INVESTIGATION OF ELECTRON BEAM IRRADIATED ACRYLONITRILE-BUTADIENE-STYRENE (ABS) UNDER OVEN TREATMENT

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

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May 2015

DECLARATION

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

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ABSTRACT

ABS is a common type of engineering plastic made up of rubbery polybutadiene and glassy phase styrene-acrylonitrile copolymer. It is a commonly used materials in the automotive and electrical industries. However, the applications of ABS are still limited as it fell short of meeting the requirements of high performance plastics. Past researches showed that the properties of the polymer could be significantly improved by the incorporation of electron beam irradiation. Therefore, this project was conducted to study the effects of electron beam irradiation and thermal ageing on the mechanical, thermal and physical properties of the ABS materials. Tensile and Izod Impact tests were adopted to measure the minimum forces that the samples could withstand before failure. The strength of the sample was seen to be improved up to certain range of irradiation dosage and it was attributed to the cross-linking effect which mitigated the deformation of the polymer matrix when forces were applied. However, the mechanical properties of polymer were observed to be deteriorated after prolonged thermal ageing. This was due to the chain scissioning of polymer chains which significantly discontinued the polymer matrix and caused the sample specimens to be broken easily. The chain scissioning effect was also verified by Differential Scanning Calorimetry (DSC) analysis and it showed that certain portions of the polymer chains were obviously shortened after the thermal ageing processes. Last but not least, the effects of electron beam irradiation and thermal ageing on the physical properties of the polymer were verified by Scanning Electron Microscopy (SEM). The amount of voids and fibrils formed were observed to increase with the irradiation dosage as well as the duration of thermal ageing. This also assured that the morphological structures of the ABS have been potentially disrupted.

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LIST OF SYMBOLS / ABBREVIATIONS

T_g	glass transition temperature, ℃
F	FWHM of the diffraction peak, radian
k	Scherrer’s constant
L	crystallite size, Å
T_m	melting temperature, ℃
T_{50}	temperature of 50 % degradation, ℃
T	temperature, K
T_c	crystallisation temperature, ℃
wt	weight percentage, %
ΔH	melting heat

λ	wavelength of Cu-Kα X-ray radiation, 1.542 Å
θ	incident angle of X-ray beam, degree

ABS	acrylonitrile-butadiene-styrene
XRD	X-ray Diffraction
SAN	styrene acrylonitrile
DSC	differential scanning calorimetry
EVA	ethylene-vinyl acetate
ENR	epoxidised natural rubber
SBR	styrene butadiene rubber
NBR	nitrile rubber
TEM	transmission electron micrograph
NBRr	acrylonitrile butadiene rubber
TMPTMA	trimethylolpropane triacrylate
FMIR	frustrated multiple internal reflection

FTIR	fourier transform infrared spectrum
SEM	scanning electron microscopy
FESEM	field emission scanning electron microscopy
HDPE	high-density polyethylene
$Mg(OH)_2$	magnesium hydroxide
PLA	polylactic acid
PC	polycarbonate
PB	polybutadiene
PP	polypropylene
PS	polystyrene
PVC	poly(vinyl chloride)
SAN	styrene acrylonitrile
TGA	thermogravimetric analysis

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CHAPTER 1

INTRODUCTION

1.1 Background

Acrylonitrile-butadiene-styrene (ABS) is a common type of polymer that comprises particulate rubber of butadiene or polybutadiene copolymer, that is dispersed in the matrix of styrene and acrylonitrile copolymer (SAN) (Kulich, et al., 2001). Its high impact resistance and toughness allow it to suit the diverse application of automotive industry including the manufacture of motorcycle helmet and car headlight housing. Over the decade, ABS has been actively involved in electrical and electronic industry such as the manufacture of telephones for impact resistance and aesthetic purposes (Adams, et al., 1993). Basically, the rigidity and chemical resistance properties of a commercial ABS is attributed to the presence of SAN (approximately 70 wt%) where the toughness of ABS depends ultimately on the content of polybutadiene. However, the applications of ABS are still limited in high performance engineering plastics as it came up short of meeting the requirement of high-end engineering plastic. Thus, many research have been done to improve the properties of polymer by taking the approach of inducing cross-linking network to the ABS matrix.

Irradiation techniques such as electron beam and gamma ray have been commonly used as an effective alternative to induce cross-linking in polymer matrix other than incorporation of chemical cross-linking agent. The irradiation applied on polymer matrix induces the formation of active free radicals. These radicals are able to bridge two long molecular chains (cross-linking) via the formation of C-C intermolecular bonds that serve to enhance the inter-chain interaction (Bee, 2014). In fact, polymers have been subjected to radiation would undergo structural change via two prominent effects: cross-linking and chain scissioning processes (Kumar, et al., 2012). Each of these processes would lead to distinct effects to the properties of polymers. For instance, if the chain scissioning process predominates over cross-linking process, polymer degradation where significant deterioration of mechanical, physical and chemical properties of the polymer will occur. On the other hand, predominant cross-linking will increase the molecular weight of cross-linked polymers in proportion to the radiation dose (Loo, Ooi and Boey, 2004). Thus, such polymers that have been cross-link have encountered improvement in their physico-mechanical properties (Rytlewski, 2010). Furthermore, the dosage of electron beam irradiation applied on the polymer must be controlled at optimum level in order to improve the properties of polymer. If the irradiation dosage applied is too low, it may not produce significant improvement on the polymer properties whereas if it is too high, the irradiated polymer may become brittle due to excessive cross-linking (Bee, 2013).

In order to verify the effects of cross-linking on improvement of polymer properties, irradiated polymers are subjected to thermal ageing process. Based on the past researches, the analysis of thermal ageing on irradiated ABS was adopted at constant temperature. However, in reality, the heat energy exerted on ABS will not remain at constant value especially when it is applied in application involving severe weather exposure such as automotive part. In the end, ABS subjected to inconsistent amount heat may be deteriorated. Hence, in this project, it is relatively important to analyse the effect of thermal ageing of ABS under different temperature.

To date, there have been very few reports regarding the properties of ABS subjected to electron beam irradiation at different dosage and thermal ageing at different temperature. The aims of this work were to investigate the effect of various electron beam irradiation dosage on ABS and the effect of various temperature thermal ageing on ABS.

1.2 Problem Statements

ABS is a common copolymer thermoplastic made by polymerising styrene, acrylonitrile and polybutadiene. It combines the strength and rigidity of acrylonitrile and styrene polymers with the toughness of polybutadiene rubber phase. These properties enable ABS to be widely used in marine, pipe, furniture, computer casing and so forth. Despite its decent mechanical properties, there is still, technically, room for improvement in order to meet the requirement of high performance engineering plastic. Thus, electron beam irradiation has been adopted to modify the mechanical properties of polymer by inducing cross-linking in polymer matrix. In this study, the effects of electron beam irradiation dosage on properties of polymer would be verified by thermal ageing process. Therefore, the problem statements of this project are as follow:

1. What are the effects of constant temperature thermal ageing on the mechanical, thermal and physical properties of irradiated ABS?
2. What are the effects of ramp temperature thermal ageing on the mechanical, thermal and physical properties of irradiated ABS?

1.3 Aims and Objectives

The aims of this project were to investigate the characteristics of ABS and effects of electron beam irradiation and thermal ageing on the mechanical, thermal and physical properties of ABS. The range of irradiation dosages required to enhance the properties of ABS would be studied. Plus, the effects of various temperature and time of thermal ageing on ABS would be investigated. In a nutshell, the main objectives were divided into the following two sub objectives:

1. To analyse the effects of constant temperature thermal ageing on the mechanical, thermal and physical properties of irradiated ABS.
2. To analyse the effects of ramp temperature thermal ageing on the mechanical, thermal and physical properties of irradiated ABS.

1.4 Scopes of Project

This project discussed on the effects of electron beam irradiation and thermal ageing on the mechanical, thermal, chemical and physical properties of irradiated ABS. The ABS samples were prepared and several characterization techniques were adopted to characterize the properties of ABS.

1.4.1 Sample Preparation

ABS was compressed into 1 mm × 15 cm × 15 cm sheets by using a hot presser. The 1 mm thick sheets were then electron beam irradiated at room temperature under an acceleration voltage of 175 kV. The irradiation dosages used were 50, 100, 150, 200 and 250 kGy with 50 kGy per pass.

1.4.2 Mechanical Properties

The mechanical properties of sample were investigated through tensile test and Izod impact strength. For tensile test, three tensile parameters, namely tensile strength, elongation at break and tensile modulus were determined for each of the samples. Tensile test was performed so that the force required to break the sample (tensile strength) and the extent to which the sample elongates until it reaches its breaking point (elongation at break) were determined by analysing the stress-strain curve generated. The sample was tested according to ASTM D1822 standard. While for Izod impact strength, it was tested according to ASTM D256 standard for the notched sample bars. The impact strength of ABS undergone thermal ageing was investigated.

1.4.3 Thermal Properties

Thermal properties of the samples were investigated through Differential Scanning Calorimetry (DSC). For DSC, two melting parameters, melting temperature and melting heat were investigated for each of the samples based on the DSC data generated.

1.4.4 Physical Properties

The crystalline structure and morphology of the sample were investigated by Scanning Electron Microscopy Analysis (SEM). For SEM, the microstructure of the fracture surface of the samples from the tensile test were scanned and analysed under the magnification of 1000×, 8000× and 15000× to study the morphology for both before and after ageing of ABS.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical Structure and Thermophysical Properties of Acrylonitrile-Butadiene-Styrene (ABS)

Acrylonitrile-Butadiene-Styrene (ABS) is a highly versatile engineering thermoplastic with large diversity of end uses. Its moderate position in terms of properties and price between expensive, high performance engineering plastic and cheaper commodity plastic are the reason why it is one of the most successful thermoplastic available. ABS is made up of rubber phase polybutadiene (PB) polymer dispersed in a thermoplastic matrix of styrene and acrylonitrile copolymer (SAN). SAN matrix was chemically grafted to PB phase so that rubber phase PB is compatible with SAN component. As a multiphase polymer, the structural effects exhibited by each of the polymer were independent. In general, rubber phase PB contributes the toughness of ABS, styrene phase contributes rigidity and processability while acrylonitrile phase exhibits the properties of resistance to chemical (Kulich, et al., 2001).

To be specific, acrylonitrile is a colourless liquid with boiling point of 77.3 ℃ and freezing point of approximately -83 ℃. It is soluble in both polar and non-polar type of solvents. Besides, it could undergoes several different types of chemical reactions, especially homopolymerisation which occurred at carbon-carbon double bond initiated by free radicals (Rutkowski and Levin, 1986). Saltman (1965) had reported that polybutadiene rubber polymer was formed by addition polymerisation of 1,3-Butadiene which is a reactive compound due to its double bonds. All polymerisation of 1,3-Butadiene requires the presence of initiator such as free-radical and ionic or coordinate mechanism. Styrene monomer on the other hand is a colourless to yellowish oily liquid with boiling point range of 145 to 146 ℃ and freezing point of -30.6 ℃ (Coulter, et al., 1970). Styrene polymerisation is slow at room temperature but can be increased with thermal treatment. Styrene requires free-radical or ionic reactions to initiate its polymerisation process (Platt and Keskkula, 1970). Chemical structures of ABS monomer is shown in Figure 2.1.

Typical densities of ABS are between 1.05 to 1.07 g/cm^3. It has heat deflection temperature of 94 to 104 ℃ and coefficient of thermal expansion of 70 to 90 parts per million per degree Kelvin. ABS is chemically resistive to chemical attack such as acid and alkali, but susceptible to severe attack by most polar solvents. The colour of ABS depends on the variation of particles distribution on its dispersed phase. The material is naturally opaque to yellowish when the dispersed phase is based on emulsion particle, whilst opaque to translucent white for bulk particles (Colborn, Buckley and Adams, 1993).

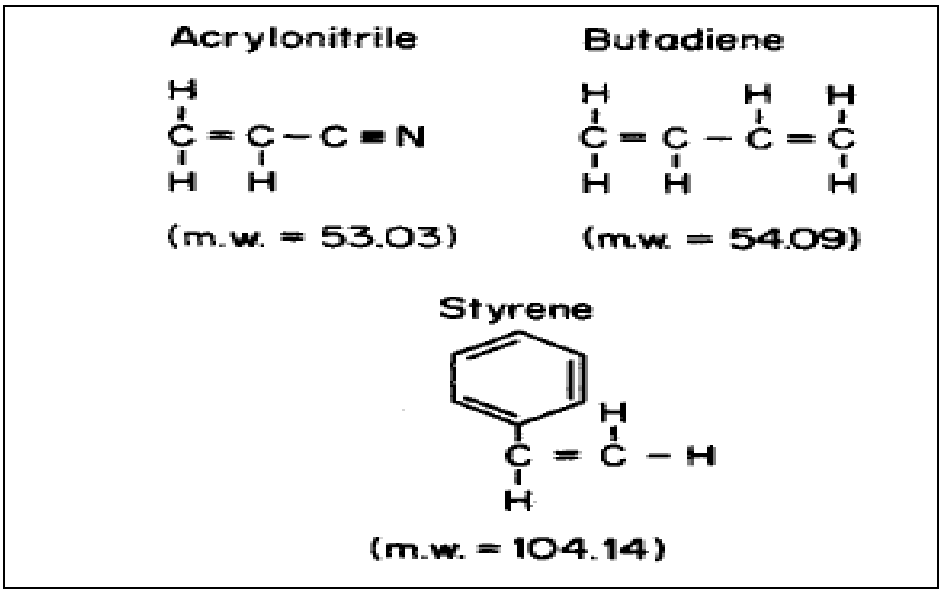


Figure 2.1: Chemical Structure of ABS Monomer (Rutkowski and Levin, 1986)

2.2 The Role of Electron Beam Irradiation on Polymer Matrix

Electron beam irradiation is an irradiation technique that has been commonly used as an effective alternative to induce cross-linking on polymer matrix rather than using traditional method of chemical cross-linking agent. Electron beam irradiation is capable of inducing polymerization, grafting, cross-linking and chain scissioning reaction on the polymer matrix. Besides, researchers had found out that irradiated polymers undergo structural changes via two important effects, cross-linking and chain scissioning (Ng, et al., 2013).

In comparison with traditional chemical cross-linking agent, irradiation cross-linking is relatively faster and more versatile, thereby leading to lesser energy consumption, occupies smaller space for processing and producing more uniform cross-linking on polymer matrix (Vijayabaskar, Tikku and Bhowmick, 2006). Besides, the inherent waste-free nature from this irradiation technique makes it less polluting than conventional chemical technologies (Cooper, et al., 1999).

Recently, there has been growing usage of electron beam irradiation in industry for cross-linking of thermoplastic. By varying the rate of irradiation dosage, rate of cross-linking and degradation of polymer can be monitored with the objective of improving properties of irradiated polymer (Landi, 2003). However, electron beam irradiation shall not be confused or mixed up with gamma irradiation method. This might be occurred as both electron beam and gamma ray irradiation were mostly used in current industrial processes. Furthermore, the principles and doctrines of interaction between these two radiation techniques with matters are of similar. The only significant difference between them was the penetration power.

Woo and Sanford (2002) concluded that gamma ray irradiation has higher penetrating power but low dose rate, whilst electron beam irradiation has lower penetrating power but compensate by high dose rate. Dose rate of electron beam was approximately ten thousand times higher than gamma irradiation. Plus, the most significant advantages of having high dose rate were to effectively modify the thermal properties of irradiated polymer matrix and reducing the exposure time needed for the same dose delivery (Woo and Sanford, 2002).

Electron beam irradiation on polymer matrix generates active free radicals that are capable of bridging two long molecular chains (cross-linking) via the formation of C-C intermolecular bond. As a result, inter-chain interaction within the polymer matrix of irradiated polymer could be enhanced effectively (Bee, 2014). In addition, electron beam irradiation with inherently high dose rate would lead to higher concentration of free-radicals produced during exposure and higher recombination reactions. Due to the fact that recombination reaction would not produce harmful product species, higher recombination would eventually lead to lesser polymer degradation and antioxidant consumption (Woo and Sanford, 2002).

2.3 Electron Beam Irradiation on Properties of Polymer Blends

Electron beam irradiation was proven to cross-link more effectively to the polymer matrix than using chemical cross-linking agent. Properties such as modulus and hardness of irradiated samples were found to be more superior to chemically cured samples at all dosage (Frounchi, Dadbin and Panahinia, 2006). Mechanical, thermal and physical properties of polymer blends can be altered by increasing the density of cross-linking in polymer matrix via electron beam irradiation process. Researches believed that the gel fraction yield, tensile strength, and stress at 100% elongation were proportional to the increasing of irradiation dose (Munusamy, et al., 2009).

Moreover, Liu and Tsiang (2002) investigated that in the aspect of microscopic level, structural changes such as macromolecular chain splitting, creation of low mass fragments, production of free radicals, oxidation and cross-linking have been found on the polymers after exposing to electron beam irradiation. Furthermore, if compare to pristine non-irradiated polymer samples, Liu and Tsiang (2002) justified that irradiated polymers have higher glass transition temperature as well as thermal decomposition temperature. In addition, mechanical properties such as elongation at break of acrylonitrile butadiene rubber blends was found to decrease in a steady manner whilst hardness and gel contents were found to increase in accordance to increasing of irradiation dosage (Yasin, et al., 2005).

2.3.1 Effect of Electron Beam Irradiation on Mechanical Properties of Polymer Blends

Mechanical properties of polymer blends can be enhanced and deteriorated depending on the predominant effect of either cross-linking or chain scissioning. The PVC/epoxidised natural rubber (ENR) blends produces radiation-induced crosslinking under electron beam irradiation improved the mechanical properties of the blends (Ratman & Zaman 1999). Both of these structural changes are varying with irradiation dosage absorbed by polymer. Landi (2003) had conducted a research on the effect of electron beam radiation on terpolymer acrylonitrile butadiene styrene (ABS). Based on the results obtained from tensile test, tensile properties such as tensile strength at break, tensile strain at break and elongation at break of both pristine and irradiated ABS samples is shown in Table 2.1.

Table 2.1: Tensile Properties of Irradiated and Non-Irradiated ABS Samples at Different Dosage of Irradiation (Landi, 2003)

Dosage (kGy)	Tensile Strength (MPa)	Elongation at Break (mm)	Strain at Break (%)
0	36	11.0	13.0
25	39	10.0	11.0
100	40	9.0	10.0
300	43	8.0	9.2
500	45	7.4	8.3

By analysing the results obtained in Table 2.1, it can be seen that as the irradiation dosage increases from 0 to 500 kGy, the number of cross-linking network increases as well, thereby leading to increment of tensile strength and decrement of both elongation at break and strain at break. The decreasing of elongation at break and strain at break could be attributed to the enhancement of cross-linking network at high irradiation dosage, thereby polymer matrix lost its flexibility and formed a larger cross-linking network that could prevent the easy slippage of intermolecular chain, resulting to lower elongation at break. The effects of irradiation dosage on tensile strength and strain at break of ABS samples are shown in Figure 2.2.

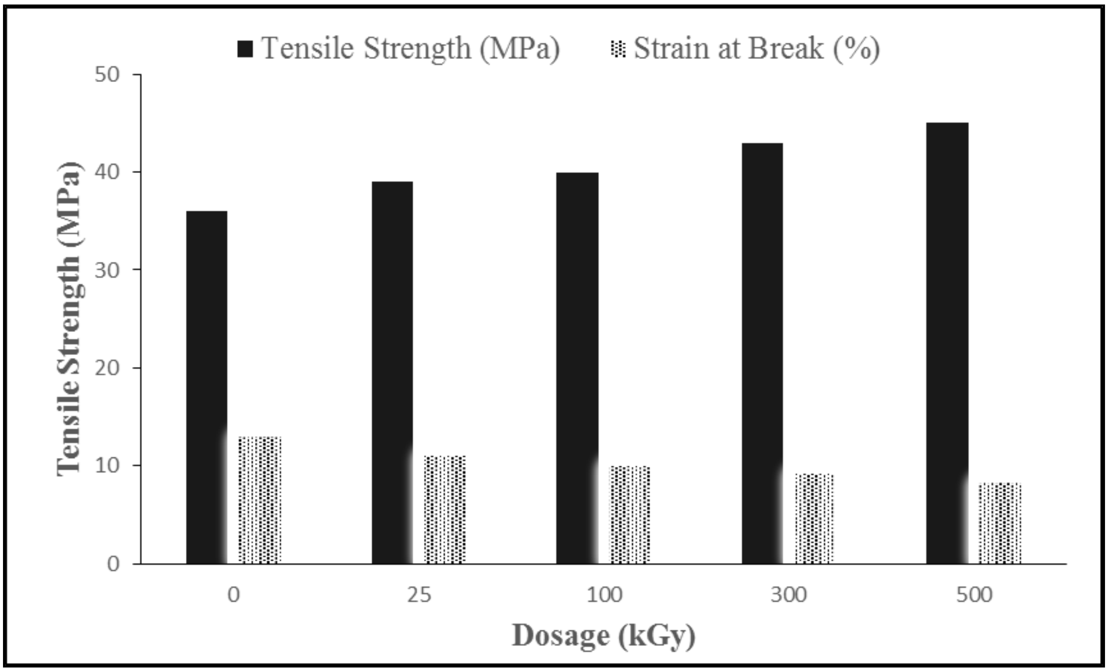


Figure 2.2: Tensile Strength and Strain at Break of ABS Samples as a function of Irradiation Dosage (Landi, 2003)

Vijayabaskar, Tikku and Bhowmick (2006) studied structure and properties of irradiated nitrile rubber with varying nitrile content in the presence and absence of trimethylolpropane triacrylate. They had concluded that the tensile strength and elongation at break (%) of nitrile rubber blends increase from the beginning and reach maximum value at around 50 kGy of irradiation dosage, but decrease subsequently with continuous increasing of dosage. However, the modulus at 100 % elongation increases continuously with irradiation dosage. This indicates that cross-linking effect is more dominant from 0 to 50 kGy, whereas cross-scissioning effect which lead to deterioration of mechanical properties predominates after 50 kGy dosage. Figure 2.3 shows the variation of tensile strength, modulus and elongation at break of nitrile rubber blends with respect to electron beam irradiation dosage.

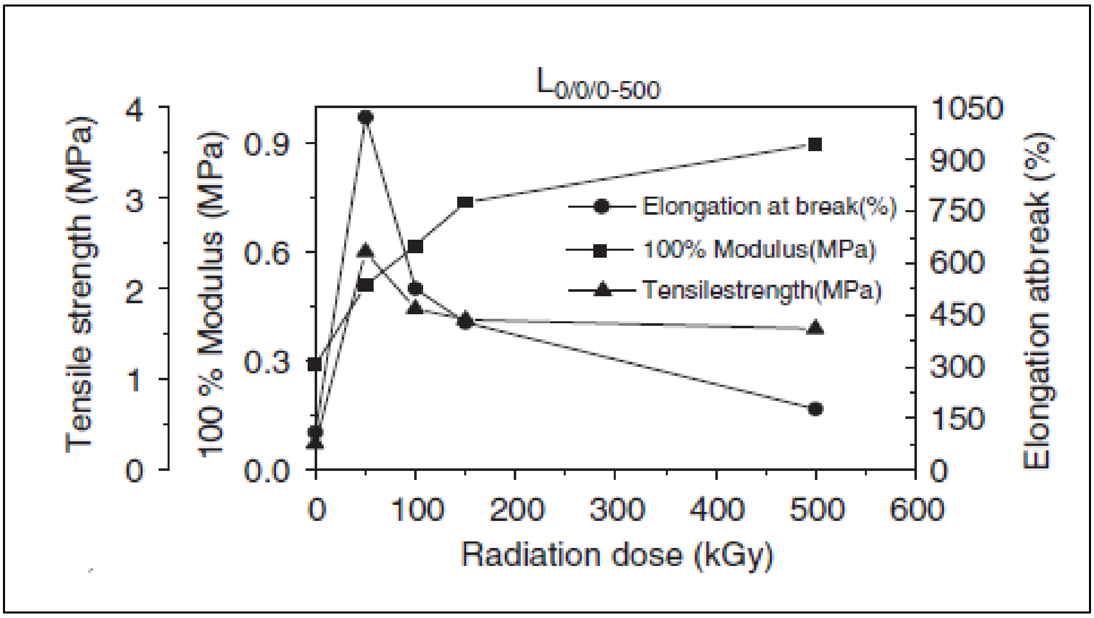


Figure 2.3: Effects of Irradiation Dosage (0-500 kGy) on Tensile Strength, Modulus and Elongation at Break of Nitrile Butadiene Blends (Vijayabaskar, Tikku and Bhowmick, 2006)

Predominant cross-linking in the polymer matrix will increase the molecular weight and intermolecular bond of cross-linked polymers. Thus, higher entanglement of polymer chains are formed to restrict the sliding of individual chain during stretching (Loo, Ooi and Boey, 2004). Thus, the enhanced of mechanical properties at higher irradiation dosage confirms the predominance of cross-linking. On the other hand, when the irradiation dosage exceeded above 50 kGy, chain scissioning was more favourable and therefore reducing the molecular weight of polymer matrix. The resulting polymer matrix with shorter chain and lower degree of entanglement would be more flexible, allowing easy slippage of chain during stretching and so weaker tensile strength. The decrement in mechanical properties at higher dosage thereby confirms the predominance of chain scissioning structural changes in polymer matrix (Vijayabaskar, Tikku and Bhowmick, 2006).

Tensile modulus of irradiated polymer blends on the other hand is proportional to the density of cross-linking formed (Bhowmick and Mangaraj, 1994), whereas the degree of cross-linking is proportional to the amount of irradiation dosage absorbed by the polymer (Vijayabaskar, Tikku and Bhowmick, 2006). Hence, continuously increase of irradiation dosage is accompanied by increase of modulus. This is because at high cross-linking density, the polymer matrix lost its mobility, thereby more stress is needed to deform the polymer leading to stiffer and less ductile polymer matrix (Yang et al., 2008).

Munusamy, et al. (2009) had conducted a research on the effect of electron beam irradiation on the properties of ethylene-(vinyl acetate)/natural rubber/organoclay nanocomposites (EVA/SMR L) blend. Electron beam accelerator with 2 MeV acceleration energy, 2 mA beam current and 50 kGy per pass for a dose range of 0 to 200 kGy was used. From the tensile results obtained, the authors reported that the effect of irradiation on tensile properties of polymer blends were not the same as compared to the trend of normal polymer blends. It was reported that the tensile strength of both pristine polymer and nanocomposites blends increase proportionally with respect to irradiation dosage (0 to 200 kGy). The improvement of tensile properties could be further supported by morphology studies on the irradiated polymer.

Tensile strength of polymer blends then achieved an optimum value when the organoclays added to the polymer blend were increased up to 4 phr. Further increment of organoclays loading in the polymer would result in deterioration of tensile strength. This indicates that organoclays may agglomerate at high loading level, whereas for low loading of polymer blend, organoclays were evenly distributed and dispersed uniformly over the entire matrix. As a result, agglomerates formed due to excessive loading of organoclay materials can act as stress concentrator which ease the pulling motion of tensile test and eventually weaken tensile strength.

Moreover, Munusamy, et al. (2009) investigated that the trend of elongation at break of irradiated EVA/ SMR L blend and nanocomposites were somehow similar to the common polymer blend. The value of elongation at break increasing gradually with the enhancement of irradiation dosage until an optimum value, then reduced again as higher dosage were applied. The increment of elongation at break could be attributed to the enhanced interaction between EVA addictive and SMR L rubbery phase due to subsequent cross-linking of electron beam irradiation. On the contrary, high cross-linking density induced by large irradiation dosage lead to stiffer polymer matrix with enhanced intermolecular bond, thereby reducing the value of elongation at break.

Yasin, et al. (2005) had conducted a research on the effect of concentration of polyfunctional monomers on the physical properties of irradiated acrylonitrile-butadiene rubber. The researchers had reported that the hardness value of polymer blends exhibit similar trend as in the case of tensile strength. Based on the results obtained, the hardness of polymer increased with increasing of irradiation dosage and filler content due to improved cross-linking network of polymer matrix. In order to verify the improvement of cross-linking network, gel fraction test had been conducted and the results obtained had shown a sharp increase of gel fraction as irradiation dosage was increased.

Moreover, Landi (2003) had studied the impact strength of ABS polymer samples prior and after electron beam irradiation and it was noticed that the Izod impact strength of ABS samples was extremely high at low irradiation dosage of 0 to 25 kGy, whereas at higher irradiation dosage (100 kGy) onwards, impact strength decreased rapidly with increasing of irradiation dosage. In general, impact strength measures the energy of polymer expended up to failure under condition of rapid loading. Impact strength of a polymer is important as it may be used to determine whether a polymer material has sufficient energy-absorbing properties useful for particular application. For impact test, the samples specimens were prepared according to ASTM D256 standard. Table 2.2 showed the value of Izod impact strength with responds to electron beam irradiation dosage. The results showed that when the dosages applied were too low (0 and 25 kGy), the impact strength of polymer samples were not known because the body of the specimen did not break during impact testing, indicating very high impact resistance. This could be attributed to the high energy-absorbing properties of polymer matrix as the density of cross-linking network formed were not sufficiently high to modify the inherent high impact strength of ABS samples. Besides, strong interfacial adhesion by grafting rubbery phase of polybutadiene and brittle matrix phase of styrene acrylonitrile (SAN) providing high impact resistance of ABS. However, as irradiation dosage kept on increasing (100 kGy and above), it had shown a rapid drop of Izod impact strength indicating that the polymer matrix had their stiffness increased at the same time becoming more fragile due to cross-linking effect (Landi, 2003).

Table 2.2: Effect of Electron Beam Irradiation Dosage on Izod Impact Strength of ABS (Landi, 2003)

Dose (kGy)	Izod Impact Strength (J/m^2)
0	-
25	-
100	63.25
300	38.81
500	15.88

2.3.2 Effect of Electron Beam Irradiation on Thermal Properties of Polymer Blends

Liu and Tsiang (2002) had conducted thermogravimetric and thermomechanical studies on irradiated ethylene-styrene interpolymer, ES140 (40 wt % styrene) and ES 169 (69 wt % styrene). About 7-9 mg of irradiated polymer samples were prepared and subjected to thermogravimetric analyser (TGA) measurement by heating at a rate of 20 ℃/min under the purging of nitrogen gas. Based on the thermograms results obtained, the initial decomposition temperature for both ES169 and ES140 were found to increase after irradiation, indicating higher thermal stability of compound. This was attributed to the higher heat transfer barrier induced by cross-linking of polymer matrix after irradiation. Other than irradiation, cross-linking structure could be induced by monomer free radical, which can be emitted through the breakage of double bond at high temperature condition (Ng, et al., 2013). The author had concluded that the irradiation dosage and degree of cross-linking have certain impact on the thermal stability of ethylene-styrene interpolymer within a dosage level of 0 to 200 kGy.

Other than that, the properties of thermal degradation of irradiated high-density polyethylene/ethylene vinyl-acetate copolymer/magnesium hydroxide composites (HDPE/EVA/$Mg(OH)_2$) was studied by Liu, et al., (2009). Thermogravimetric analyser (TGA) and Differential Scanning Calorimetry (DSC) were adopted to assist on the investigation of thermal properties. For TGA, thermogravimetric analysis was conducted at temperature from 50 to 600 ℃ with nitrogen purging and scanning rate of 20 ℃/min. Based on the thermograms results obtained, it can be seen that as the irradiation dose increases, weight loss of polymer composites postponed, thereby improved thermal stability properties. The thermogravimetry curves for both pristine and irradiated polymer composites are shown in Figure 2.4.

Based on the thermogravimetry curves, it can be seen that the weight of polymer composites with higher irradiation dosage appeared to be higher than polymer with lower irradiation dosage at the same temperature parameter. The weight loss associated to thermal decomposition of polymer blend occurred by two-step process, loss of acetic acid from EVA and dehydration of $Mg(OH)_2$ in the first step followed by formation of chain scissioning process in the second step. For instance, the temperature at 85 % weight of polymer composites under 50 kGy irradiation was 410 ℃, whilst the temperature required to decompose polymer irradiated at 200 kGy at same amount of weight was 440 ℃. The enhancing of thermal stability properties of irradiated polymer was attributed to higher cross-linking structure induced by irradiation.

However, researches had investigated that cross-linking structure may not formed solely under treatment of electron beam irradiation. In fact, it could be induced by monomer free radical at high temperature condition. For instance, the application of hot press compression-moulding could lead to formation of cross-linking on the polymer matrix. A merely small amount of monomer free radicals are sufficiently strong enough to form an extensive cross-linking network (Bee, et al., 2013).

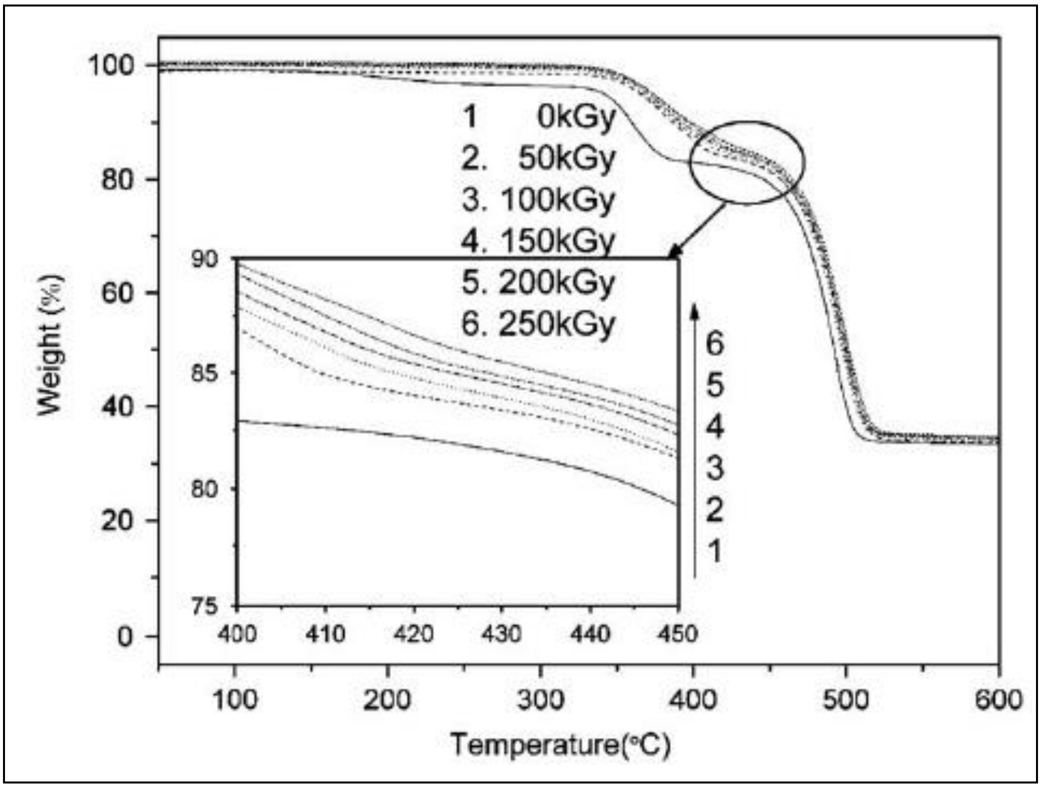


Figure 2.4: Thermogravimetry Curves For Pristine and Irradiated HDPE/EVA/Mg(OH)2 Polymer Composites (Liu, et al., 2009)

Other than TGA analysis, DSC analysis was carried out as well to further study the thermal properties of polymer samples. Liu, et al., (2009) had conducted the DSC analysis at a heating rate of 10 ℃/min in temperature range of 20 to 150 ℃ in the presence of nitrogen gas. Thermal properties such as melting point (T_m) could be obtained from the peak of the DSC thermo-gram curve whereas melting heat (ΔH) could be determined by automatic integration of the area under the melting thermo-gram curve. Figure 2.5 clearly shown the melting point and melting heat of the polymer composites increases marginally with the increment of irradiation dosage. The increased of both T_m and ΔH could be attributed to the improved intermolecular bonding of polymer matrix due to cross-linking effect. The resulting modification of polymer structure would restrict the growth of melting, thereby increasing T_m as more heat energy is needed to break the stronger intermolecular bond.

Besides, there were noticeably two peaks along the DSC curve indicating two melting process. The author of the report discussed that the first peak was the melting temperature of EVA at 87 ℃, whilst the second peak with higher amplitude was attributed to the melting of HDPE at temperature of 128 ℃. The fact that EVA was decomposing at faster rate or at lower temperature than HDPE could be attributed to the lower degree of crystallinity and consequently reduction in chain mobility.

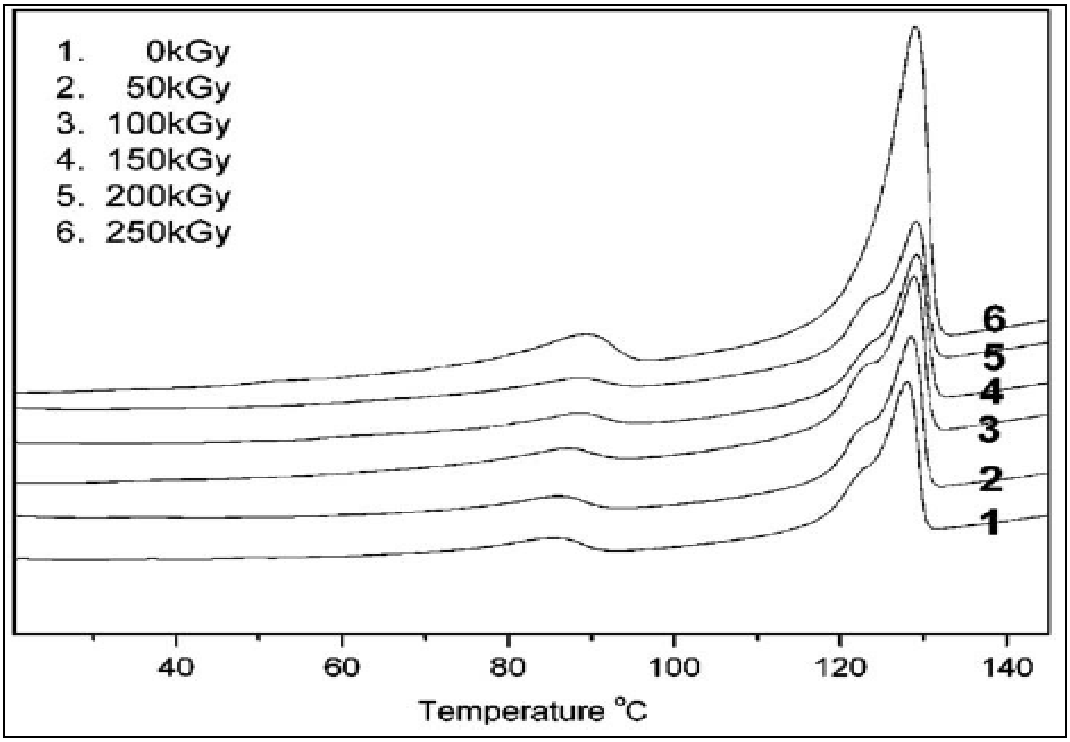


Figure 2.5: DSC curves of non-irradiated and irradiated HDPE/EVA/Mg(OH)$_2$ Polymer Composites (Liu, et al., 2009)

Crystallisation temperature (T_c) of polymer blends can be obtained from DSC thermogram analysis as well. Crystallisation process was believed to take place in polymer blends due to the alignment of polymer chain which lead to formation of a semi-crystalline phase (Noriman and Ismail, 2011). Based on the research done by Noriman and Ismail, styrene butadiene rubber/acrylonitrile butadiene rubber (SBR/NBRr) blends with different blend ratio of trimethylolpropane triacrylate (TMPTMA) had recorded similar results of T_c and only slight difference of ΔH due to cross-linking effect of irradiated polymer blends. The authors of the research had adopted both DSC and TGA characterisation technique. For DSC analysis, measurements were conducted at scan rate of 20 ℃/min under nitrogen atmosphere. Polymer samples were at first heated until 250 ℃ to nullify the influence of mechanical and thermal history, followed by cooling from 250 ℃ to 30 ℃ at constant scan rate.

Noriman and Ismail (2011) had believed that irradiated polymer blends tend to have higher heat enthalpy than non-irradiated as more polymer chains were aligned on the irradiated polymer. Besides, the authors also reported that the addition of filler TMPTMA helps to enhance the alignment of polymer chain via cross-linking. Based on the results obtained, as the amount of TMPTMA blend ratio increases, T_c of polymer occurred at higher temperature. These results could be attributed to the strong compatibility of NBRr and TMPTMA and higher degree of cross-linking aided by TMPTMA upon irradiation. This also indicates that dispersion and concentration of filler may influence the thermal properties of polymer blends (Colonna, et al., 2010; Uddin and Sun, 2010).

2.3.3 Effect of Electron Beam Irradiation on Physical Properties of Polymer Blends

The morphology studies of polymer blends are usually used to support the significant improvement or deterioration in tensile properties of irradiated polymer. Munusamy, et al. (2009) had adopted Scanning Electron Microscopy Analysis (SEM) to study the morphology of the fractured surface of EVA/SMR L blend. Based on the morphology results investigated, fibril-like structures were formed and distributed throughout the polymer matrix of irradiated polymer nanocomposites. It was noticed that polymer matrix irradiated at 200 kGy dosage were elongated and stretched at higher extent when compared with 100 kGy. As a result, the fibril surfaces were noticeably longer and finer, indicating a more ductile surface and higher resistance towards failure. These surface phenomenon could be used to support the results of higher tensile properties of exhibited by nanocomposite polymers at higher irradiation dosage.

Ng, et al., (2013) had conducted a similar research to investigate the effect of electron beam irradiation on morphology structure of polylactic acid (PLA) with TMPTMA blend. Scanning Electron Microscope (SEM) was used to record images at magnification of 500 to 1000x. Based on the images obtained from SEM, it can be observed that at low radiation dosage (25 kGy), discontinuous phase and fiber-like structures were formed. Nevertheless, small voids were noticed on the polymer matrix as well. These result could be explained by the fact that volatile-by products were released as a result of chain scissioning induced by irradiation. On the other hand, the formation of voids were relatively more critical at high irradiation dosage (150 to 250 kGy). This could be attributed to the trapping of gas within the discontinuous phase of polymer matrix. The gas trapped was a product of removal of ester bond via backbone chain scissioning. However, cavities were found absent in pure PLA subjected to same irradiation dosage. This absence was because pure PLA samples without addictive tend to have lower degree of cross-linking, high energy of irradiation could easily broke the entanglement of long chain, allowing the trapped gas to escape.

2.4 Thermal Ageing on Properties of Polymer Blends

The biggest challenge faced by the industry of plastic nowadays is the long term stability of moulded plastic part. Due to the increasing utilisation of plastic part in applications involving severe ageing problem such as vehicle parts, piping and furniture, the long term stability of polymer has always been a major concern for both manufacturers and end users. By exposing to different environmental conditions, it is inevitably for polymers to lose their properties due to intermolecular chain degradation. Heat, on the other hand, is one of the degrading agents and the impacts imposed by thermal treatment are often studied by thermal ageing. Several prominent effects are initiated during thermal ageing, chain scissioning, cross-linking and cross-linking breakage (Varghese, Bhagawan and Thomas, 2010). The stability of plastic is very susceptible to degradation by exposing to high temperature environment which lead to oxidative degradation, stress cracking, crystallization and loss of volatile compounds (Wyzgoski, 1976). Degradation can take place during drying process of polymerisation as well. Polymerisation is normally conducted at the presence of nitrogen gas so that the amount of oxygen could be suppressed to reduce the likelihood of oxidative degradation (Casale, Salvatore and Pizzigoni, 1975).

For polymers such as ABS, degradation of polymer is initiated by hydrogen abstraction in the secondary or tertiary carbon atoms of its main chain (Guyot, 1986). For instance, in ABS sample, hydroperoxide radicals produced via hydrogen abstraction from the α carbon atom next to trans-1,4 and 1,2 unsaturation sites in polybutadiene phase is the main factor contributing to thermal degradation of ABS. When the radicals generated combine with oxygen atom in the air, carbonyl and hydroxyl products will be produced (Tiganis, et al., 2002). Thermal degradation of polymer generally impose changes on its surface layer only without affecting the bulk layer. In fact, thickness of this degraded surface layer depends on the temperature and duration of exposure to heat (Wolkowicz and Gaggar, 1981).

Polymers that have been subjected to degradation, due to environmental factor will have lower performance than normal polymers (Reich and Stivala, 1971). Wyzgoski (1976) had reported that constant temperature ageing induced the decrement of tensile properties such as elongation at break due to the thermal embrittlement of polymer matrix. Impact resistance of aged polymer was shown to decrease slightly for times up to 1500 h at constant heating condition (Guest and Van Daele, 1995). In addition, morphology studies had shown that colour changes (discolouration) was limited on the surface of aged polymer while bulk phase of polymer was totally free of oxygen diffusion. Furthermore, microindentation was noticed on aged polymer surface which indicates brittle features (Tiganis, et al., 2002).

Guest and Van Daele (1995) had concluded that ageing temperature could be used to vary the surface morphology and properties of aged polymers. If the ageing temperature fall below the polymer’s glass-transition temperature (*Tg*), physical ageing of the amorphous polymer would take place. On the other hand, if ageing of polymer was conducted at temperature higher than *Tg*, thermo-oxidative degradation is alleged to have taken place (Tiganis, et al., 2002; Wyzgoski, 1986). In fact, even if physical ageing and thermo-oxidative degradation on SAN phase may contribute to deterioration of polymer's mechanical properties, the effect was still insignificant as compared to degradation on PB phase (Kulich, Wolkowicz and Wozny, 1993). Physical ageing is normally occurred when the amorphous polymer was cooled rapidly from temperature above *Tg* to certain range of temperature below *Tg* which provide sufficient intermolecular mobility for the rearrangement of structure to achieve thermodynamic equilibrium. Selection of ageing condition especially temperature is of vital as each of the reactants has unique and distinct mass diffusion rate and solubility which lead to different rate of polymer degradation. Apart from the effect of elevated ageing temperature and time, thermal degradation at ambient temperature was proposed to include both surface and bulk degradation (Tiganis, et al., 2002).

2.4.1 Thermal Ageing on Mechanical Properties of Polymer Blends

Mechanical properties of polymer are subjected to either improvement or reduction as polymer materials are very likely to degrade upon the exposure at elevated temperature. Thermally aged polymer samples would encounter either crosslinking or chain cleavage effects. Thermally aged polymers that subjected to chain cleavage (chain scissioning) would have its molecular weight reduced, whilst cross-link could induce embrittlement of polymer chain (Kader and Bhowmick, 2002). Chain scissioning can either takes place at the chain end to form a totally new product or at any position along the polymer chain to form lower molecular weight product (random scissioning) (Madras and McCoy, 1999). The impact strength of ABS was found to decrease upon oven ageing at temperature of 70 ℃ onwards (Golden, Hammant and Hazell, 1967; Wyzgoski, 1976).

Wolkowicz and Gaggar (1981) had studied the effect of thermal ageing on ABS terpolymer and reported that upon the exposure to heating environment, rubbery phase of polymer was subjected to degradation, as a result significant drop of impact strength was noticed on the aged polymer. Oven ageing was adopted in this experiment to heat the high impact grade ABS under various temperature and subsequently allowed to cool to room temperature. Upon ageing, ABS samples was taken for puncture impact testing. Based on the results obtained, when ABS was heated at constant temperature of 190 ℃, its impact strength dropped drastically at 30 minutes of ageing time. In fact, all ABS samples showed sign of brittle failure after 30 minutes of ageing time. Nonetheless, the impact strength of ABS samples was found to remain constant regardless of ageing time by heating at lower temperature of 90 ℃ (Tiganis, et al., 2002). Then, by continuously heating up to 1 hour, the impact strength of ABS decreased to nearly zero which indicates complete failure. By analysing the morphology of fractured surfaces, it was observed that the thickness of degraded surface layer increases with ageing time. A critical surface thickness in which polymers surface change from ductile to brittle failure was estimated at approximately 0.02 mm at all 190 ℃, 215 ℃ and 232 ℃ ageing temperature. Ultimate thickness of degraded layer at which polymer samples became total failure occurred at 0.2 mm.

Besides, the authors of report had investigated the molecular weight of polymer drop gradually up to 30 minutes of ageing time, but decreases rapidly after 30 minutes. The minor surface embrittlement of polymers along with very minimal molecular weight change noticed at the first 30 minutes may be occurred as a result of graft phase separation between polybutadiene rubber and matrix phase. After 30 minutes ageing time, chain scissioning take place which further deteriorate the energy absorbing efficiency of polymer.

Moreover, ABS blends were reported to exhibit strong and high mechanical properties such as impact strength due to the combination effect of each of unique components (Balart, et al., 2006). In ABS terpolymer, acrylonitrile contributes the chemical and heat resistance, while styrene contributes polymer rigidity and improved processability and polybutadiene provides the toughness and impact strength. Golden, Hammant and Hazell (1967) studied the thermal ageing of polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) blends. In order to evaluate the structural properties changes during thermal ageing, dynamic mechanical spectroscopy (DMS) was used. From the data generated by DMS, ABS has a Tg value of about 110 ℃ while Tg associated to PC is 155 ℃. Three ageing temperature which are 90, 110 and 130 ℃ were tested for each ABS blends.

In general, ABS blends subjected to high ageing temperature of below its *Tg* were found to have its tensile and flexural yield strength improved but lower ductility. Based on the results of impact test, the impact strength of ABS blends were found to decrease significantly only after 5 hours of ageing time for all three heating temperature. Ageing at 110 ℃ showed a larger and more significant decreased of impact strength compared to 90 ℃, whilst decrement of impact strength at 130 ℃ was similar to 110 ℃. This could be attributed to formation of crazing along with void and fibril-like structure on the polymer surface due to cross-linking (Donald and Kramer, 1982). Besides, the decrease in toughness of pure ABS was noticed for ageing temperature below *Tg* and it was projected to be attributed to physical ageing process. Nevertheless, for ABS/PC blends, toughness reduction of polymer was not merely caused by physical ageing but the oxidation of butadiene rubber as well. In fact, the loss of mechanical properties of aged ABS blends does not restricted to the thermo-oxidative degradation within PB phase but also physical ageing in SAN phase (Tiganis, et al., 2002).

Other than loss of impact strength, thermally aged polymers are susceptible to decrease of tensile properties as well. Wyzgoski (1976) had conducted research on effect of oven ageing on poly(acrylonitrile-butadiene-styrene) and reported the loss of tensile elongation but enhancement of yield strength and modulus of thermally aged ABS sample. The author then concluded that the effect of loss of elongation was greatest during ageing at 70 to 90 ℃, moderate during 50 and 60 ℃ and no significant changes for 40 ℃. As thermal ageing of ABS was conducted at temperature below its *Tg*, the resulting loss of elongation could be attributed to the embrittlement of glassy matrix phase (Golden, Hammant and Hazell, 1967; LeGrand, 1969). The author then investigated that oxidative and thermo-oxidative degradation of ABS induced chemical changes in its elastomeric structures, thereby carbonyl and hydroxyl groups were formed which further promote the breakage of double bond and improve cross-linking in matrix. In spite of that, all of these samples were heated for merely one hour and therefore samples aged at low temperature such as 40 ℃ might be noticeable after long period of time.

Tensile strength of ABS decreased rapidly upon heating under sunshine temperature which is about 20 to 40 ℃ up to 500 hours. It can be seen that tensile properties of polymer would decrease eventually even at inconsistent and low range of temperature for a long period of time (Casale, Salvatore and Pizzigoni, 1975). However, Kader and Bhowmick (2003) had studied that tensile strength of acrylate rubber polymer blends was shown to improve up to 3 days of constant heating environment at 150 ℃ before it started to decrease permanently. The modulus of rubber blends on the other hand increased steadily throughout the ageing period. The corresponding improvement of modulus could be attributed to the increased of polymer density by cross-linking induced by thermo-oxidative degradation (Tiganis, et al., 2002).

The improvement of both modulus and tensile strength at the earlier stage (up to 3 days) could be attributed to the complete polymerisation of monomer acrylates and minimal crosslinking effect of the blends. Tensile strength of acrylate rubber blends then decreased gradually from 150 ℃ to 200 ℃ at constant ageing time of 36 hours while modulus was reported to increase from 150 to 180 ℃, followed by slight reduction at 200 ℃. Tensile strength of nitrile rubber (NBR) blends showed significant improvement after ageing at 50 ℃ but decreased to an extent which is even lower than unaged samples upon heating at 100 ℃ (Varghese, Bhagawan and Thomas, 2001). The increased of tensile strength at 50 ℃ could be explained by higher degree of cross-linking in polymer matrix as evidenced in gel fraction test.

The relationship between impact strength of pure polymer with exposed sunshine hours has always been a major concern for the plastic industry. Variation of impact strength with exposed sunshine hours is relatively important so that the behaviour of polymer when subjected to elevated temperature for a longer period of time could be predicted. Casale, Salvatore and Pizzigoni (1975) had reported that the Izod impact strength of ABS polymer was decreasing rapidly ever since it started to expose to sunshine and reached lowest impact strength by 600 sunshine hours. However, if ABS was continuously heated for more than 600 hours under constant temperature, impact strength stopped decreasing but remain constant permanently which lead to high impact resistance.

2.4.2 Thermal Ageing on Thermal Properties of Polymer Blends

Apart from mechanical properties, the effects of thermal ageing on thermal properties of polymer blends must not be neglected, in fact it should be studied and properly monitored to meet the desired specifications and safety requirement for its vast applications. For instance, one of the biggest challenges encountered by polymer manufacturers and end-users is the variation of melting temperature of polymers during thermal ageing process.

Wyzgoski (1986) had adopted Differential Scanning Calorimetry (DSC) to analyse the effect of thermal ageing on ABS terpolymer under heating condition of 10 ℃/min in a nitrogen atmosphere. Based on the DSC measurements, glass-transition temperature (*Tg)* of ABS sample varied accordingly to its structural components and phases. *Tg* of polybutadiene (PB) phase was found to remain constant at -91℃ throughout ageing process while in styrene-acrylonitrile (SAN) phase, *Tg* of polymer increased rapidly with ageing time up to 300 hours at heating temperature of 90 ℃. DSC curve for the traces of both unaged and aged ABS samples after heating at 90 ℃ for 50 hours are shown in Figure 2.6. Based on the curve, it was noticeable that a large endotherm was noticed at temperature of approximately 100 ℃, which is very close to the *Tg* of SAN phase. The author of the report had concluded that the large endotherm plotted was not attributed to melting process as ABS is a fully amorphous polymer with no crystalline structure. In fact, the large endotherm could be attributed to the transition from glass to plastic phase. Large endotherm of aged samples occurred at higher temperature indicates a slower rate of transition from glass to plastic phase. As a result, the increment of brittle features of thermally aged polymers can be attributed to the changes of *Tg* induced by SAN glassy matrix. However, if ageing was conducted at temperature of 190 ℃, *Tg* of PB phase increased as a function of ageing time rather than remain constant as compared to previous study which use ageing temperature of 90 ℃.

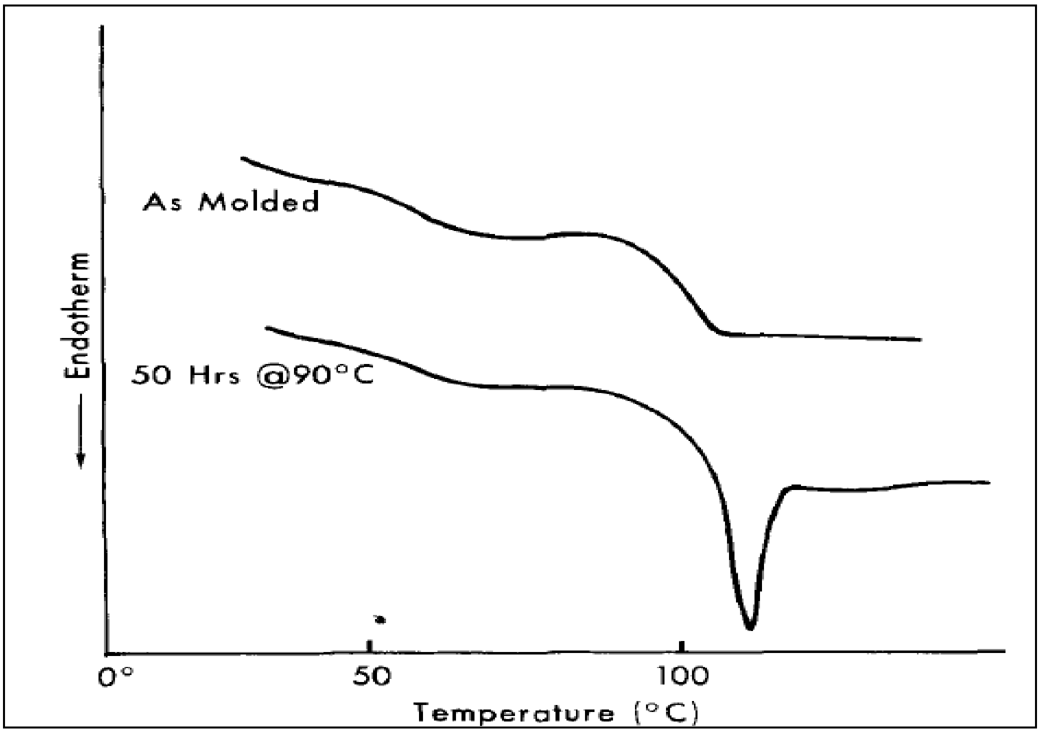


Figure 2.6: Differential Scanning Calorimeter (DSC) Curve for Traces of Unaged and Aged ABS Samples (Wyzgoski, 1986)

Other than DSC, thermogravimetric analysis (TGA) was often adopted to study the thermal properties such as degradation initiation temperature and temperature of 50 % degradation (T_{50}) of thermally degraded polymer. It has proved to be a good method to determine the thermal stability of polymer. Kader and Bhowmick (2003) found that the degradation initiation temperature of aged acrylate rubber blends increased up to 407 ℃ which is very much higher than unaged polymer blends, whilst T_{50} of acrylate rubber blends increased from 418 to 502 ℃, indicating higher thermal stability of polymer blends after ageing. The shifting of initiation of degradation to higher temperature was attributed to the formation of three dimensional network structure of polymer blends containing multifunctional polyacrylate. Kader and Bhowmick (2003) also concluded that polyacrylate is a polyfunctional monomer with large number of available cross-linking site. Thus, the formation of polyacrylate in rubber blends would improve the degree of cross-linking network and therefore enhanced the resistance of intermolecular chain breakage during degradation process.

Varghese, Bhagawan and Thomas (2001) had conducted a research on the thermogravimetric analysis and thermal ageing of crosslinked nitrile rubber/poly(ethylene vinyl acetate) blends (NBR/EVA). NBR/EVA blends with different blend ratio and filler content were subjected to ageing process at 50 ℃ and 100 ℃ for duration of 72 hours. TGA method was used to heat up the sample from 30 to 750 ℃ at heating rate of 10 ℃ /min. Based on thermograms data obtained, degradation of EVA blends occurred at two-stage in which first stage degradation started at 310 ℃ while second-stage occurred at 446 ℃. The initial degradation step could be attributed to the removal of acetic acid and degradation of polyethylene segment as a result of chain scissioning of vinyl acetate chain. The second stage of degradation occurred due to the elimination of polyene molecule after first degradation process. Nevertheless, for the case of NBR, two-step degradation process was observed as well. First and second degradation took place from 427 to 536 ℃ and 584 to 706 ℃ with a mass loss of 80.5 % and 18% respectively. Furthermore, degradation temperature of polymer blend strongly depend on the ratio of NBR blend. As the blend composition of NBR increases, initial and final decomposition temperature of polymer blends improved slightly, thereby enhancing thermal stability. Nonetheless, temperature of 50 % degradation (T_{50}) of NBR blends reduced gradually with NBR mass ratio until maximum level at 50 % NBR. As the mass ratio of NBR increased above 50 %, T_{50} of polymer blend recovered back to its original value.

Balart, et al., (2006) had studied the effect of thermal degradation of polycarbonate/acrylonitrile-butadiene-styrene (PC-ABS) blends. PC-ABS samples were prepared according to four different weight ratio (%). TGA with heating rate of 2 ℃/min was carried out to investigate the thermal properties of PC-ABS blends subjected to thermal degradation. Figure 2.7 shows the TGA curves of PC-ABS blends at different blend ratio. Based on the results obtained, PC-ABS blends exhibit very similar thermal properties regardless of the blend ratio as the temperature range for all the polymer blends was relatively narrow. Among all four polymer samples, pure PC samples was observed to have higher temperature at any degree of conversion as compared to pure ABS samples or PC-ABS blend samples. This indicates that pure PC has the highest thermal stability.

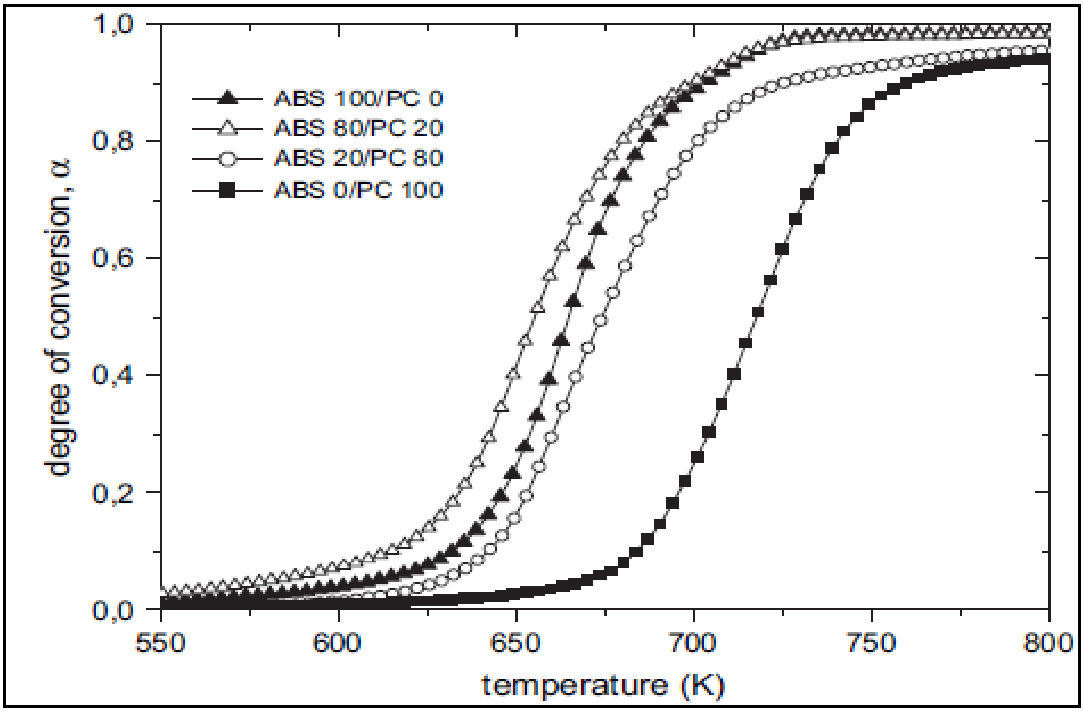


Figure 2.7: TGA Curves of PC-ABS Blends at Different Weight Ratio (Balart, et al., 2006)

Horrocks, et al., (1998) had conducted a research on the influence of carbon black on thermal degradation of oriented polypropylene (PP). DSC was adopted to study the crystallinity changes on the polymer samples upon thermal degradation. PP samples were subjected to oven ageing at 130 ℃ followed by DSC testing with heating rate of 10 K/min. The endotherm area of DSC data curve was calculated to measure the enthalpy heat of fusion, which representing the crystallinity of polymer samples. Based on the DSC-derived crystallinity curve, the degree of crystallinity was increasing steadily with respect to oven ageing time. The increased of crystallinity structures upon thermal ageing could be attributed to chain scissioning effect initiated by thermal oxidative environment. Polymers subjected to chain scissioning then allowed to undergo recrystallization process to rearrange their crystalline structure during exposure (Horrocks, et al., 1999). However, PP/carbon black blends on the other hand showed a lower value of crystallinity as compared to pure PP samples regardless of the duration of ageing. This could be attributed to the alteration of highly oriented crystalline structures upon the addition of carbon black filler.

2.4.3 Thermal Ageing on Physical Properties of Polymer Blends

Surface morphology or physical properties of thermally aged polymer samples are often studied to find out the modified phase and properties changes on the surface of polymer. Besides, the products formed as a result of thermal degradation would contribute to inconsistent surface microstructure which eventually lead to formation of stress concentration site (Tiganis, et al., 2002). Wyzgoski (1986) had investigated that ABS samples subjected to oven ageing at temperature of 90 ℃ would not produce any significant changes in term of the shape or size of polymer and distribution of rubber particles. Transmission electron micrograph (TEM) with extensively large magnification power was adopted for morphology studied of aged polymer. Based on the micrograph, there was no obvious changes on the number of rubber particle near the outer surface of ABS before and after ageing. Furthermore, frustrated multiple internal reflection (FMIR) was used to provide information regarding the distribution of polybutadiene rubber particle near the polymer surface. Based on the results measured by FMIR, distribution of rubber particles near the polymer surface decreased after ageing. This could be attributed to the degradation induced by oxidative environment.

Tiganis, et al., (2002) had investigated the mechanism of degradation on the surface of ABS blends via Fourier Transform Infrared Spectrum (FTIR). Based on the results obtained, the surface spectrum of ABS decreased rapidly in the absorbance bands at 966.92 cm^{-1} and 911.43 cm^{-1} which corresponds to trans C=C unsaturation (vinyl) in polybutadiene and 1,2 butadiene terminal vinyl C-H. This could be attributed to modifications of surface structure of polybutadiene phase as a result of either chain scissioning or cross-linking. In addition, hydroperoxide species was observed by absorbance bands at 1724.4 cm^{-1} and 3473.49 cm^{-1} which indicates carbonyl and hydroxyl group atom respectively. This result was supported by the research that has been done by Shimada and Kabuki (1968) which proposed that degradation at rubber phase of ABS would lead to generation of hydroperoxide.

CHAPTER 3

METHODOLOGY

3.1 Materials

The polymeric material used in this project was Acrylonitrile-Butadiene-Styrene (ABS). The specifications of the material were discussed in the following sections.

3.1.1 Acrylonitrile-Butadiene-Styrene (ABS)

In this project, general purpose ABS with grade of TOYOLAC 500 322 produced by Toray Plastic (Malaysia) Sdn. Bhd. was used. The mixtures in the ABS resin are acrylonitrile-butadiene-styrene copolymer (95 % or more), additives (5 % or less) and styrene (0.05 to 0.2 %). The resins used would be palletised with mass density of 1050 kg/m^3 and melt flow index of 20 g/10 min.

3.2 Formulation

The following tables show the formulation of electron beam irradiation dosage on ABS samples.

Table 3.1: Formulation Table for Electron Beam Irradiation Dosage on Samples

Sample	Electron Beam Irradiation Dosage (kGy)
S0	0
S50	50
S100	100
S150	150
S200	200
S250	250

3.3 Sample Preparation

ABS was compressed into 1 mm × 15 cm × 15 cm sheets by using Lotus Scientific L5-11009 hot presser. After carried out hot press process, dumbbell shape specimen was then obtained by cutting the compression moulded sheets with Cometech QC-603A pneumatic tensile cutter according to ASTM D1822 standard. The sample specimen prepared was electron beam irradiated at room temperature using an accelerating voltage of 175kV. The irradiation dosages were 50, 100, 150 and 200 kGy with 50 kGy per pass. After irradiation, the samples were then subjected to thermal ageing by using Memmert Universal Oven at four heating conditions for a duration of 2, 4, 6 and 8 days.

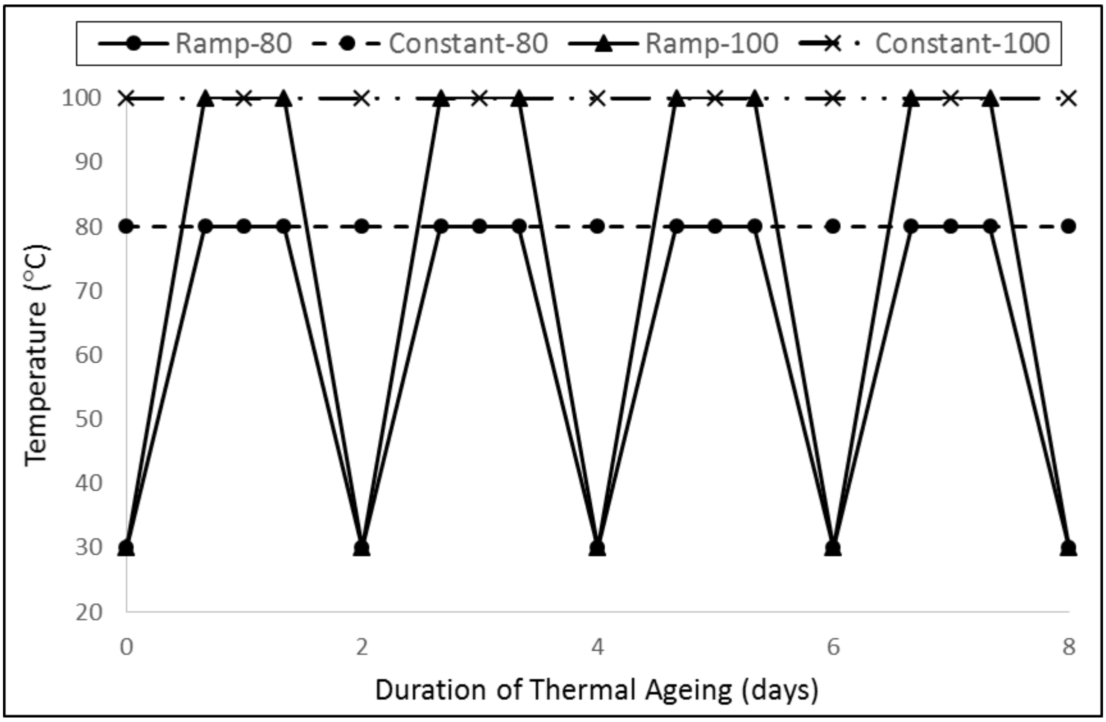


Figure 3.1: The Profile of Four Heating Conditions throughout the 8 Days Thermal Ageing Operation

For the first heating condition (Ramp-80), the samples were heated linearly from 30-80 ℃ for 16 hours, followed by constant heating at temperature of 80 ℃ for another 16 hours and lastly linear cooling from 80-30 ℃ for the last 16 hours of the cycle. For second heating condition (Constant-80), the samples were subjected to constant heating at temperature of 80 ℃. While for the third heating condition (Ramp-100), samples were heated linearly from 30-100 ℃ for 16 hours, followed by constant heating at temperature of 100 ℃ for another 16 hours and lastly linear cooling of samples from 100-30 ℃ for the same amount of time. For the fourth heating condition (Constant-100), the samples were heated constantly at temperature of 100 ℃. Same heating conditions were carried out by samples for duration of 4, 6 and 8 days as well.

3.4 Characterization Techniques

Each of the samples upon electron beam irradiation was subjected to various kind of characterization tests to analyse their mechanical, thermal and physical properties. The characterization tests used were tensile test, Izod impact strength, Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy Analysis (SEM).

3.4.1 Tensile Test

For tensile test, mechanical properties of the samples such as tensile strength, elongation at break and tensile modulus were evaluated. Samples subjected to tensile test were tested according to ASTM D1822 standard by using Instron Universal Testing Machine 5582 Series IX tensile tester configured with Bluehill software. The test was carried out at room temperature by using 2 kN of load cell and 50 mm/min of crosshead speed. The datasheet of tensile stress at maximum load (tensile strength), tensile strain at maximum tensile stress (elongation at break) and tensile modulus were generated by Bluehill software.

3.4.2 Izod Impact Test

For impact test, it was performed in accordance to ASTM D 256 standard for the notched sample bars with different irradiation dosage and ageing conditions. The machine being used in this test was Izod impact tester XJU-22 manufactured by Beijing United Test Co., Ltd. This machine consists of a big foundation base with a vise to clamp on the sample and ensure that the sample bar is placed in an upright vertical position during the test. Impact was exerted to the notched side of the sample bar when a pendulum-type of hammer connected to the impact tester is released to break the sample bar. The energy utilized by pendulum hammer to break the sample bar is equated with the impact strength of the sample.

3.4.3 Differential Scanning Calorimetry

In order to study the melting behaviours of polymer samples such as melting temperature and melting heat, each of the samples was subjected to Differential Scanning Calorimetry (DSC) analysis by using Mettler Toledo DSC821^e analyser. In order to conduct this analysis, 5-8 mg of polymer sample was heated from 30 to 200 ℃ through constant heating at 10 ℃/min. In addition, nitrogen gas was applied for purging purpose throughout the entire process at constant volumetric flow rate of 20 ml/min.

3.4.4 Scanning Electron Microscopy Analysis

After undergoing tensile test, the fractured surface of the samples would be tested with Scanning Electron Microscopy (SEM) to study the effect of thermal ageing on the surface morphology of the samples. Before conducting the test, a small part of the fractured sample was cut and placed on the sample holder with the fractured surface facing up. A thin layer of gold was coated on the sample surface before inserting it into the microscope chamber for analysis. The microscope being used was S-3400N scanning electron microscope from Hitachi. Lastly, microphotographs of the samples were generated at magnifications of 1000×, 8000× and 15000× respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Impact Test

Impact strength is the ability of a material to withstand rapid shock and loading preceding fracture of the material. It is commonly express as amount of energy absorbed by material before failure. Figure 4.1 shows the curve of impact strength against irradiation dosage for ageing condition of Constant-80 where the polymers have been subjected to thermal ageing at constant temperature of 80 ℃ for 2, 4, 6 and 8 days. For unaged sample (0 day thermal ageing), it can be observed that the impact strength increased when the irradiation dosage increased from 0 to 50 kGy and then decreased from 50 kGy to 250 kGy. In fact, the impact strength exhibited by unaged ABS samples were significantly higher than all the thermally aged samples. The trend of lower impact strength upon thermal ageing was consistent with the researchers conducted by Golden, Hammant and Hazell (1967) and Wyzgoski (1976) which concluded that the impact strength of ABS was found to decrease upon oven ageing at temperature of 70 ℃ onwards.

The improvement of impact strengths upon irradiation at 50 kGy was attributed to craze formation at the crosslinked polybutadiene rubbery phase. Such newly-formed surface with enormous craze is capable of sustaining loading by absorbing energy and toughening of material (Smallman and Bishop, 2013). Besides that, it is estimated that certain degree of cross-linking has occurred in the polymer matrix to enhance the interfacial adhesion along with reduction of stress concentration in notch region. This phenomenon was found consistent with the research that had been done by Baker, Bellare and Pruitt (2013) in which they had concluded that a low cross-link density (<100 kGy) may improve the resistance of crack initiation and propagation of polymer, not to mention the density of cross-linking at 50 kGy were too low to deteriorate the inherently high energy absorbing properties of grafted copolymer ABS.

Meanwhile, impact strengths of irradiated ABS samples were declining progressively as the irradiation dosage increased above 50 kGy. This could be occurred due to poor interfacial adhesion between rubbery PB and glassy SAN phase associated with irradiation degradation at high irradiation dosage (Chaudhari, et al., 2007). In addition to poor interfacial adhesion, with increasing cross-linking density at high irradiation dosage (>100kGy), resistance to crack propagation reduced, thereby lesser stress intensity is needed for crack growth (Baker, Bellare and Pruitt, 2003). Besides, this phenomenon might be attributed to excessively high energy of irradiation induced intensive degradation to the polymer matrix rather than cross-linking (Zenkiewicz and Dzwonkowski, 2007).

Furthermore, Figure 4.1 also shows that for higher irradiation dosage (>50 kGy), ABS samples undergone thermal ageing of 4 days and above would have remarkably lower value of impact strength as compared to samples with 2 days of thermal ageing. This indicates that the crack propagation resistance and interfacial adhesion of polymer matrix have been severely disrupted after prolonged thermal ageing. As a consequences, low crack initiation and propagation energy were expected to cause embrittlement and degradation of material’s impact strength (Baker, Bellare and Pruitt, 2003).

In addition, it can be observed that for the first 2 days of thermal ageing, all the samples possessed slight reduction of impact strength. This could be attributed to the reduction of interfacial adhesion between terpolymer due to the heating effect of ageing. In addition, the impact strength of high dosages(>100 kGy) irradiated ABS seen to be independent to the duration of ageing as their impact strength were declining at very minimal rate throughout 8 days of ageing. This could be occurred as the polymer matrix has been severely disrupted by excessively high irradiation energy. Consequently, the linkages of grafted copolymer PB and SAN were broken down, thereby aiding the stress concentrator notch region to fail prior to the operation of thermal ageing. Besides, the weak heating effect at 80 ℃ could induce minor surface embrittlement and very minimal reduction of molecular weight, therefore decreasing impact strength of polymer (Tiganis, et al., 2002).

Meanwhile, the impact strengths of low dosages (<50 kGy) irradiated ABS samples decreased from the beginning of day 2 to 4 and subsequently increased from day 4 to 6. It can be seen that significant loss of impact strength would only occur after 2 days of thermal ageing and regain back right after 4 days of ageing. This could be attributed to the low temperature of heating effect which required longer hours of ageing period to deteriorate the interfacial adhesion of majority polymer matrix. On the other hand, it is suggested that rearrangement of polymer chain has occurred due which caused the polymer to gain sufficient energy to withstand rapid loading of impact and subsequently regained impact strength.

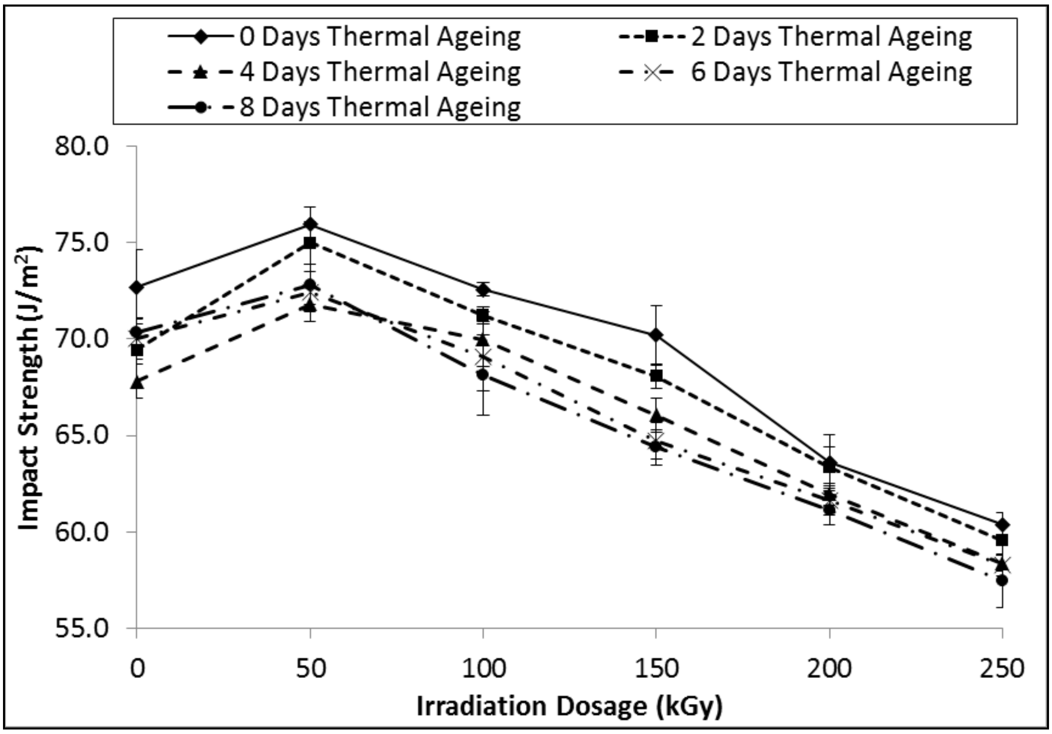


Figure 4.1: Impact Strength against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Constant-80

Figure 4.2 shows the graph of impact strength against irradiation dosage for condition Ramp-80 in which all the samples were heated in a cyclic manner which they were heated from 30 ℃ to 80 ℃ for 16 hours, followed by constant temperature heating at 80 ℃ for 16 hours and decreased linearly from 80 ℃ to 30 ℃ for another 16 hours. By analysing the curve, it can be seen that the trend of impact strength decreased linearly with increasing of irradiation dosage which was consistent with the research that have been done by Pramanik, et al. (2009) where the impact strength of Nylon 6 has fallen with increasing of irradiation dosage.

However, at low irradiation dosage (50 kGy), ABS sample subjected to 2 days of thermal ageing had shown improvement of impact strength as compared to other samples (4, 6 and 8 day thermal ageing) which possessed insignificant changes. This could be attributed to the cross-linking imposed to the polymer matrix which strengthened the adhesion of polymer matrix and minimize void formation (Baker, Bellare and Pruitt, 2003). As a result, such crosslinked polymer is said to exhibit high crack initiation energy when it was subjected to impact. On the other hand, samples with thermal ageing of more than 4 days possessed no significant improvement of impact strength may be attributed to reduction of interfacial adhesion effect as the effect of prolonged thermal ageing became more significant than cross-linking of polymer.

Furthermore, the trend of impact strength against duration of thermal ageing could be observed from the curve as well. The trend of impact strength decreased slightly after 2 days of thermal ageing and remained almost unchanged as the duration of thermal ageing prolonged to 8 days. For the first 2 days of thermal ageing, irradiated samples of 50 and 100 kGy decreased gradually while others (>100kGy) remain stagnant. This was attributed to the elevation of temperature which disrupted the graft phase separation of rubber and matrix phase, thereby leading to higher stress concentration during impact. On the other hand, the trend of impact strength for ABS irradiated at 200 and 250 kGy remained stagnant throughout the ageing process. This indicates that their polymer chains have been severely degraded by excessively high irradiation induced chain scissioning which eventually deteriorates the energy absorbing efficiency of polymer (Tiganis, et al., 2002).

In addition, for ABS samples irradiated at 50 kGy, the trend of impact strength were similar to that of condition Constant-80 where the impact strength decreased after certain duration of thermal ageing followed by increment as the thermal ageing prolonged to 8 days. In fact, it could be noticed that the ABS samples of condition Constant-80 required longer time (4 days) in order to have its impact strength recovered while ABS of Ramp-80 spent 2 days in advance to achieve the same outcome. This phenomenon was attributed to the fact that recrystallization of polymer occurred earlier for the case of condition Ramp-80 as polymer samples were cooled down after 36 hours of ageing within each cycle as compared to constant temperature for condition Constant-80.

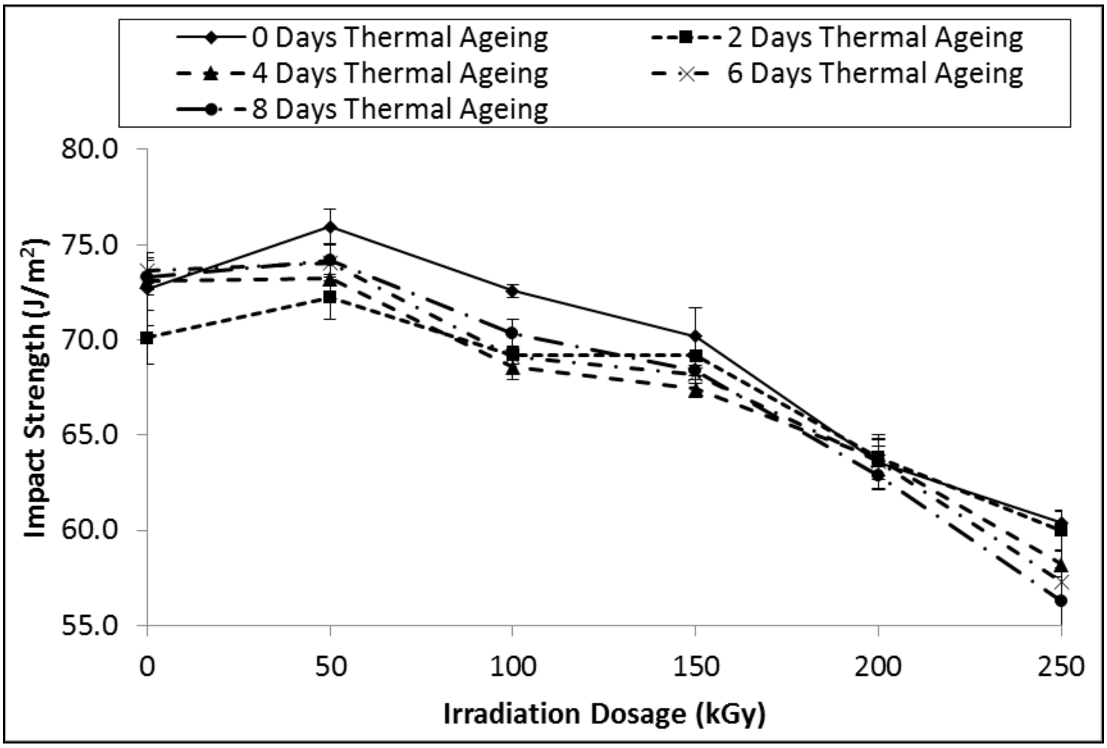


Figure 4.2: Impact Strength against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Ramp-80

The effect of impact strength upon irradiated at various dosages for condition Constant-100 thermal ageing can be observed from Figure 4.3. From the curves, it can be seen that the trends of impact strength were similar to that of condition Constant-80 where the impact strength of most of the samples were decreasing with increment of irradiation dosage. However, the average impact strength values for all the samples of condition Constant-100 were generally lower than of condition Constant-80. By referring to APPENDIX A, it can be seen that the value of impact strength after condition Constant-100 fell within the range of 54 – 72 J/m^2 as compared to 57 – 75 J/m^2 of condition Constant-80. This indicates that apart from dosage of irradiation and duration of thermal ageing, temperature of thermal ageing is also one of the factors that could affect the impact strength properties of material.

However, in contrast to condition Constant-80, ABS sample irradiated at 50 kGy exhibited a reduction of impact strength after 6 and 8 days of thermal ageing. This indicates that the heating effect from elevated temperature has altered the mechanisms of cross-linking process as the degradation effect from thermal ageing was more dominant than cross-linking. In addition, it can be observed that impact strength of ABS samples irradiated at 50 kGy were lower than non-irradiated samples. This can be explained by the formation of crazing with microvoids and fibril-like structures along the surface of polymer induced by chain scissioning at high temperature (Donald and Kumar, 1982).

Besides, the effects of impact strength against duration of thermal ageing for condition Constant-100 at various irradiation dosages were studied as well. From the curves, it can be noticed that the impact strength of samples irradiated at 50-150 kGy decreased progressively throughout the duration of 8 days thermal ageing. However, ABS samples irradiated at 200 kGy were experiencing improvement of impact strength after 4 days of thermal ageing. This could be attributed to recrystallization of polymer chains which enhanced interfacial adhesion and reduced stress concentration of polymer.

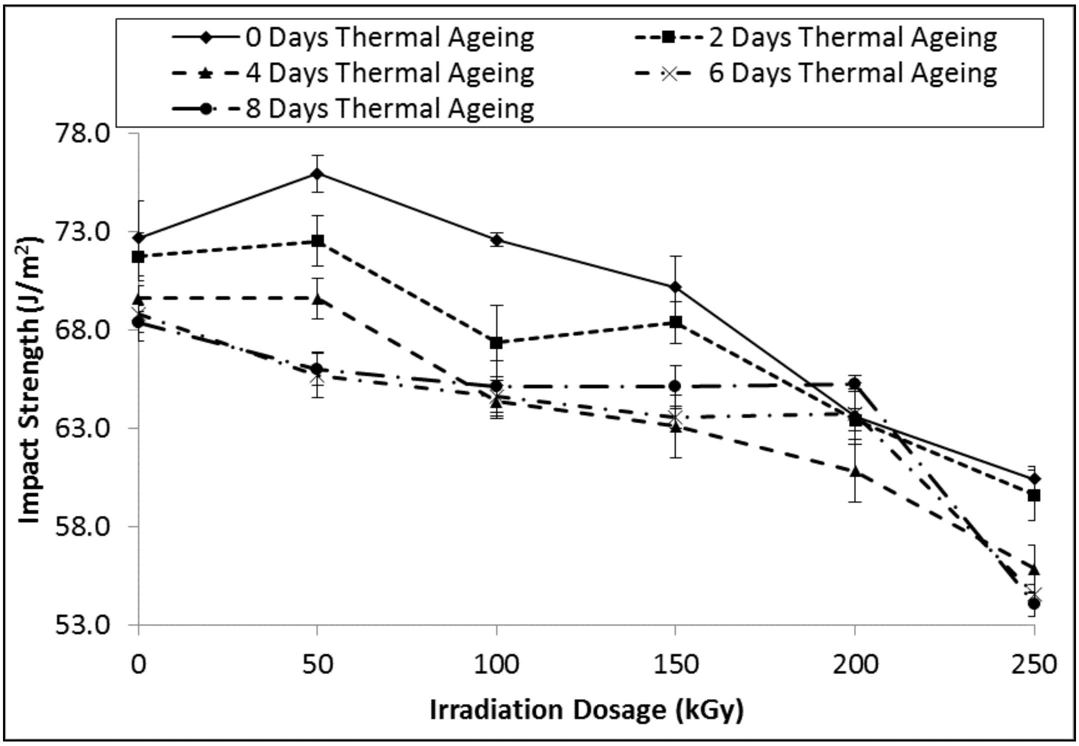


Figure 4.3: Impact Strength against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Constant-100

Figure 4.4 shows the graph of impact strength against irradiation dosage for condition Ramp-100 thermal ageing. Similar to the unaged samples, when the irradiation dosage increased to 50 kGy, impact strength of ABS samples improved. This might be attributed to cross-linking which effectively reinforced the interfacial interaction of grafted and polymer matrix. Furthermore, when the irradiation dosage increased from 50 to 150 kGy, impact strength decreased rapidly. This indicates that the reduction of crack initiation and propagation resistance were initiated when chain scissioning mechanisms was more dominant within the polymer matrix.

However, when polymer samples were irradiated at 200 kGy, impact strength of ABS samples subjected to more than 4 days of thermal ageing increased slightly. This phenomenon was attributed to certain degree of crosslinking which strengthened interfacial adhesion and minimized void formation of polymer. As the irradiation dosage further increased to 250 kGy, all the samples experienced fell of impact strength due to excessively high energy of irradiation which severely damaged the polymer chains.

Besides, Figure 4.4 also shows the effect of impact strength against duration of thermal ageing for condition Ramp-100 at various irradiation dosage. From the curves, the impact strength of polymer samples decreased when the thermal ageing prolonged to 4 days. This was attributed to the breakage of graft interface between rubbery and matrix phase of ABS by thermally heating at high temperature.

Apart from that, it can be observed that impact strength of samples subjected to 50 kGy irradiation dosage was higher than non-irradiated samples. This indicates that cross-linking has promoted the reinforcement effect to the polymer interface, therefore enhanced the energy absorbing efficiency of polymer. In addition, when the duration of thermal ageing prolonged to 6 days, most of the samples were experiencing improvement of impact strength. This indicates samples started to undergo recrystallization and therefore showed an overall increment of impact strength. As the duration of thermal ageing further prolonged to 8 days, the impact strength fell off again as the reduction of interfacial adhesion from prolonged thermal ageing outweigh the recrystallization effect.

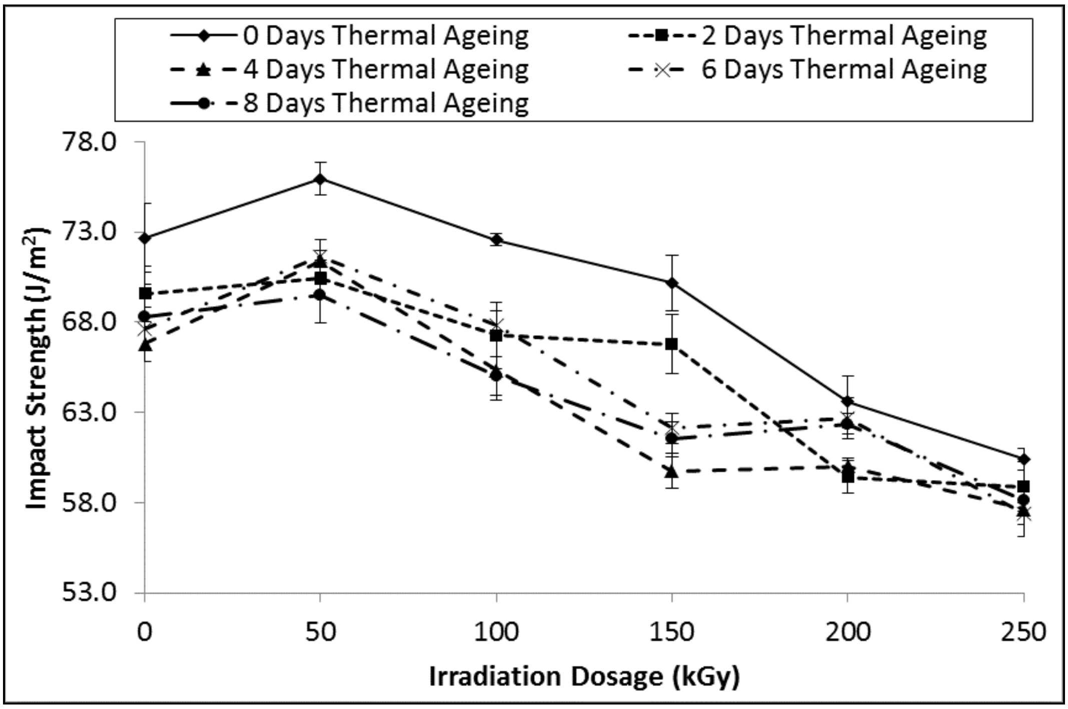


Figure 4.4: Impact Strength against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Ramp-100

As a conclusion, it should be noted that impact strength test is still a controversial method of evaluating mechanical properties of a material as compared to other traditional methods such as tensile test. In fact, it relies on the notch region in the centre of specimen to help induce crack initiation and propagation which eventually acts as a failure point. However, it could be possible for polymer sample to fails at any other spot rather than at the stress concentration notch region. Thus, the accuracy and reliability of impact test in determining the mechanical properties of material are doubted and remained sceptical for researchers.

4.2 Tensile Test

4.2.1 Thermal Ageing and Various Irradiation Dosages on Tensile Strengths

Tensile strength is the maximum stress that a material can withstand before being pulled to fracture or breakage. It is one of the most important and common methods of measuring a material’s ability to perform in particular operation. In this project, tensile test is conducted to investigate the effect of tensile properties of ABS with various electron beam irradiation dosage before and after thermal ageing. Figure 4.5 shows the graph of tensile strength against irradiation dosage for condition Constant-80 at various duration of thermal ageing. Based on the curves, it can be seen that the tensile strength for unaged (0 day thermal ageing) samples remained higher than aged samples throughout the duration of thermal ageing. In fact, the tensile strength of unaged samples increased drastically from the beginning (0 kGy) and reached maximum at around 100 kGy, but decreased as irradiation dosage increased further from 100 to 250 kGy. The trend displayed by unaged samples was consistent with the research that has been done by Vijayabaskar, Tikku and Bhowmick (2006) in which the tensile strengths of material increased with increment of irradiation dosage, followed by reduction at higher dosage. This increment of tensile strength by from 0 to 100 kGy could be attributed to cross-linking of polymer whereas fell of tensile strength at higher dosage (>100 kGy) was attributed to irradiation induced chain scissioning.

In fact, cross-linking induced by certain range of irradiation energy would increase the molecular weight and intermolecular bonding of polymer matrix. Hence, stable polymer chains with higher degree of entanglement formed to restrict the sliding of macromolecular chains during stretching, thereby leading to a relatively stronger tensile strength (Loo, Ooi and Boey, 2004). Chain scissioning on the other hand reduced the molecular weight of polymer. The resulting polymer with shorter chain and lesser entanglement allows easy slippage during stretching and therefore lower tensile strength.

For aged samples subjected to 0 to 100 kGy irradiation dosage, tensile strength of samples increased due to restriction of intermolecular chain sliding from cross-linking. However, when irradiation dosage increased up to 150 kGy, most of the aged samples were experiencing loss of tensile strength. This was attributed to the ease of intermolecular sliding during stretching by chain scissioning effect. Despite chain scissioning occurred at 150 kGy, further increased of irradiation dosages from 150 to 250 kGy significantly improved the tensile strength of aged ABS samples from range of 44-47 MPa to 48-52 MPa. This could be attributed to cross-linking induced by irradiation became more dominant than chain scissioning, therefore more stress is needed to break the larger and higher entanglement polymer chains. In addition, the tensile strength of non-irradiated sample was significantly lower than irradiated samples throughout the duration of thermal ageing. This indicates that cross-linking upon electron beam irradiation improved the tensile strength of samples despite significant loss of tensile strength upon thermal ageing.

In addition, the trend of tensile strength of all samples decreased upon thermal ageing for 2 days, followed by slight increased from 2 to 4 days. The loss of tensile strength for the first 2 days of thermal ageing could be attributed to heating effect of thermal ageing which decomposed polymer chains that have relatively weaker intermolecular bonding. On the other hand, the slight improvement of tensile strength at 4 days of thermal ageing indicates that small scale of recrystallization were occurred where molecules gained sufficient energy to rearrange themselves into uniform and stable polymer structure which resisted easy slippage during stretching. As the duration of thermal ageing prolonged to 4 days and above, tensile strength of polymer samples decreased again. This could be explained by the breakage of polymer chains as thermal degradation appeared to be more significant than recrystallization of chain molecules.

Furthermore, it could be noticed that tensile strength of samples with high dosages (>200 kGy) were significantly higher than low dosages (<200 kGy) samples when the duration of thermal ageing prolonged for more than 2 days. This was attributed to the higher degree of cross-linking density in polymer matrix of high dosages samples induced by thermo-oxidative degradation (Tiganis, et al., 2002). On the other hands, thermal decomposition of low dosages samples to shorter and weaker chains via chain scissioning became more significant after prolonged therma ageing.

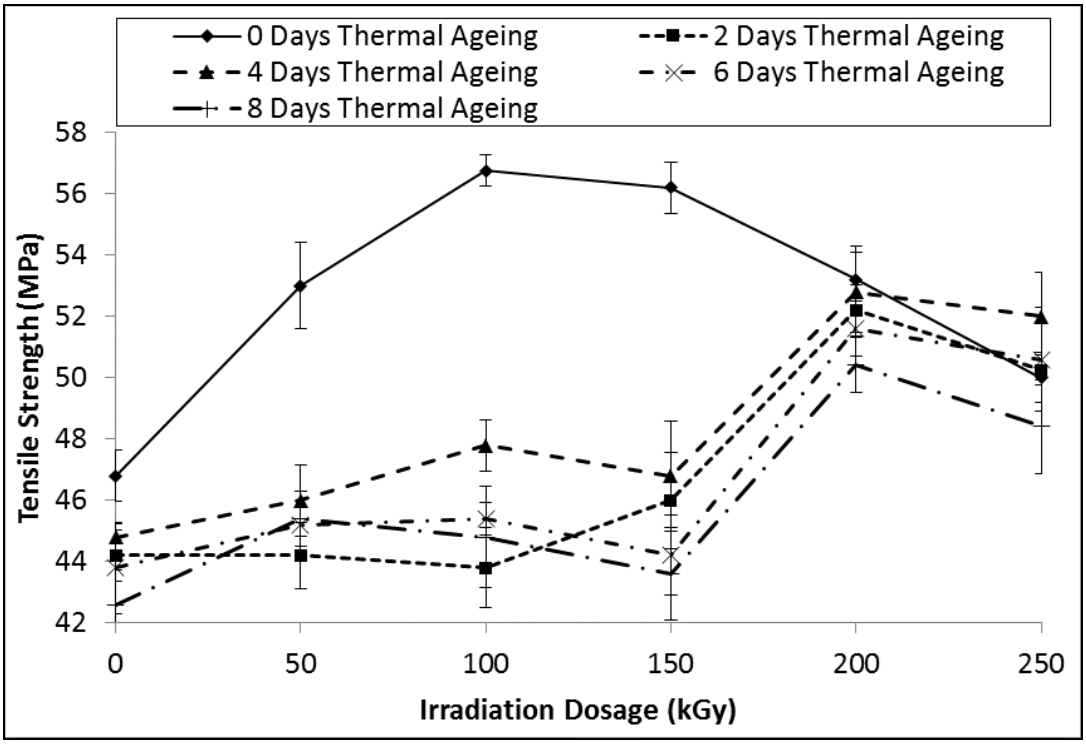


Figure 4.5: Tensile Strength against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Constant-80

Figure 4.6 shows the graph of tensile strength against irradiation dosages for condition Ramp-80. Similar to unaged samples, it can be seen that the trends of tensile strength for all the aged samples increased gradually with irradiation dosages from 0 to 100 kGy. This can be explained by cross-linking effect which strengthen the entanglement and intermolecular bonding of polymer chain. In addition, samples subjected to 2 and 8 days of thermal ageing were experiencing slightly loss of tensile strength when irradiation dosage increased up to 150 kGy despite improvement of tensile strength shown by samples aged for 4 and 6 days. This could be attributed to the degradation of weak polymer chains when they were first heated at elevated temperature, whereas when thermal ageing prolonged to 8 days, chain scissioning of polymer matrix became more dominant than cross-linking.

When irradiation dosage was higher than 150 kGy, tensile strength started to increase again before falling off slightly at 250 kGy. This phenomenon was similar to the case of condition Constant-80 as a certain degree of cross-linking has occurred which lead to improvement of tensile strength. However, as compared to condition Constant-80, tensile strength values of polymers were significantly lower. By referring to APPENDIX B, tensile strength value after condition Ramp-80 fell within the range of 39 – 45 MPa as opposed to 42 – 52 MPa of condition Constant-80. This indicates that apart from the effect of irradiation dosage and duration of thermal ageing, the temperature of thermal ageing was one of the crucial factors in manipulating the tensile strength behaviour of material as well.

Other than that, Figure 4.6 also shows the trend of tensile strength as a function of duration of thermal ageing for condition Ramp-80. For the first 2 days of thermal ageing, the tensile strengths for all the samples fell drastically. This could be attributed to the decomposition of weaker polymer chains by heating effect of thermal ageing. It could be noticed that the tensile strength of irradiated samples were significantly higher than non-irradiated samples. This indicates that despite the cross-linking effect initiated upon electron beam irradiation of polymers, the degradation effect from thermal ageing was more dominant than cross-linking. Moreover, as similar to condition Constant-80, the tensile strength of majority samples improved after thermally aged for 4 days. This phenomenon was attributed to the recrystallization effect which strengthened the intermolecular bonding of polymers through the formation of stable crystalline structure. Thus, more stress is needed to stretch the polymer chains with stronger bonding and structure. Apart from that, when thermal ageing prolonged to 6 days and above, tensile strengths of most of the aged samples remained constant or showed insignificant changes as compared to ageing at 2 and 4 days. This can be explained by no further recrystallization occurred within the polymer matrix after long period of ageing.

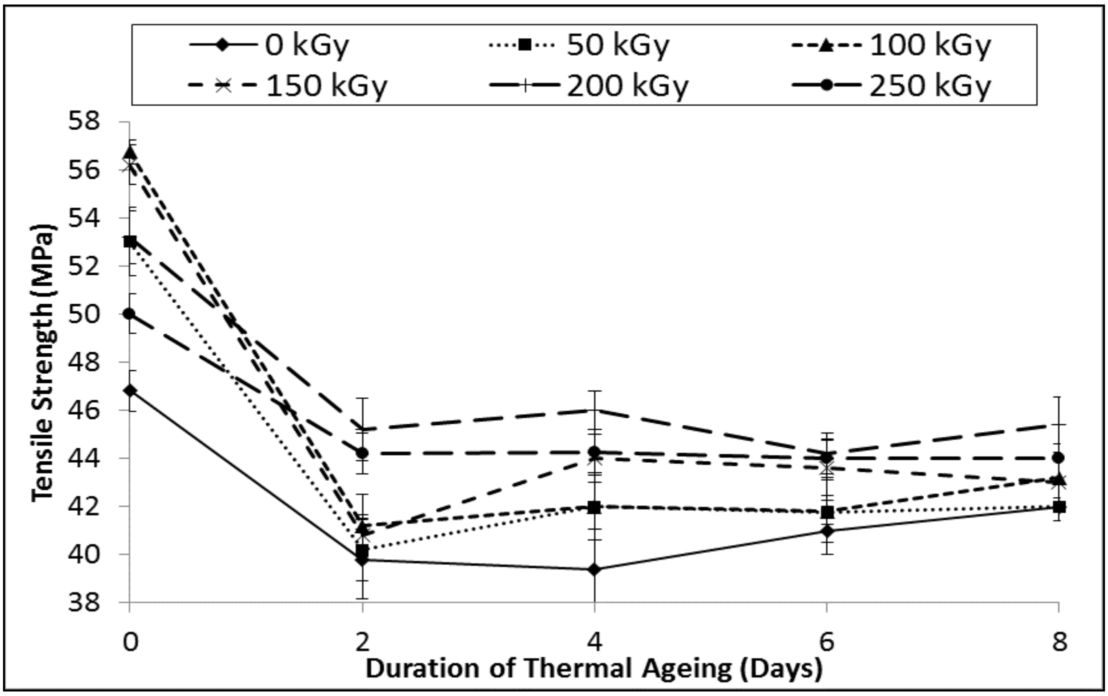


Figure 4.6: Tensile Strength against Duration of Thermal Ageing at Various Irradiation Dosage for Condition Ramp-80

The effect of various irradiation dosages on tensile strength of polymers subjected to thermal ageing for 2 to 8 days at constant 100 ℃ were explained in Figure 4.7. From the curves, it can be seen that the trend of the tensile strength curves were increasing with irradiation dosage up to 100 kGy. The increment of tensile strengths upon irradiated up to 100 kGy were attributed to higher molecular weight and stronger entanglement of polymer matrix upon cross-linking by electron beam. When irradiation dosages further increased up to 250 kGy, tensile strength fell off significantly. This could mean that chain scissioning mechanisms have occurred and was more dominant than cross-linking at high irradiation dosages (>100 kGy), thereby reduced size and entanglements of polymer matrix.

In addition, it can be seen that at lower dosage (50 kGy), tensile strength of sample subjected to 8 days thermal ageing was falling off instead of improving as shown by other samples. This indicates that long duration of thermal ageing decomposed the intermolecular bonding of polymer chains which lead to lower tensile energy during stretching. Nevertheless, as compared to condition Constant-80, the degree of tensile strength reduction were significantly higher. This phenomenon could be attributed to higher heating effect of condition Constant-100, which subsequently altered the chain scissioning and cross-linking mechanisms of polymers. Thus, it could be presumed that temperature of thermal ageing is one of the factors that could alter the tensile properties of material despite irradiation dosage and duration of thermal ageing.

Besides, it could be observed that for samples subjected to 2 and 8 days thermal ageing, the trend of tensile strength curves were consistent with unaged samples. Besides, when thermal ageing prolonged up to 6 days, tensile strength increased gradually. This can be explained by the fact that recrystallization of polymer structure had started which allowed them to restructure and gained sufficient energy to prevent easy slippage upon tensile stretching. When thermal ageing prolonged for more than 6 days, all the irradiated samples had their tensile strength reduced significantly. This could mean that cleavage of grafted polymer chains has occurred after overly long period of ageing duration. This phenomenon was consistent with the research by Tiganis, et al., 2002 which concluded that the tensile stress of ABS samples significantly deteriorates at higher temperature and ageing duration.

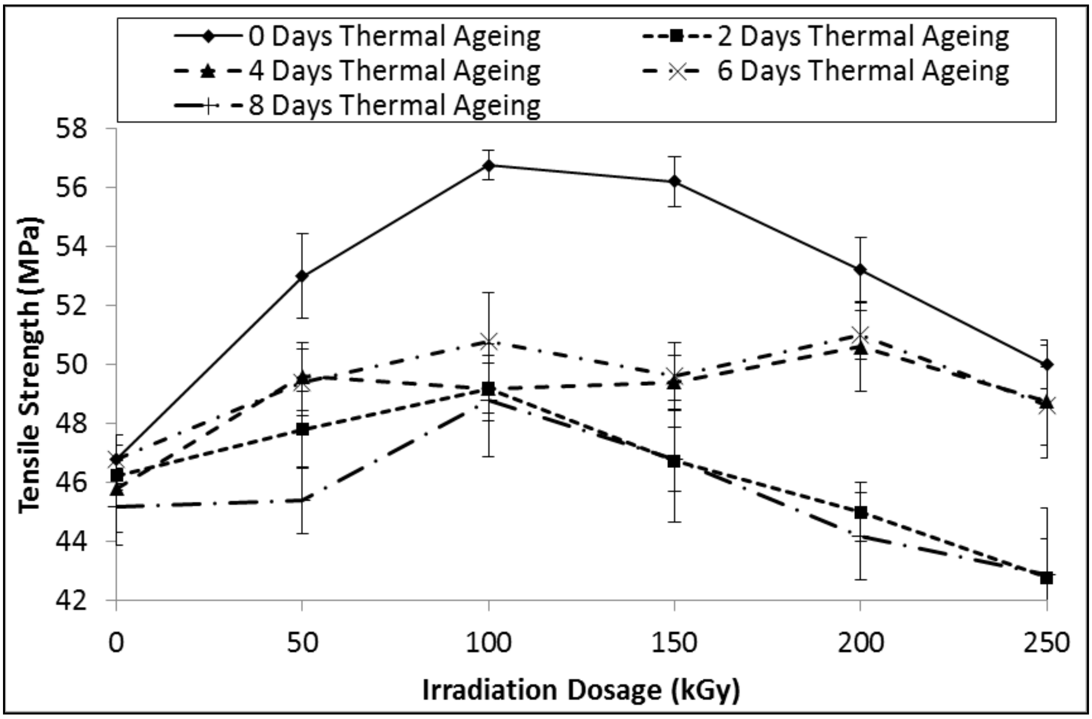


Figure 4.7: Tensile Strength against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Constant-100

While for condition Ramp-100, the graph of tensile strength against irradiation dosage was shown in Figure 4.8. Based on the curves, tensile strengths of samples increased gradually up to 150 kGy, followed by reduction at higher dosage. It can be observed that tensile strength of samples thermally aged for 2 days increased at significantly high extent as compared to other samples with longer ageing period. This phenomenon could be attributed to the fact that the intermolecular bonding and entanglement of polymer matrix were still high and intact after 2 days of ageing.

In contrast, as duration of thermal ageing prolonged, polymer matrix lost its intact bonding and chains entanglement, thereby allowing easy stress stretching. When irradiation dosage increased from 150 kGy onwards, polymers lost their tensile strength properties due to the fact that at such ageing condition, chain scissioning was more dominant than cross-linking at higher dosage (>50 kGy). Nevertheless, it could be noticed that samples thermally aged for 8 days possessed different trend as compared to other samples. This could be attributed to the uneven heating and cooling effect of Ramp condition thermal ageing.

Figure 4.8 also explained the variation of tensile strength under various duration of thermal ageing at condition Ramp-100. From the curves, it could be observed that the tensile strength for all the samples were pretty consistent and seemed to be independent of the dosages of electron beam irradiation. In addition, trend of decreasing tensile strength was noticed when the duration of thermal ageing prolonged from 0 to 4 days for every single polymer samples. This indicates that degradation of polymer chains due to high temperature ageing was so dominant that the effect of cross-linking on polymers has been nullified.

As thermal ageing prolonged to 4 days and above, polymer samples gained back tensile strength and subsequently increased with time due to the recrystallization effect which reinforced stable crystalline structure. After 8 days of thermal ageing, tensile strength of samples eventually varied or became dependant to their respective irradiation dosage as compared to short duration ageing. It is observed that samples irradiated at higher dosage were experiencing stronger tensile strength which was consistent with the trends exhibited by irradiated polymers. This phenomenon explained that there were no further intensive thermal decomposition of polymer matrix, therefore cross-linking became more significant than thermal degradation effect.

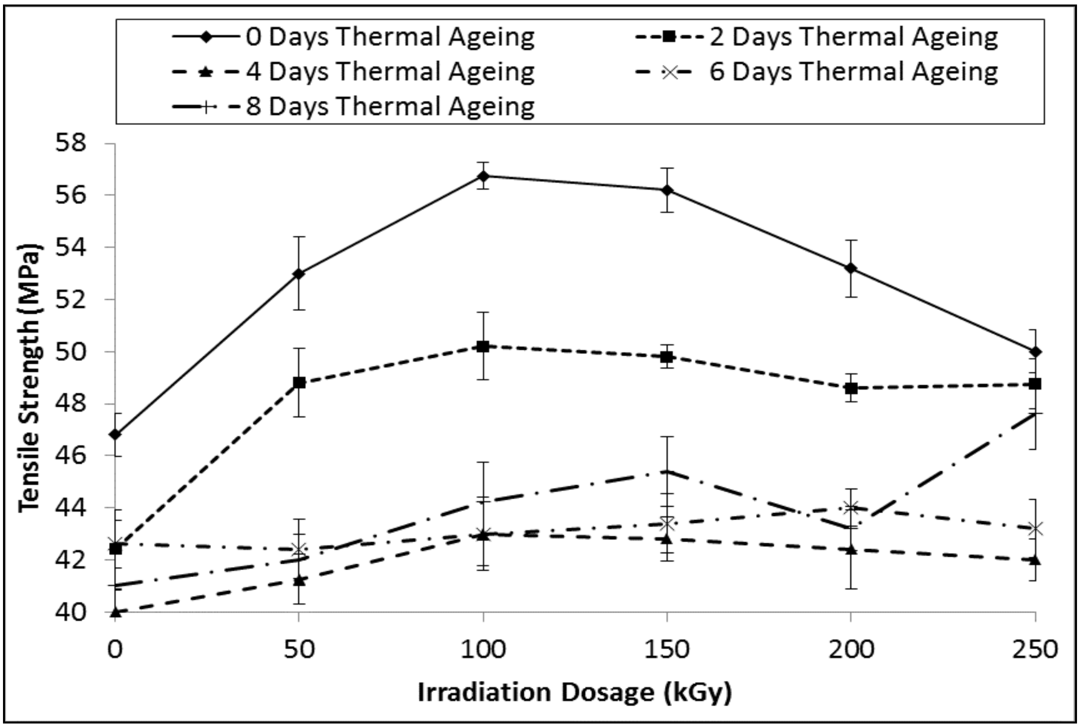


Figure 4.8: Tensile Strength against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Ramp-100

4.2.2 Thermal Ageing and Various Irradiation Dosages on Elongation at Break

Other than tensile strength, another crucial tensile properties of material would be elongation at break. The effects of thermal ageing and various irradiation dosages on elongation at break of polymer samples were showed in Figure 4.9. Based on the curves, it can be noticed that the values of elongation at break of samples varied progressively with increasing irradiation dosages. For the unaged sample, elongation at break increased drastically and reached maximum value at 50 kGy. This result was consistent with the research that has been done by Vijayabaskar, Tikku and Bhowmick, 2006. This phenomenon can be explained by certain degree of cross-linking network in the polymer matrix which enhanced the flexibility of polymer chains during stretching.

When the irradiation dosage increased up to 100 kGy, elongation at break of samples decreased. This could be attributed to random scissioning of polymer matrix which lead to easy breakage with lower elongation. When the irradiation dosage further increased to 150 kGy, elongation at break of samples showed significant improvement due to higher cross-linking network in polymer matrix. At higher dosage (>150 kGy), elongation at break of samples remained constant with slight decrement in between. This phenomenon could be attributed to chain scissioning mechanism induced by high irradiation energy, therefore leading to chain cleavage. Besides, it could be noticed that elongation at break of all the aged samples were remaining at lower value than unaged samples for the entire range of dosages. This was attributed to restriction of chain mobility upon irradiation on polymer matrix. Moreover, at low dosages (<150 kGy), the elongation at break of samples aged for 2 days remained at relatively low values as the effect of thermal degradation upon ageing was more significant than cross-linking of irradiation dosage. When dosage increased for more than 150 kGy, elongation at break improved gradually as cross-linking density was more dominant.

Other than variation of irradiation dosage, Figure 4.9 also described the effect of duration of thermal ageing on elongation at break of samples under condition Constant-80. From the curves, it can be seen that upon thermal ageing for 2 days, elongation at break for samples decreased rapidly due to the thermal embrittlement induced in glassy matrix of SAN phase (Golden, Hammant and Hazell, 1967; LeGrand, 1969).Furthermore, as duration of thermal ageing prolonged to 4 days, samples showed slight improvement of elongation at break. This indicates that under proper condition and duration of thermal ageing, the orientation of chain structures would be modified in certain way to improve the chain mobility. As thermal ageing prolonged to 4 days and above, elongation at break fell off significantly. This can be explained by alteration of chain scissioning mechanism after long period of thermal ageing which lead to easy fracture of samples at low elongation.

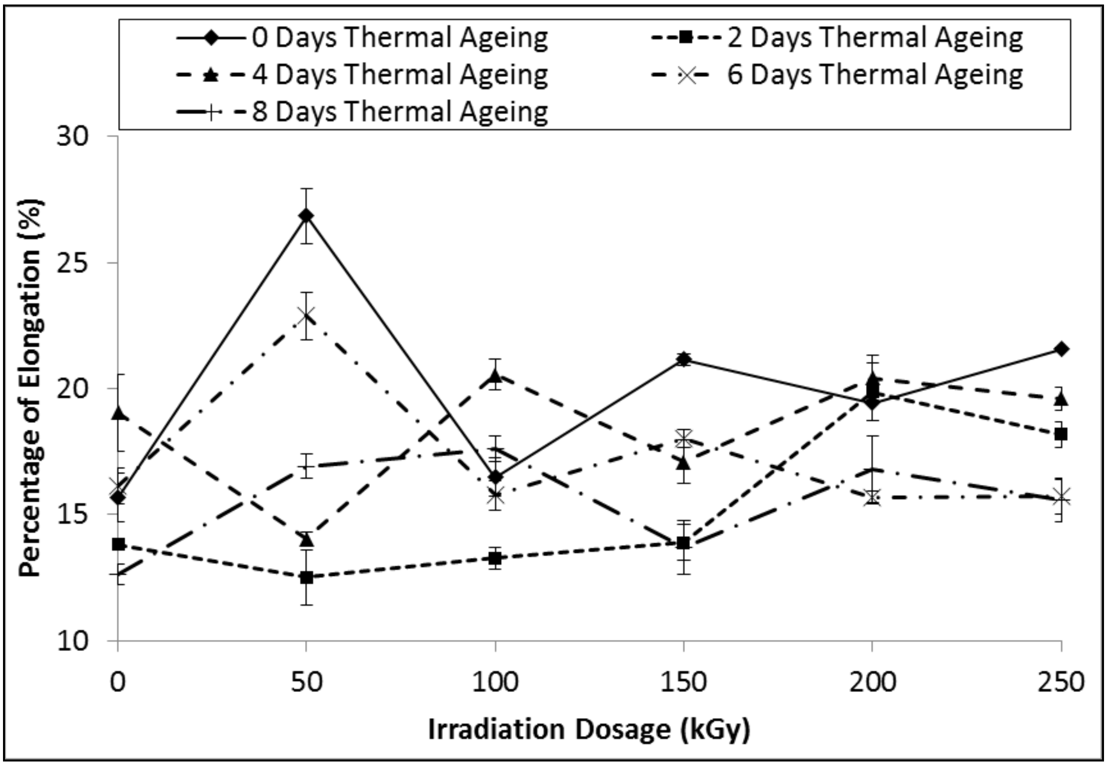


Figure 4.9: Elongation at Break against Irradiation Dosage at Various Durations of Thermal Ageing for Condition Constant-80

Figure 4.10 shows the trend of elongation at break versus irradiation dosage for thermal ageing of condition Ramp-80. It can be observed that the elongation at break decreased upon irradiation at 50 kGy. This was attributed to degradation of polybutadiene phase which eventually reduced chain mobility of polymers, thereby polymer elongated lesser at fracture. As irradiation dosages increased up to 150 kGy, values of elongation at break of samples were noticed to increase gradually. This indicates the formation of cross-linking network within polymer matrix induced by higher irradiation energy. When dosage of electron beam irradiation further increased to 200 kGy, samples subjected to more than 2 days thermal ageing had their elongation at break decreased. This was attributed to altered chain scissioning mechanism at high irradiation dosage which eventually caused cleavage of polymer chains.

Above 200 kGy, elongation at break improved slightly again as interfacial interaction within polymer matrix was promoted to ease the chain movement at the same time mitigating chain restriction. Besides, it could be noticed that for Ramp temperature ageing, elongation at break for samples were independent of duration of thermal ageing at low dosages (<100 kGy) which opposed the trend showed by condition Constant-80 ageing. This could be explained by the periodical heating and cooling effect of Ramp condition, thereby polymer samples required relatively more time to vary the chain mobility as compared to constant heating.

Besides, Figure 4.10 also shows elongation at break against duration of thermal ageing for condition Ramp-80. Based on the curves, it was noticed that the trend of elongation at break was pretty consistent for all the samples. As thermal ageing prolonged to 4 days, elongation at break decreased gradually due to embrittlement of glassy phase matrix, thereby polymer chains were more easily broken at fracture. When thermal ageing continued up to 6 days, elongation at break started to bounce up slightly as polymer matrix gained sufficient energy and strengthened upon cross-linking. With stronger polymer structure, greater amount of stress is needed to elongate the samples which lead to larger strain and eventually fracture. After 6 days of thermal ageing, there were no significant changes on the elongation at break for most of the samples due to the fact that there were no further weak polymer chains for chain scissioning to be taken place.

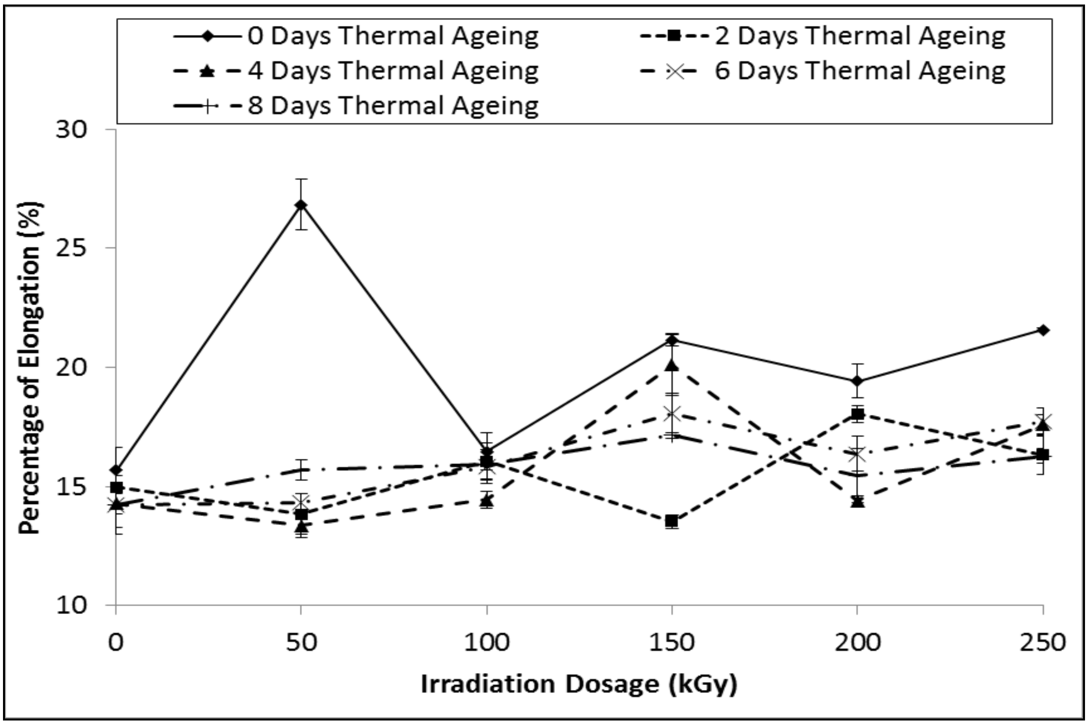


Figure 4.10: Elongation at Break against Irradiation Dosage at Various Durations of Thermal Ageing for Condition Ramp-80

In addition, the effect of elongation at break upon at various irradiation dosage for thermal ageing at constant 100 ℃ was showed in Figure 4.11. Basically, polymer samples subjected to 4 and 8 days of thermal ageing exhibited similar trend of elongation at break as to unaged sample. When irradiation dosage increased from 0 to 250 kGy. However, thermally aged samples of 2 and 6 days on the other hand possessed significant reduction of elongation at break when they first irradiated at 50 kGy. This could be attributed random scissioning mechanism which allowed easy cleavage of chains during stretching, thereby lowered the elongation prior to fracture.

When dosage increased to 100 kGy, both of the samples experienced higher elongation at break, followed by rather stable values of elongation at higher dosages (>100 kGy). These phenomenon indicate the modification of polymer structures and alteration of chain scission mechanism. Moreover, it can be seen on the curve that sample subjected to 2 days thermal ageing had the highest elongation before irradiation, followed by gradual loss and eventually remained at range of values higher than other aged samples. This phenomenon can be explained by the alteration of chain scissioning process at dosages higher than 50 kGy which promoted the flexibility of chain movements.

Besides, by analysing Figure 4.11, the trend of elongation at break at different duration of thermal ageing for condition Constant-100 could be evaluated. According to the curves, the elongation at break of non-irradiated sample increased sharply from 15-27 % upon thermally aged for 2 days whereas irradiated samples were found to have slightly lower elongation values. This might be attributed to the insignificant effect of chain scissioning process at early stage of thermal ageing, thereby polymer chains would have intact mobility and structures.

When duration of thermal ageing prolonged from 2 to 6 days, loss of elongation were experienced by all the thermally aged samples. This suggests that the degree of embrittlement of glassy matrix phase of ABS increased with prolonged duration of thermal ageing. With brittle and crack scattered structure, the resulting polymers could be easily broken when subjected to stress. For sample irradiated at 50 kGy, elongation at break reduced severely from 27-12 % for 6 days, before bouncing back to 17 % after 8 days. The rapid fell of elongation at break could be attributed to the intensive scission mechanisms, eventually lead to progressive cleavage of chains with time. Nevertheless, the increment of elongation at break after 8 days indicates no further chain scissioning as the molecule structures started to rearrange themselves into more ordered state, thereby mitigating the restriction of polymer chain mobility.

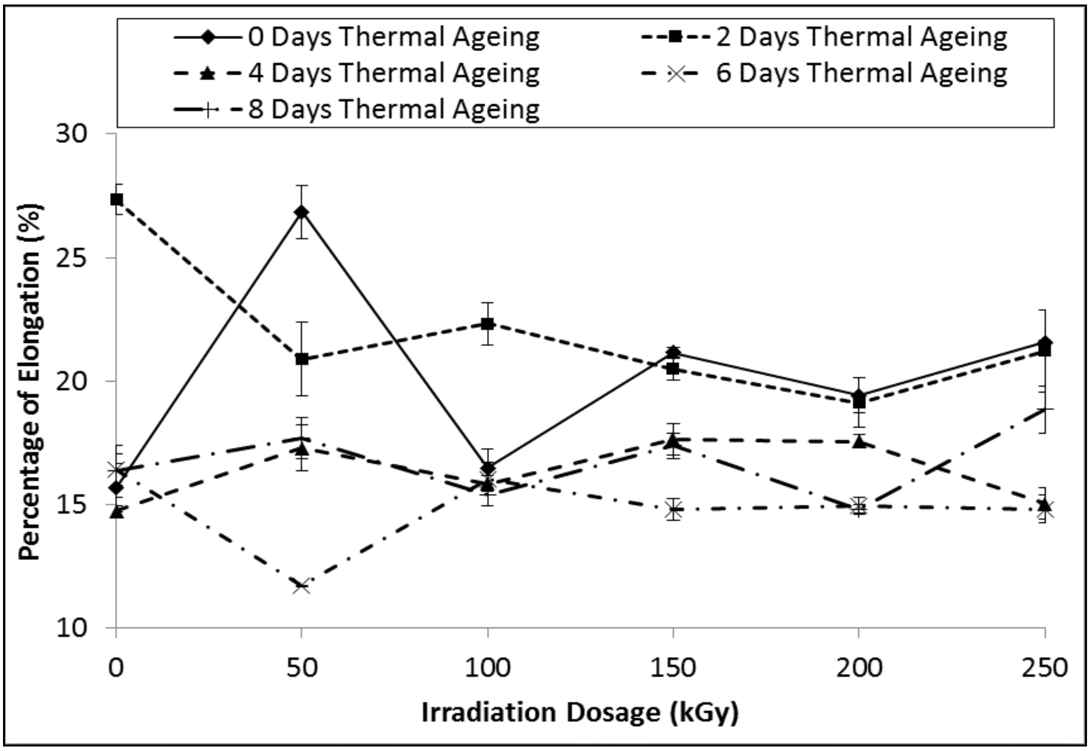


Figure 4.11: Elongation at Break against Irradiation Dosage at Various Durations of Thermal Ageing for Condition Constant-100

Figure 4.12 shows the trend of curves for elongation at break against various irradiation dosage for different duration of thermal ageing at condition Ramp-100. It can be seen that the values of elongation at break for most of the samples possessed no significant changes for whole range of irradiation dosages. For samples irradiated at 50 kGy, the elongation at break were relatively low rather than the extensively high elongation at break showed by non-irradiated samples and samples thermally aged at condition Constant-100. This can be explained by the limited chains movement of polymers under on and off heating environment during Ramp condition thermal ageing. When irradiation dosages increased from 50 to 150 kGy, all the samples possessed remarkably constant values of elongation at break as compared to significant variation during condition Constant-100 thermal ageing. This indicates that elongation at break of samples were independent of either variation of irradiation dosages or duration of thermal ageing. At higher dosages (>150 kGy), variation of elongation at break was more profound despite insignificant effect of thermal ageing duration.

Furthermore, Figure 4.12 also shows the elongation at break as a function of thermal ageing duration for condition Ramp-100 thermal ageing. Based on the curves of the graph, elongation at break of polymers decreased drastically after they have been subjected to first thermal ageing cycle (2 days). This indicates chain scissioning induced by thermal embrittlement of samples at elevated temperature. As thermal ageing prolonged 3 cycles (6 days), elongation at break of samples decreased in progressive manner, followed by stagnant and consistent value during the last cycle of thermal ageing. This could mean that as thermal ageing prolonged, thermal decomposition of molecular chains increased as well, and therefore shorter elongation and easy breakage would be occurred prior to fracture. While for the last cycle of thermal ageing, no further changes had been observed as there were no remaining of weak polymer chains to be decomposed.

Apart from that, it can be observed that for non-irradiated sample, the elongation at break value was relatively lower than irradiated samples at the early cycles of thermal ageing. This could be attributed to more dominant random scissioning process which impede the elongation of polymers prior to fracture. In other words, chain scission mechanisms were less significant for irradiated polymers at short duration of thermal ageing. However, as thermal ageing prolonged to higher cycles (4 days and above), elongation at break of non-irradiated samples bounced up to higher value than remaining irradiated samples. This concluded that the degree of chain scissioning on irradiated polymers were more profound at prolonged duration of thermal ageing. For samples irradiated for 50 kGy, it could be observed that the elongation at break decreased at range of 27-14 % as compared to 27-11 % of condition Constant-100. The extent of elongation at break loss were slightly lower due to the periodical heating and cooling of samples which resulted in polymers to fracture at shorter elongation.

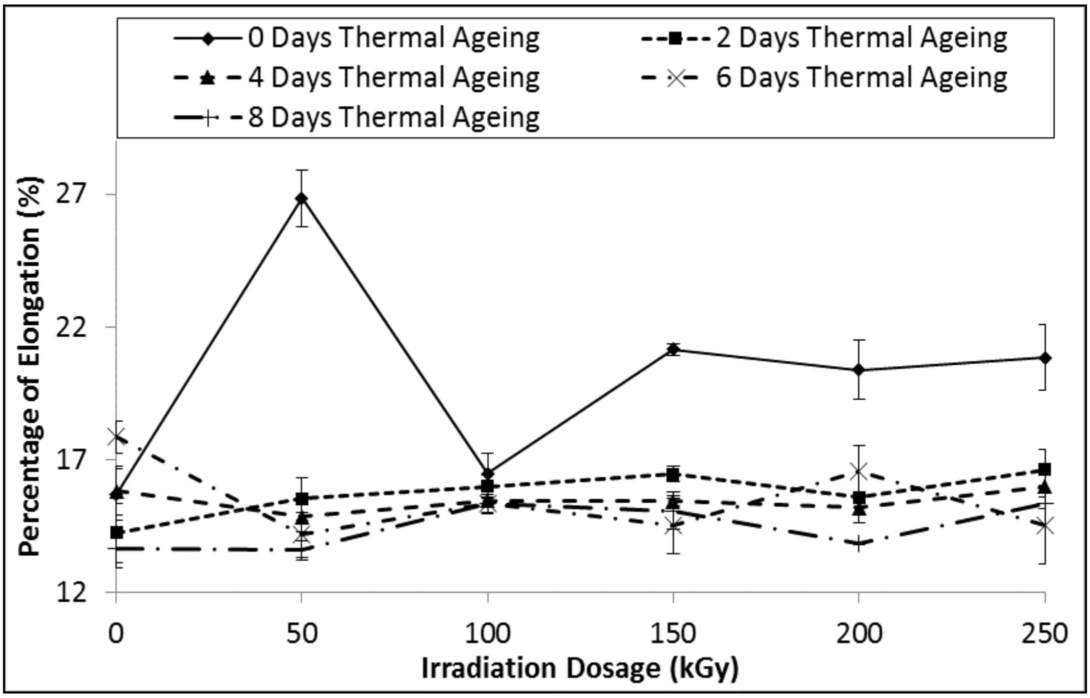


Figure 4.12: Elongation at Break against Irradiation Dosage at Various Durations of Thermal Ageing for Condition Ramp-100

4.2.3 Thermal Ageing and Various Irradiation Dosages on Tensile Modulus

Tensile modulus (also known as Young's modulus) is the ratio of tensile stress over tensile strain under the proportional limit of a particular material. In this project, the tensile modulus for irradiated ABS samples subjected to various duration of thermal ageing was evaluated.

Figure 4.13 shows the curves of tensile modulus versus various irradiation dosage of thermally aged samples under condition Constant-80. Based on the curves, it could be observed that the tensile modulus of unaged sample increased drastically at low dosages (<100 kGy). This could be attributed to the increment of cross-linking density at higher irradiation dosages. Thus, polymer chains lost its mobility as they have been entangled into larger molecule size, thereby more stress is needed to deform the polymer indicating stiffer and less ductile polymer matrix (Yang et al., 2008). As irradiation dosages increased from 100 to 200 kGy, there were no significant changes of tensile modulus as they were maintained at value of about 175 to 177 MPa. When dosage further increased to 250 kGy, tensile modulus decreased as chain scissioning induced by high irradiation energy was more dominant. Hence, shorter and smaller polymer structures formed would have better flexibility and lesser restriction to slide past the chains of each other; thus, lower stress is required to break the samples.

As similar to unaged samples, all the aged samples were found to have their tensile modulus increased with irradiation dosages up to 100 kGy. The tensile modulus of sample subjected to 4 days thermal ageing increased at highest extent from 145 to 186 MPa after irradiated at 100 kGy, whereas for sample of 8 days thermal ageing, the increment of tensile modulus were the least from 145 to 153 MPa. This phenomenon indicates the chain mobility of polymer with 4 days thermal ageing were restricted by large density of cross-linking, whereas sample that has been thermally aged for 8 days were decomposed into shorter structures with better chain mobility.

At high dosages (>100 kGy), tensile modulus of aged samples decreased gradually as a result of better chain flexibility induced by high cross-linking density. By comparing with non-irradiated polymer sample, it can be seen that the tensile modulus of irradiated samples were relatively higher than non-irradiated. This could be attributed to overall improvement of modulus through cross-linking from thermo-oxidative degradation (Tiganis, et al., 2002).

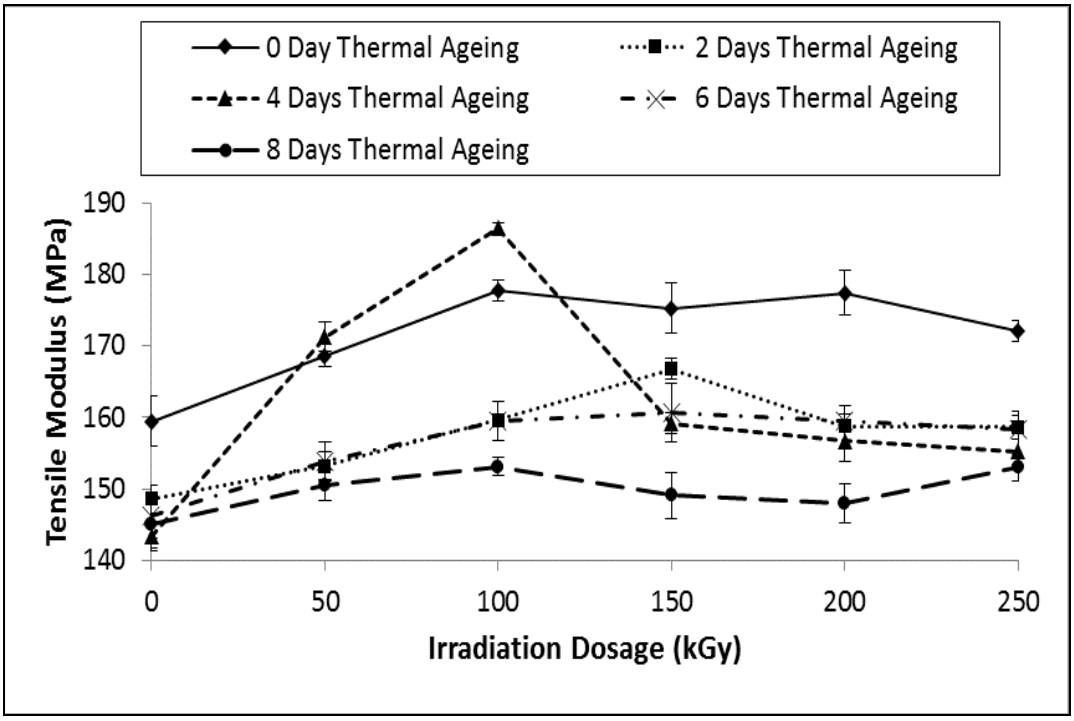


Figure 4.13: Tensile Modulus against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Constant-80

Figure 4.14 shows the curves of tensile modulus against various irradiation dosages for condition Ramp-80 thermal ageing. For non-irradiated sample, tensile modulus of samples subjected to 6 days thermal ageing were highest at value of 139 MPa, followed by samples with 4 and 8 days of thermal ageing at modulus values of 129-137 MPa, and lastly sample of 2 days thermal ageing. The increment of tensile modulus upon thermally aged from 2 to 6 days could be explained by rearrangement of molecules from unordered melt structure to more uniform and stable structure. Besides, the initial loss of tensile modulus from 159 to 126 MPa after 2 days thermal ageing could be attributed to the decomposition of long chains into shorter and more flexible structures when polymer first started to heat.

In addition, when irradiation dosage increased up to 200 kGy, tensile modulus of samples were pretty consistent with unaged samples where modulus value increased in a progressive manner. However, it could be noticed that polymer thermally aged for 2 days had its tensile modulus improved rapidly at 100 kGy, and sooner possessed highest modulus at 200 kGy. This phenomenon was consistent with the research that has been done by Bhowmick and Mangaraj, 1994 where tensile modulus is proportional to density of cross-linking formed. Thus, larger polymer with rigid three dimensional cross-linked network was formed to restrict the chain mobility and prevent easy sliding of intermolecular chains during stretching (Loo, Ooi and Boey, 2004). At higher dosage (>200 kGy), tensile modulus of all the polymer samples reduced due to the chains cleavage from dominant chain scissioning mechanism induced by high energy radiation.

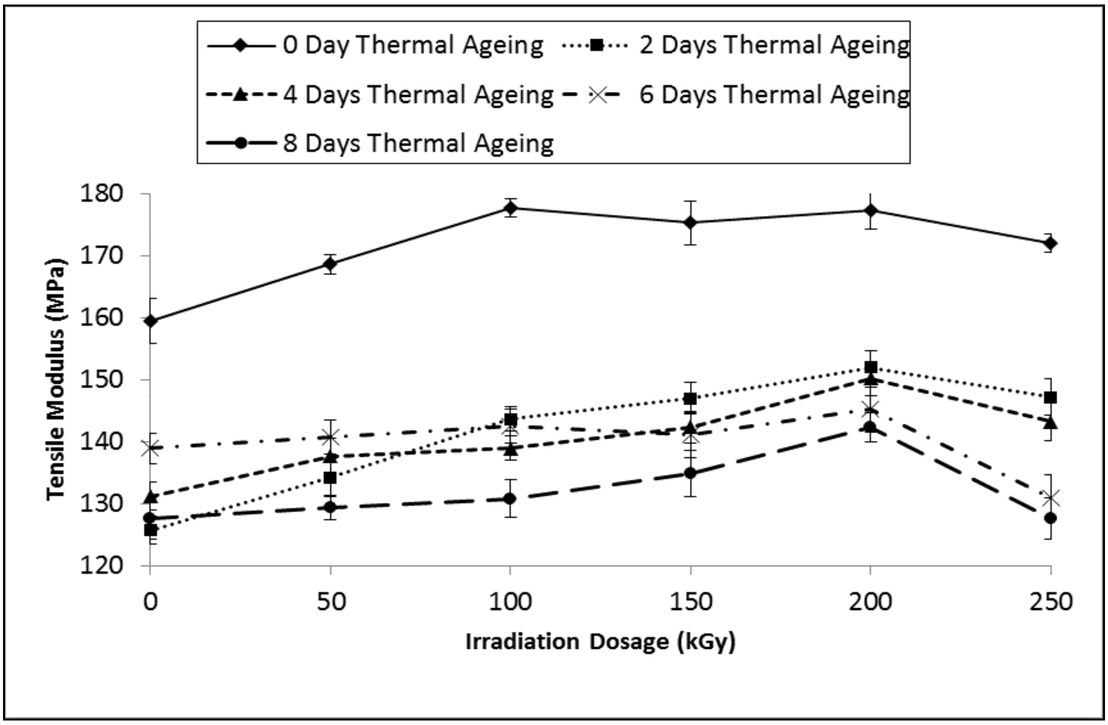


Figure 4.14: Tensile Modulus against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Ramp-80

Figure 4.15 shows tensile modulus versus irradiation dosage of samples subjected to condition Constant-100 thermal ageing. Based on the curves, it can be seen that the tensile modulus exhibited by non-irradiated sample was consistent with the modulus trend of Ramp-80 thermal ageing where samples that have been thermally aged at 4 and 6 days possessed higher tensile modulus than other samples of 2 and 8 days ageing. Furthermore, when irradiation increased to 50 kGy, all the samples possessed similar tensile modulus values despite subjected to different duration of thermal ageing. When irradiation dosages increased from 50 to 200 kGy, tensile modulus of samples increased gradually before falling off at 250 kGy again. Besides, it was notably that samples subjected to 6 days thermal ageing showed significant of modulus improvement of tensile modulus from 100 kGy and above. However, as compared to condition Constant-80, the increment of tensile modulus for condition Constant-100 was significantly lower. This was attributed to strict heating environment of condition Constant-100 which impeded the intermolecular bonding of polymer matrix, eventually allowed easy sliding between molecules. At high irradiation dosage of 250 kGy, tensile modulus of samples were consistent irrespective of the duration of thermal ageing. This phenomenon further explained the fact that chain scissioning had taken place on most of the polymer matrix which lead to lower stress needed to deform the sample.

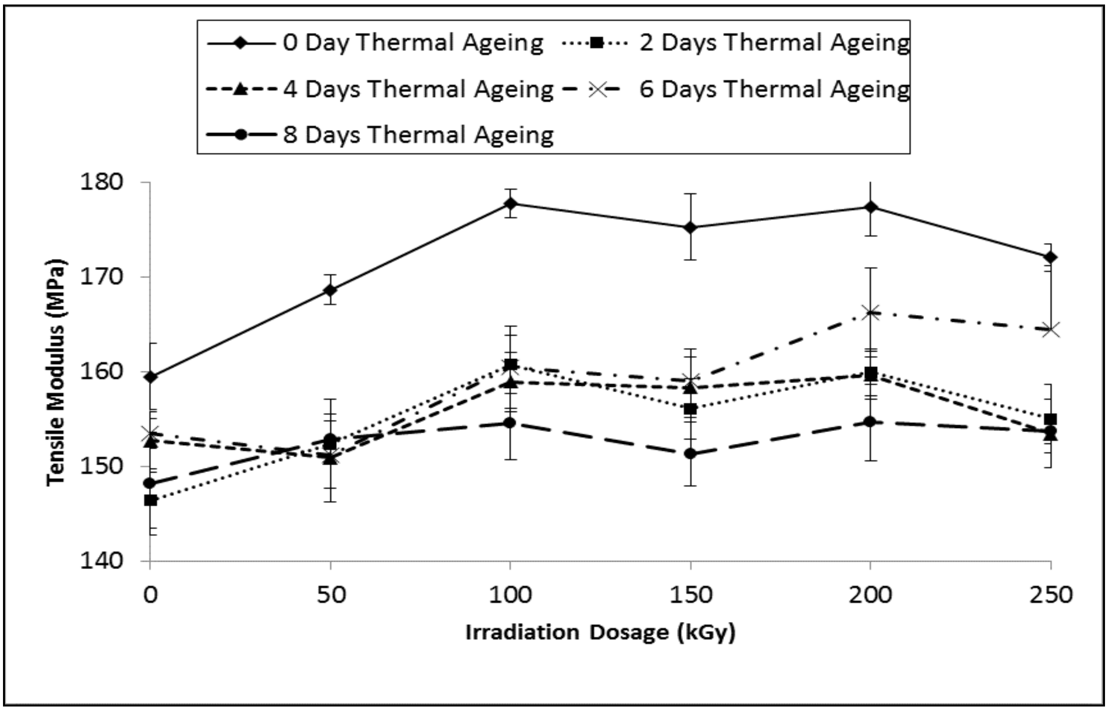


Figure 4.15: Tensile Modulus against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Constant-100

Figure 4.16 shows the curves of tensile modulus for thermal ageing of condition Ramp-100. Based on the curves, the trend of tensile modulus for non-irradiated sample decreased upon thermally aged for 4 days. This may be attributed to the breakage of chain induced by altered chain scissioning mechanisms. As duration of thermal ageing further prolonged to 6 days, tensile modulus of sample increased slightly, followed by reduction at 8 days and above. The improvement of tensile modulus noticed by 6 days of thermal ageing could be attributes to the rearrangement of molecules into uniform structures, thereby reduced the chain mobility during stretching. When irradiation dosage increased to 100 kGy, trend of tensile modulus for most of the samples increased, followed by flattened out at 150 kGy. The improvement of tensile modulus properties of samples was consistent with the research that has been done by Tiganis, et al., 2002 where tensile modulus of polymer increased as a result of cross-linking of rubbery polybutadiene phase. Therefore, phase transformation of ductile to brittle transition was noticed prior to failure. At dosages higher than 200 kGy, tensile modulus decreased significantly. This could mean that breakage of polymer chains became more significant than cross-linking at high dosage. Thus, shorter polymer chains with weaker intermolecular bonding would be formed.

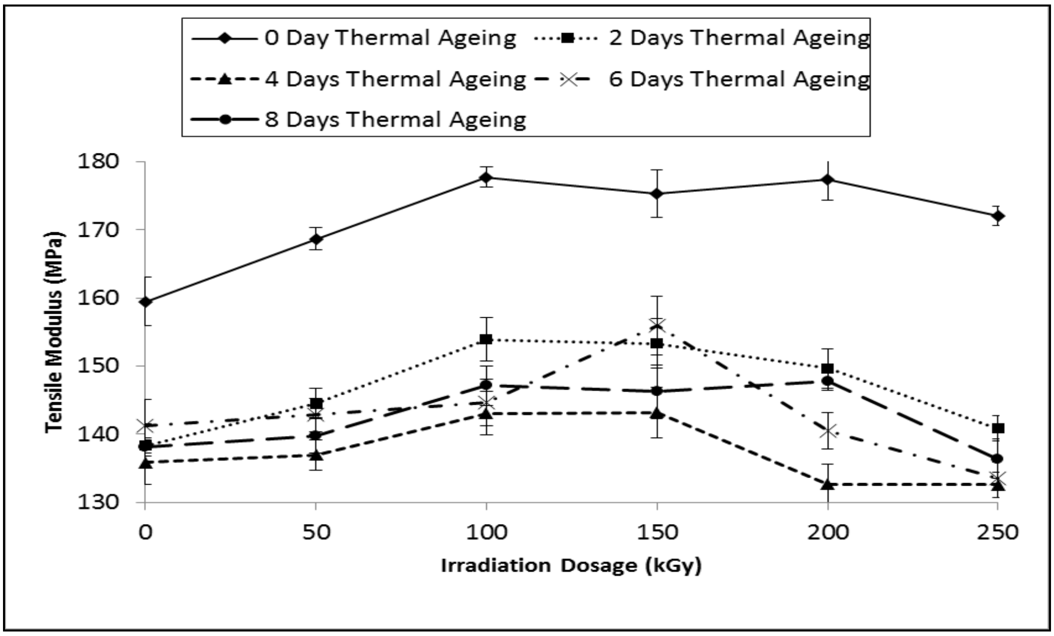


Figure 4.16: Tensile Modulus against Irradiation Dosage at Various Duration of Thermal Ageing for Condition Ramp-100

4.3 Differential Scanning Calorimetry

4.3.1 Thermal Ageing and Various Irradiation Dosages on Melting Temperature

Differential Scanning Calorimetry is one of the most widely used thermal analysis methods to study the thermal stability and melting behaviour of polymer subjected to high temperature heating. In this project, thermal properties of polymer samples such as melting temperature (T_m) could be obtained from the peak of DSC thermograms curve, whereas melting heat of polymers were determined by area under the curve of thermograms. Table 4.1 shows the curve of T_m of irradiated ABS samples of 0, 100 and 200 kGy upon thermal ageing from 2 to 8 days at constant temperature of 100 ℃. It can be observed that the results of T_m against various irradiation dosages were consistent with the research that have been done by Liu, et al., 2009 in which melting point of the polymers increased marginally with higher irradiation dosages. This phenomenon could be attributed to the formation of stronger intermolecular bonding within polymer matrix as a result of cross-linking effect. Thus, the resulting polymers with their structure modified became more resistant to melting.

Moreover, as the duration of thermal ageing prolonged from 2 to 6 days, the polymer samples showed a slight improvement of T_m up to 3 ℃. This can be explained as the duration of thermal ageing increased, polymer matrix would have sufficient time to vaporize all the polymer chains with weaker intermolecular bonding. As a result, the rest of the polymer chains with stronger bond strength and intact structure required more heat energy to melt. Apart from that, when thermal ageing prolonged to 8 days, T_m decreased due to chain scissioning effects induced by thermal degradation at high temperature.

Other than constant temperature thermal ageing at 100 ℃, the trend of T_m of samples subjected to condition Ramp-100 thermal ageing were showed in Table 4.2. As similar to condition Constant-100, the T_m of polymers at Ramp condition increased with irradiation dosage due to reinforcement of intermolecular bond by cross-linking effect. However, when duration of thermal ageing prolonged to 4 days, the resulting polymer samples experienced decrement of T_m. This indicates that the structures of polymer matrix were decomposed by chain scissioning mechanisms at elevated temperature. After 4 days of thermal ageing operation, T_m of all the polymer samples increased again. This was attributed to the rearrangement of molecules to form consistent and ordered structures in polymer matrix. As a result, melting of the polymers were required to take place at higher temperature which indicates higher T_m.

Table 4.1: Melting Temperature of Samples subjected to Condition Constant-100 Thermal Ageing at Various Irradiation Dosage

Irradiation dosage (kGy)	Melting Temperature (℃)				
	Un-aged Samples	2 Days Thermal Ageing	4 Days Thermal Ageing	6 Days Thermal Ageing	8 Days Thermal Ageing
0	106.24	108.10	108.30	109.25	109.88
100	107.76	108.56	111.14	111.10	110.76
200	111.43	111.41	111.14	111.99	111.25

Table 4.2: Melting Temperature of Samples subjected to Condition Ramp-100 Thermal Ageing at Various Irradiation Dosage

Irradiation dosage (kGy)	Melting Temperature (℃)				
	Un-aged Samples	2 Days Thermal Ageing	4 Days Thermal Ageing	6 Days Thermal Ageing	8 Days Thermal Ageing
0	106.24	108.57	108.17	108.74	109.05
100	107.76	110.71	110.5	110.95	111.2
200	111.43	111.73	109.72	111.43	111.23

4.3.2 Thermal Ageing and Various Irradiation Dosages on Melting Heat

Apart from the analysis of T_m, melting heat (ΔH) of the melted samples could be obtained from the integrated area under the curve of DSC thermograms as well. Figure 4.17 shows the ΔH of ABS samples subjected to condition Constant-100 and Ramp-100 thermal ageing at irradiation dosages of 100 and 200 kGy. Based on the curve, it can be seen that for non-irradiated samples thermally aged under condition C-100, the area under the curve (*ΔH*) of sample decreased with prolonged duration of thermal ageing and reached minimum value at 6 days of ageing. This indicates that the bonding spectrum of ABS molecules became narrower with time. This phenomenon implies that as duration of thermal ageing prolonged, polymer chains with weaker intermolecular bonding would be vaporised due to high temperature heating effect. Therefore, the remaining polymers with relatively stronger and larger molecule size resulted in narrower bond spectrum.

As thermal ageing prolonged up to 8 days, area under the curve of non-irradiated samples increased. This could be attributed to the cleavage of polymer chains induced by random scissioning mechanisms as a result of prolonged duration of thermal degradation. Moreover, the area under the curve of samples irradiated at 100 kGy was highest as compared to non-irradiated sample and sample irradiated at 200 kGy throughout 4 days of ageing. This implies that the amount of heat energy required to melt sample irradiated of 100 kGy was relatively higher than as needed by other samples.

As duration of thermal ageing further prolonged to 8 days, area under the curve of high dosage samples (200 kGy) decreased progressively. It was believed that a larger portion of weaker polymer chains have been vaporized due to prolonged thermal ageing, resulted in further narrowing of molecules bonding spectrum. However, as similar to non-irradiated sample, area under the curve of 200 kGy irradiation sample was found to increase after thermally aged for 4 days and above. This could be explained by random scissioning of polymer matrix which contributed to wider bond spectrum. In contrast, sample of 100 kGy irradiation dosage had smaller area under the curve after 4 days. This phenomenon shows that vaporization of weaker polymer chains occurred in conjunction with prolonged duration of thermal ageing, ended up narrowing the bonding spectrum.

On the other hand, it can be observed that the trend of area under the curve of non-irradiated samples thermally aged under condition Ramp-100 remained constant throughout 6 days of thermal ageing. This indicates that the area under the curve of sample was independent at short duration of thermal ageing (less than 6 days). However, when thermal ageing prolonged to 8 days, area under the curve of sample reduced drastically, indicating smaller bonding spectrum of molecules. This was attributed to significant loss of weak polymer chains as a result of continuous vaporisation throughout long duration of thermal ageing. For irradiated sample of 100 and 200 kGy, the area under the curve increased and decreased respectively at small scale from 2 to 4 days of thermal ageing.

Nevertheless, as thermal ageing further prolonged to 4 days and above, there were no significant changes on area under the curve for both irradiated samples as compared to the significant changes showed by condition Constant-100 thermal ageing. This phenomenon indicates that bonding spectrum of the sample molecules remained unchanged as they were independent to the prolonged duration of thermal ageing.

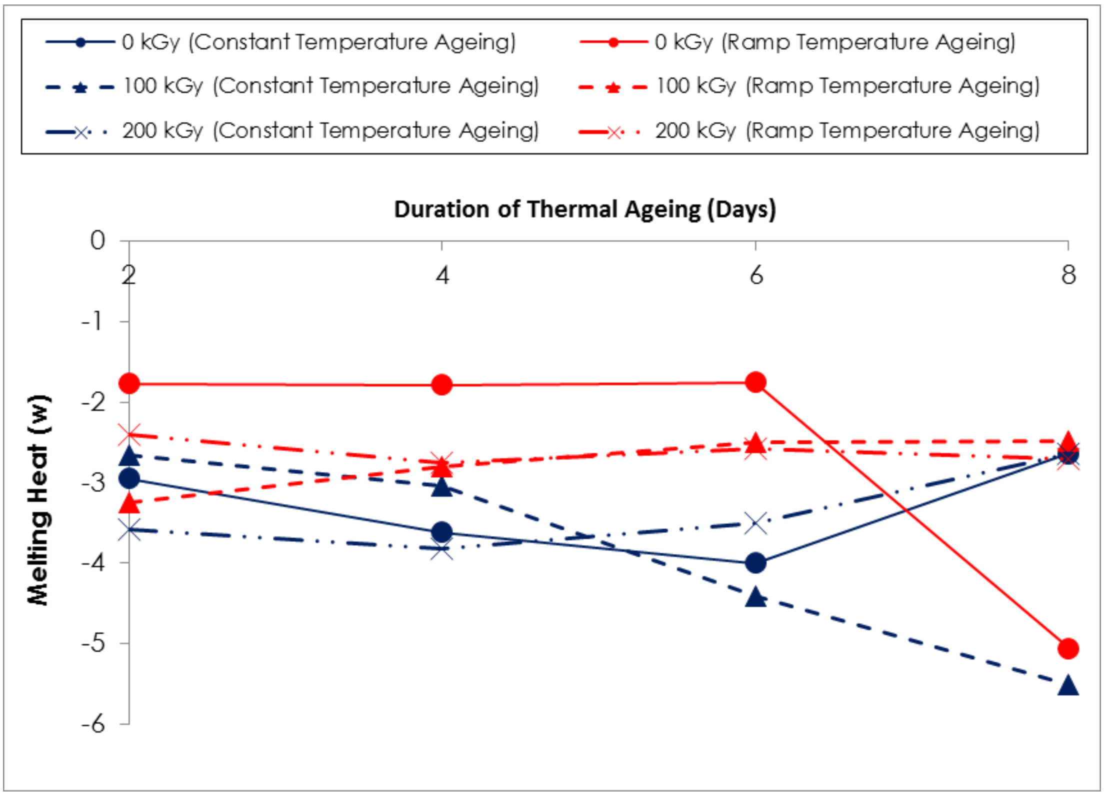


Figure 4.17: Melting Heat against Duration of Thermal Ageing at Various Irradiation Dosage for Condition Constant-100 and Ramp-100

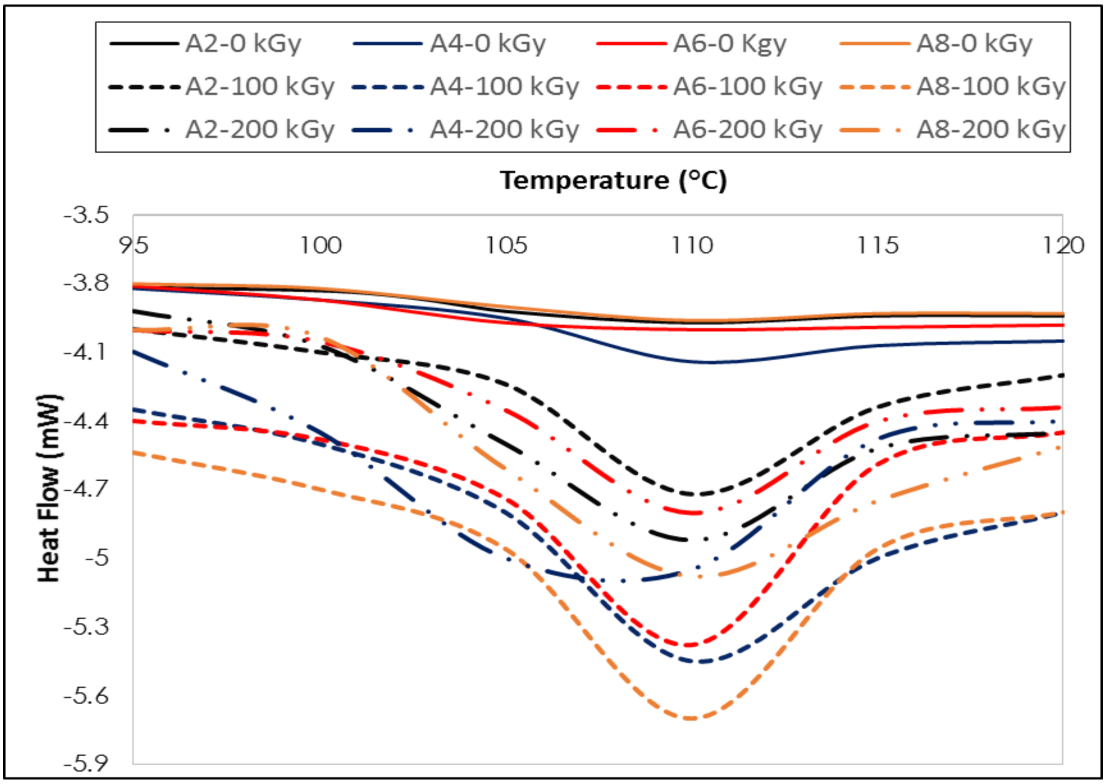


Figure 4.18: DSC Thermograms for Condition Constant-100

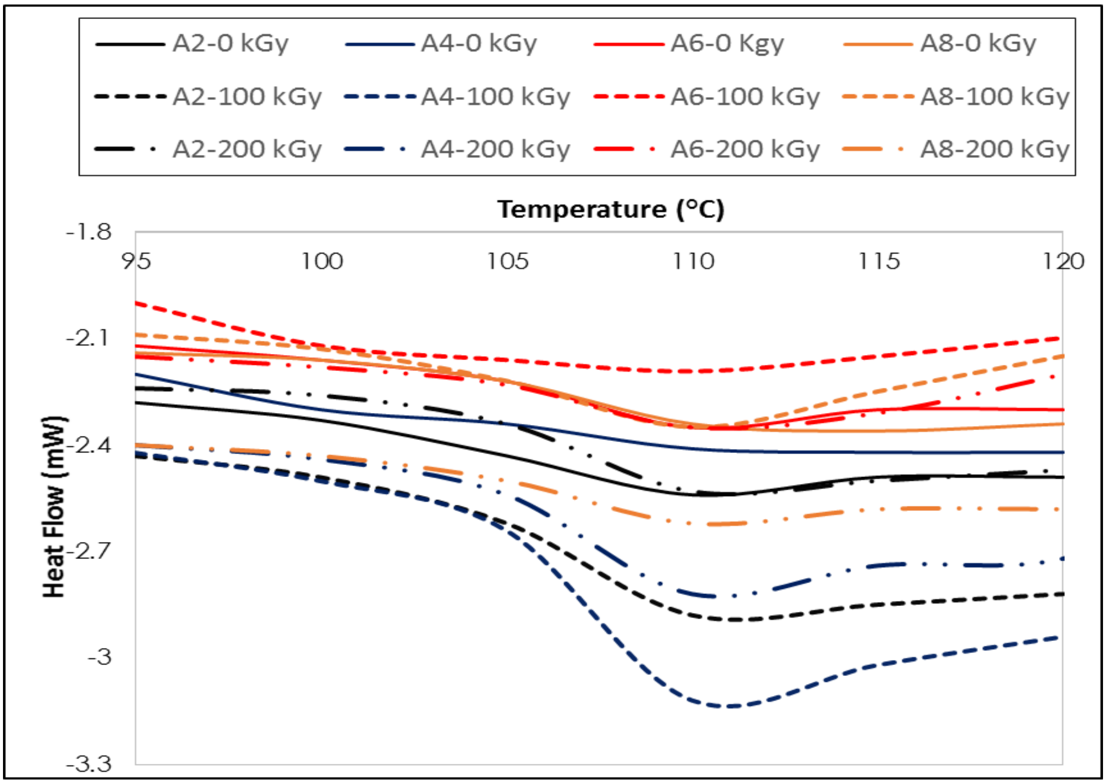


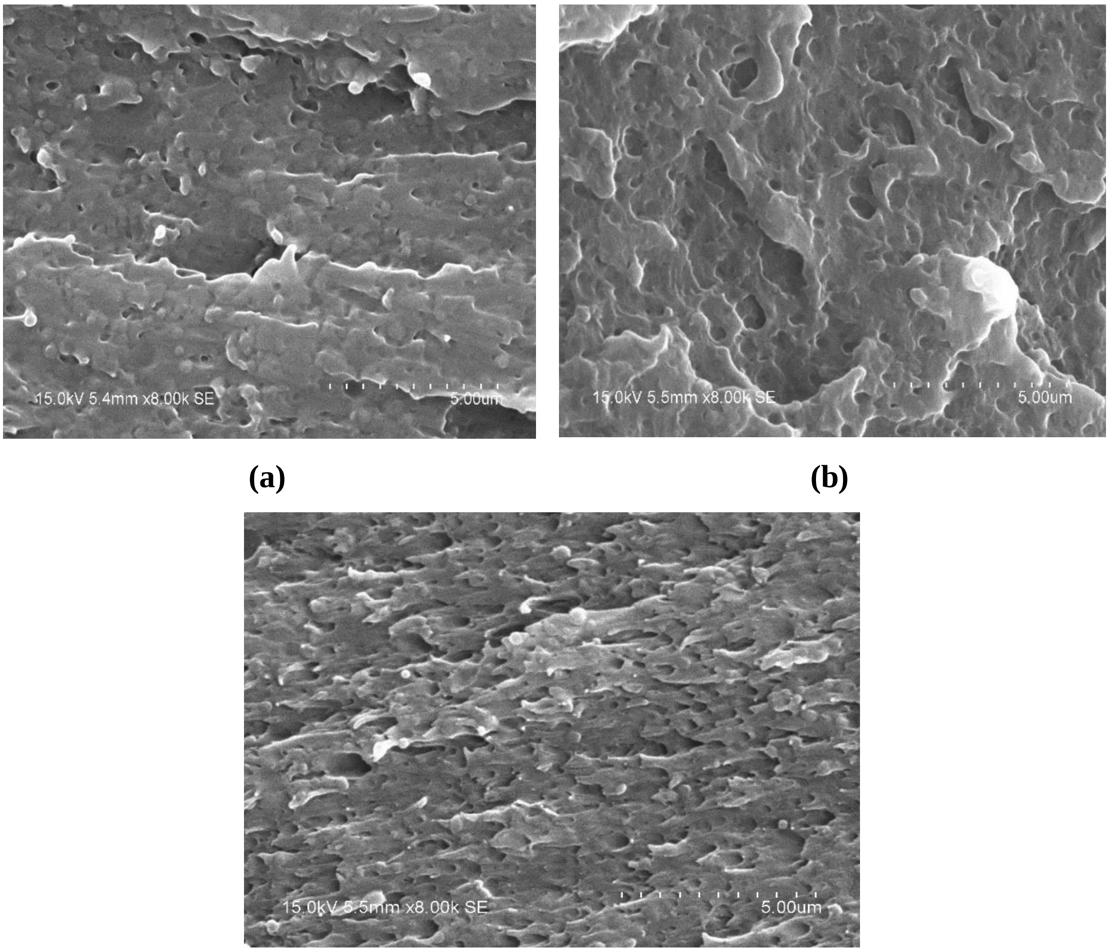
Figure 4.19: DSC Thermograms for Condition Ramp-100

4.4 Scanning Electron Microscopy

4.4.1 Thermal Ageing and Various Irradiation Dosages on Surface Morphologies

SEM analysis was used to verify and assure the effects of thermal ageing and various irradiation dosages on surface morphologies of polymer samples. Besides, mechanical properties of polymer materials such as tensile strength and elongation at break could be verified by evaluating the surface morphologies at fracture region of polymer sample as well. Figure 4.20 shows the surface morphologies of unaged samples (0 days thermal ageing) irradiated at 0, 100 and 200 kGy dosages. From the images, it can be observed that non-irradiated sample (as shown in Figure 4.20(a)) showed matrix continuity and intact layer. This shows that the relevant polymer is capable to perform at good mechanical properties.

When the irradiation dosage incorporated into polymer samples increased to 100 kGy, a clear phase separation and less continuity structures were found at the fractured regions (Figure 4.20(b)). This indicates that cross-linking structures induced by irradiation released monomer free radical, eventually broke the large pendant group of styrene ring within the PB phase. As irradiation further increased up to 200 kGy (Figure 4.20(c)), discontinuous matrix phase along with small voids were noticed distributed throughout the fractured surface. This indicates that the some of the regions have been oxidized via chain scissioning process. Therefore, a significant deterioration of mechanical properties could be observed on the sample.



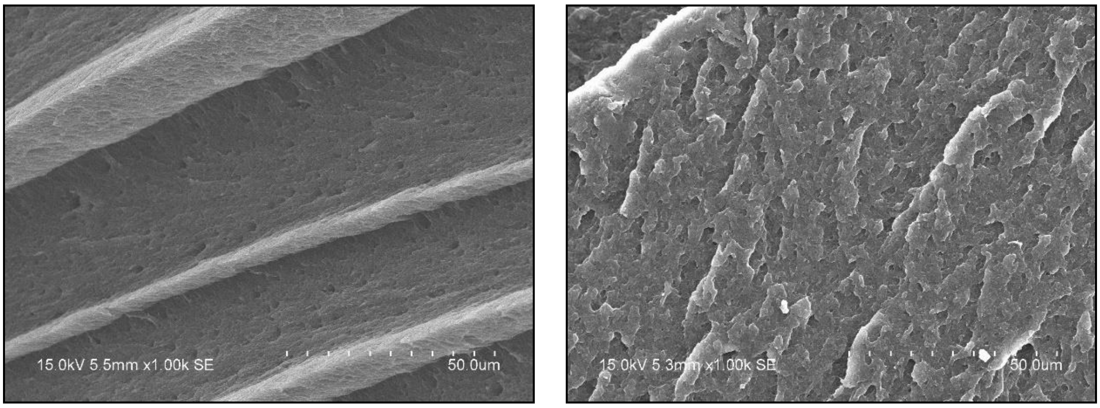
(a) **(b)**

(c)

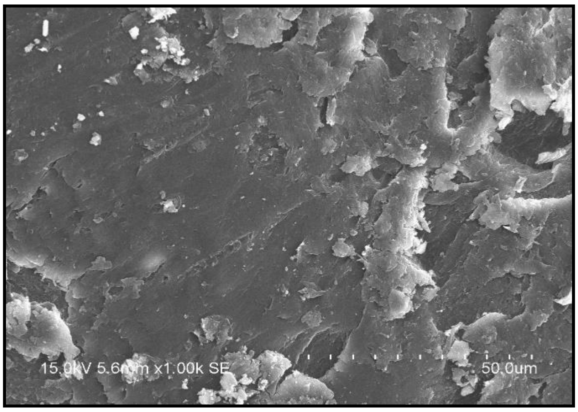
Figure 4.20: SEM Images of Unaged (0 Day Thermal Ageing) Samples irradiated at (a) 0 kGy (Non-Irradiated) (b) 100 kGy (c) 200 kGy

Figure 4.21 shows the images of non-irradiated and irradiated samples (100 and 200 kGy) that have undergone condition Constant-100 thermal ageing for 2 days. For non-irradiated sample that have been thermally aged for 2 days, the surface morphology was relatively smooth with continuity structures. This implies that the polymer exhibited good mechanical properties as their structures remained intact (Figure 4.21(a)). Furthermore, when irradiation was introduced at 100 kGy (Figure 4.21 (b)), it could be observed that the size of continuity structures decreased as compared to Figure 4.21(a). However, it can be seen that small amount of globules were found on the fractured region as well. This indicates that sample irradiated at 100 kGy possessed better mechanical properties as the formation of globules was due to the cross-linking network incorporated into rubbery polybutadiene phase. Hence, fractured region would return back to its original position, thereby exhibiting elastic behaviour (Yamanaka and Inoue, 1988).

In addition, this phenomenon also implies that rubbery polybutadiene phase of ABS has been cross-linked, thereby improving the extend ability of polymer prior to fracture. When irradiation dosage further increased to 200 kGy (Figure 4.21(c)), no continuity structures were found on the fractured surface as they were severely degraded by heating effect at elevated temperature. In addition, larger size of voids were formed at the fracture surface as compared to unaged sample (Figure 4.20(c)). This indicates that at high irradiation dosages, chain scissioning was more dominant and thereby promoting the oxidation of short chain polymers. Apart from that, discontinuous matrix and surface discoloration to white could be attributed to thermal oxidation and degradation of rubbery PB phase of ABS (Tiganis, et al., 2002). Hence, polymer with higher volume of void was expected to possess weaker tensile strength and elongation at break.



(a) **(b)**

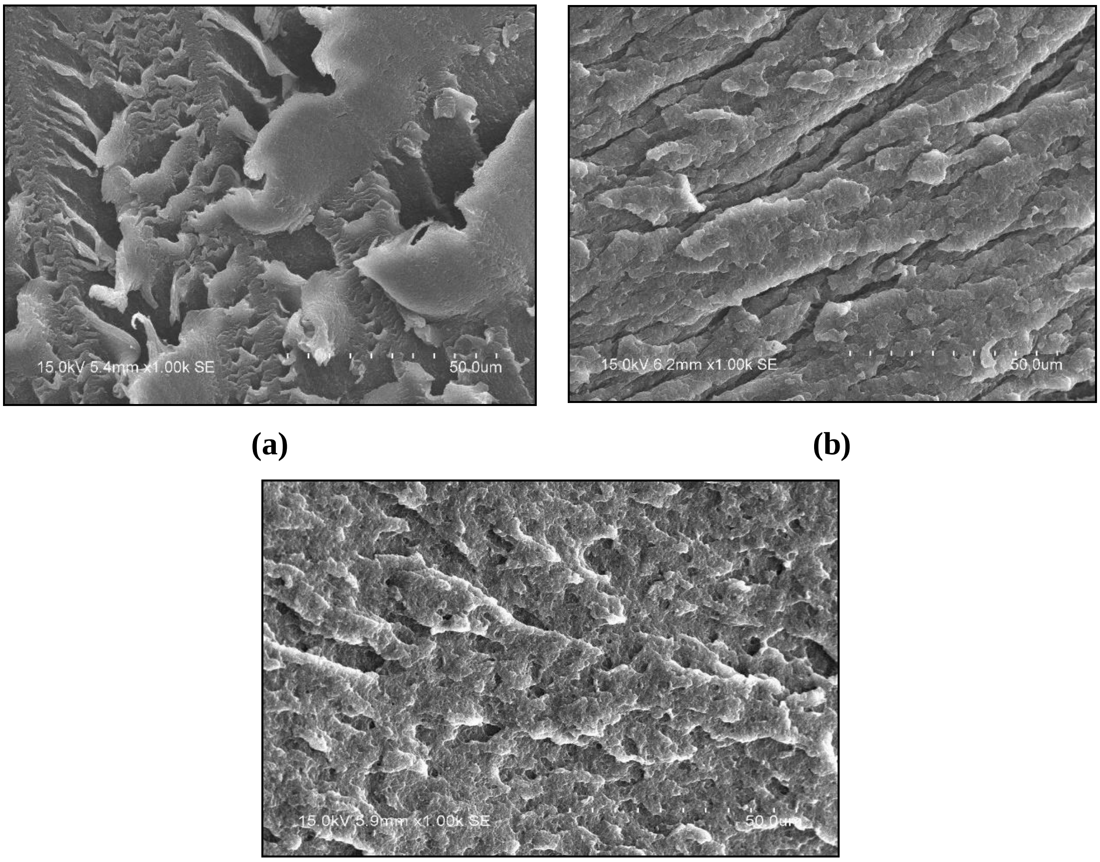


(c)

Figure 4.21: SEM Images of Condition Constant-100 Thermal Ageing for 2 Days (a) 0 kGy (Non-Irradiated) (b) 100 kGy (c) 200 kGy

When duration of thermal ageing prolonged to 8 days (Figure 4.22(a)), all polymer samples showed significant changes on fractured region. It could be observed that non-irradiated sample showed lower continuity as compared to sample thermally aged for 2 days (Figure 4.21(a)). Besides, thin fibrils were found on the fracture region as well. This indicates that the interfacial adhesion between polymer chains was disrupted by thermal degradation and resulted in discontinuous matrix phase (Bee, et al., 2013). This phenomenon was consistent with the lower tensile strength and elongation at break as compared to sample thermally aged for 2 days.

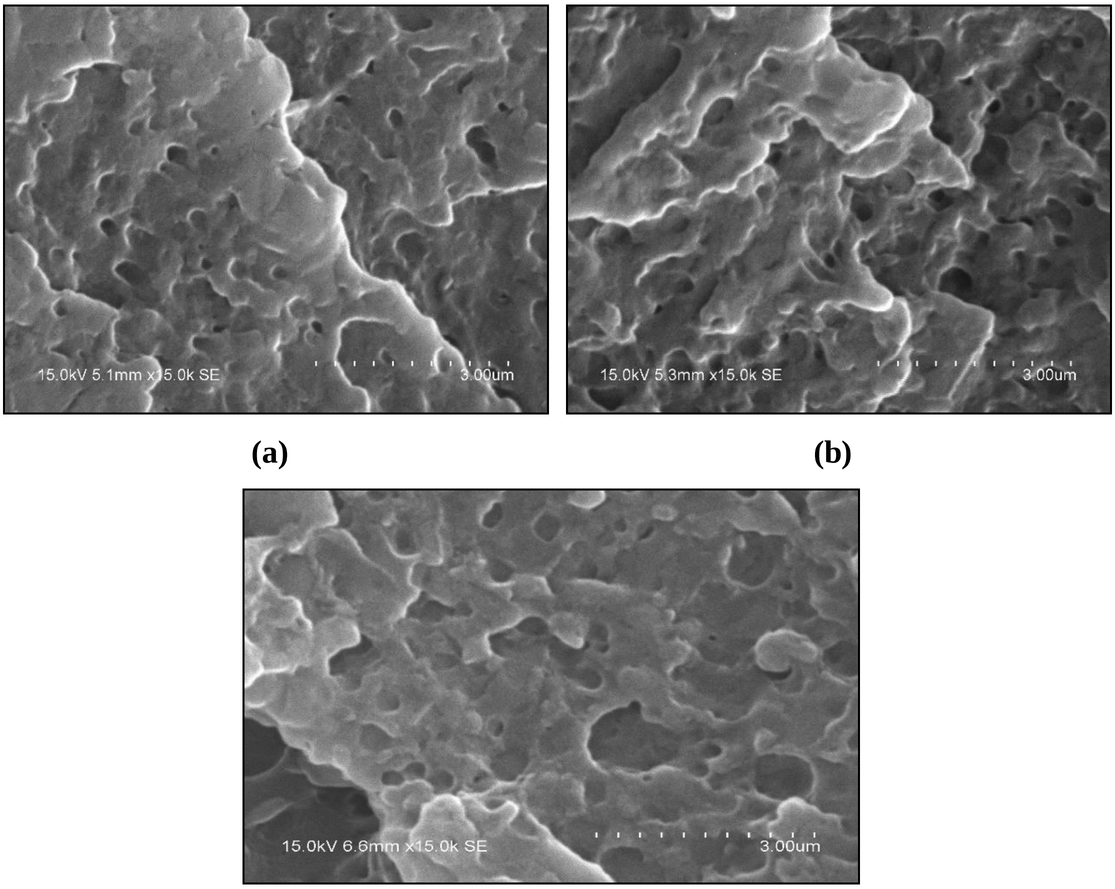
When irradiation dosage increased to 100 kGy (Figure 4.22(b)), matrix continuity of irradiated sample increased. The number of fibrils were significantly reduced as compared to non-irradiated sample (Figure 4.22(a)). This implies that the polymer possessed better mechanical properties than non-irradiated sample. At high dosage (200 kGy), the surface morphologies of polymer were severely disrupted as shown in Figure 4.22 (c) where no continuity structures were found on surface, along with long and thin flakes distributed all over the fractured region as compared to Figure 4.22(a)). This implies that most of the polymer chains have undergone intensive chain scissioning which broke the entangled amorphous melt into large number of short polymer chains at high irradiation dosage and prolonged duration of thermal ageing. As a consequence, gaseous released upon oxidation of short polymer chains were trapped within the polymer matrix and resulted the formation of void all over the fractured region (as shown in Figure 4.22(c)). This phenomenon was consistent with the tensile test results where the tensile strength and elongation at break of sample thermally aged for 8 days appeared to be lowest.



(a) **(b)**

Figure 4.22: SEM Images of Condition Constant-100 Thermal Ageing for 8 Days (a) 0 kGy (Non-Irradiated) (b) 100 kGy (c) 200 kGy

In addition, the images of ABS samples irradiated at 100 and 200 kGy and subjected to thermal ageing of condition Ramp-100 for 2 and 8 days were showed in Figure 4.23. For non-irradiated sample, it could be noticed that surface continuity was poor and filled with small voids. This indicates that thermal degradation of polybutadiene phase resulted in microstructural inconsistencies or stress concentration site. Thus, polymer subjected to thermal ageing for 2 days showed lower tensile strength and elongation at break as compared to unaged sample. At low dosage of 100 kGy (Figure 4.23(b)), phase separation and small voids were found on the fracture region. This implies that despite thermal degradation for 2 days, higher degree of cross-linking induced by irradiation was more significant than thermal degradation effect. Therefore, tensile strength and elongation at break of polymer increased as more stress is needed to deform cross-linked structures. As irradiation dosage increased up to 200 kGy (Figure 4.23(c)), the number and size of voids distributed over the fracture region were larger as compared to that of Figure 4.23(b). This implies that the effect of high irradiation dosage has caused the chain scissioning more significantly and thus the polymer chains undergone oxidation more easily.



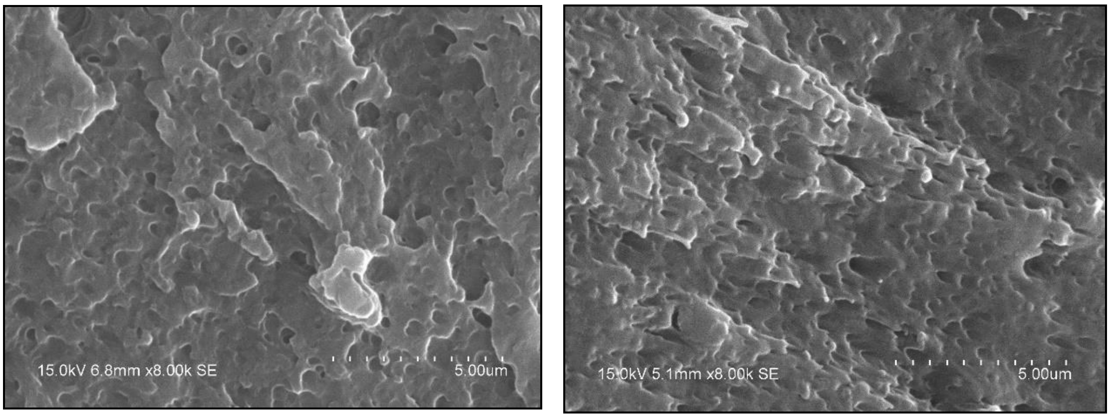
(a) **(b)**

(c)

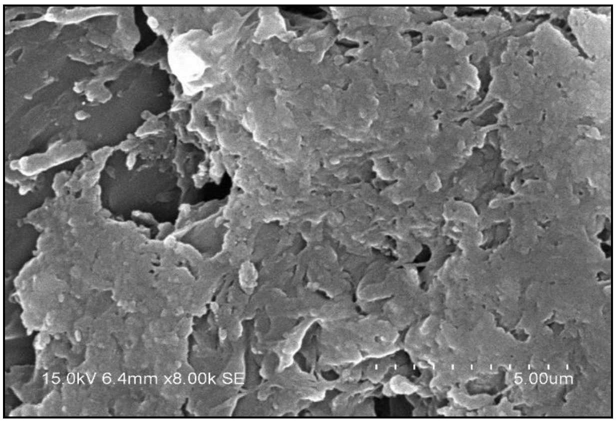
Figure 4.23: SEM Images of Condition Ramp-100 Thermal Ageing for 2 Days (a) 0 kGy (Non-Irradiated) (b) 100 kGy (c) 200 kGy

Figure 4.24 shows the SEM images of irradiated polymers subjected to condition Ramp-100 thermal ageing for 8 days. It could be observed that none of the sample possessed smooth and high continuity structures due to severe thermal degradation after 8 days of ageing. For Figure 4.24(a), non-irradiated sample showed relatively smaller portion of continuity and more voids. This was consistent with the results that the polymers possessed lower elongation at break as compared to condition Constant-100 sample as of Figure 4.22(a). This could be attributed to the chain scissioning mechanisms which restricted the polymer chain mobility became more significant. Hence, the polymer chains hardly slipped against each other during stretching and this led to easy fracture at low elongation. In addition, when irradiation dosages incorporated to samples increased to 100 kGy, it can be observed from Figure 4.24(b) that the aged sample showed higher continuity matrix. This indicates that cross-linking has been incorporated into polymer chain as a result of higher irradiation dosage.

Thus, polymer irradiated at 100 kGy showed improvement of tensile strength and elongation at break as compared to non-irradiated sample. When irradiation dosage further increased up to 200 kGy (Figure 4.24(c)), it was noticed that the size void present in the fracture region was significant large as compared to Figure 4.22(c). This implies that the polymer thermally aged at condition Ramp-100 possessed weaker mechanical properties as compared to sample of condition Constant-100.



(a) **(b)**



(c)

Figure 4.24: SEM Images of Condition Ramp-100 Thermal Ageing for 8 Days (a) 0 kGy (Non-Irradiated) (b) 100 kGy (c) 200 kGy

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This project has studied the mechanical and thermal properties of irradiated ABS samples at various condition of thermal ageing. Besides, physical properties of fractured regions has also been evaluated by conducting SEM analysis.

The incorporation of electron beam irradiation has significantly affected the mechanical properties of polymer samples. The impact strength values of unaged sample increased upon irradiation at 50 kGy, followed by progressive reduction when irradiation dosage further increased. This could be attributed to formation of cross-linking network which restricted the chain mobility at 50 kGy. In addition, the minimum impact strength (60 J/m^2) was achieved by sample irradiated at 250 kGy as interfacial adhesion of polymer was severely disrupted by excessively high irradiation energy. For tensile test, tensile strength value increased with respect to irradiation dosage up to 100 kGy, where maximum tensile value was achieved at 56.75 MPa. However, when irradiation dosage further increased at 100 kGy and above, rapid reduction of tensile strength was found on the material. In addition, elongation at break of unaged sample increased drastically from 16.5 MPa to maximum value of 26.8 MPa after irradiated at 50 kGy dosage. This indicates cross-linking effect has occurred within polymer matrix which promoted the chain mobility.

On the other hand, for condition C-100 thermal ageing, the impact strength of samples decreased drastically with higher dosage and reached minimum value of 54

J/m^2 at 250 kGy. For tensile test, the tensile strength value for ABS samples thermally aged for 2 and 8 days decreased significantly (49-43 MPa) at high dosages (>100 kGy). This could be attributed to altered chain scissioning process initiated by heating effect and prolonged duration of thermal ageing. Nevertheless, for thermal ageing of condition Ramp-100, the trend of impact strength was similar to condition Constant-100. However, it could be concluded that the impact strength of condition Ramp-100 decreased at lower degree (72-58 J/m^2) as compared to condition Constant-100 (73-54 J/m^2). This was attributed to harsh and constant heating environment of condition Constant-100 as compared to discontinuous heating and cooling environment of Ramp-100.

Moreover, when the samples have been subjected to thermal ageing for 4 to 8 days under condition Ramp-100, no significant changes of tensile strength could be found as compared to condition Constant-100. This indicates that the impacts of thermal degradation and chain scissioning mechanisms were less significant during Ramp condition thermal ageing as the heat applied to the sample was not fixed at constant temperature. Apart from that, the effects of irradiation dosage and thermal ageing on thermal properties have been verified by DSC analysis. For unaged samples, the melting temperature (106.24 ℃) was remained at significantly low level. As irradiation dosage increased up to 100 and 200 kGy, melting temperature rose to 107.76 ℃ and 111.43 ℃ respectively. This could be attributed to the strengthening of intermolecular bond by higher cross-linking network formed at higher irradiation dosage. When duration of thermal ageing prolonged, melting temperature of samples increased as well due to the vaporization of most of the weaker polymer chains. Thus, more heat energy was required to break the stronger bond of remaining polymer.

Lastly, the effects of irradiation dosage and thermal ageing on the physical properties of polymer sample could be verified by SEM. By analysing the images of unaged samples, it can be concluded that more continuity matrix structures were found on the surface which indicated good mechanical properties of the polymer. At low irradiation dosage (<100 kGy), cross-linking of the polymer matrix occurred and resulted improvement of mechanical properties. On the other hand, at high irradiation dosage, mechanical properties of polymer further deteriorated again as chain scissioning mechanism induced by high irradiation dosage was more dominant and resulted in surface structures filled of voids.

Apart from that, when polymer samples were subjected to condition Constant-100 and Ramp-100 thermal ageing, the morphological structures of polymer samples were disrupted by thermal degradation at elevated temperature. Thus, mechanical properties such as tensile strength and elongation at break of polymer further deteriorated as compared to unaged samples. In addition, as the duration of thermal ageing further prolonged, it could be concluded that surface continuity of samples would be further destroyed along with significantly larger and more voids distributed all over the surface. Therefore, this led to deterioration of mechanical properties of the polymer samples as most of the polymer chains were severely disrupted and became discontinued.

In conclusion, the effects of various irradiation dosages and thermal ageing on the mechanical, thermal and physical properties of ABS samples have been verified. It could be concluded it is very important to incorporate a proper dosage of electron beam irradiation in order to enhance the mechanical, thermal and physical properties of polymer material. Besides, prolonged duration of thermal ageing would cause potential deterioration of mechanical, thermal and physical properties of polymer.

5.2 Recommendations

It is recommended that the analysis of X-Ray Diffraction is applied to this project as it will be a useful characterization technique to analyse crystallite size and degree of crystallinity of polymer subsequent to thermal ageing process. Furthermore, it is suggested that Fourier Transform Infrared (FTIR) analysis could be carried out in this project in order to verify the formation of new functional groups within the polymer matrix after being thermally aged.

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APPENDICES

APPENDIX A: Impact Strength

Condition Constant-80

Irradiation Dosage (kGy)	0	50	100	150	200	250
0 Day Ageing	72.66	75.93	72.57	70.17	63.59	60.40
2 Days Ageing	69.44	74.98	71.22	68.06	63.35	59.56
4 Days Ageing	67.79	71.79	69.97	66.05	61.96	58.38
6 Days Ageing	70.03	72.43	69.08	64.71	61.62	58.30
8 Days Ageing	70.33	72.81	68.12	64.39	61.15	57.46

Condition Ramp-80

Irradiation Dosage (kGy)	**0**	**50**	**100**	**150**	**200**	**250**
0 Day Ageing	72.66	75.93	72.57	70.17	63.59	60.40
2 Days Ageing	70.11	72.25	69.22	69.16	63.81	60.00
4 Days Ageing	73.08	73.20	68.57	67.42	63.71	58.20
6 Days Ageing	73.63	74.03	69.14	68.15	63.64	57.26
8 Days Ageing	73.27	74.19	70.35	68.38	62.85	56.27

Condition Constant-100

Irradiation Dosage (kGy)	**0**	**50**	**100**	**150**	**200**	**250**
0 Day Ageing	72.66	75.93	72.57	70.17	63.59	60.40
2 Days Ageing	71.73	72.52	67.34	68.37	63.42	59.58
4 Days Ageing	69.60	69.60	64.33	63.10	60.82	55.85
6 Days Ageing	68.77	65.70	64.61	63.55	63.72	54.54
8 Days Ageing	68.33	65.96	65.12	65.08	65.25	54.01

Condition Ramp-100

Irradiation Dosage (kGy)	**0**	**50**	**100**	**150**	**200**	**250**
0 Day Ageing	72.66	75.93	72.57	70.17	63.59	60.40
2 Days Ageing	69.58	70.41	67.26	66.77	59.41	58.88
4 Days Ageing	66.79	71.37	65.32	59.75	60.01	57.64
6 Days Ageing	67.61	71.63	67.79	62.10	62.65	57.40
8 Days Ageing	68.30	69.52	65.01	61.50	62.36	58.09

APPENDIX B: Tensile Strength

Condition Constant-80

Irradiation Dosage (kGy)	**0**	**50**	**100**	**150**	**200**	**250**
0 Day Ageing	46.80	53.00	56.75	56.20	53.20	50.00
2 Days Ageing	44.20	44.20	43.80	46.00	52.20	50.25
4 Days Ageing	44.80	46.00	47.80	46.80	52.80	52.00
6 Days Ageing	43.80	45.20	45.40	44.20	51.60	50.60
8 Days Ageing	42.60	45.40	44.80	43.60	50.40	48.40

Condition Ramp-80

Irradiation Dosage (kGy)	**0**	**50**	**100**	**150**	**200**	**250**
0 Day Ageing	46.80	53.00	56.75	56.20	53.20	50.00
2 Days Ageing	39.80	40.20	41.20	40.80	45.20	44.20
4 Days Ageing	39.40	42.00	42.00	44.00	46.00	44.25
6 Days Ageing	41.00	41.75	41.80	43.60	44.20	44.00
8 Days Ageing	42.00	42.00	43.20	43.00	45.40	44.00

Condition Constant-100

Irradiation Dosage (kGy)	**0**	**50**	**100**	**150**	**200**	**250**
0 Day Ageing	46.80	53.00	56.75	56.20	53.20	50.00
2 Days Ageing	46.25	47.80	49.20	46.75	45.00	42.80
4 Days Ageing	45.80	49.60	49.20	49.40	50.60	48.75
6 Days Ageing	46.80	49.40	50.80	49.60	51.00	48.60
8 Days Ageing	45.20	45.40	48.80	46.80	44.20	42.90

Condition Ramp-100

Irradiation Dosage (kGy)	**0**	**50**	**100**	**150**	**200**	**250**
0 Day Ageing	46.80	53.00	56.75	56.20	53.20	50.00
2 Days Ageing	42.40	48.80	50.20	49.80	48.60	48.75
4 Days Ageing	40.00	41.25	43.00	42.80	42.40	42.00
6 Days Ageing	42.60	42.40	43.00	43.40	44.00	43.20
8 Days Ageing	41.00	42.00	44.25	45.40	43.20	47.60