus, it was implied that the char of PVOH/APP could not isolate flame, combustion-supporting and flammable gases from the inner polymeric material due to the lack of compact outer surface. On the contrary, LDH functions in catalyzing the polyphosphate or the phosphate to cross-link with PVOH during combustion to form expansion charred layer with close outer surface which is helpful in protecting and insulating the underlying polymeric materials from further pyrolysis and burning.



**Figure 2.7 SEM micrograph of char residues for (a) outer surface of PVOH/APP (b) inner surface of PVOH/APP, (c) outer surface of PVOH/APP added with nickel-aluminium LDH, (d) inner surface of PVOH/APP added with nickel-aluminium LDH (Zhao, et al., 2008)**

Lin, et al. (2011) have explored the flame retardancy of PVOH through the addition of APP. Not only this, they have further inspected the effect of MMT towards the mechanical and thermal properties of PVOH and APP composites. According to their study, the LOI for pure PVOH was 19.7 % while the incorporation of 15 wt% of APP increased the LOI to 27.9 % although a V-0 rating was still unable to achieve. To increase the flame retardancy of PVOH/APP to a greater extent, small loading of MMT can be applied. It has been declared that LOI values increased gradually with the amount of MMT in the composites up to a maximum of 30.8 %. However, the LOI values of PVOH/APP/MMT composites were reduced when the weight ratio of APP to MMT was lower than 20:1. Therefore, it was concluded that



optimum synergistic effect was achieved at APP:MMT of 20:1. No visible dripping occurred during the UL-94 test and the burning of composites specimen ceased within 10 seconds after two applications of flame with 10 seconds each on the test specimen. Furthermore, it has been proven by Wang, et al. (2007) that ammonium salt of 2-hydroxyl-5,5-dimethyl-2,2-oxo-1,3,2-dioxaphosphorinane was able to improve the flame retardancy of PVOH in combination of APP and nickel chelate. The optimum formulation of the IFR used in PVOH composites was found to be: 7 wt% APP, 0.5 wt% nickel chelate and 7.5 wt% 2-hydroxyl-5,5-dimethyl-2,2-oxo-1,3,2-dioxaphosphorinane. With the formulation, LOI as high as 34.2 % was obtained.

#### **2.4 Electron Beam Irradiation**

The application of high energy irradiation such as the electron beam to modify the properties of polymer compound has been the topic of studies for different researchers in the past few decades. By introducing electron beam irradiation, cross-linking of polymer chains in the blends can be triggered. It is crucial to note that although the employment of electron beam irradiation could potentially enhance the mechanical properties of polymer blends, the irradiation dosage applied must be controlled and kept at optimum level to prevent excessive and over cross-linking of polymer blends, causing the blends to become brittle. As shown by Dalai and Wenxiu (2002), irradiation on LDPE/EVA blends has improved the tensile strength which made it to be widely used in heat shrinkable materials for wire and cable insulation. Besides

that, for blends of polylactic acid (PLA) and LDPE, it was concluded that the sizes of all PLA/LDPE crystalline structure were greatly increased with irradiation dosage up to 100 kGy, implying a good interaction between the recently formed crystalline structures and the original crystalline structures (Bee, et al., 2014).

The effect of cross-linking density on some properties of electron beam irradiated styrene-butadiene rubber (SBR) has been studied (Wang, Wang and Cheng, 2009). It was concluded that both radiation sensitizer loading and electron beam irradiation dosage play vital roles in the determining the cross-linking density of SBR. The cross-linking density of SBR was found to increase with irradiation and later decrease upon reaching optimum dosage of 150 kGy. The increased cross-linking density of SBR has shown to have higher tensile strength, elongation at break and thermal stability. On the other hand, as shown by Youssef (2009), electron beam irradiation is proven to be a suitable mean of inducing curing to polycarbonate (PC) and acrylonitrile butadiene rubber (NBR) blends up to dosage of 150 kGy. It was also concluded that enhancement of tensile properties and hardness could be attained after curing of PC/NBR blends through irradiation with respect to blank NBR.

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Materials**

The polymeric materials used in this project were polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) supplied by Toray Plastic (Malaysia) Sdn Bhd. The used flame retardant was ammonium polyphosphate (APP) with nitrogen content of about 14 % and more than 200 % degree of polymerization. Montmorillonite (MMT) with grade of Nanomer 1.3P was purchased from Nanocor, Arlington Height and used as reinforcing filler in this study. Methyl ethyl ketone (MEK) solution with concentration of about 40 % was used as solvent in gel content test of the polymer blends.

#### **3.2 Formulation of PC/ABS Blends**

Table 3.1 shows the formulation of PC/ABS blends with different loading levels of APP and MMT.

**Table 3.1: Formulation of PC/ABS Blends with Different Loading Levels**

PC (phr)	ABS (phr)	APP (phr)	MMT (phr)
50	50	0	0
			2
			4
			6
			8
50	50	10	0
			2
			4
			6
			8
50	50	15	0
			2
			4
			6
			8
50	50	20	0
			2
			4
			6
			8
50	50	25	0
			2
			4
			6
			8

### 3.3 Sample Preparation

During blending process, PC/ABS blends added with different loading levels of APP and MMT as shown in Table 3.1 were prepared by using a brabender mixer with model of Brabender<sup>®</sup> Plasti-Corder<sup>®</sup> Lab-Station. All zones and die in the mixer were set to 190 °C in order to reach the suitable melt temperature. The rotor speed was set at 50 rpm and the mixing duration was fixed at 10 minutes.

After the blending, all the flame retarded PC/ABS blends were compression moulded into a 150 mm × 150 mm plate with thickness of 1 mm

by using a L5-11009 hot press machine from Lotus Scientific. The temperature used was 170 °C. Pneumatic specimen press with model of QC-603A by Comotech was used to cut the compression moulded piece into a number of smaller dumbbell shapes. The dumbbell shape specimens were then used for tensile testing purpose.

For impact testing, all the flame retarded PC/ABS blends were compression moulded to sheet with 3 mm in thickness. Vertical band saw of model T-JAW 360 manufactured by T-Jaw Machinery Works Co., Ltd. was used to cut the mould into a number of smaller bars. Notching machine by BeiJing United Test Co., Ltd. with model of ZQK-20 was used to make a notch at the center of the sample bar.

For limiting oxygen index (LOI) testing, sample sheets with 1 mm in thickness from compression moulding process were cut into smaller sample size with dimension of 150 mm × 50 mm × 1mm.

### **3.4 Electron Beam Irradiation of PC/ABS Blends**

All the flame retarded PC/ABS blends were electron beam irradiated at 50 kGy, 100 kGy, 150 kGy, 200 kGy and 250 kGy with dosage of 50 kGy per pass using an IMPELA 10/50 electron beam accelerator. The beam voltage and current chosen was 2 MeV and 5 mA while the speed of the accelerator used was 0.94 m/min.

### **3.5 Testing and Characterization**

#### **3.5.1 Limiting Oxygen Index (LOI) Test**

The LOI test was conducted using an equipment from Rheometer Scientific, United Kingdom following ASTM D2863. This test was used to examine the flame retardancy or flammability of certain materials and substances. To test for the LOI, the specimen with dimension of 150 mm × 50 mm × 1mm was fixed vertically in a transparent test column. Mixture of oxygen and nitrogen was introduced into the column to produce an atmosphere with oxygen and nitrogen. After that, the upper end of the specimen was ignited to observe the subsequent burning behaviour and burning period. The minimum oxygen concentration in which a specimen was just sufficient to sustain burning was determined and denoted as the LOI. The LOI values obtained from the test indicate the minimum oxygen concentration from the mixture of oxygen and nitrogen needed to support or sustain the combustion and burning behaviour of the material. Thus, higher LOI value implies that the sample has a rather high fire retardancy or low flammability.

#### **3.5.2 Tensile Test**

Instron 5582 tensile machine configured with Bluehill<sup>®</sup> software was used to access the tensile strength (maximum tensile stress sustained by a specimen under a tensile test) and elongation at break of the flame retarded PC/ABS blends. This test was conducted by following the ASTM D 638.

Dumbbell-shaped specimens were cut out from the compression moulded sheets and tested under a strain rate of 50 mm/min. Precaution must be taken during the initial stage of tensile testing to ensure that the test specimen was held in a fixed position with minimum slippage relative to the grips. The tensile strength and elongation at break were recorded from the average value of 6 specimens.

### **3.5.3 Izod Impact Test**

Izod impact test was performed in accordance to the ASTM standard D 256. In this test, Izod impact tester with model of XJU-22 manufactured by BeiJing United Test Co., Ltd. was used. Flame retarded PC/ASB sample bars with 3 mm in thickness was cut out from the compression moulded sheets. After that, a notch was made at the centre of the sample bar to act as the stress concentrator. Pendulum-type of hammer which is connected to the impact tester would be used to provide the necessary energy to break the sample bar. The Izod impact test determines the amount of energy per unit area that was absorbed by certain material during fracture.

### **3.5.4 Gel Content Test**

Gel content test was conducted following ASTM D2765 to obtain the degree of cross-linking for flame retarded PC/ABS blends. In this test, samples of flame retarded PC/ABS blends were immersed in methyl ethyl ketone (MEK) and heated at temperature of 80 °C for 24 hours. After the

extraction process, the samples were washed with clean MEK to remove the remaining stain of soluble materials on the surface of the samples. After that, the washed samples were soaked in methanol for about 30 minutes before they were dried in vacuum oven for 3 hours. Finally, the weight of dried PC/ABS samples were measured to obtain the gel content percentage as shown in equation 3.1. Three specimens were used in each formulation of PC/ASB and the average reading was recorded.

$$\text{Gel content percentage (\%)} = \frac{W_f}{W_i} \times 100 \% \quad (3.1)$$

where,

$W_i$  = initial weight of the samples before extraction (g)

$W_f$  = final weight of the dried samples after extraction (g)

### **3.5.5 Scanning Electron Microscopy (SEM)**

The fractured surface of flame retarded PC/ABS blends after tensile test was studied by using S-3400N scanning electron microscope from Hitachi. About 3 mm in length was cut out from the point of fracture before being placed into the sample holder by double-sided sticker. After coating a layer of gold on the surface of the sample, the sample holder was inserted into the microscope chamber to examine the morphology with magnifications of 1000×, 8000× and 15000× respectively.



### **3.5.6 X- Ray Diffraction (XRD)**

XRD test is used to determine the dispersion of a particular material or substance. In this report, X-ray diffractometer of model XRD-6000 equipped with Cu K $\alpha$  generator of 40 kV and 30 mA was employed to study the structure of flame retarded PC/ABS blend samples. A certain length was cut out from the fractured sample after performing tensile testing and attached into the sample holder by double-sided sticker. X-ray beam was irradiated onto the sample surface and the  $2\theta$  scan data were collected at 1.20 degree/min over a range of 0° to 40°.

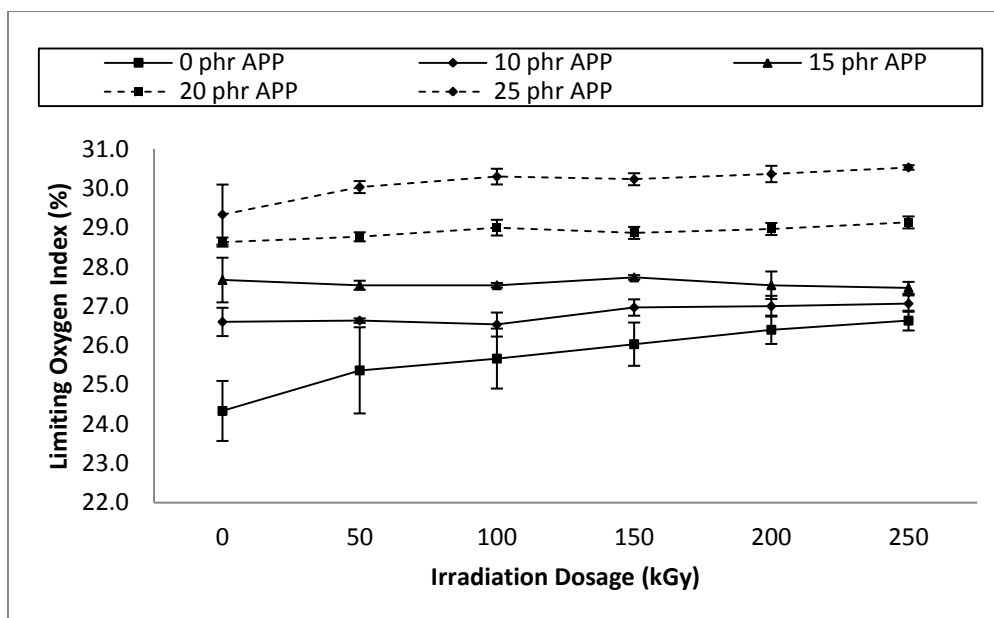
## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Flame Retardancy

##### 4.1.1 Limiting Oxygen Index (LOI)

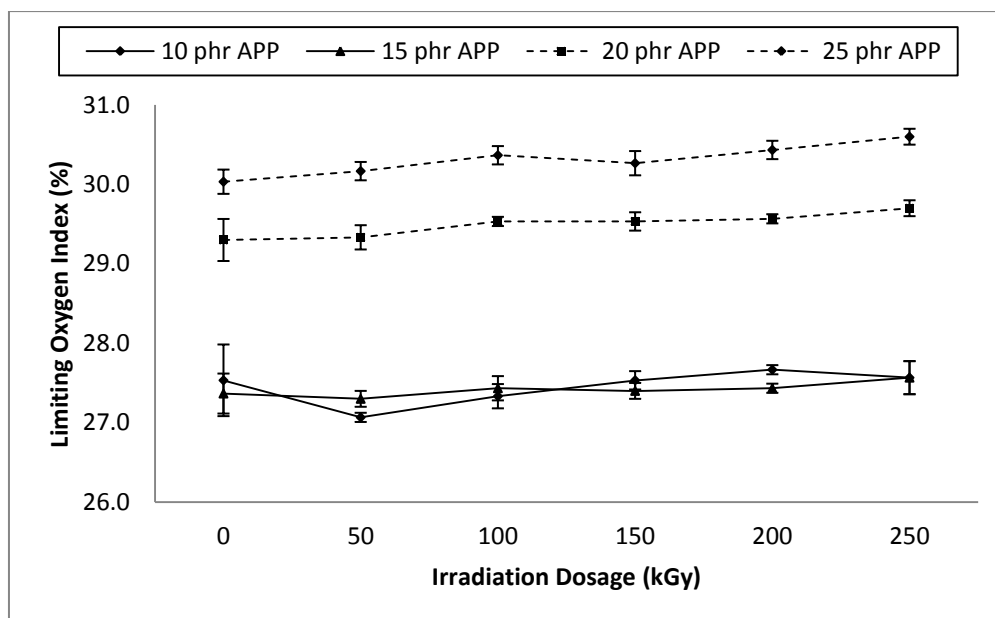
Figure 4.1 shows the effect of APP loading level on LOI of PC/ABS blends when subjected to various irradiation dosages. It can be noticed that the LOI values of the PC/ABS blends increase with the APP loading level. This is in agreement with the study that addition of flame retardant could improve the flame retardancy of polymer blends that give a higher LOI value. Besides that, it can be seen that the LOI values of the PC/ABS blends increase gradually with irradiation dosage. Higher percentage of LOI increment was found in the PC/ABS blend without APP and PC/ABS blend added with 25 phr APP when they were irradiated under 50 kGy. This can be explained by the effect of cross-linking happened in the polymer chains through the electron beam irradiation. With the existence of cross-linking network, the chains of PC and ABS can be bonded together, thereby reducing the melt dripping phenomenon during the combustion process (Szép, et al., 2006). Consequently, the flammability of the PC/ABS polymer blends is retarded and hindered.



**Figure 4.1: The effect of APP loading level on LOI of PC/ABS blends without MMT and subjected to various electron beam irradiation dosages**

For PC/ABS blends added with 2 phr MMT, the LOI profile shows some differences as compared to the previous plot. As depicted in Figure 4.2, the LOI values of the PC/ABS blends with 10 phr and 15 phr APP are relatively lower than those of 20 phr and 25 phr APP added PC/ABS blends. It can be seen that for 10 phr APP added PC/ABS blends, no irradiation and irradiation at higher dosages (150 kGy and 200 kGy) give relatively higher LOI values than 15 phr APP added PC/ABS blends under the same irradiation condition. For non-irradiated 15 phr APP added PC/ABS blend, the poor dispersion of APP and MMT particles in the polymer matrix has resulted in weak interfacial adhesion between the polymer phase of PC and ABS with the APP particles by forming aggregates of APP. In this case, the APP could not function properly as intumescent flame retardant in the polymer blend, thus giving a lower LOI value. On the other hand, for PC/ABS blends added with 15 phr of APP at high irradiation of 150 kGy and 200 kGy, degradation of

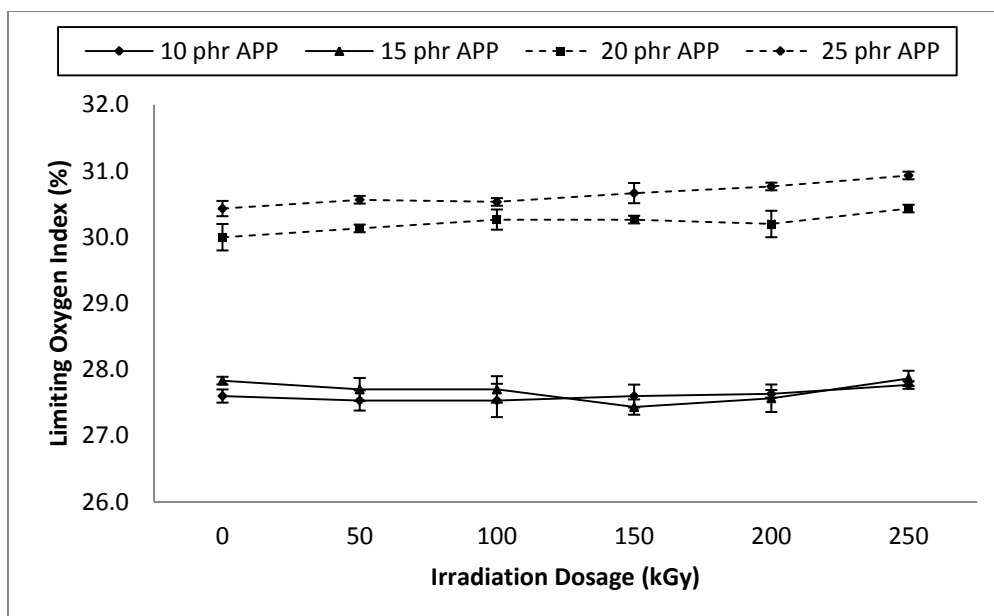
polymer due to the chain scissioning of PC/ABS in the polymer blend has occurred. Therefore, the polymer blend could not sustain the fire or combustion process and fail at preliminary stage when it was under the LOI test.



**Figure 4.2: The effect of APP loading level on LOI of PC/ABS blends added with 2 phr of MMT and subjected to various electron beam irradiation dosages**

Figure 4.3 shows the effect of APP loading level and electron beam irradiation dosage on LOI of 4 phr MMT added PC/ASB blends. It can be seen that the LOI values of PC/ABS blends with 20 phr and 25 phr of APP are relatively higher as compared to the PC/ABS blends with APP loading of 10 phr and 15 phr. This indicates the positive enhancing effect of blending 20 phr and 25 phr of APP into PC/ABS with 4 phr MMT. The APP in the PC/ABS blend is able to function effectively as intumescent flame retardant which is able to form a carbonaceous foam that acts as a barrier to prevent heat, air and pyrolysis product from entering the surface of the material (Camino, Costa and

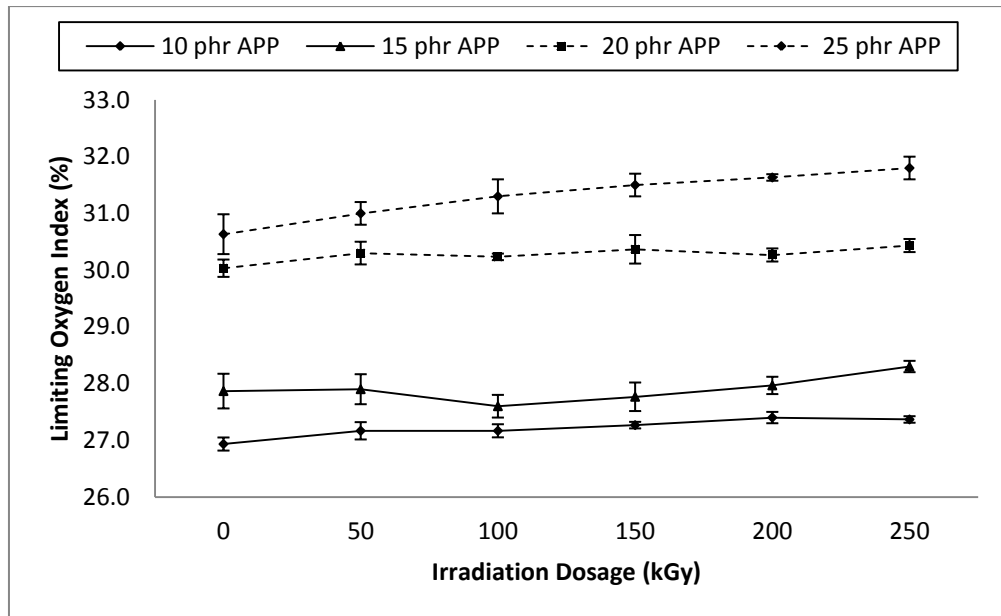
Luda, 1993). As shown by Le Bras, Bourbigot and Revel (1999), the mechanism of APP as intumescent flame retardant is further developed. At first, the intumescence state was started during the combustion process. There was a formation of phosphocarbonaceous structure which trap the polymer chains. Then, the structure was degraded and the polymer chains were evolved. Lastly, a carbonaceous residue was formed. The combustion process ceased when there was no polymer chains left that would act as the fuel to the combustion. Apart from that, it is obvious in Figure 4.3 that PC/ABS blends added with 15 phr of APP exhibits lower LOI values when it was irradiated at 150 kGy and 200 kGy. This is because of a slight degradation caused by higher irradiation dosage that happened in the polymer structure of PC and ABS. Thus, the PC/ABS blends could not sustain for a longer time during combustion as compared to the PC/ABS blends added with 10 phr of APP and irradiated at same dosages of 150 kGy and 200 kGy, resulting a lower LOI value.



**Figure 4.3: The effect of APP loading level on LOI of PC/ABS blends added with 4 phr of MMT and subjected to various electron beam irradiation dosages**

The effect of APP loading and electron beam irradiation on 6 phr MMT added PC/ABS blends is depicted in Figure 4.4. Generally, it is observed that the LOI of the PC/ABS blends increases with increasing of APP loading level and irradiation dosage. However, exception is given to the case of PC/ABS blends added with 15 phr of APP and irradiated at 100 kGy. It is clear to notice that there is a sharp decline of LOI when the irradiation was raised from 50 kGy to 100 kGy. At this stage, the PC/ABS blend is unable to withstand the electron beam irradiation and experienced premature degradation before it is being cross-linked by the radicals from electron beam (Tseng, et al., 2001). Hence, the flame retardancy of the PC/ABS blend is hindered and a lower LOI value is obtained. Aside from that, it can be observed that application of electron beam irradiation do not impose any huge effect on PC/ABS blends added with 10 phr of APP as the LOI values do not change significantly with increasing irradiation dosage. It can be postulated

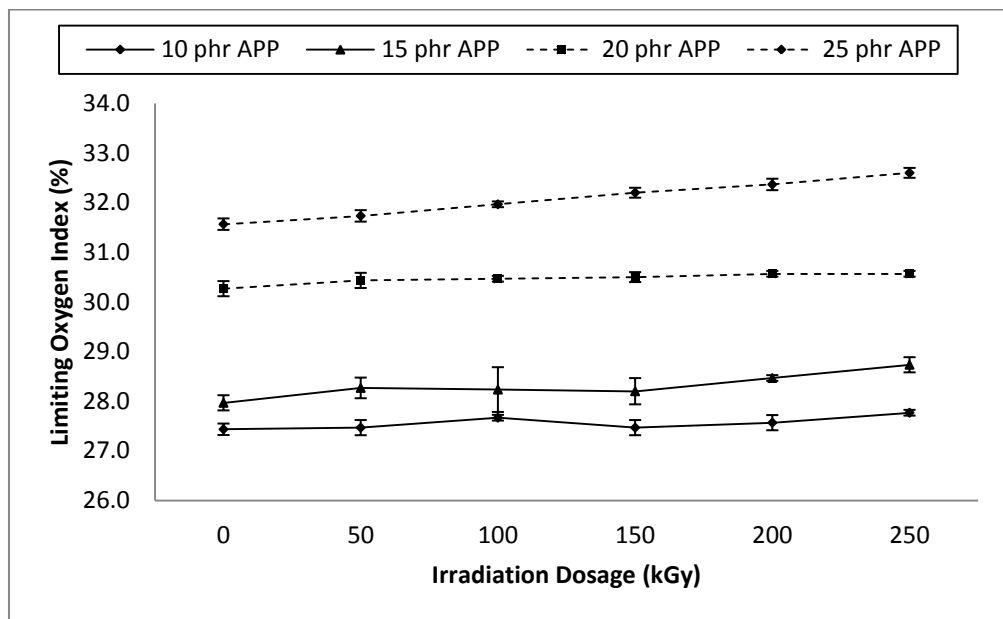
that although the flame retardancy of PC/ABS blends added with 10 phr of APP could not be enhanced through the application of electron beam irradiation, its inherent flame retardancy could stay almost constant without being affected by the adverse effect of irradiation.



**Figure 4.4: The effect of APP loading level on LOI of PC/ABS blends added with 6 phr of MMT and subjected to various electron beam irradiation dosages**

Figure 4.5 demonstrates the effect of APP loading level and electron beam irradiation dosage on the LOI of PC/ASB blends added with 8 phr MMT. It can be seen that the LOI values of PC/ABS blends increase with increasing APP loading and electron beam irradiation dosage. Nevertheless, it is important to note that PC/ABS blends added with 10 phr of APP display some discrepancies as compared to other polymer blends. The LOI value 10 phr APP added PC/ABS blend is found to be higher when it was irradiated at 100 kGy and 250 kGy. Thus, it can be postulated that irradiation dosages of 100 kGy and 250 kGy would be more suitable to be applied on PC/ABS blends

added with 10 phr APP and 8 phr MMT. Suitable choice of irradiation could promote the cross-linking of polymer chains in the PC/ABS blends which could enhance the flame retardancy and flammability when it is subjected to fire. Additionally, it can be seen that PC/ABS blend added with 20 phr APP and 8 phr MMT do not have any significant change in the LOI values when it was subjected to different irradiation dosages. Hence, this PC/ABS blend is able to withstand the application of electron beam irradiation up to higher dosages without any enhancing or deteriorating effect on its flame retardancy.



**Figure 4.5: The effect of APP loading level on LOI of PC/ABS blends added with 8 phr of MMT and subjected to various electron beam irradiation dosages**



## **4.2 Mechanical Properties**

### **4.2.1 Tensile Strength**

The effects of APP loading level and electron beam irradiation dosage on the tensile strength of PC/ABS blends is presented in Figure 4.6 and Figure 4.7. From Figure 4.6 (a), it can be seen that the tensile strength of 10 phr APP added PC/ABS blends decreased significantly regardless of the irradiation dosage. This can be attributed to the addition of APP that has significantly reduced the amount of base polymer (PC and ABS). As a result, the continuity of the polymer matrix has been disrupted. For PC/ABS blend without MMT and irradiation, the tensile strength decreased when 10 phr of APP was added. When 15 phr of APP was used instead, the tensile strength increased by about 13 % from 39.0 MPa to 43.9 MPa. This can be explained by the proper fitting of APP particles into the interface of PC and ABS which leads to the enhanced continuity of the PC/ABS blends. However, as APP loading level continued to increase up to 25 phr, the tensile strength of the PC/ASB blends has showed weakening properties. For the case of PC/ABS blends without MMT and irradiated at 50 kGy, the tensile strength decreased up to 15 phr of APP. Further addition of APP increased the tensile strength relative to 15 phr APP but lower compared to 0 phr APP and 10 phr APP. Based on this observation, it can be concluded that minimum APP loading level of 10 phr would be sufficient to impart certain flame retardancy on the PC/ABS blends without further weakening the tensile strength.

In Figure 4.6 (a), the trend of tensile strength assumed similar patterns for all PC/ABS blends irradiated at 100 kGy, 150 kGy, 200 kGy and 250 kGy. The overall tensile strength of PC/ABS blends without MMT was observed to undergo a gradual decrease when added with 15 phr of APP. The tensile strength of non-irradiated PC/ABS blend added with 15 phr of APP has achieved the highest value while the 15 phr APP added PC/ABS blend has obtained the lowest tensile strength when irradiated to 200 kGy. At this point, severe degradation and chain scission have occurred in the PC/ABS blend (Kalkar, et al., 1992). Besides that, it can be inferred that for 15 phr added PC/ABS blend, application of electron beam irradiation would decrease the tensile strength as the non-irradiated blend has the highest tensile strength among the irradiated blends. On the other hand, when 20 phr of APP was added in the PC/ABS blends, significant increase in tensile strength was observed especially for the case of 200 kGy irradiation. This can be assigned to the successful cross-linking happened in the 20 phr APP added PC/ABS blend induced by electron beam irradiation. However, maximum APP loading of 25 phr reduced the tensile strength of the blends back to the level of PC/ABS blend added with 10 phr of APP. Lastly, it can be seen in Figure 4.6 (a) that the effect of electron beam irradiation is more significant and profound at APP loading level of 15 phr. For PC/ABS blends with other APP loading level, the tensile strength do not differ significantly when different irradiation dosages were employed.

For PC/ABS blends added with 2 phr of MMT irradiated under different dosages, there is some discrepancies exist as compared to the

PC/ABS blends without MMT. As shown in Figure 4.6 (b), the tensile strength of non-irradiated PC/ABS blends added with 2 phr MMT decreases when APP was added up to the loading level of 20 phr. However, when 25 phr of APP was used in the PC/ABS blend, highest tensile strength was achieved. This is due to the excellent dispersion of 25 phr APP and 2 phr MMT in the PC/ABS blends that gives a rather continuous structure with good interfacial adhesion between the APP and MMT particles to the PC/ABS polymer matrix. For flame retarded PC/ABS blend added with 2 phr of MMT and irradiated at 50 kGy, the tensile strength decreases when APP increased from 10 phr to 15 phr. In fact, this situation happened for every PC/ABS blends added with 15 phr of APP and 2 phr of MMT regardless the irradiation dosage. The increment of APP amount has reduced the main polymer base of PC and ABS which is responsible for the high tensile strength of the blends. Hence, the combination of 15 phr APP and 2 phr MMT was not suitable in increasing the tensile strength even with the application of electron beam irradiation. Moreover, the effect of irradiation dosage was most significant when PC/ABS blends was added with 20 phr APP and 2 phr MMT. By introducing electron beam irradiation, all the tensile strength of all irradiated PC/ABS blends recorded were higher than non-irradiated PC/ABS blends. This suggests that cross-linking induced by irradiation happened in PC/ABS blends with 20 phr APP and 2 phr MMT at all irradiation dosages from 50 kGy to 250 kGy (Rivaton, Sallet and Lemaire, 1983; Bee, et al., 2014). Apart from that, by referring to PC/ABS blends added with 25 phr APP and 2 phr MMT, it can be observed that the tensile strength decreases when irradiation was applied into the blends. Hence, it can be implied that application of electron beam irradiation is

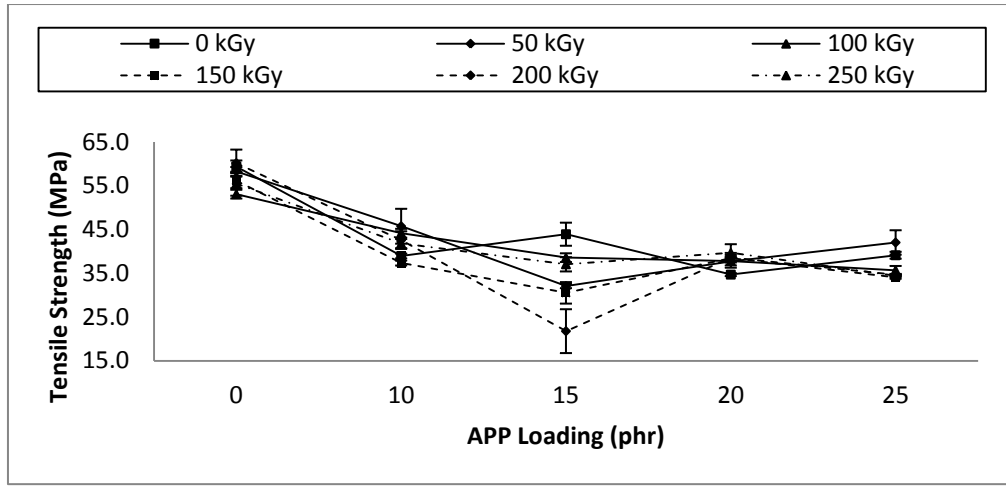
detrimental when it was used in PC/ABS blends with 25 phr APP and 2 phr MMT.

Figure 4.6 (c) shows the tensile strength profile for PC/ABS blends added with 4 phr of MMT under different APP loading level and irradiation dosages. It can be seen that the tensile strength profiles for PC/ABS blends at irradiation of 0 kGy, 150 kGy, 200 kGy and 250 kGy reported the same trend. Incorporation of 25 phr APP and 4 phr MMT into PC/ABS blends has achieved the highest tensile strength. This shows that combination of 25 phr APP and 4 phr MMT resulted in a homogeneous dispersion in the PC/ABS blends. Besides that, intercalation of PC/ABS polymers into the MMT layers has occurred as well. On the other hand, it is revealed in Figure 4.6 (c) that the effect of electron beam irradiation is more noticeable when 10 phr and 15 phr of APP was added in PC/ABS blends. For 10 phr APP added PC/ABS blends, irradiation of 50 kGy and 100 kGy have enhanced the tensile strength, while irradiation of 250 kGy has decreased the tensile strength of the blends. For 15 phr APP added PC/ABS blends, irradiation of 250 kGy gave the highest tensile strength while 100 kGy gave the lowest tensile strength. Therefore, it can be stipulated that application of electron beam irradiation is highly dependent on the loading level of APP when 4 phr of MMT is added in the PC/ABS blends. For PC/ABS blends added with 20 phr and 25 phr APP, application of irradiation gave almost similar tensile strength values except for the case of 150 kGy.

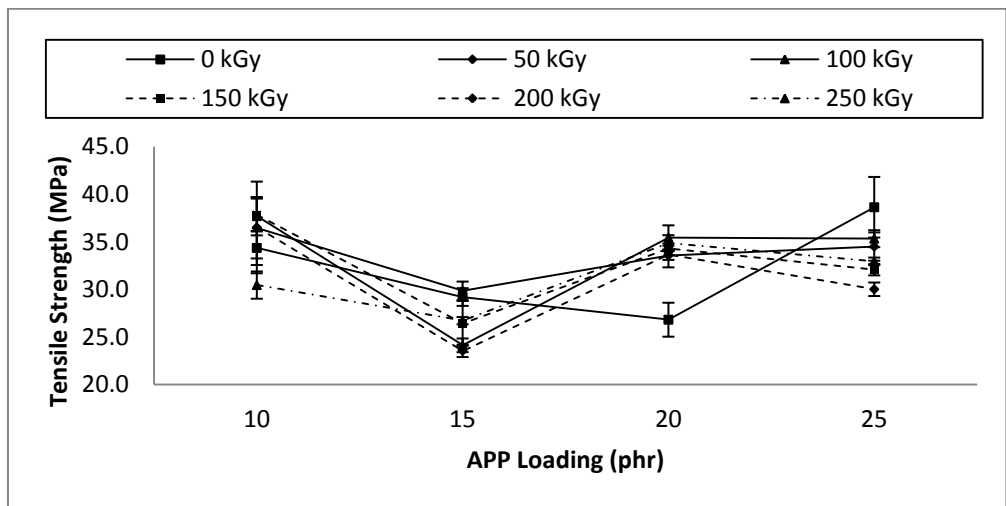
The tensile strength graph of PC/ABS blends added with 6 phr MMT at different APP loading level and irradiation dosages is given in Figure 4.7 (a). It is noted that all the PC/ABS blends are having similar pattern of tensile strength curve for all irradiation range except 250 kGy. For PC/ABS blends added with 6 phr MMT and irradiated at 250 kGy, direct upward trend of tensile strength was observed. Highest tensile strength was obtained when 25 phr APP was added into the PC/ABS blends. Hence, increasing APP loading could increase the tensile strength when the PC/ABS blends added with 6 phr MMT was irradiated at 250 kGy. As confirmed by Acierno, et al. (1980), the high irradiation dosage works well with the combination of 6 phr MMT in flame retarded PC/ABS blends that helps in forming cross-linking network inside the polymer chains of the blend.

Figure 4.7 (b) shows the plot of tensile strength against APP loading for PC/ABS blends added with 8 phr MMT under different irradiation dosages. It can be seen that for APP loading of 15 phr and 20 phr, highest tensile strength was resulted when irradiation dosage of 250 kGy was used. Thus, it is implied that for PC/ABS blends added with 15 phr and 20 phr APP combined with 8 phr MMT, 250 kGy is chosen over other irradiation dosages in order to improve the tensile strength. Application of high electron beam irradiation has triggered proper cross-linking in the PC/ABS blends. In addition, it can be observed that flame retarded PC/ABS blends added with 8 phr MMT and irradiated at 100 kGy gave an increasing upward trend of tensile strength when the APP loading is increased. Nevertheless, for APP loading of 20 phr and 25 phr, irradiation of 100 kGy results in almost similar tensile strength although

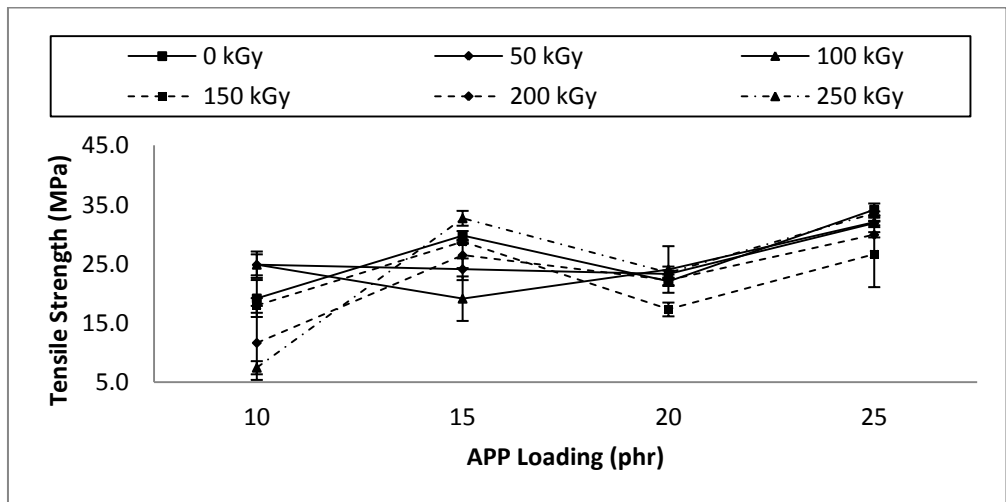
slight increment is obtained. Thus, it is implied that increasing APP loading from 20 phr to 25 phr APP does not help very much in enhancing the tensile strength when PC/ABS blend was added with 8 phr MMT and irradiated at 100 kGy.



(a)

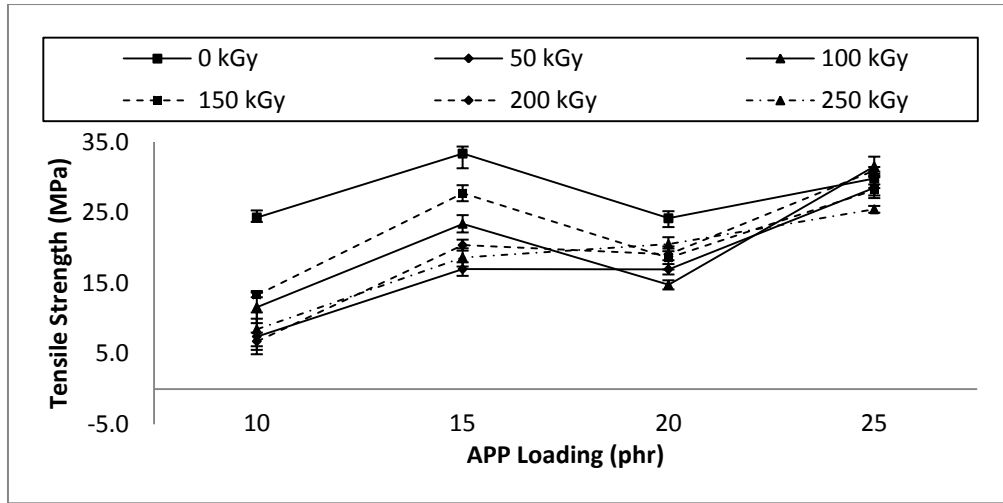


(b)

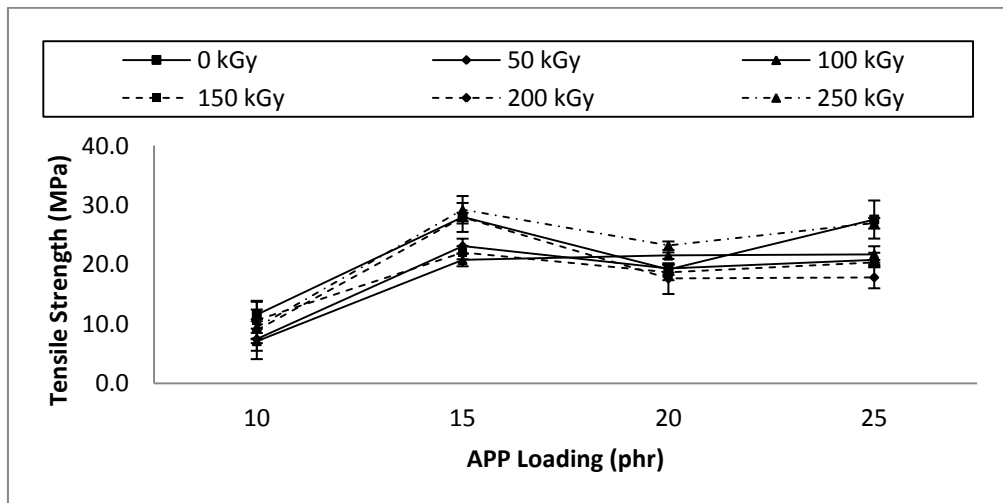


(c)

**Figure 4.6: Effect of APP loading level on tensile strength of PC/ABS blends (a) without MMT, (b) added with 2 phr MMT, (c) added with 4 phr MMT under different irradiation dosages**



(a)



(b)

**Figure 4.7: Effect of APP loading level on tensile strength of PC/ABS blends (a) added with 6 phr MMT, (b) added with 8 phr MMT under different irradiation dosages**

To examine the effects of MMT loading level and electron beam irradiation dosage on the tensile strength of the PC/ABS blends, tensile strength was plotted against the MMT loading by fixing the amount of APP. Based on Figure 4.8 (a), it is demonstrated that PC/ABS blends irradiated at 50 kGy and 200 kGy display similar trend of tensile strength. At first, the tensile strength for both 50 kGy and 200 kGy irradiated PC/ABS blends decreases with increasing MMT loading level up to 6 phr. This can be



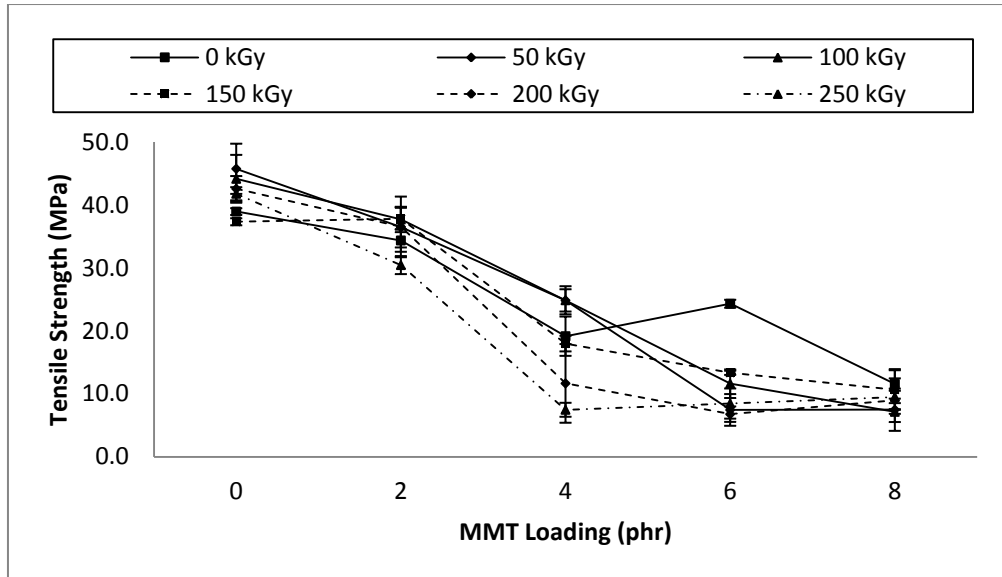
attributed to the poor interfacial adhesion between the PC/ABS polymer matrix with MMT, which is further deteriorated by the application of electron beam irradiation (Meri, et al., 2015). In addition, it can be seen that MMT loading of 2 phr has decreased the tensile strength when compared to PC/ABS blend without MMT. This applies for all the irradiation dosages except for the case of 150 kGy where PC/ABS blend experienced a slight increase in tensile strength when the MMT loading increased from 0 phr to 2 phr. Thus, in this scenario, it is presumed that addition of 2 phr MMT in the PC/ABS blend has reduced the tensile strength when irradiation dosages other than 150 kGy was used. At this stage, agglomeration of MMT has occurred in the PC/ABS polymer matrix.

Figure 4.8 (b) illustrates the tensile strength profile for PC/ABS blends added with 15 phr APP under different MMT loading level and irradiation dosages. It can be observed that when MMT loading increased from 0 phr to 2 phr, the tensile strength for all irradiation dosages decreased with the exception of 200 kGy. In fact, for PC/ABS blends added with 15 phr of APP and irradiated at 200 kGy, the tensile strength increases with MMT loading up to 4 phr. After that, the blend experienced a minor decrease in tensile strength when added with 6 phr of MMT before it achieved the highest tensile strength of 28.0 MPa with MMT addition of 8 phr. Hence, it can be concluded that under the same irradiation dosage of 200 kGy, highest tensile strength can be achieved when PC/ABS blend was added with 15 phr APP and 8 phr MMT. Excellent intercalation of polymers (PC and ABS) into the MMT layers and successful cross-linking induced by electron beam irradiation are the factors

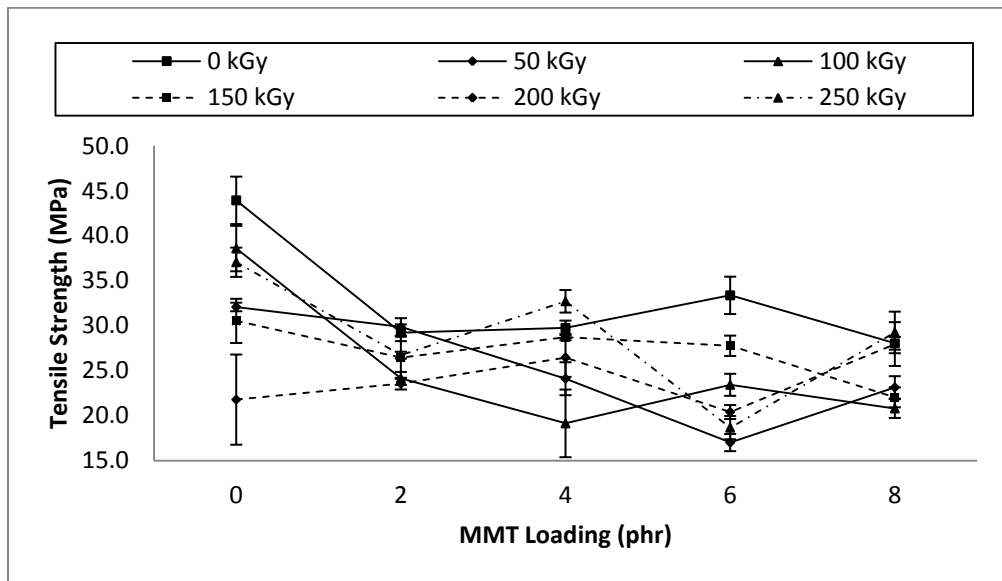
behind the enhanced tensile strength (Wang, et al., 2003). Furthermore, for both flame retarded PC/ABS blends without MMT addition and added with 6 phr of MMT, it can be noticed that all electron beam irradiation dosages has significantly reduced the tensile strength of the blends. It is inferred that application of electron beam irradiation is not suitable for PC/ABS blends without MMT and added with 6 phr MMT. This might be due to the poor blending of PC/ABS blends with the APP and MMT particles that lead to premature degradation of the polymer chains when the blend was subjected to electron beam irradiation.

The tensile strength profile for PC/ABS blends added with 20 phr APP under different MMT loading and irradiation dosages is depicted in Figure 4.9 (a). It is reported that electron beam irradiation did improve the tensile strength of 20 phr APP added PC/ABS blend when it is blended with 0 phr MMT and 2 phr MMT respectively. Homogenous blending of PC/ABS blends with the APP and MMT components is the reason behind this observation. As a result, the excellent interfacial adhesion between the polymer phase and the particles (APP and MMT) could be further enhanced through cross-linking prompted by electron beam irradiation. On the other hand, for PC/ABS blends added with 20 phr APP and 6 phr MMT, irradiation at all dosages has weakened the tensile strength of the blends. Therefore, it is anticipated that electron beam irradiation is helpful in strengthening PC/ABS blend when it is added with 20 phr APP accompanied by no MMT or minimum MMT addition of 2 phr. Cross-linking would favour MMT loading of 0 phr and 2 phr instead of 6 phr.

Figure 4.9 (b) shows the tensile strength profile of PC/ABS blends added with 25 phr APP under different loading level of MMT and electron beam irradiation dosages. It can be seen that non-irradiated PC/ABS blends and PC/ABS blends irradiated at 50 kGy and 100 kGy have the same declining trend of tensile strength with MMT loading up to 8 phr. The declining tensile strength of the PC/ABS blends can be attributed to the agglomeration of high MMT amount in the polymer structure. Consequently, the effective interfacial adhesion between the polymer (PC and ABS) and the particles (APP and MMT) has decreased drastically, leading to lowest tensile strength as low stress is needed to break the PC/ABS blends. Apart from that, for PC/ABS blends added with 25 phr APP under irradiation dosages of 150 kGy and 200 kGy, identical trend of tensile strength was obtained. The tensile strength was found to be decreasing with the MMT loading up to 4 phr before it was increased relatively again in MMT addition of 6 phr. Maximum MMT loading of 8 phr into the blends resulted in the lowest tensile strength for both of the irradiation dosages. Consequently, it is deduced that PC/ABS blends without MMT addition would give the optimum mechanical properties in terms of tensile strength. If addition of MMT is inevitable, low MMT loading of 2 phr is used to alleviate the further weakening of tensile strength.

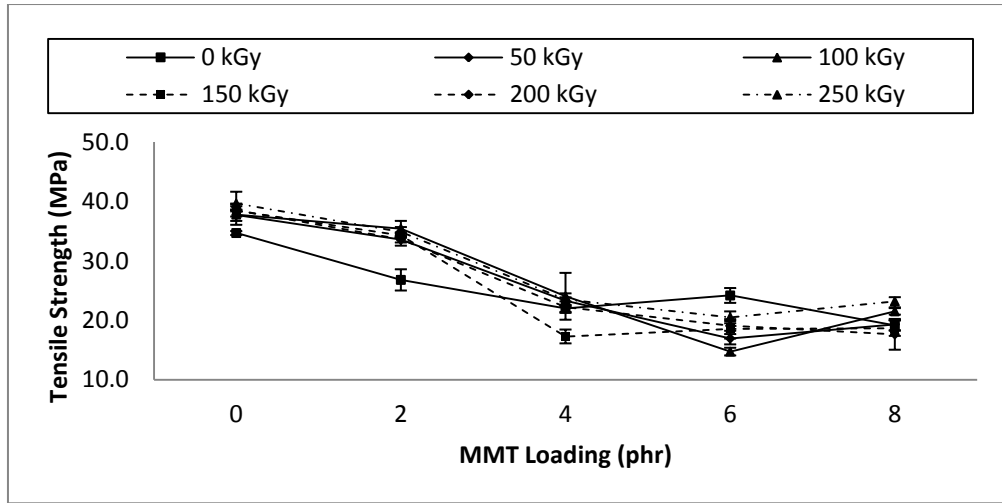


(a)

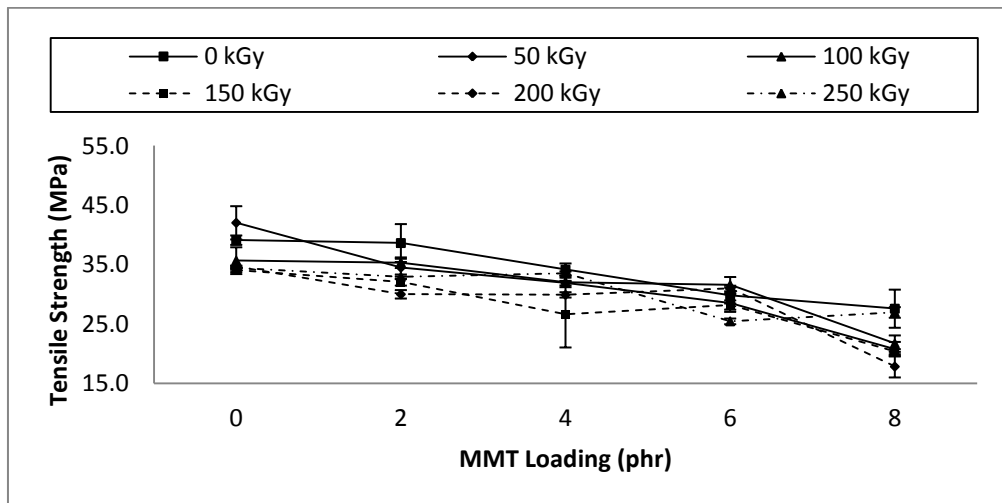


(b)

**Figure 4.8: Effect of MMT loading level on tensile strength of PC/ABS blends (a) added with 10 phr APP, (b) added with 15 phr APP under different irradiation dosages**



(a)



(b)

**Figure 4.9: Effect of MMT loading level on tensile strength of PC/ABS blends (a) added with 20 phr APP, (b) added with 25 phr APP under different irradiation dosages**

#### 4.2.2 Elongation at Break

When the test specimen subjected to tension finally ruptures or breaks, the final value of the percentage of elongation is termed the elongation at break. Generally, elastic material has a higher value of elongation at break while brittle material has a lower value.

The effect of increasing APP loading level and irradiation dosage on the elongation at break of PC/ABS blends were plotted in Figure 4.10 and Figure 4.11. From Figure 4.10 (a), it can be seen that the elongation at break of unfilled PC/ABS blends recorded the highest values for most irradiation ranges. The overall elongation at break values of the PC/ABS blends with APP loading ranging from 10 phr to 25 phr are comparatively low. This is in agreement with the general theory that pure PC/ABS without additives has higher elasticity. However, exception is given to the PC/ABS blends added with 10 phr of APP without MMT and irradiated at 50 kGy and 250 kGy. Based on Figure 4.10 (a), it can be observed that the elongation at break of PC/ABS blend filled with 10 phr APP without MMT irradiated at 50 kGy and 250 kGy are higher than their respective blend without the addition of APP. This can be explained by the excellent interfacial adhesion between the APP and the polymer base of PC and ABS that has enhanced the elasticity of the blend. Besides that, cross-linking induced by irradiation has occurred between the polymer chains and strengthen the polymer structure (Acierno, et al., 1981). With a rather strong polymer structure, more stress would need to be applied to elongate and eventually rupture the sample, resulting in a higher elongation at break. Moreover, it is interesting to note that PC/ABS blends irradiated at 100 kGy, 150 kGy and 200 kGy possess the same trend of elongation at break. From the observation, it can be concluded that if addition of APP is necessary in order to enhance the flame retardancy of PC/ABS blends, 10 phr APP is a better alternative over 15 phr, 20 phr and 25 phr to avoid further reduction of elongation at break.

Figure 4.10 (b) shows the elongation at break for PC/ABS blends added with 2 phr MMT under different APP loading and electron beam irradiation. It can be seen that PC/ABS blends irradiated at 150 kGy, 200 kGy and 250 kGy recorded similar pattern of elongation at break. For PC/ABS blends irradiated at 150 kGy and 200 kGy, optimum elongation at break was found when 10 phr APP was added with 2 phr MMT. Thus, it can be verified that minimum incorporation of APP flame retardant and MMT into PC/ABS blends could reduce the further decreasing effect on the mechanical properties of the blend, in particularly the elongation at break. Meanwhile, for 250 kGy irradiated PC/ABS blend, highest elongation at break is reported when the blend was added with 25 phr APP and 2 phr MMT. Thus, when PC/ABS blends were to be irradiated under 250 kGy, maximum APP loading of 25 phr and minimum MMT loading of 2 phr would be more effective to obtain a higher elongation at break. In addition, it can be seen that all the PC/ABS blends added with 15 phr APP and 2 phr MMT exhibit low elongation at break regardless of the irradiation. Lowest values of elongation at break were achieved when 15 phr APP and 2 phr MMT added PC/ABS blends were irradiated under 150 kGy and 200 kGy. This indicates that the application of electron beam irradiation is unable to provide significant effect on the elongation at break of PC/ABS blends added with 15 phr APP.

From Figure 4.10 (c) which shows the elongation at break for PC/ABS blends added with 4 phr MMT under different APP loading and electron beam irradiation, it is obvious that for PC/ABS blends irradiated at 50 kGy, 200 kGy and 250 kGy, increasing profile of elongation at break was obtained along

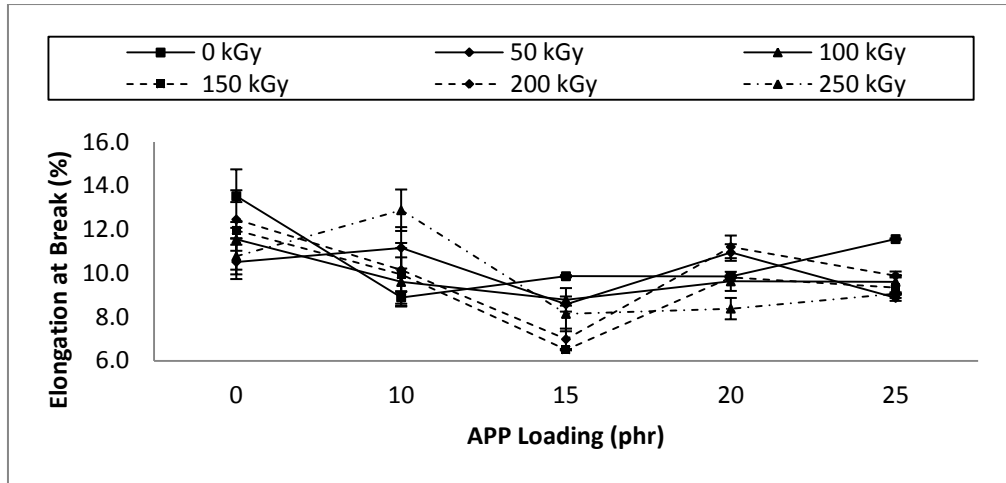
with the increase of APP loading. The enhancement of elasticity of PC/ABS blends can be attributed to the intercalation of PC and ABS into the MMT which is further strengthened by electron beam irradiation. Hence, it can be deduced that 4 phr of MMT and 25 phr of APP is the optimum way of enhancing the elongation of PC/ABS blends when they were to be irradiated at 50 kGy, 200 kGy and 250 kGy.

Figure 4.11 (a) shows the elongation at break plot for PC/ABS blends added with 6 phr MMT under different APP loading and irradiation. From Figure 4.11 (a), the influence of electron beam irradiation seems to be inconsistent for different APP loading. PC/ABS blends irradiated at 150 kGy and 200 kGy was observed to give the similar growing trend of elongation at break with increasing APP loading. However, for non-irradiated PC/ABS blends and PC/ABS blends irradiated to 100 kGy, the elongation at break generally undergoes a severe decrement when APP loading increased from 10 phr to 15 phr. After that, the elongation at break increases in tandem with APP loading up to 25 phr to reach the highest elongation at break values of 8.3 % and 8.2 % respectively. Therefore, it can be deduced that high APP loading of 25 phr would be more preferable for 6 phr MMT added PC/ABS blend without irradiation and 6 phr MMT added PC/ABS blend irradiated at 100 kGy in order to achieve higher elongation at break.

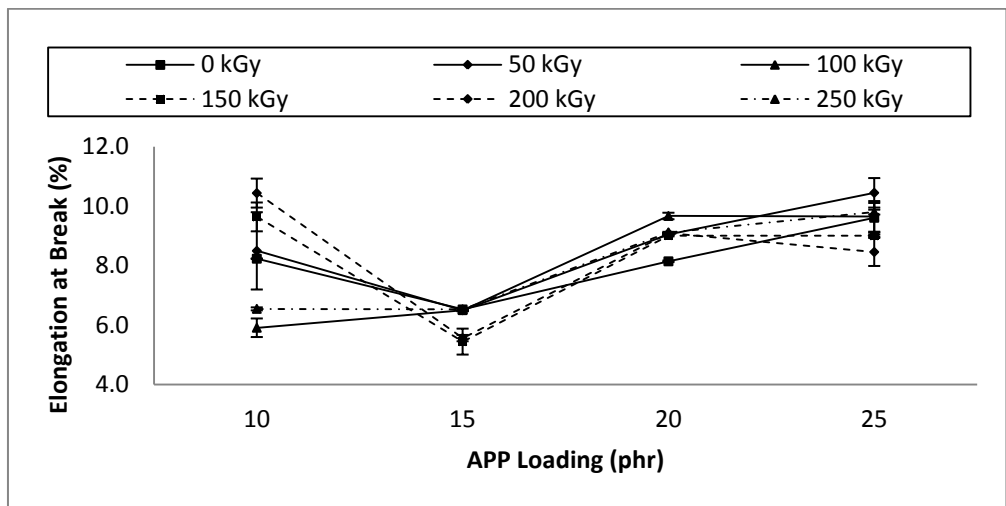
According to Figure 4.11 (b), it is important to note that non-irradiated PC/ABS blends and PC/ABS blends irradiated at 100 kGy, 200 kGy and 250 kGy are having the same pattern of elongation at break. Maximum elongation



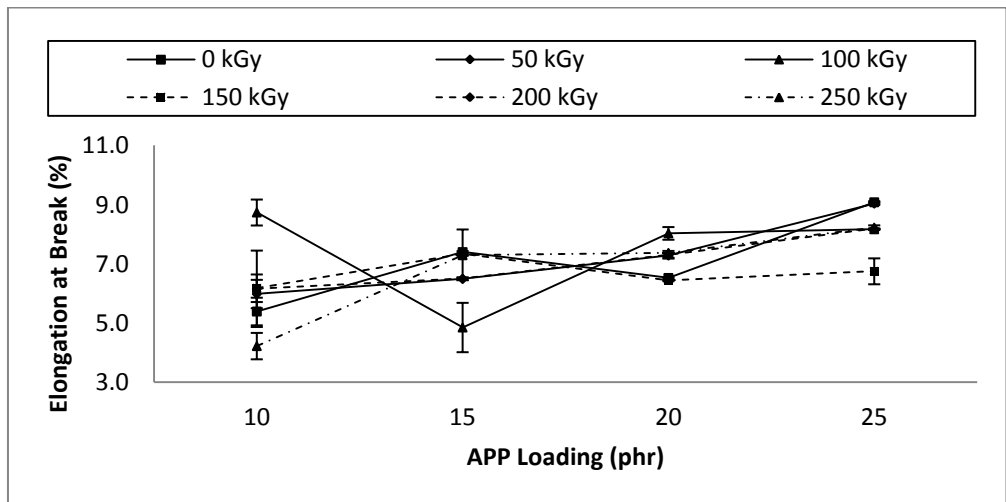
at break was obtained by increasing APP loading from 10 phr to 15 phr. Apart from that, it can be seen in Figure 4.11 (b) that PC/ABS blend added with 15 phr APP and 8 phr MMT obtained the highest elongation at break in all irradiation ranges. This can be explained by the proper selection of MMT and APP loading which lead to positive effect on the elongation of the blend. The orientation of the PC/ABS polymer structure is modified to a certain point where it starts to show elastic behaviour with increment of elongation at break. Besides that, excellent intercalation of polymers into the MMT layers has enhanced the overall strength of the PC/ABS blends added with APP. As a result, the specimens of 15 phr APP and 8 phr MMT added PC/ABS blend can withstand for a longer duration before they finally ruptures, giving a higher elongation at break values.



(a)

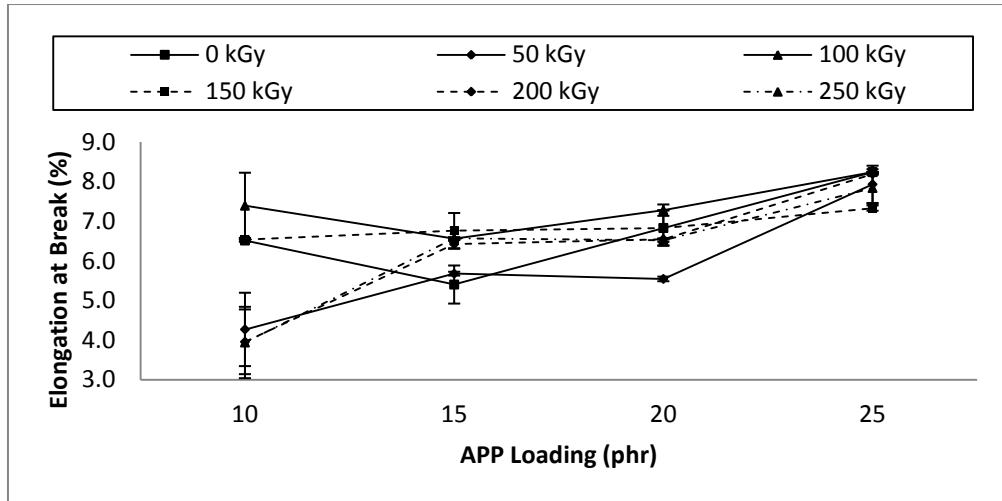


(b)

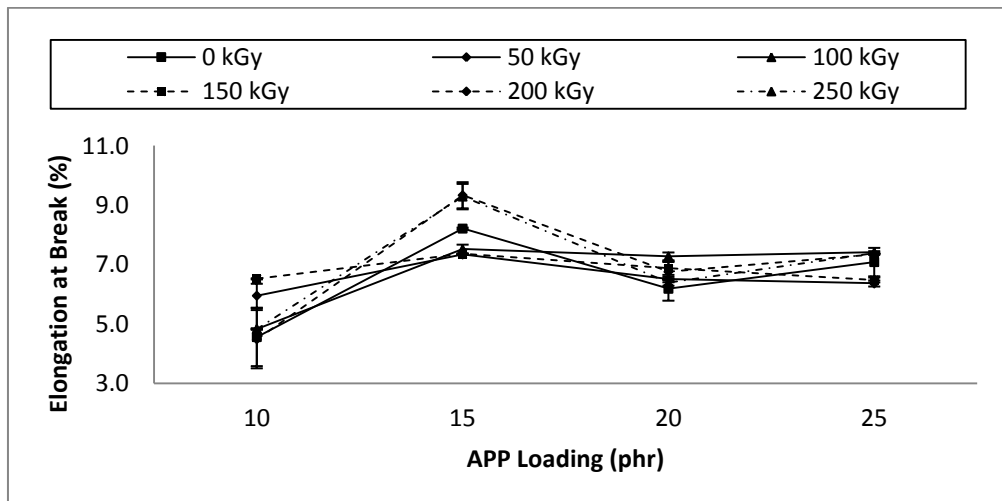


(c)

**Figure 4.10: Effect of APP loading level on elongation at break of PC/ABS blends (a) without MMT, (b) added with 2 phr MMT, (c) added with 4 phr MMT under different irradiation dosages**



(a)



(b)

**Figure 4.11: Effect of APP loading level on elongation at break of PC/ABS blends (a) added with 6 phr MMT, (b) added with 8 phr MMT under different irradiation dosages**

Based on Figure 4.12 (a) which shows the effect of increasing MMT loading and electron beam irradiation on the elongation at break of PC/ABS blends, several observations can be made. First, for 10 phr APP added PC/ABS blend without MMT loading, irradiation at all dosages from 50 kGy to 250 kGy have enhanced the elongation at break of the blends. At this point, cross-linking has occurred in the polymer matrix of PC/ABS blends which is triggered by electron beam irradiation. For MMT loading of 2 phr instead,

irradiation has increased the elongation at break of PC/ABS blends except for the case of 100 kGy and 250 kGy. For MMT loading of 4 phr into PC/ABS blends, irradiation dosage from 50 kGy to 200 kGy have improved the elongation at break. However, maximum irradiation of 250 kGy has lowered the elongation of the blend to 4.2 %. Random chain scission has happened in the 4 phr MMT added PC/ABS blend irradiated at 250 kGy which incur to premature failure of the blend when it was subjected to tensile test. Apart from that, PC/ABS blends added with 10 phr APP and 6 phr MMT showed increment of elongation at break when irradiation of 100 kGy and 150 kGy were applied. Higher irradiation dosages of 200 kGy and 250 kGy could disrupt the polymer chain of the PC/ABS. Lastly, electron beam irradiation in PC/ABS blends with APP loading of 10 phr and MMT loading of 8 phr displayed positive improvement in elongation at break of the blends except for the case of 200 kGy.

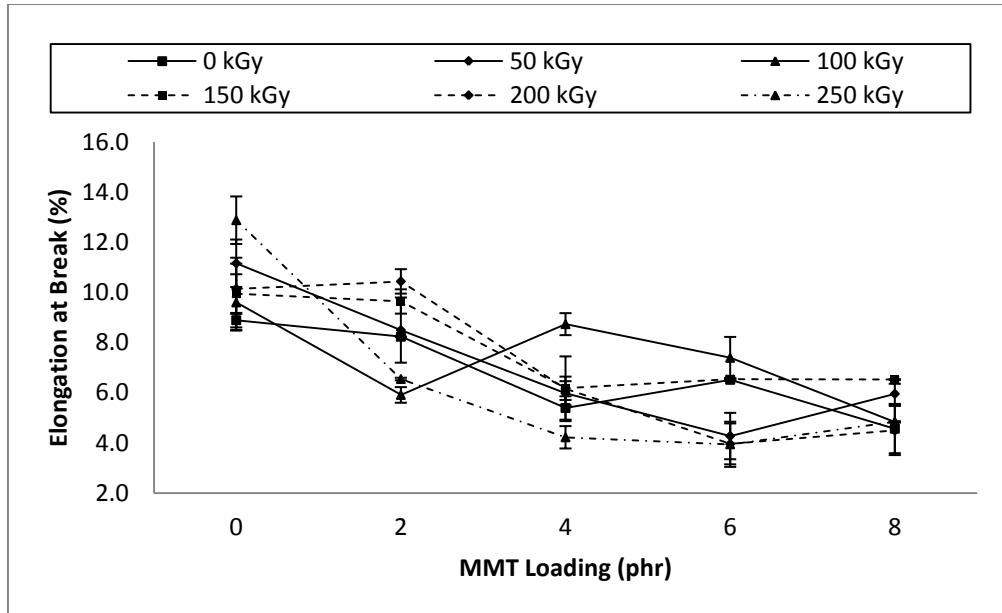
Figure 4.12 (b) shows the elongation at break for PC/ABS blends added with 15 phr APP under different MMT loading and electron beam irradiation. It is shown that non-irradiated PC/ABS blend and PC/ABS blends irradiated at 150 kGy, 200 kGy and 250 kGy exhibit identical trend of elongation at break. It can be concluded that when PC/ABS blends were to be irradiated at 150 kGy, 200 kGy and 250 kGy, MMT loading level of 4 phr and 8 phr are more suitable to be used over 2 phr and 6 phr when PC/ABS blends were added with 15 phr APP. Excellent intercalation of polymer PC and ABS into the nanoclay MMT could impart the enhancement of elongation at break

of the PC/ABS blends, which is further supported by successful cross-linking induced by suitable irradiation.

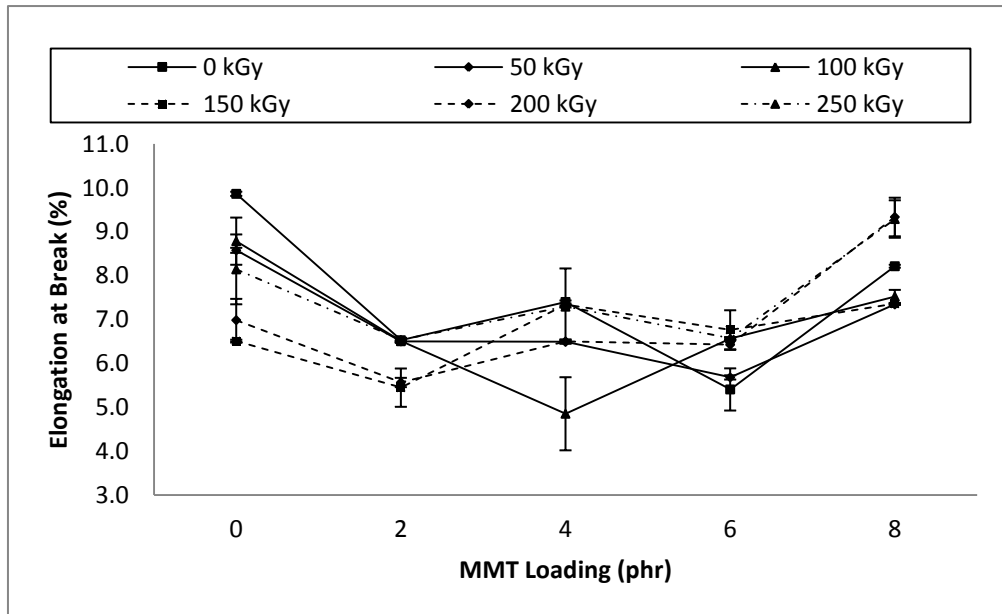
According to Figure 4.13 (a), a seemingly decreasing trend of elongation at break with MMT loading is obtained. This indicates that for PC/ABS blends added with 20 phr of APP, increasing the MMT loading level would only weaken the elongation of the blends. This can be attributed to the agglomeration of MMT particles in the polymer matrix of PC/ABS blends added with APP. Upon closer inspection, it can be noticed that increasing the MMT loading from 0 phr to 2 phr did not help in improving the elongation at break except for the case of PC/ABS blends irradiated at 100 kGy and 250 kGy. Hence, suitable dosage of electron beam irradiation can help in mitigating the adverse effect of MMT agglomeration towards the PC/ABS blend, as seen for the case of 100 kGy and 250 kGy. On the other hand, it can be observed that electron beam irradiation at all ranges has increased the elongation at break of the flame retarded PC/ABS blends added with MMT of 2 phr, 4 phr and 8 phr. This proves the presence of cross-linking which could possibly be induced by proper selection of irradiation dosage. With the help of secondary reinforcement, premature failure of PC/ABS blends added with APP and MMT was hindered when it was subjected to tensile testing.

Figure 4.13 (b) shows the elongation at break graph for PC/ABS blends added with 25 phr APP under different MMT loading and irradiation. It is disclosed that application of electron beam irradiation has affected the PC/ABS blends added with 25 phr of APP without MMT. Irradiation at all

dosages has disrupted the elongation at break of the PC/ABS blends, which is due to the severe chain scission that happened in the PC/ABS polymer chains. Secondly, it can be seen that by increasing the amount of MMT from 0 phr to 2 phr, the elongation at break of the PC/ABS blends were increased as well for irradiation of 50 kGy, 100 kGy (with slight increment) and 250 kGy. Formation of cross-linking networks by suitable irradiation dosage and effective intercalation of polymer matrix into the MMT interlayer galleries would further provide the enhancement effect to the elongation at break.

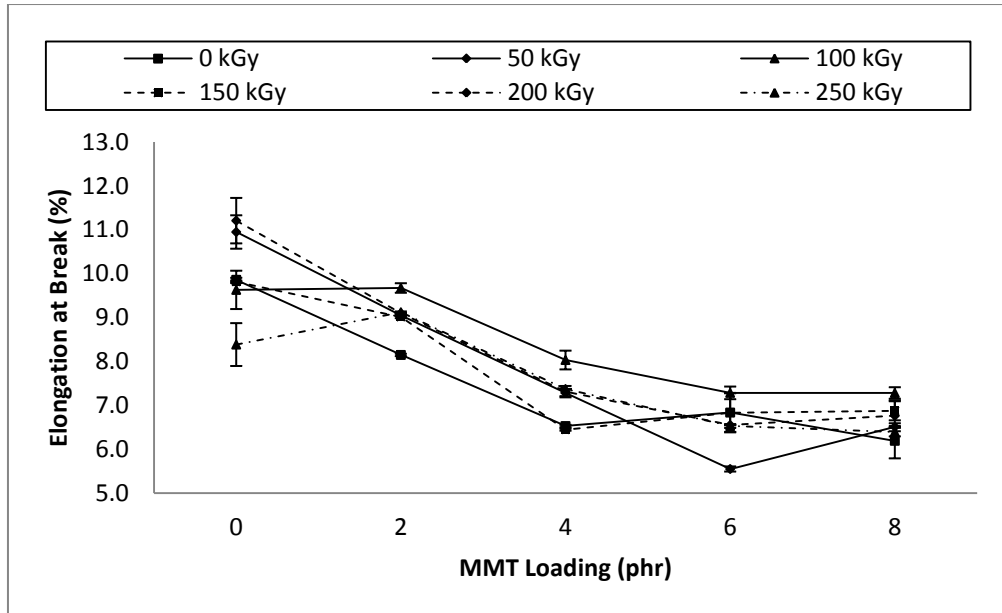


(a)

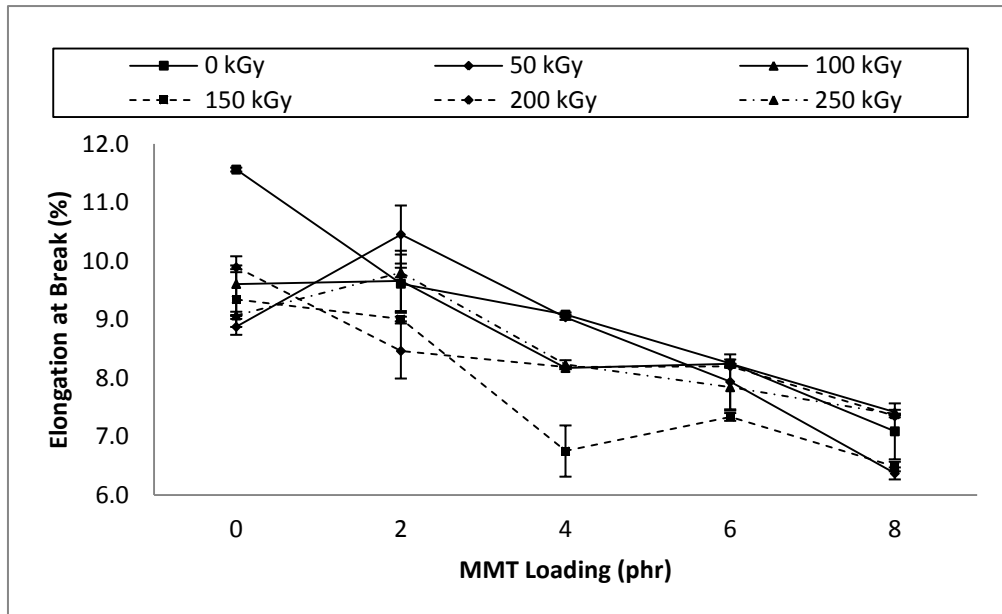


(b)

Figure 4.12: Effect of MMT loading level on elongation at break of PC/ABS blends (a) added with 10 phr APP, (b) added with 15 phr APP under different irradiation dosages



(a)



(b)

Figure 4.13: Effect of MMT loading level on elongation at break of PC/ABS blends (a) added with 20 phr APP, (b) added with 25 phr APP under different irradiation dosages



### 4.2.3 Izod Impact Strength

The impact strength reflects the ability of a certain material to absorb energy at fracture when it is exposed to sudden impact or rapid loading (Park, et al., 2010). Figure 4.14 (a) shows the Izod impact strength for PC/ABS blends added with different amount of APP and under different electron beam irradiation dosages without the presence of MMT. It can be observed that for unfilled PC/ABS blends, application of electron beam irradiation has significantly reduced the impact strength. Chain scissioning caused by the electron beam irradiation has occurred in the polymer structure of PC/ABS blends. As a result, the shorter chains of polymer in the PC/ABS matrix are not able to effectively absorb and dissipate more energy while it is subjected to impact test, giving a lower Izod impact strength value (Yin and Wang, 2010). However, for PC/ABS blend added with 15 phr of APP, the application of irradiation shows positive results in impact strength. In this case, electron beam irradiation at all dosages has strengthened the PC/ABS blends. Some degree of cross-linking is imparted into the PC/ABS polymer structure via the electron beam irradiation.

As given in Figure 4.14 (b), it is observable that when APP loading increased from 10 phr to 15 phr, the impact strength of the blends decreased drastically for all irradiation dosages. The addition of APP has reduced the overall impact strength of the PC/ABS blends as the amount of polymer base PC and ABS is reduced. Moreover, as shown in PC/ABS blends added with 10 phr of APP and 2 phr of MMT, the impact strength is very dependent on the

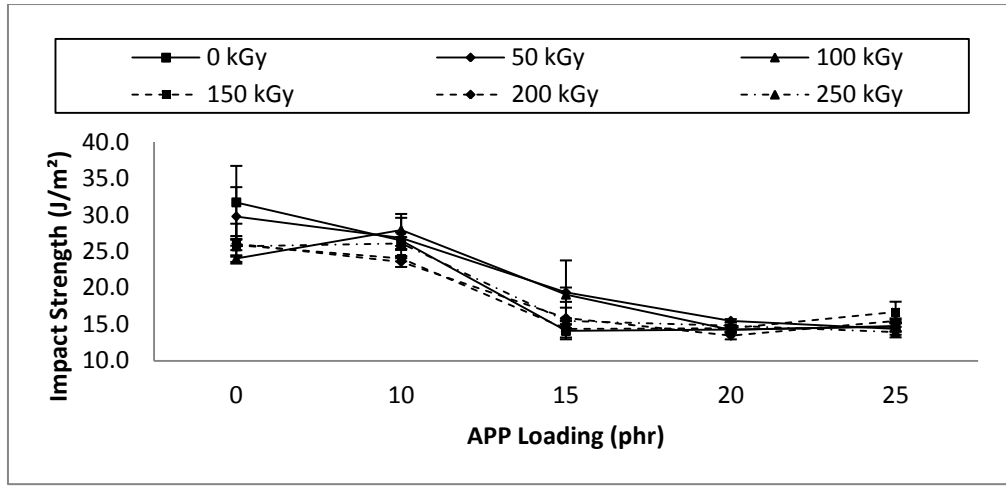
dosage of electron beam irradiation. High Izod impact strength values were obtained when irradiation from 0 kGy to 150 kGy were used while lower values were recorded when high irradiation of 200 kGy and 250 kGy were applied. At this stage, severe degradation of PC/ABS chains has happened in the blends irradiated at 200 kGy and 250 kGy. This causes the inability of the specimens of 200 kGy and 250 kGy irradiated PC/ABS blends to absorb sufficient energy when they were subjected to impact test, resulting lower Izod impact strength values.

The Izod impact strength profile for PC/ABS blends added with 4 phr MMT at different APP loading and irradiation dosages is depicted in Figure 4.14 (c). It is noticed that for PC/ABS blends added with APP loading of 10 phr and 15 phr, all electron beam irradiation dosages have weakened the impact strength of the blends as compared to their primitive blend without irradiation. It is postulated that for 10 phr APP and 15 phr APP added PC/ABS blends, implementation of electron beam irradiation would degrade the polymer blend instead of enhancing the impact strength of the blends. On the other hand, for PC/ABS blends added with 20 phr of APP, the use of irradiation at all range has improved the impact strength. Therefore, it can be deduced that the increment of Izod impact strength in PC/ABS blends are very dependent on the APP loading and irradiation dosages. Besides that, application of electron beam irradiation might not be suitable for low APP loading level of 10 phr and 15 phr in PC/ABS blends.

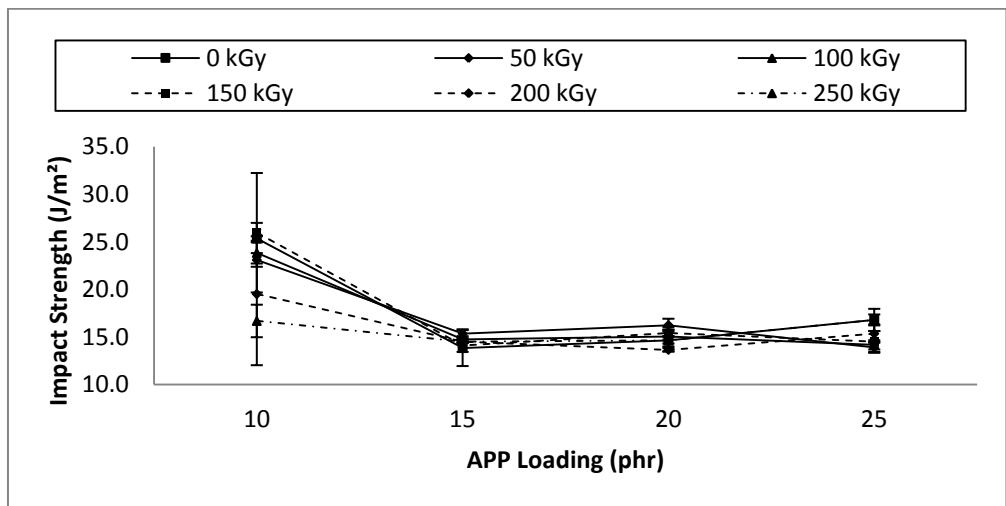
Figure 4.15 (a) depicts the Izod impact strength for PC/ABS blends added with 6 phr of MMT under different APP loading and electron beam irradiation dosages. It can be observed that the impact strength values of PC/ABS blends without irradiation (0 kGy) and PC/ABS blends irradiated at 200 kGy do not differ very much with increasing APP loading level. Thus, if the PC/ABS blends were to be left without irradiation or irradiated at 200 kGy, the increase of APP loading in PC/ABS blends would neither enhance nor deteriorate the impact strength of the blends. Meanwhile, it can be seen that for PC/ABS blends irradiated under 50 kGy, the impact strength decreased with increasing of APP loading up to 20 phr. With maximum APP loading of 25 phr, the impact strength showed some improvement as compared to the previous 20 phr APP. On the contrary, for PC/ABS blends irradiated at 100 kGy, the impact strength is enhanced with increasing of APP loading up to 20 phr before it is weakened by APP loading of 25 phr that gives the lowest impact strength. Additionally, it can be seen that for PC/ABS blends irradiated 150 kGy, direct decreasing trend of impact strengths with APP loading is obtained. Hence, it can be established that for 6 phr MMT added PC/ABS blends irradiated at 150 kGy, increasing the APP loading would weaken the impact strength of the blends.

Figure 4.15 (b) shows the Izod impact strength for PC/ABS blends added with 8 phr MMT under different APP loading and irradiation. It can be observed that when APP loading increased from 10 phr to 15 phr, most of the impact strengths of PC/ABS blends decreased gradually even with the application of electron beam irradiation. However, for PC/ABS blend filled

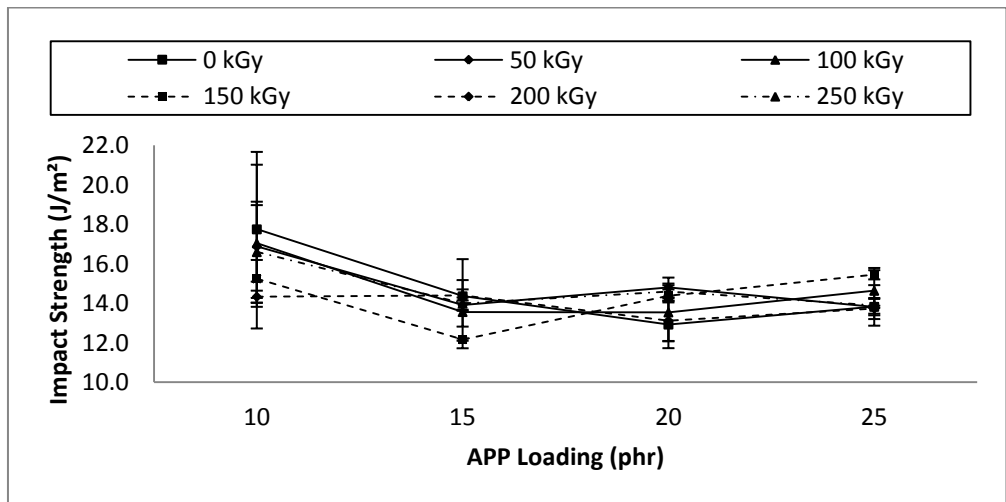
with 8 phr of MMT, irradiation of 200 kGy has increased the impact strength of the blend by 11.6 % when the APP increased from 10 phr to 15 phr. In fact, it can be seen that application of electron beam irradiation does assist in improving the impact strength of PC/ABS blends added with 15 phr as all the impact strength values at all irradiation dosages are higher than the blend without irradiation. Thus, it can be anticipated that application of electron beam on PC/ABS blends added with 15 phr is beneficial in order to achieve a higher impact strength. With the occurrence of cross-linking networks promoted by irradiation, the interfacial adhesion between the polymer phase together with APP and MMT has been significantly improved. As a result, the stress concentration of the PC/ABS blends will be reduced, giving higher impact strength (Dong, Greco and Orsello, 1993). Conversely, for PC/ABS blends added with 20 phr of APP, it can be noticed that irradiation has reduced the impact strength of the blends. At this stage, severe degradation caused by the chain scission of PC/ABS polymer chains has occurred. Hence, it can be concluded that application of electron beam is advantageous to PC/ABS blends added with 15 phr of APP but detrimental to PC/ABS blends added with 20 phr of APP.



(a)

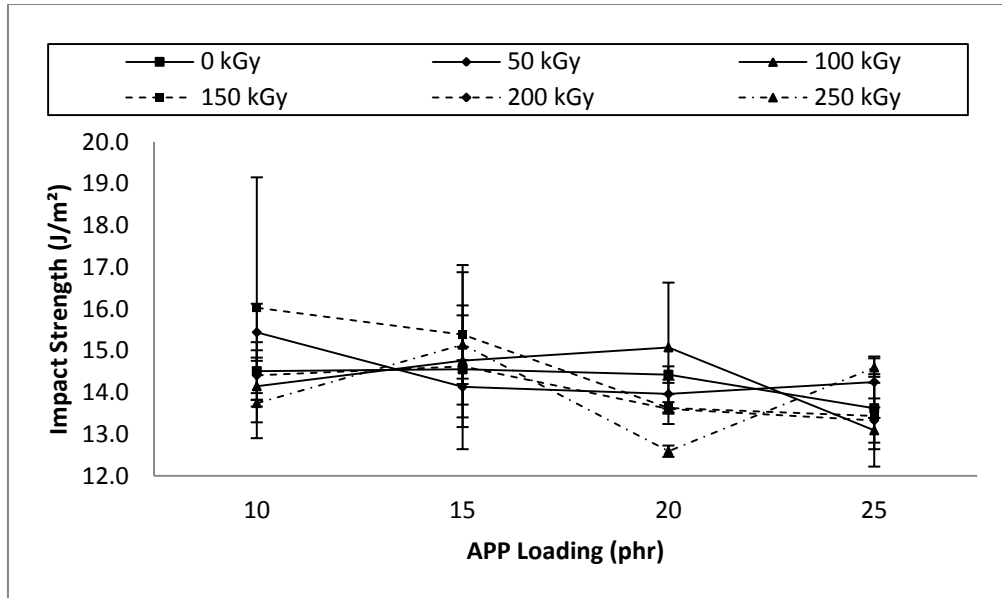


(b)

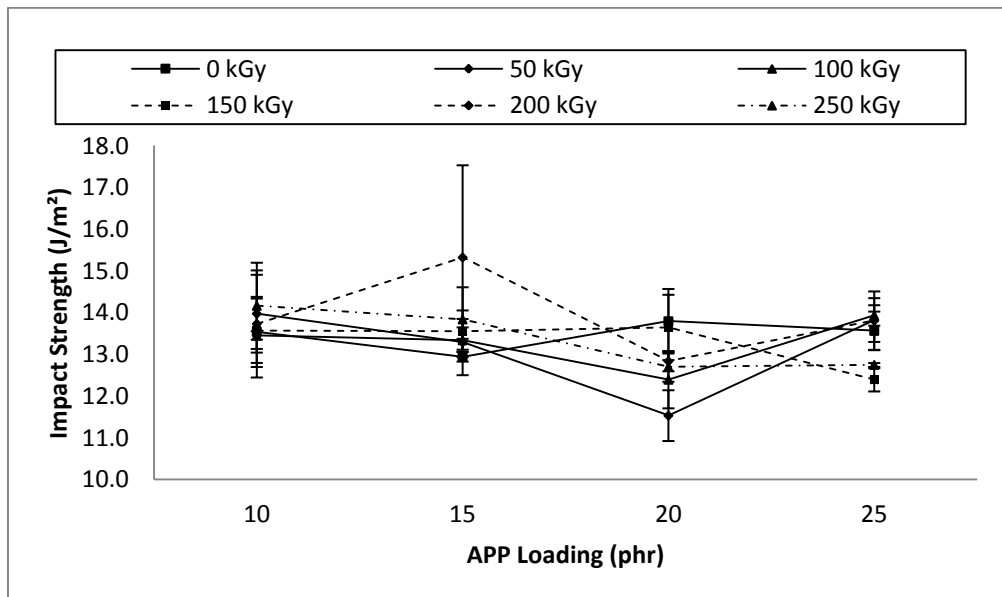


(c)

**Figure 4.14: Effect of APP loading level on Izod impact strength of PC/ABS blends (a) without MMT, (b) added with 2 phr MMT, (c) added with 4 phr MMT under different irradiation dosages**



(a)



(b)

**Figure 4.15: Effect of APP loading level on Izod impact strength of PC/ABS blends (a) added with 6 phr MMT, (b) added with 8 phr MMT under different irradiation dosages**

Based on Figure 4.16 (a), it can be noted that non-irradiated PC/ABS blends and PC/ABS blends irradiated at 50 kGy, 100 kGy and 200 kGy exhibit the same decreasing trend of impact strength with increasing MMT loading. This shows that increasing the amount of MMT in flame retarded PC/ABS blends followed by irradiation in 0 kGy, 50 kGy, 100 kGy and 200 kGy would reduce the impact strength due to the reduced amount of base polymer in the PC/ABS blends. Besides that, the MMT in PC/ABS blends has agglomerated with increasing MMT loading (Zhang, et al., 2015). Apart from that, PC/ABS blends added with 10 phr APP and 8 phr MMT showed negligible change in the impact strength when different dosages of electron beam irradiation was applied. It can be inferred that the impact strength of PC/ABS blend added with 10 phr of APP and 8 phr MMT is independent of the electron beam irradiation.

Figure 4.16 (b) shows the Izod impact strength for PC/ABS blends added with 15 phr APP under different MMT loading and electron beam irradiation. It can be found out that for both PC/ABS blends without MMT and PC/ABS blends added with 2 phr MMT, irradiation at all dosages has enhanced the impact strength of the blends. This can be attributed to the successful cross-linking of the blends triggered by electron beam irradiation. The effective linkage between the PC and ABS polymer phase has been bonded strongly, which eventually reduced the overall stress concentration of the blend. Consequently, more energy would be needed to break the specimen of the blends, giving higher impact strength. For PC/ABS blend added with 4 phr of MMT instead, the application of irradiation has weakened the impact

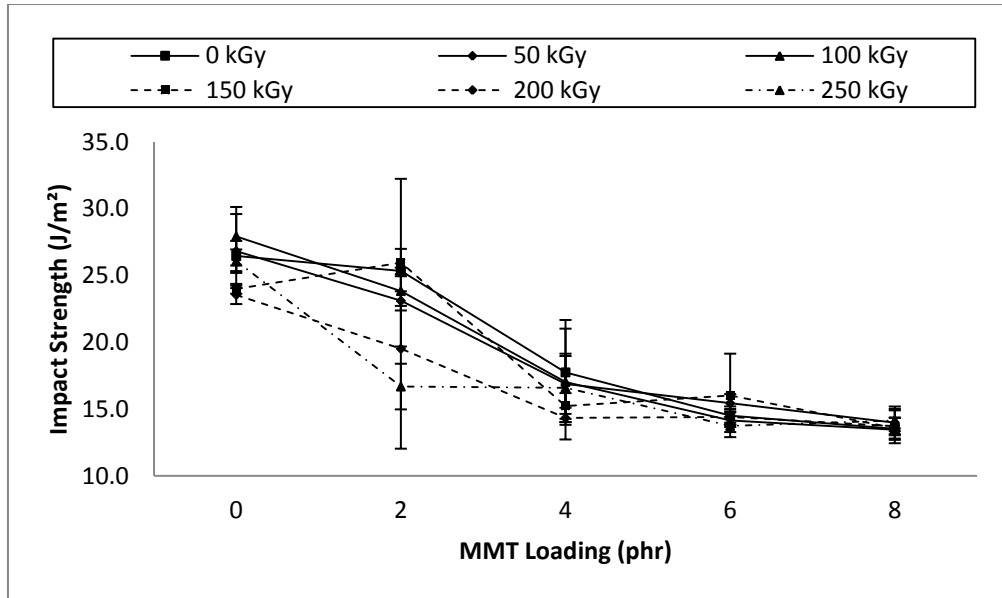
strength of the blend. At this point, severe degradation of PC/ABS blend is the reason behind the results. Hence, it can be concluded that the use of electron beam irradiation is more appropriate for no MMT or low MMT loading in PC/ABS blends.

The Izod impact strength for 20 phr APP added PC/ABS blends with different MMT addition and electron beam irradiation dosages is summarised in Figure 4.17 (a). It can be observed that for PC/ABS blends added with 20 phr of APP and 4 phr of MMT, electron beam irradiation at any dosages has increased the impact strength of the blends. This proves the successful application of irradiation towards the increment of impact strength in PC/ABS blends. Apart from that, it can be noticed that for PC/ABS blends added with 20 phr APP and 6 phr MMT, high irradiation of 150 kGy, 200 kGy and 250 kGy has weakened the impact strength as compared to the original blend without irradiation. For PC/ABS blend irradiated under 250 kGy, it has recorded the lowest impact strength of only 12.6 J/m<sup>2</sup>, which is about 12.8 % of reduction from its blend without irradiation. Thus, it can be inferred that high irradiation dosage on PC/ABS blends added with 20 phr APP and 6 phr MMT would deteriorate the impact strength due to the degradation of polymer chain in the blends.

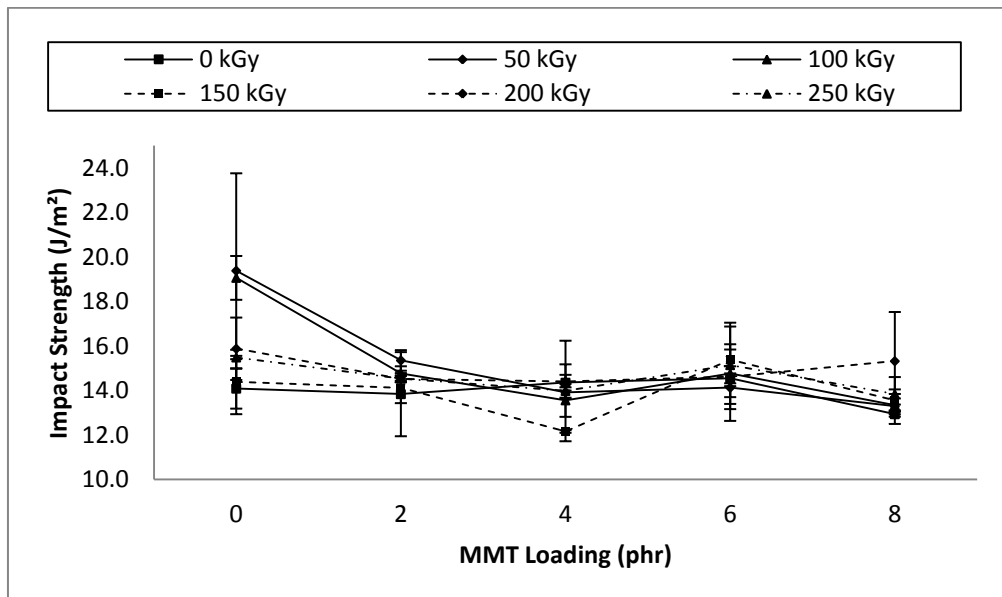
Figure 4.17 (b) demonstrates the Izod impact strength of PC/ABS blends added with 25 phr APP under different MMT loading and irradiation. It can be seen that PC/ABS blends without MMT and PC/ABS blends added with 2 phr show higher dependency on the irradiation as their impact strength



values vary in a much greater extent than the other blends. For PC/ABS blend without MMT, irradiation of 250 kGy gives the lowest impact strength while for PC/ABS blend added with 2 phr of MMT, irradiation of 250 kGy gives the highest impact strength. Therefore, it can be implied that MMT loading level and electron beam irradiation dosage are dependent to each other. Proper selection of MMT loading and irradiation dosage would need to be taken into account in order to prepare flame retarded PC/ABS blends with higher mechanical properties reinforced by MMT. In addition, it is noted that for both PC/ABS blends without irradiation and irradiated at 250 kGy, increasing MMT loading from 0 phr to 2 phr has increased the impact strength significantly. This suggest that when electron beam irradiation dosages of 0 kGy and 250 kGy were applied, increment of MMT loading from 0 phr to 2 phr would yield positive effect in the impact strength.

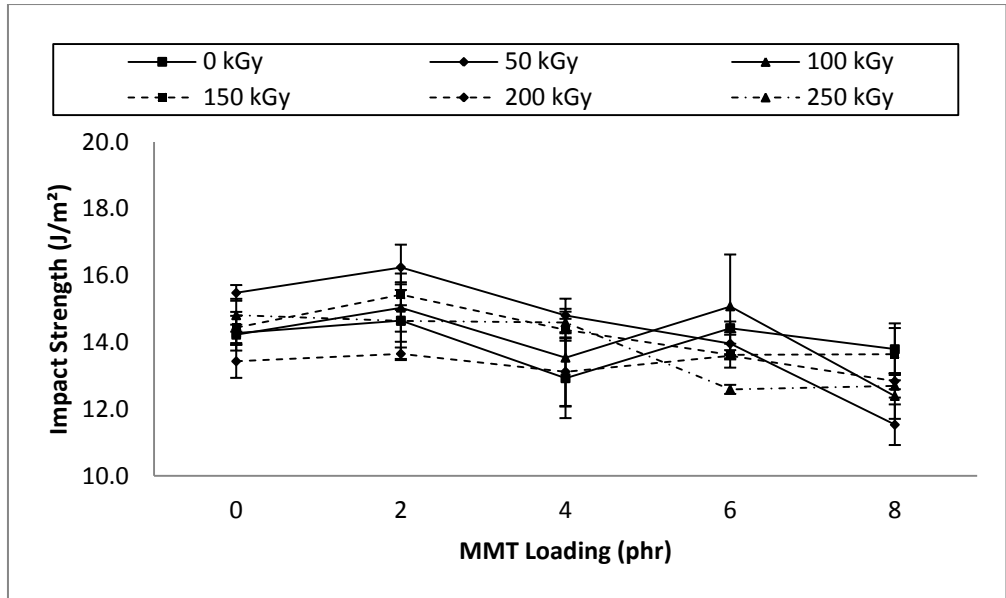


(a)

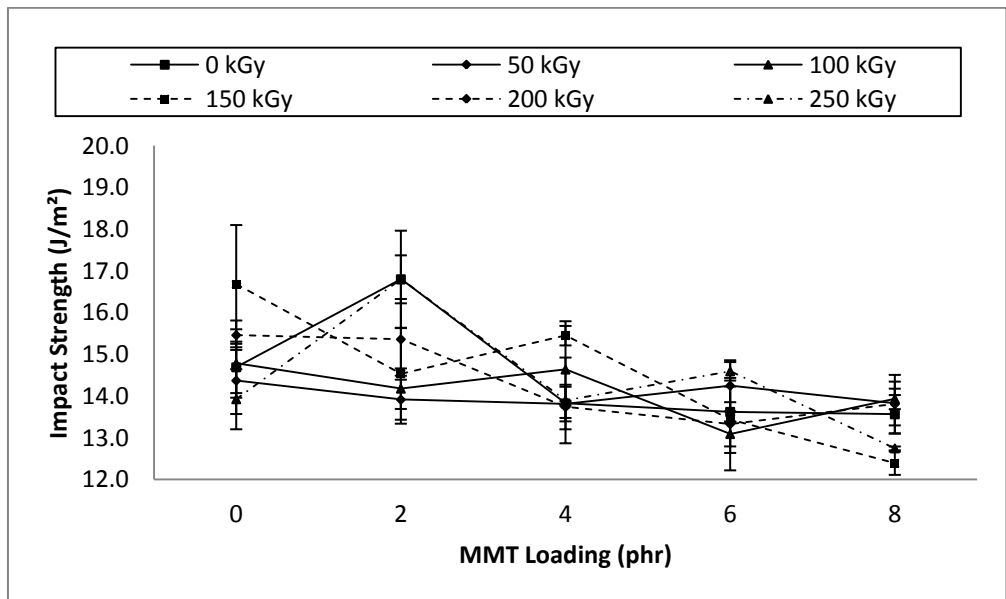


(b)

Figure 4.16: Effect of MMT loading level on Izod impact strength of PC/ABS blends (a) added with 10 phr APP, (b) added with 15 phr APP under different irradiation dosages



(a)



(b)

Figure 4.17: Effect of MMT loading level on Izod impact strength of PC/ABS blends (a) added with 20 phr APP, (b) added with 25 phr APP under different irradiation dosages

### **4.3 Physical Properties**

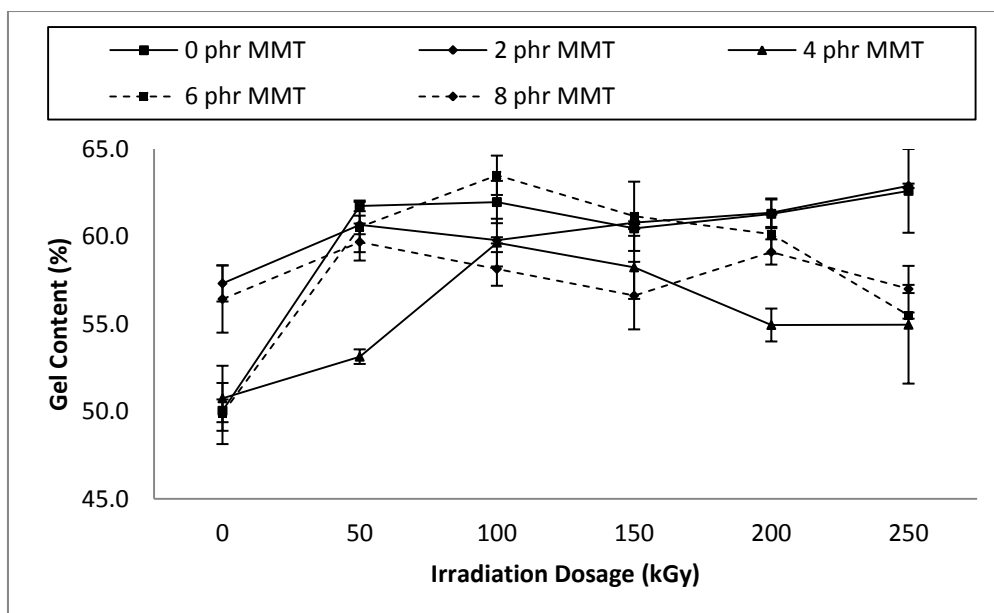
#### **4.3.1 Gel Content**

Generally, the degree of cross-linking formed in a polymer structure can be determined through the gel content test (Munusamy, et al., 2009). It is well known that the degree of cross-linking is mainly dependent on the application of electron beam irradiation while some degree of cross-linking might be due to the addition of reinforcing fillers such as MMT.

Figure 4.18 shows the percentage of gel content for PC/ABS blends with 10 phr of APP under different loading level of MMT and irradiation dosages. It is important to note that all the PC/ABS blends with electron beam irradiation are having higher values of gel content than their respective blends without irradiation. Basically, the gel content test is based on the inability of PC/ABS blends added with APP and MMT to completely dissolve in the methyl ethyl ketone (MEK) due to the insolubility of inorganic APP and MMT in the MEK which is an organic solvent. Thus, a higher gel content value implies that less amount of PC and ABS have been dissolved in the MEK while a lower gel content implies that large amount of PC and ABS have been dissolved. For PC/ABS blends irradiated with electron beam, formation of a three-dimensional network structure or cross-linking in the polymer matrix of PC and ABS can be triggered by the free radicals generated via the radical reaction (Tseng, et al., 2001). As a result, the matrix of PC/ABS blends are

bonded strongly where the possibility of PC and ABS being dissolved in the MEK solvent is reduced, giving a higher gel content value.

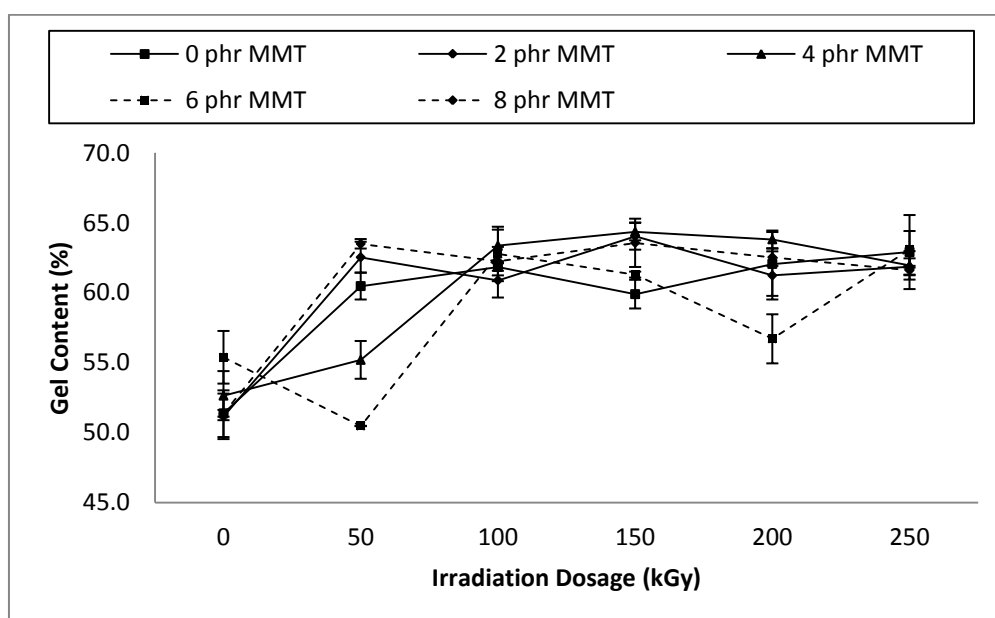
Based on Figure 4.18, it can be observed that PC/ABS blends added with 10 phr APP and 4 phr MMT has the lowest gel content among its peer when it was irradiated at 50 kGy. At this stage, possible agglomeration of MMT has occurred in the PC/ABS blends whereby the intercalation effect of MMT could not be initiated (Romanov, et al., 2015). Eventually, more PC and ABS were dissolved in the MEK solvent that leads to a lower gel content. Besides that, for PC/ABS blends under high electron beam irradiation dosage of 250 kGy, low MMT loading of 0 phr and 2 phr are more preferred as the blends were able to give higher gel content values compared to their respective with high MMT loading. This can be attributed to the cross-linking network formed between the polymer chains for PC/ABS blends added with only 10 phr APP and PC/ABS blends added with 2 phr MMT and 10 phr APP.



**Figure 4.18: Gel content profile for PC/ABS blends with 10 phr of APP under different MMT loading level and electron beam irradiation dosages**

Figure 4.19 demonstrates the gel content for PC/ABS blends with 15 phr of APP under different MMT loading and irradiation dosages. It can be seen that although most of the PC/ABS blends experienced an increment of gel content with increasing irradiation from 0 kGy to 50 kGy, one exception can be seen in PC/ABS blend added with 15 phr APP and 6 phr MMT as its gel content was found to be lower after 50 kGy of irradiation. This can be attributed to the poor blending of PC/ABS blends with 15 phr APP and 6 phr MMT has resulted a poor interaction effect between the APP and MMT with the polymer matrix. Consequently, the PC and ABS macromolecules are not able to bond together effectively and this would give a rather low percentage of gel content owing to the fact that more PC and ABS were dissolved in the MEK solvent.

Furthermore, it can be observed in Figure 4.19 that for PC/ABS blends irradiated under 50 kGy, the gel content is more dependent on the MMT loading while for PC/ABS blends irradiated under 250 kGy, the gel content is almost independent of the MMT loading as their gel content values are roughly the same. This is due to the intensive cross-linking network formed by the 250 kGy irradiation in the polymer matrix of PC/ABS where increasing the MMT loading would not impart any further intercalation effect (Dadbin, et al., 2002). Thus, it is implied that with application of high irradiation dosage, increasing the MMT loading would neither strengthen nor weaken the bonding of PC and ABS, resulting a rather constant gel content values.



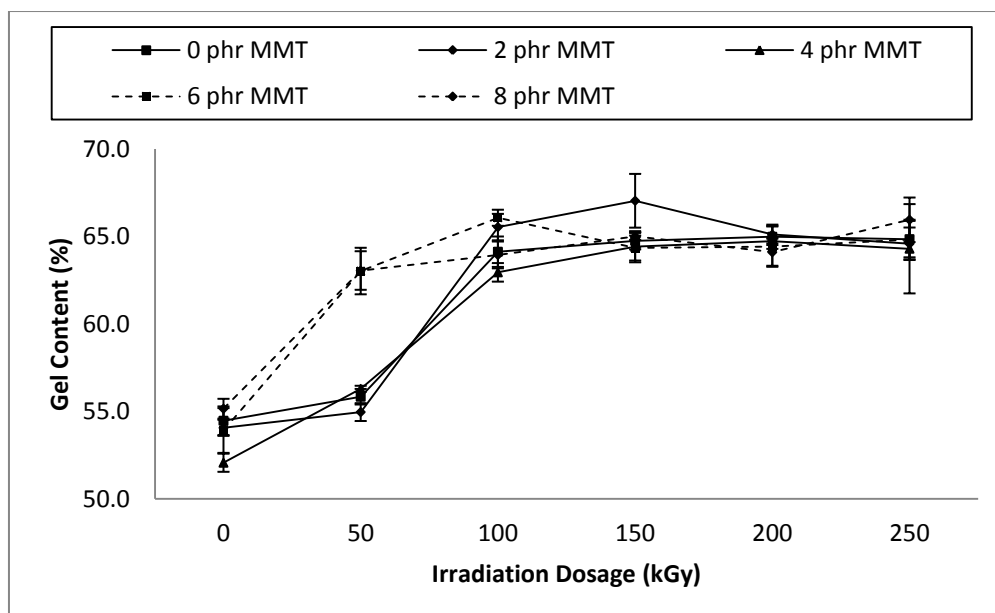
**Figure 4.19: Gel content profile for PC/ABS blends with 15 phr of APP under different MMT loading level and electron beam irradiation dosages**

The gel content for PC/ABS blends with 20 phr of APP under various MMT loading and irradiation dosages is depicted in Figure 4.20. It is discovered that flame retarded PC/ABS blends added with high MMT loading

of 6 phr and 8 phr gave a rather high gel content compared to PC/ABS blends with low MMT loading when they were irradiated under 50 kGy. This can be attributed to the intercalation effect in the polymer matrix due to the addition of suitable MMT amount, which could be further enhanced by the formation of cross-linking through electron beam irradiation. In this case, it is suggested that combination of high MMT loading combined with 50 kGy irradiation would be more appropriate to be applied when the PC/ABS was blended with 20 phr of APP.

It is shown that when the electron beam irradiation dosage increased from 200 kGy to 250 kGy, the gel content of PC/ABS blends do not show any significant changes. This can be explained by the saturation stage of the cross-linked PC/ABS blends. Originally, the gel content of the PC/ABS blends can be increased by suitably increasing the MMT loading and electron beam irradiation. However, with further increasing of irradiation dosages, the movement of the generated free radicals have been restricted by the cross-linking networks which was formed at previous irradiation from 50 kGy to 150 kGy. These trapped free radicals inside the cross-linked network of polymer matrix are less likely to cause the formation of bonding in between the cross-linked polymer chains. Not only this, the availability of free volumes to form cross-linking within the chains of PC/ABS matrix has reached a critical point whereby formation of new cross-linking network is not possible (Sabet, Hassan and Ratnam, 2012). Even if the formation of cross-linking is possible, the contribution of the new cross-linking would be insignificant to the increment of cross-linking density of the PC/ABS blends.

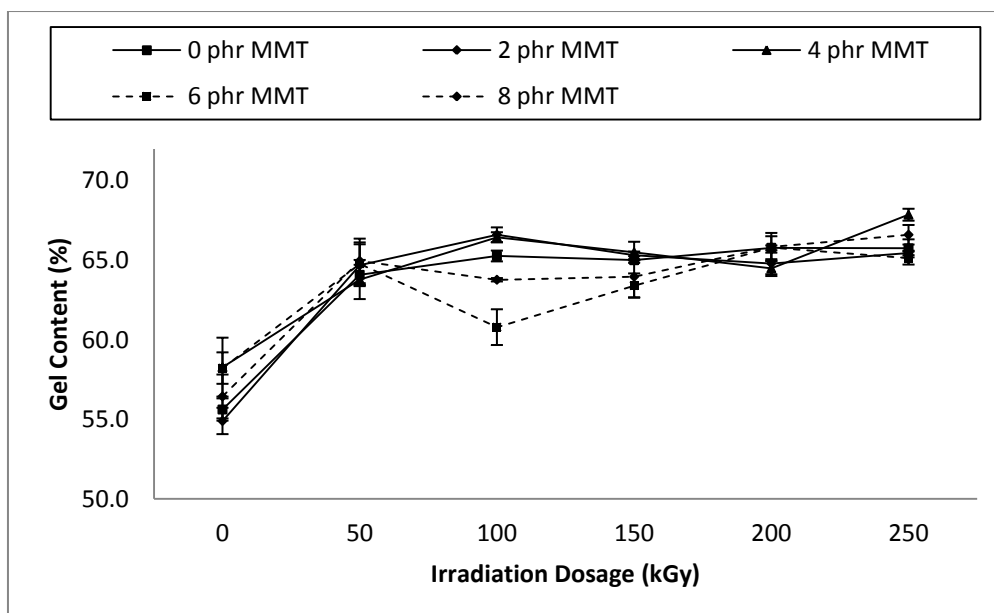




**Figure 4.20: Gel content profile for PC/ABS blends with 20 phr of APP under different MMT loading level and electron beam irradiation dosages**

Figure 4.21 displays the effects of increasing MMT loading and electron beam irradiation dosage on the gel content of PC/ABS blended with 25 phr of APP flame retardant. By referring to Figure 4.21, the percentage of gel content for non-irradiated PC/ABS blends are relatively low. However, increasing the MMT loading was observed to increase the gel content of PC/ABS blends added with high APP loading of 25 phr. It is commonly known that addition of mineral or inorganic fillers such as APP and MMT into the PC/ABS blends are insoluble in the organic solvent. Therefore, increasing the MMT loading would slightly reduce the solubility of the blends into the MEK solvent. Besides that, the intercalation of PC and ABS polymer chains into the layers of MMT has further enhanced the interaction between the MMT and PC/ABS matrix (Isitman and Kaynak, 2011). Consequently, lower percentage of PC and ABS would be dissolved by the MEK organic solvent, showing a higher gel content value.

It is demonstrated in Figure 4.21 that the gel content values of PC/ABS blends do not change significantly with the MMT loading for all irradiation dosages except for the case of PC/ABS blends irradiated at 100 kGy. It can be observed that flame retarded PC/ABS blends added with high MMT loading of 6 phr and 8 phr showed lower gel content when they were irradiated to 100 kGy. This is because of the agglomeration of high MMT loading in the polymer matrix of PC/ABS, which is further deteriorated by improper cross-linking of the agglomerated MMT. Therefore, more PC and ABS were dissolved in the MEK solvent, leading to a lower gel content value. On the other hand, it can be noticed that PC/ABS blends added with high MMT loading of 6 phr and 8 phr were able to withstand the high irradiation dosage of 200 kGy as their gel content exhibited highest gel content with no significant changes. Hence, it can be concluded that for PC/ABS blends added with high MMT loading of 6 phr and 8 phr, 200 kGy irradiation would be more suitable to be applied instead of 100 kGy in order to ensure a higher percentage of gel content.

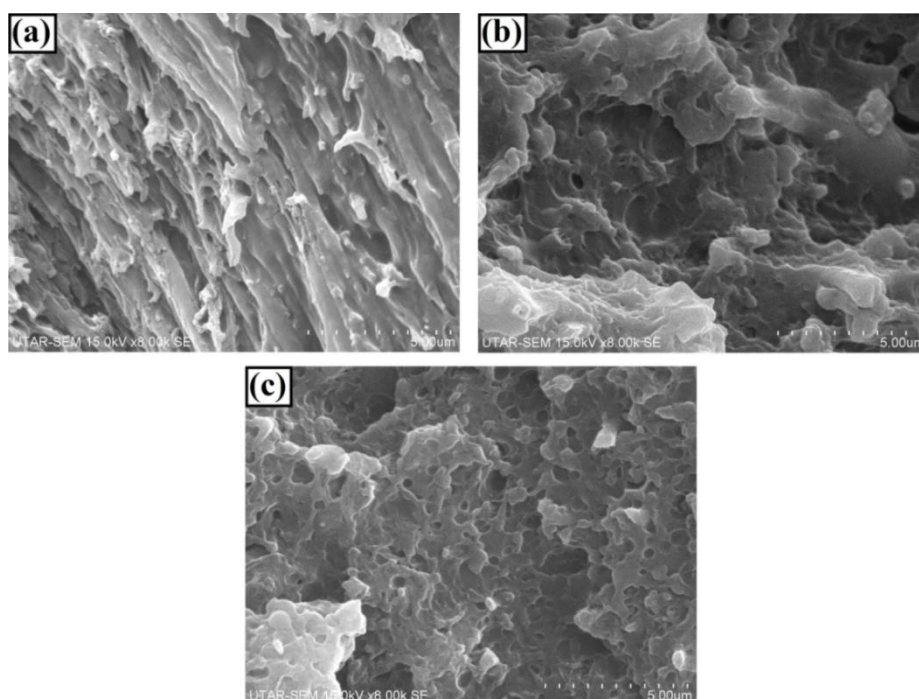


**Figure 4.21: Gel content profile for PC/ABS blends with 25 phr of APP under different MMT loading level and electron beam irradiation dosages**

### 4.3.2 Morphology

Figure 4.22 shows the SEM micrographs of unfilled PC/ABS blends under irradiation dosages of 0 kGy, 50 kGy and 250 kGy. From Figure 4.22 (a), it can be seen that for non-irradiated PC/ABS blend, the polymer matrix of unfilled PC/ABS blend appears to be discontinuous with the presence of high amounts of elongated fibrils. This is in agreement with the tensile results as the elongation at break for non-irradiated PC/ABS blend is higher than PC/ABS blends irradiated at 50 kGy and 250 kGy. The formation of fibrils in the structure of PC/ABS could be due to the tearing of polymer matrix during the tensile extension in order to resist the straining stress suffered by the blend (Bee, et al., 2013). From Figure 4.22 (b) and 4.22 (c), it can be discovered that electron beam irradiation of 50 kGy and 250 kGy gave a continuous phase of PC and ABS. This shows that application of electron beam irradiation could

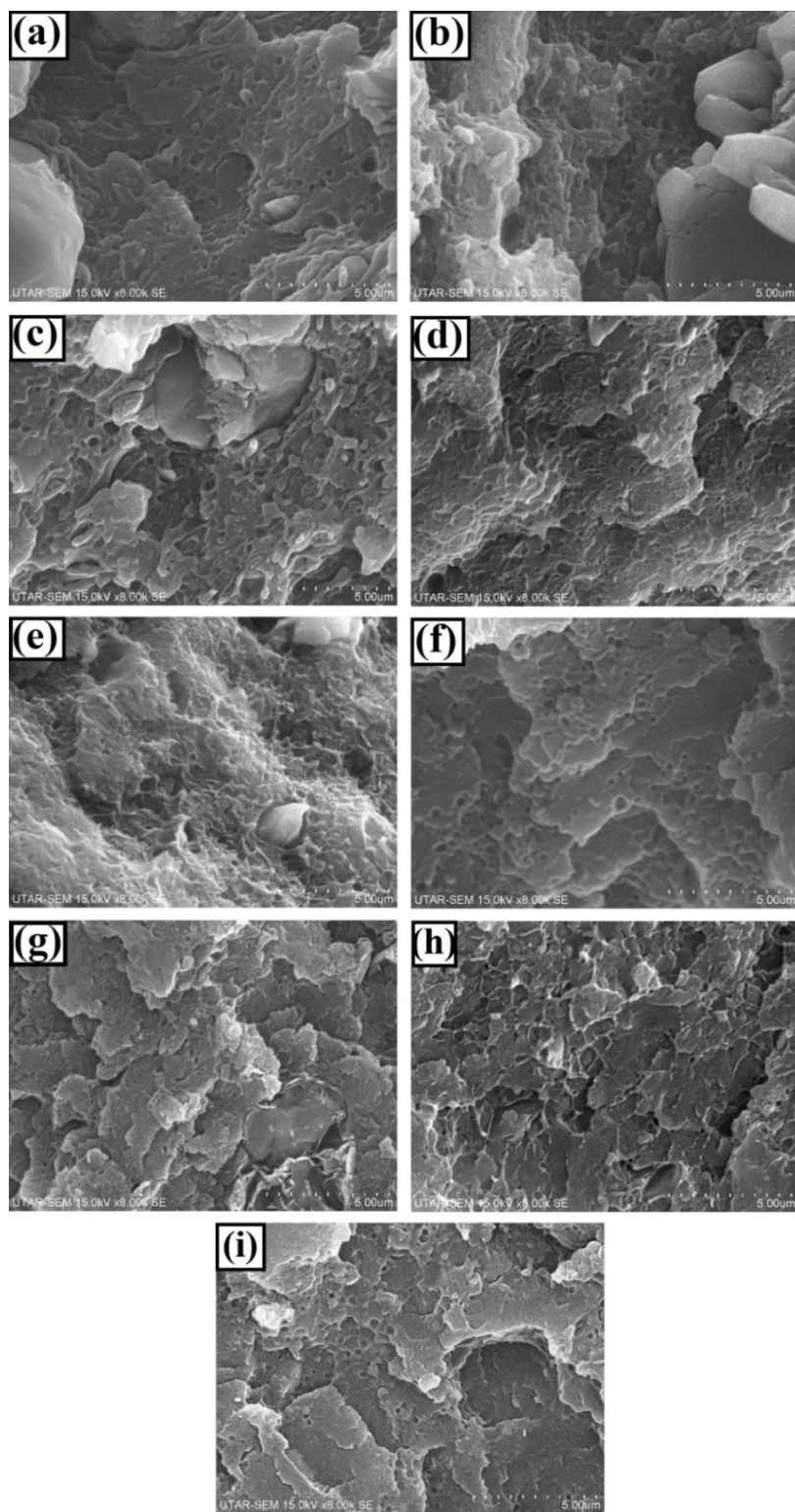
improve the continuity of polymer matrix of PC/ABS blends by forming cross-linking network. However, when PC/ABS blend irradiated to 250 kGy, voids can be observed as shown in Figure 4.22 (c), implying the presence of severe polymer degradation caused by the application of high electron beam irradiation dosage (Bhattacharya, 2000). The voids are formed by the volatiles liberated from the polymer structure after gaining enough energy from the irradiation.



**Figure 4.22: SEM micrographs of PC/ABS blends without APP and MMT under electron beam irradiation of (a) 0 kGy, (b) 50 kGy, (c) 250 kGy**

The SEM micrographs of PC/ABS blends added with low APP loading of 10 phr and MMT loading of 0 phr, 2 phr and 8 phr under irradiation of 0 kGy, 50 kGy and 250 kGy are shown in Figure 4.23. From Figure 4.23 (a) to Figure 4.23 (c), it can be noted that APP added PC/ABS blends gave a rather continuous structure compared to unfilled PC/ABS blends as shown in Figure

4.22 (a). For PC/ABS blend added with 10 phr of APP and 2 phr of MMT, it can be observed in Figure 4.23 (d) to Figure 4.23 (f) that the PC/ABS blend gave a more continuous phase. At this point, it can be stipulated that the intercalation effect of MMT could improve the interfacial adhesion between the polymer matrix of PC/ABS and the APP flame retardant, resulting an excellent dispersion with good continuity (Wang, et al., 2012). However, for PC/ABS blend added with 10 phr of APP and 2 phr of MMT irradiated to 250 kGy, flakes-like structure of PC/ABS can be seen in Figure 4.23 (f). This indicates the brittle behaviour of 10 phr APP and 2 phr MMT added PC/ABS blend irradiated at 250 kGy. In fact, this observation agrees very well with the tensile results as the 10 phr APP and 2 phr MMT added PC/ABS blend irradiated at 250 kGy has a lower elongation at break as compared to the same formulation of blend without irradiation and irradiated at 50 kGy. On the other hand, based on Figure 4.23 (g) to Figure 4.23 (i) which displays the polymer matrix of PC/ABS added with 10 phr of APP and 8 phr of MMT, almost similar flakes-like structures were obtained as for the case of Figure 4.23 (f). At this stage, severe embrittlement effect has been imparted to the polymer matrix of PC/ABS blend added with 8 phr of MMT. This can be proven in the tensile results as both the tensile strength and elongation at break of the PC/ABS blend added with 8 phr of MMT were relatively lower than PC/ABS blend added with 2 phr of MMT even with the same irradiation dosages of 0 kGy, 50 kGy and 250 kGy. It is concluded that overloading of MMT into the PC/ABS blends could lead to reduced interfacial adhesion between the polymer matrix and APP, thereby affecting the intercalation effect of PC/ABS polymers into the MMT.



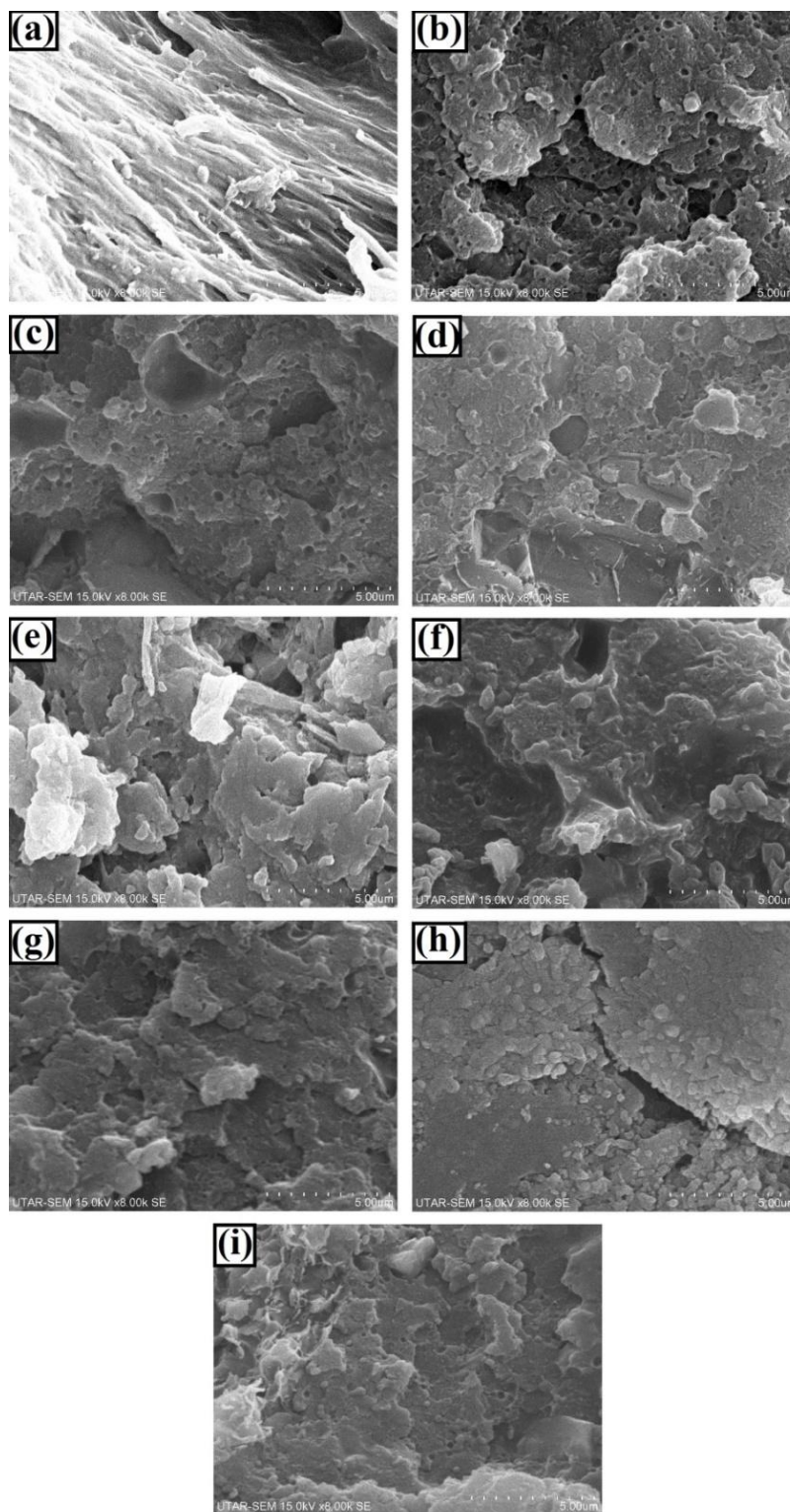
**Figure 4.23: SEM micrographs of PC/ABS blends with low APP loading level of 10 phr and different MMT loading level and irradiation (a) 0 phr MMT at 0 kGy, (b) 0 phr MMT at 50 kGy, (c) 0 phr MMT at 250 kGy, (d) 2 phr MMT at 0 kGy, (e) 2 phr MMT at 50 kGy, (f) 2 phr MMT at 250 kGy, (g) 8 phr MMT at 0 kGy, (h) 8 phr MMT at 50 kGy, (i) 8 phr MMT at 250 kGy**

Figure 4.24 illustrates the SEM micrographs of PC/ABS blends added with high APP loading of 25 phr and MMT loading of 0 phr, 2 phr and 8 phr under irradiation of 0 kGy, 50 kGy and 250 kGy. It can be noticed in Figure 4.24(a) that non-irradiated 25 phr APP added PC/ABS blend gave a discontinuous phase of polymer matrix with elongated fibrils (Bee, et al., 2014). This conforms to the tensile results as non-irradiated PC/ABS blend has higher elongation at break compared to PC/ABS blends irradiated at 50 kGy and 250 kGy. Besides that, some agglomerated APP particles can be observed as well, which corresponds to the lower tensile strength than the same blend with irradiation dosages of 50 kGy and 250 kGy. Moreover, based on Figure 4.24 (b) and Figure 4.24 (c), continuous structure of PC/ABS can be detected with some amounts of voids left by the APP due to the poor interfacial adhesion between the polymer and the APP flame retardant. For PC/ABS blends irradiated at 250 kGy shown in Figure 4.24 (c), the number of voids present in the structure are higher because of the degradation of polymer that releases some volatiles to the surroundings.

The incorporation of MMT also found to be effective in improving the continuity of the PC/ABS blends as the amount of voids are lesser by comparing Figure 4.24 (d) to Figure 4.24 (f) (PC/ABS blends added with both APP and MMT) with Figure 4.24 (b) (PC/ABS blends added with APP only). This can be attributed to the intercalation of PC/ABS polymer matrix into the MMT layers, thus filling the empty spaces and reducing the amount of cavities, subsequently enhancing the interfacial adhesion between the MMT and APP with the polymer matrix (Sharif, Dahlan and Yunus, 2007). However, as seen

in Figure 4.24 (e), addition of APP loading level up to 25 phr was observed to result in severe agglomeration of APP in the structure of the blend when irradiated to 50 kGy. For 25 phr APP and 8 phr MMT added PC/ABS blends, flakes-like structure can be found in Figure 4.24 (g) to Figure 4.24 (i). Visible crack formation can be seen in PC/ABS blend irradiated under 50 kGy as displayed in Figure 4.24 (h). It is deduced that excessive loading of APP and MMT in PC/ABS blends would give flame retarded polymer composites with brittle behaviour. By referring to the tensile results, it is clear that under the same irradiation dosage, both the tensile strength and elongation at break of 8 phr MMT added PC/ABS blend are lower as compared to the PC/ABS blend added with lower MMT loading of 0 phr and 2 phr. Hence, it is concluded that high loading of APP and MMT gives a rather brittle polymer composites.





**Figure 4.24: SEM micrographs of PC/ABS blends with high APP loading level of 25 phr and different MMT loading level and irradiation (a) 0 phr MMT at 0 kGy, (b) 0 phr MMT at 50 kGy, (c) 0 phr MMT at 250 kGy, (d) 2 phr MMT at 0 kGy, (e) 2 phr MMT at 50 kGy, (f) 2 phr MMT at 250 kGy, (g) 8 phr MMT at 0 kGy, (h) 8 phr MMT at 50 kGy, (i) 8 phr MMT at 250 kGy**

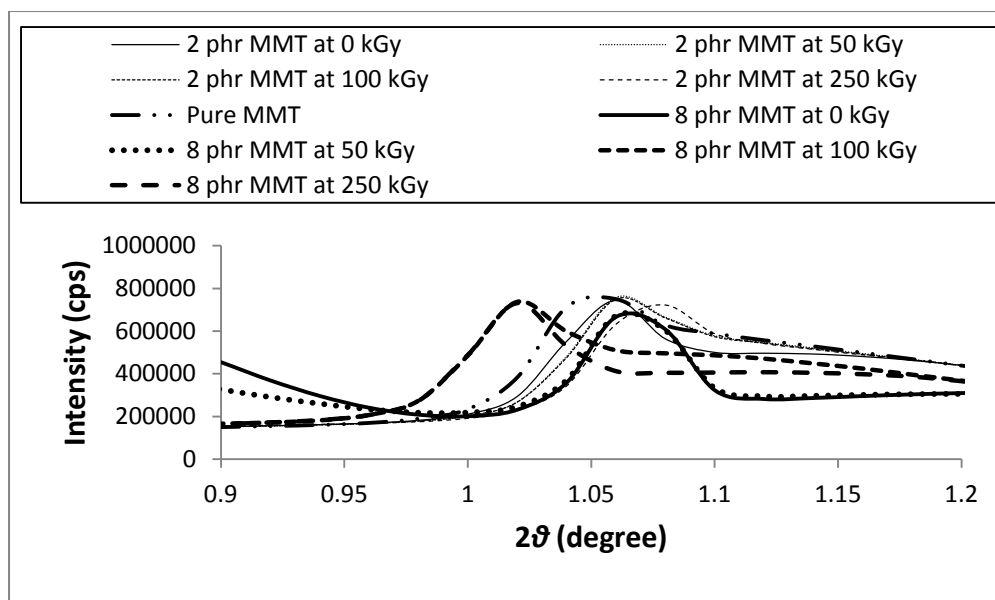
### 4.3.3 X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis was conducted to examine the dispersion and intercalation state of MMT in the PC/ABS polymer matrix by obtaining the d-spacing and the inter-chain separation. Basically, d-spacing indicates the interlayer spacing of the MMT while inter-chain separation implies the distance between the APP particles and the PC/ABS chains (Akhlaghi, et al., 2012).

Figure 4.25 shows the XRD curves of PC/ABS blends with low APP loading of 10 phr added with 2 phr and 8 phr MMT loading level under electron beam irradiation of 0 kGy (no irradiation), 50 kGy, 100 kGy and 250 kGy. Besides that, the XRD pattern of pristine MMT was included at the bottom of all XRD curves for reference purpose. From Figure 4.25, it can be observed that for non-irradiated PC/ABS blends, the diffraction peaks of the blends have shifted to a lower  $2\theta$  value as compared to the diffraction peak of pristine MMT. This indicates that the PC/ABS blends have intercalated into the interlayer galleries of the MMT particles. To further verify this statement, the d-spacing and inter-chain separation of different PC/ABS blends are tabulated in Table 4.1. From Table 4.1, it can be discovered that the d-spacing of non-irradiated PC/ABS blends added with 2 phr MMT and non-irradiated PC/ABS blends added with 8 phr MMT were higher than the d-spacing of pristine MMT. This indicates that intercalation effect of MMT has happened in the polymer matrix of PC/ABS. Furthermore, non-irradiated PC/ABS blends added with 8 phr of MMT recorded higher d-spacing and inter-chain

separation than non-irradiated PC/ABS blends added with 2 phr of MMT. This implies that for PC/ABS blends added with low APP loading of 10 phr, higher MMT loading level of 8 phr is more preferred in order to give a better intercalation result and better inter-chain separation between the APP particles and the PC/ABS polymer chains.

The effect of electron beam irradiation on the 10 phr APP added PC/ABS blends can be examined in Figure 4.25 and Table 4.1. Based on Table 4.1, it can be observed that for 10 phr APP and 2 phr MMT added PC/ABS blend, increasing the irradiation from 0 kGy to 100 kGy has reduced the d-spacing values and inter-chain separation of the blends. This is due to the improper cross-linking happened in the polymer matrix causing the intercalation effect to be ineffective. However, high irradiation of 250 kGy increased the d-spacing and inter-chain separation in relative to the previous 100 kGy but are still lower compared to PC/ABS blends without irradiation and irradiated at 50 kGy. On the other hand, for PC/ABS blends added with 10 phr APP and 8 phr MMT, increasing the irradiation from 0 kGy to 100 kGy has increased the d-spacing values and inter-chain separation. This suggests that cross-linking network formed as a result of irradiation could assist in improving the intercalation effect of PC/ABS matrix into the MMT layers (Yang, et al., 2011). However, application of high irradiation dosage of 250 kGy on 10 phr APP and 8 phr MMT added PC/ABS blend shows reduction in d-spacing and inter-chain separation, implying the presence of polymer degradation.



**Figure 4.25: XRD curves of pristine MMT and PC/ABS blends added with low APP loading level of 10 phr under different MMT loading level and irradiation dosages**

**Table 4.1: d-spacing and inter-chain separation of pristine MMT and PC/ABS blends added with low APP loading level of 10 phr under different MMT loading level and irradiation dosages**

APP Loading (phr)	MMT Loading (phr)	Irradiation dosage (kGy)	2θ (°)	d-spacing (Å)	Inter-chain Separation (Å)
-	Pristine MMT	-	1.1494	76.80	96.00
10	2	0	1.1453	77.07	96.34
		50	1.1464	77.00	96.25
		100	1.1658	75.72	94.65
		250	1.1532	76.54	95.68
10	8	0	1.1251	78.46	98.07
		50	1.1237	78.55	98.19
		100	1.1218	78.69	98.36
		250	1.1231	78.60	98.25

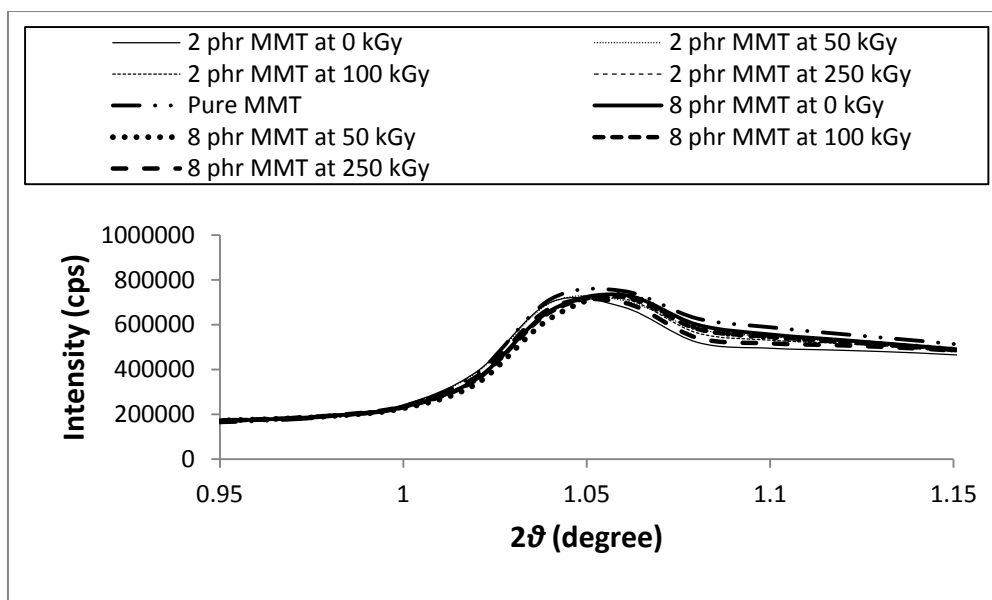
The XRD curves of PC/ABS blends with high APP loading of 25 phr added with 2 phr and 8 phr MMT loading level under electron beam irradiation of 0 kGy (no irradiation), 50 kGy, 100 kGy and 250 kGy is depicted in Figure 4.26. It can be discovered that all the diffraction peaks of

PC/ABS blends shifted to a lower  $2\theta$  value as compared to the pristine MMT. This indicates the effective intercalation of the PC/ABS polymer into the interlayer of MMT particles. In addition, it can be seen in Table 4.2 that the d-spacing values for all APP and MMT added PC/ABS blends are higher than pristine MMT. The increment of d-spacing for all PC/ABS blended with APP and MMT is in agreement with the shifting of diffraction peaks relative to the pristine MMT. In fact, the shifting of diffraction peaks and increment in d-spacing can be explained by the intercalation of PC/ABS into the interlayer of MMT particles. When PC/ABS matrix was inserted and fitted into the MMT interlayer, the distance between the two layers of MMT would be widened and extended, resulting a higher d-spacing value with shifting of  $2\theta$  (Wang, et al., 2012).

By referring to Table 4.2, it is revealed that non-irradiated PC/ABS blend added with 8 phr of MMT recorded lower d-spacing than non-irradiated PC/ABS blend added with 2 phr of MMT. This signifies that for PC/ABS blend added with high APP loading level of 25 phr, higher MMT of 8 phr could weaken the effective intercalation of PC/ABS matrix into the MMT particles. MMT might have higher tendency to agglomerate when excessive MMT loading level was added in the blends (Bee, et al., 2013). The agglomeration of MMT particles could reduce the number of effective intercalated MMT within the PC/ABS blends. Moreover, it is found in Table 4.2 that the inter-chain separation of non-irradiated PC/ABS blend added with 8 phr of MMT recorded lower value than non-irradiated PC/ABS blend added with 2 phr of MMT. This shows that the separation distance between the APP

and the PC/ABS chains is reduced with higher MMT loading of 8 phr, indicating a poor distribution of MMT and APP in the PC/ABS blend (Ahmadi, et al., 2009). Thus, it can be deduced that for non-irradiated PC/ABS blends added with high APP loading of 25 phr, lower MMT loading of 2 phr would be more suitable to be used in order to produce a well-intercalated PC/ABS blend with better dispersion.

The effect of electron beam irradiation on the 25 phr APP added PC/ABS blends can be examined in Table 4.2. It is obvious in Table 4.2 that for PC/ABS blends added with 25 phr APP and 2 phr MMT, increasing the irradiation from 0 kGy to 50 kGy has promoted the intercalation effect with increasing d-spacing and inter-chain separation. However, further increasing of irradiation from 50 kGy to 100 kGy and 250 kGy has decreased both the d-spacing and inter-chain separation. It is implied that polymer degradation and chain scission has occurred in the polymer structure of PC/ABS (Kalkar, et al., 1992). On the other side, for PC/ABS added with 25 phr APP and 8 phr MMT, irradiation of 100 kGy has the highest d-spacing and inter-chain separation. The increase of inter-chain separation is the result of proper fitting of MMT particles into the spaces between the surface of APP particles and PC/ABS chains. For maximum irradiation of 250 kGy on PC/ABS blend added with 25 phr APP and 8 phr MMT, the d-spacing and inter-chain separation was seen to be deteriorated due to the adverse effect of MMT agglomeration and polymer degradation. Hence, it can be concluded that for PC/ABS blends added with high APP loading of 25 phr, irradiation of 100 kGy would give an optimum state of PC/ABS blend with good intercalation and uniform dispersion.



**Figure 4.26: XRD curves of pristine MMT and PC/ABS blends added with high APP loading level of 25 phr under different MMT loading level and irradiation dosages**

**Table 4.2: d-spacing and inter-chain separation of pristine MMT and PC/ABS blends added with high APP loading level of 25 phr under different MMT loading level and irradiation dosages**

APP Loading (phr)	MMT Loading (phr)	Irradiation dosage (kGy)	2θ (°)	d-spacing (Å)	Inter-chain Separation (Å)
-	Pristine MMT	-	1.1494	76.80	96.00
25	2	0	1.1230	78.60	98.25
		50	1.1171	79.02	98.77
		100	1.1301	78.11	97.64
		250	1.1406	77.39	96.74
		0	1.1405	77.40	96.75
25	8	50	1.1450	77.10	96.37
		100	1.1126	79.34	99.17
		250	1.1345	77.81	97.26

## CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

This project has studied the flame retardancy, mechanical and physical properties of PC/ABS blends added with APP flame retardant and reinforced with MMT at suitable irradiation dosage. Based on the study, it was concluded that non-irradiated 50/50 PC/ABS blend without APP and MMT addition has low flame retardancy with LOI of only 24.3 %. By incorporation of suitable APP flame retardant and MMT, the LOI of the blends can be enhanced. For instance, it is shown that addition of 25 phr APP and 8 phr MMT into PC/ABS blend combined with electron beam irradiation of 250 kGy has resulted in the highest flame retardancy with LOI of 32.6 %. However, the mechanical properties of this formulation of blend are rather low with tensile strength of 26.97 MPa and elongation at break of only 7.4 %.

On the other hand, it is indicated that addition of 25 phr APP without MMT into the PC/ABS blend under high irradiation of 250 kGy gave a satisfying LOI of 30.5 % with tensile strength of 34.5 MPa, elongation at break of 9.1 % and Izod impact strength of 13.9 J/m<sup>2</sup>. Although this formulation of blend is considered to be satisfactory, there is some tolerance that could be made further. For PC/ABS blends added with APP of 25 phr and



MMT of 2 phr under irradiation of 50 kGy, it has a lower LOI of 30.2 % and same Izod impact strength of 13.9 J/m<sup>2</sup> compared to the previous blend. However, the tensile properties have been enhanced with tensile strength of 34.6 MPa and elongation at break of 10.5 %. Hence, it can be concluded that with slight reduction of LOI from 30.5 % to 30.2 %, the tensile strength and elongation at break of the PC/ABS blends can be enhanced. The optimum formulation is the PC/ABS blend added with 25 phr of APP and 2 phr of MMT under irradiation of 50 kGy.

The study has shown that increasing APP loading level has different effects on the flame retardancy, mechanical and physical properties of PC/ABS blends under various electron beam irradiation. Addition of appropriate amount of APP flame retardant into PC/ABS blends could help in reducing the adverse effect of high flammability due to the hydrocarbon origins of PC and ABS polymers. With proper addition of APP into the PC/ABS blend, the flame retardancy can be increased, giving a higher LOI value with lowered possibility of the polymer blend susceptible to fire. It is important to note that the amount of APP added has to be controlled to avoid the deterioration of mechanical properties of PC/ABS blends. Furthermore, it is concluded that increasing MMT loading level and irradiation dosage could provide secondary reinforcement which would improve the flame retardancy, mechanical and physical properties of PC/ABS blends. With the addition of suitable amount of MMT into the PC/ABS blends, intercalation effect could be triggered in the polymer matrix. As a result, the polymer structure can be strengthened by intercalation of PC/ABS polymer into the MMT layers. For

electron beam irradiation, it is shown that cross-linking network can be formed and induced with proper application of irradiation under suitable dosage. This could help in enhancing the overall properties of PC/ABS blends without degrading the polymer chains.

## **5.2 Recommendations**

By taking into accounts all the flame retardancy, mechanical properties and physical properties of PC/ABS blends, it is concluded that 25 phr APP and 2 phr MMT added into the PC/ABS blends at 50 kGy irradiation is the optimum formulation of blend. For further study, coupling agent can be added into the blends to investigate the effect on improving the mechanical performance of PC/ABS blends. The coupling agent could function as binder through the formation of a durable linkage between the organic material (polymer phase) and inorganic material (such as APP in this case). Aside from coupling agent, small amount of interfacial agents or compatibilizers can be incorporated to further enhance the interfacial adhesion between the polymer blends. Lastly, it is recommended that intumescent system additives consist of APP, pentaerythritol and melamine could be used as flame retardant system in PC/ABS blends.

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