

The effects of high energy electron beam irradiation on the thermal, mechanical, structural and physicochemical properties of polypropylene

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ABSTRACT

Polypropylene (PP) is occasionally used for packaging and manufacturing medical devices. Such applications require sterilisation to be carried out prior to use and a method that is becoming widely established is radiation due to its reliability and effectiveness. The aim of this paper is to investigate the potential effects of electron beam irradiation ranging between 25 and 200kGy for unstabilised PP. Samples of PP were subjected to a wide range of extensive characterisation techniques such as tensile strength, impact strength, modulated differential scanning calorimetry, melt flow index, Fourier transform infrared spectroscopy, rheology, x-ray diffraction, colorimetry, Shore D hardness, oxidative inductive time, goniometry and accelerated aging. The results demonstrated that a series of changes occurred due to electron bombardment. Mechanical properties such as percentage elongation at break and impact strength were mainly affected which decreased significantly with increased irradiation. Modifications to the melt strength were evidently seen from the results of the melt flow index technique, which illustrated a dramatic decrease. Fourier transform infrared spectroscopy indicated that the structural properties of the irradiated material were modified due to formation of carbonyl groups. Irradiated polypropylene material changed from a white colour to a dark yellowish colour due to post irradiation effects. Electron beam irradiation has a considerable effect on polypropylene material demonstrating poor irradiation resistance.

Keywords - Polypropylene, Biomedical, Degradation, Material Properties.

INTRODUCTION

Polypropylene (PP) has become widely used as a biomedical polymer in the medical device industry for various applications such as catheters, syringes, needle shields, auxiliary connectors, infusion bags and packaging [1, 2] This is mainly due to availability and low cost of the material, but more importantly its “resistance to softening at elevated temperatures” [3]. Radiation sterilisation of

medical devices by means of gamma ray and electron beam, has been implemented for well over fifty years [4, 5]. During sterilisation, radiation from both techniques destroys the reproductive cells of microorganisms by decomposing DNA molecules that are present. Radiation has become a popular method of sterilisation because no chemicals are used which in turn leaves no residues. However, high energy electrons can produce ionisation events throughout the material being sterilised [6]. This is readily seen in unstabilised PP material, where such events as chain scission, crosslinking and long chain branching occur due to the free radicals produced after radiation exposure [7]. The alkyl radical is a primary species of chain scission reactions which sequentially cause extensive degradation by abstracting hydrogen's from the main polymer chain [8, 9]. In addition, electron beam irradiation induces oxidation embrittlement and discoloration of PP which has been observed by [10, 11]. Post irradiation effects promote development of such groups as aldehydes and ketones, which suggest the reason for yellowing colour formation on the material. The rationale for the presence of oxidation in PP material is mainly down to an auto-oxidation process of active radical sites during irradiation. The peroxide radicals that are produced undergo further reactions which cause carbonyl compounds to form.[11-14] Oxidation continues for long periods of time after irradiation which is perhaps a reason for the presence of free radicals in the crystalline area [15, 16]. Although, the effects of high energy electron beam irradiation on polypropylene have been extensively studied, the majority of results have been discussed through a limited number of results. The present paper investigates the effects that different dose rates can have on the properties of polypropylene. It also focuses on aging samples in order to identify whether the self life has been modified after the exposure of radiation. A total of twelve characterisation techniques have been implemented to investigate modifications that occurred throughout the process.

EXPERIMENTAL

Materials

This study was carried out using a polypropylene material which is an impact copolymer grade (PP7043L1) manufactured by ExxonMobil Chemical Company (Huston, USA). The melt flow index (MFI) was 8.0g/10min under loading of 2.16kg at 230°C and the density was 0.9 g/cm³. Impact strength of the material was 13kJ/m² at 23°C while a melting temperature of 161°C was specified.

Method

Injection Moulding and Packaging

An Arburg injection moulder was used to manufacture type IV ASTM (American Society for Testing and Materials) testing specimens with the polypropylene

material. Packaging of the testing specimens and the material granules, play an important role in achieving a consistent irradiation dose. Low density polyethylene bags were used to contain the samples for each irradiation dose. Each bag had the same sample size, orientation and weight.

Electron Beam Irradiation

Firstly, dose mapping was conducted on the ASTM testing specimens and polypropylene granules in order to establish the max and min dose zones and reproducibility. Irreversible temperature labels were placed on each of the samples before irradiation in order to identify the max temperature achieved. A MEVEX high energy electron beam irradiator (combined 10/12MeV unit, 30KW) was used to irradiate the samples at doses of 25, 50, 75, 100, 150 and 200 kGy. The dose rate was approximately 12.5kGy per pass on each side for uniformity. Other dose rates were implemented to identify any changes to the material properties. For example, to obtain a 50kGy dose the sample were exposed to a 25kGy dose rate per pass each side. To obtain 75 kGy dose, the samples were exposed to a 25kGy dose rate per pass each side to make 50kGy and a further 12.5kGy per pass each side to obtain the target dose of 75kGy. This procedure was also conducted to obtain doses of 25, 50, 75, 100, 150 and 200. The irradiation of all the samples was performed at room temperature in the presence of air at the Isotron plant (Tullamore, Ireland). The dosimeters were read using a genesis 20 spectrophotometer in order to ensure that the samples received the min dose required and that the max dose was not exceeded. The non-irradiated samples served as the baseline for each of the result obtained from the characterisation techniques. Subsequent to irradiation, the temperature indicated on the irreversible temperature labels were recorded. The maximum temperature achieved during the irradiation of the samples was approximately 57° which was received by the 200kGy polypropylene sample.

Tensile Test

Type IV ASTM dumbbell specimens with dimensions of 33mm x 6mm x 3mm were used to measure the tensile strength, Young's modulus and percent elongation at break. The experiment was carried out according to ASTM D638-03. An Instron 3365 (Instron Ltd, UK) universal testing machine was used to conduct the experiment with a gripping distance of 40mm. The experiment was carried out at room temperature with a crosshead speed of 50mm/min. Five tests were executed on each sample throughout the different dose ranges and the mean was obtained from each of the five results.

Impact Test

The Charpy impact test was conducted on the ASTM specimens to establish the impact resistance of the material. Specimens with typical dimensions 124 x 12 x 6

mm were notched at half length with a 45° notch having a 2 mm depth. It was carried out according to ASTM D6110 with the exception of not using the specified anvil distance and striking edge. The anvils were 62mm apart and a 4J striking edge was used. A CEAAT 6545 impact tester was used to execute the experiment.

Modulated Differential Scanning Calorimetry (MDSC)

MDSC analysis was performed on the non-irradiated and irradiated polypropylene samples ranging from 25kGy to 200kGy, through the use of a modulated differential scanning calorimeter (TA Instrument DSC 2920 Modulated DSC). The MDSC was calibrated with indium and tin standards. All samples had a weight range between 8 and 10mg. Aluminium pans were used to contain the samples for the MDSC experiment. The non irradiated and irradiated samples were examined under a pure nitrogen atmosphere. Each of the PP samples was ramped from 40°C up to 200°C at a rate of 3°C/min and then cooled down 40°C again at the same rate. Scans for both processes were conducted twice on each sample. The first scan was performed in order to remove any thermal and aging history, while the second scan was performed to provide results during its relaxation stage. The onset temperatures, peak temperatures and enthalpy were determined from the data of both the first and second scans. Percentage crystallinity was determined by MDSC using the following formula:

$$\Delta \tau = \frac{\Delta_{fus}^H - \Delta_{fus}^{H^*}}{\Delta_{fus}^H} \times 100,$$

Where $\Delta_{fus}^{H^*}$: fusion enthalpy of irradiated polypropylene and Δ_{fus}^H : fusion enthalpy of polypropylene non – irradiated. 207J/g.

Melt Flow Index (MFI)

Melt Flow Index of the irradiated PP granules were measured by means of a CEAAT Melt Flow Quick Index (Italy).The MFI measurements of the non – irradiated and irradiated granules were performed according to the ASTM standard D 1238 – 04 with the exception of not using the standard conditional weight. For all samples, the melted material flowed through an orifice of 2.00mm diameter during 10mins (g/10mins) under loading of 0.325 kg at 230 °C

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra analysis was carried out on the non – irradiated and irradiated polypropylene samples. The results were recorded with a Perkin-Elmer Spectrum One machine which has a universal ATR (attenuated total reflection) sampling

accessory incorporated. All samples were conducted at ambient temperature, in the spectral range of $4000 - 650 \text{ cm}^{-1}$, utilising a 16 scan per sample cycle at 4 cm^{-1} resolution and a fixed universal compression force of 80N. Software such as IR Mentor and Spectrum were used to investigate the peaks that materialised throughout the irradiation process.

Rheological analysis

Rheological measurements were performed on the non – irradiated and irradiated polypropylene samples with an AR1000™ rheometer from TA instruments, which is fitted with an environmental test chamber (ETC). All experiments were conducted on a parallel plate of 25mm with a gap of 1mm. A strain sweep test was conducted in order to establish a suitable strain value within the viscoelastic region. A value of 5% was obtained for strain. Dynamic frequency sweeps were carried out in the frequency range of 0.1 – 100rad/s while using a temperature of 200°C. All samples were tested in a nitrogen atmosphere, to avoid degradation.

X-ray Diffraction (XRD)

The XRD of the polypropylene samples were examined via a Bruker axS D8 DISCOVER diffractometer. This characterisation technique was used to investigate the modifications induced by irradiation such as crystallite size and relative crystallinity. All samples were positioned onto the sample loading plate located in the XRD chamber. During setup, the loading plate was set to oscillation mode (x,y axis movement) with an amplitude of 0.5mm. The value of 2θ ranged from 5 to 35°. The GADDS and Eva software were used to analyse the recorded results.

Colorimetry

Yellowness index was carried out according to ASTM D 1925 with a Lovibond RT600 sphere spectrophotometric colorimeter. All samples were measured in terms of L from black (0) to white (100), a from green (-) to red (+) and b from blue (-) to yellow (+). Calibration was conducted on the instrument prior to testing by means of a calibration unit that was provided with the equipment ($L = 94.91$, $a = -1.01$, $b = +0.09$). Five tests were measured from each sample which was later used to calculate the average value of the yellowness index.

Shore D Hardness

A Shore durometer scale (CV Instruments) was used to establish the hardness of the polypropylene samples. It was carried out according to ASTM D 2240. All samples were exposed to room temperature for 24 hours prior to the experiment for preconditioning purposes. Each sample was measured for 30 seconds and this was completed three times in order to obtain an overall average value. The results were

recorded in inches. A type D indenter with a diameter of 1.40mm and a cone of 30° was used. A standard weight of 5kg was used to conduct the test.

Oxidative Inductive Time (OIT)

A Perkin Elmer DSC 7 was used to carry out the experiment in accordance with ASTM D3895-03. A sample of weight 8-10mg was placed into an open aluminium pan which was then positioned in the chamber of the DSC. A reference aluminium pan was also placed in the chamber in order to conduct the test. The sample were ramped up from 30°C to 200°C at a rate of 20°C per minute. The temperature was held at 200°C for 3 minutes to maintain equilibrium and this was all done under a nitrogen atmosphere. After 3 minutes elapsed, the nitrogen supply was changed over to oxygen. The temperature was held at 200°C for 30 minutes under an oxygen atmosphere.

Goniometry

The contact angle and the interfacial tension was measured using an FTA (First Ten Angstroms, Virginia) 1000 machine. Each sample was measure three times in the same order for consistency. For contact angle measurements a 0.002ml droplet of distilled water was ejected out of the micrometer syringe (GS-1200) onto the sample while using a 27 gauge needle. Images of the droplet on the surface of the sample were taken over a period of approximately 20 seconds and the FTA software was used to investigate the outcome results.

Table 1: Effects of non-accelerated aged, accelerated aged and different dose rates on the mechanical properties of irradiated polypropylene

Property	Method	0kGy	25kGy	50kGy	100kGy	200kGy
Tensile Stress (Mpa)	Non-Accelerated Aged	36.96	36.74	36.3	36.83	37.68
	Accelerated Aged	33.31	36.36	36.77	36.89	37.35
	Different dose rate	36.96	36.69	36.51	37.04	37.5
Elongation at Break (%)	Non-Accelerated Aged	172.65	110.3	73.93	28.3	9.46
	Accelerated Aged	127.78	79.98	52.45	27.15	9.33
	Different dose rate	172.65	106.94	63.42	28.97	9.02
Young's Modulus (Mpa)	Non-Accelerated Aged	976.96	978.37	1028.48	1044.29	1058.1
	Accelerated Aged	926.99	990.36	1005.77	1018.67	1044.8
	Different dose rate	976.96	895.63	881.71	878.36	892.34

Accelerated Aging

Polypropylene ASTM tensile specimens were placed into an incubator (air circulated oven) for 24 days at a temperature of 60°C which is the equivalent of one year aging. The samples were preconditioned at ambient temperature (21°C)

for 24 hours prior to the test. This test is particularly important for the shelf life of medical devices. Its helps understand the effects of one year aging on various properties of the material with regards to mechanical and structural. The 0, 25, 50, 100 and 200kGy samples were subjected to accelerated aging while the tensile test and FTIR characterisation techniques were implemented to discover any changes that may be present. The following equations was formulated to identify the required time and temperature required to achieve one year aging [17].

$$\text{AAR} = \text{Q10}^{((\text{AAT} - \text{AT})/10)} \quad (1)$$

$$\text{AATD} = \text{DRTA} / \text{AAR} \quad (2)$$

AR Accelerated Aging Rate

ATD Accelerated Aging Time Duration

RTA Desired Real Time Aging

AT Accelerated Aging Temperature

T Ambient Temperature

Q10 Accelerated Aging Factor

Q10 = 2 – Industry standard

Q10 = 1.8 – More conservative option

RESULTS AND DISCUSSION

Tensile Test

Table 1 illustrates the influence of absorbed irradiation dose, the effects of different dose rates and aging on the mechanical properties of polypropylene. It can be seen that the tensile stress for the non – accelerated samples was not significantly affected as the irradiation dose increased. Controversially, elongation at break had a dramatic decrease of approximately 120% which is in agreement with the results from [11, 18], while Young's modulus increased by 81Mpa with an increase in irradiation dose. The tensile stress for the accelerated aged samples, increase by approximately 4Mpa with an increase in irradiation dose. Again the elongation at break was most affected by the irradiation while the Young's modulus increased with an increase in radiation. Lastly, the results for the samples that were subjected to different dose rates per pass had similar trends to that of the standard dose rate per pass (12.5kGy) samples except for the Young's modulus. The Young's modulus decreased from 0 – 100kGy but increased at 200kGy.

Electron beam irradiation in the presence of air induced brittle failure under the experimental conditions. The change in the mechanical properties of the polypropylene samples can be attributed to the radiation induced oxidation degradation [13, 19]. This degradation initiates a process known as chain scission to occur which reduces the tie chains between crystal blocks. In addition, it

increases the stress concentration of the crystals and lowers the molecular weight to promote a brittle material [7, 20]. The values for the accelerated aged samples were dissimilar due to the long life free radicals present in the crystalline domain. They migrate slowly towards the crystalline /amorphous interface where they react with the accessible oxygen to create peroxy and hydroperoxy radicals and initiate degradation near the interface [21, 22]. Dose fractionation is another area which is focused on as it can form embrittlement in the material. Basically it involves multiple passes through the beam and the samples that are heated during the irradiation process are allowed to cool before going through the irradiator again to be reheated [11].

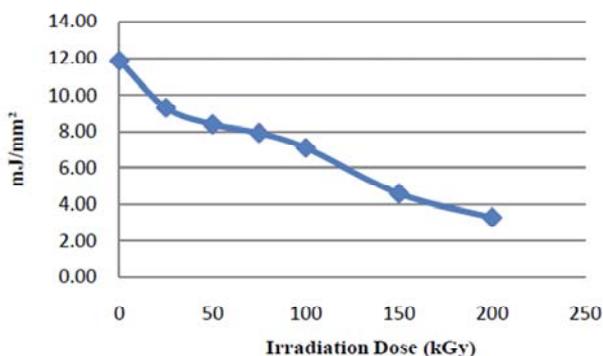


Figure 1: Impact Strength Verses Irradiation Dose

This is one of the reasons why a different dose rate was implemented to establish any improvements in the process. When the polymer crystallinity is lower the oxidation is potentially higher due to the restriction of the oxygen penetrating the crystalline region of polymers [13, 14, 19, 23]. If the material requires sterilisation, it is clear that additives need to be implemented in order to protect it against degradation produced from the electron beam irradiator.

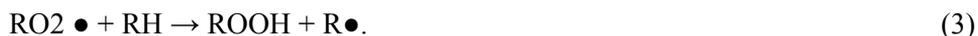
Impact strength

Fig.1 represents the results that were recorded from the impact test. It indicates that irradiation of the polypropylene ASTM testing bars had a considerable effect on the impact resistance. As the radiation dose increased the impact strength greatly decreased which is in accordance with the trend observed of tensile strength.. The present results are in agreement with the data [3, 24]. The change in the properties is down to the oxidation which forms peroxy radicals leading to chain scission and resin embrittlement [3]. Oxidation due to post irradiation effects on polymers is a multistage process which can be described as the same reaction for normal oxidation processes [25-27]:

Initiation:



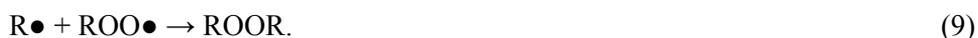
Propagation of the chain:



Branching of the chain:



Termination reactions:



Here the R and R• represent the polymer chain and polymer radical respectively

Modulated Differential Scanning Calorimetry (MDSC)

Results of the MDSC study are illustrated in Table 2. Table 2 deals with the polypropylene samples that were exposed to a dose rate of 12.5kGy per pass and the samples that were exposed to a number of diverse dose rates. This technique was performed on non-irradiated and irradiated samples where the first and second scan was observed.

Table 2: MDSC results for the irradiated polypropylene under the standard and diverse dose rate method

Sample	H_m (J/g)	Onset T_m °C	Peak T_m °C	Onset T_c °C	Peak T_c °C	% Crystallinity	Crystallinity degree variation (%)
Non-irradiated	87.56	159.10	165.06	126.78	120.82	42.30	0.00
25kGy/Standard	84.26	155.95	162.69	125.60	120.32	40.71	15.74
50kGy/Standard	83.49	155.17	160.25	124.05	119.55	40.33	4.65
75kGy/Standard	81.57	153.47	158.89	123.51	119.10	39.41	6.84
100kGy/Standard	81.05	151.55	157.54	122.48	117.90	39.15	7.43
150kGy/Standard	74.16	149.41	154.98	121.60	117.32	35.83	15.30
200kGy/Standard	71.10	147.20	153.02	120.81	116.62	34.35	18.80
25kGy/Diverse	81.36	155.82	160.55	122.60	117.97	39.31	7.07
50kGy/Diverse	76.41	153.36	158.53	122.22	117.59	36.91	12.74
75kGy/Diverse	72.86	153.81	158.26	123.36	119.12	35.20	16.78
100kGy/Diverse	71.99	152.54	157.76	122.64	118.33	34.78	17.78
150kGy/Diverse	70.40	150.04	155.09	121.54	117.19	34.01	19.60
200kGy/Diverse	68.47	148.18	152.97	120.02	115.77	33.08	21.80

In Figure 2 the first scan indicated that an increase in irradiation dose decreased the melting temperature (T_m) and the temperature crystallinity (T_c).

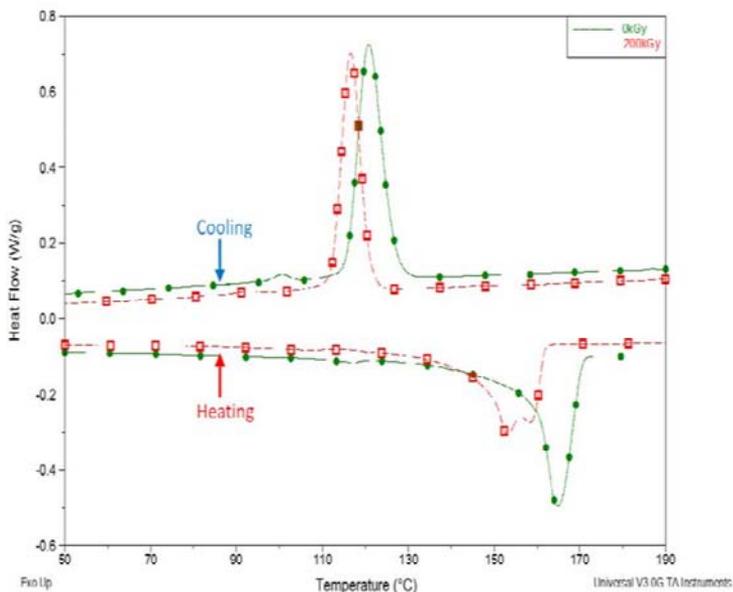


Figure 2: First scan cycle for the non-irradiated & the 200kGy PP samples

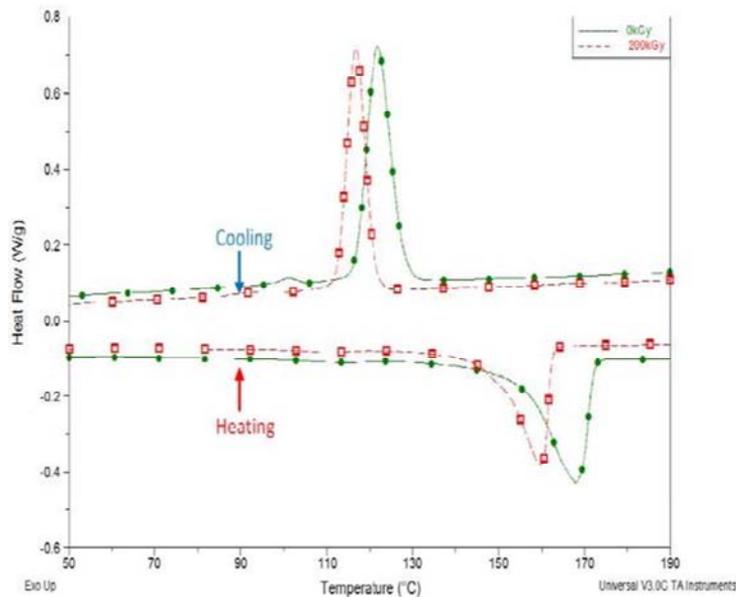


Figure 3: Second scan cycle for the non-irradiated & the 200kGy PP samples

The second scan illustrated in Figure 3 also showed a decrease in the T_m and T_c but this time the temperatures were further reduced. Similar behaviour was reported by reference [28]. This can be attributed to the formation of free radicals in the crystalline zone during irradiation, which moves more freely due to the melting process. For this reason chain scission reactions are produced which decreases the T_m and T_c [7]. This result was the same case for both methods (standard dose rate and diverse dose rates) which may be attributed to the re-crystallisation process during melting and the thermal history. Figure 3 clearly shows the re-crystallisation process during the heating up stage. The second peak becomes more pronounced as the irradiation dose is increased. The standard and diverse dose rate in table 2 follow the same trend but the results for the standard dose rate do not seem to be affected by the irradiation as much. The crystallinity decreased in both methods as the irradiation dose increased which is perhaps due to the decrease in the ability of crystallisation caused by chain branching. In addition to this, the chain branches that are formed due to irradiation induced reactions reduce the thickness and the perfection of crystallites. This in turn causes the T_m to decrease also as the irradiation dose increases in the second scan heating process [18]. Therefore, it is apparent that the polymer becomes more amorphous throughout the irradiation process [10].

Melt flow index (MFI)

Due to the high concentration of free radicals produced in the polypropylene blend [29], the melt flow index (MFI) test was performed on all non- irradiated and irradiated granule samples. Figure 4 shows a plotted graph for the MFI verses irradiation dose. It clearly demonstrates that the MFI of the PP material increases as the irradiation dose increases, which imply that a pronounced decrease in the weight average molecular weight took place as a consequence of an intense degradation (chain scission) process. These results correspond with the results from [7, 29, 30].

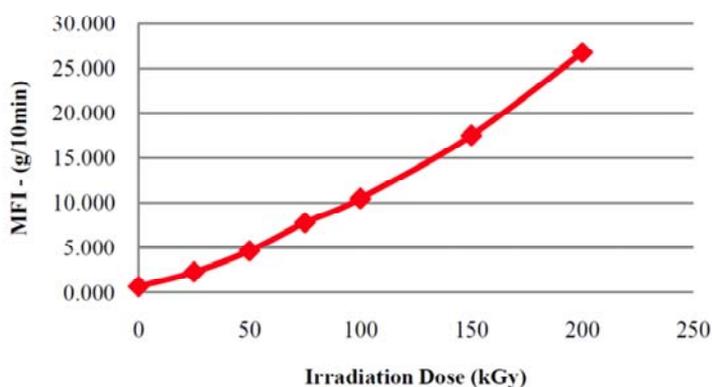


Figure 4: MFI verses Irradiation Dose

Since post irradiation increases the MFI of PP granules, the melting strength/temperature decreases which correlates with the results from the MDSC experiment. Reference [31] explains that the melting temperature (T_m) decreases steadily with irradiation dose due to chain scission. A reduction in chain scission can be achieved by irradiating the polypropylene samples in an inert atmosphere such as nitrogen. Nitrogen removes the oxygen from the area being treated, which in turn decreases the concentration of free radicals, therefore giving a greater melting strength.

Fourier transform infrared spectroscopy (FTIR)

FTIR was used to characterise the non-irradiated and irradiated polypropylene samples. This technique is an effective way in investigating the chemical structure of polymers. This technique was carried out on the standard and diverse dose rate samples and also the accelerated aged samples. The standard and diverse dose rate samples (Non- accelerated aged) had the same results but the accelerated aged samples highlighted that a significant amount of degradation occurred.

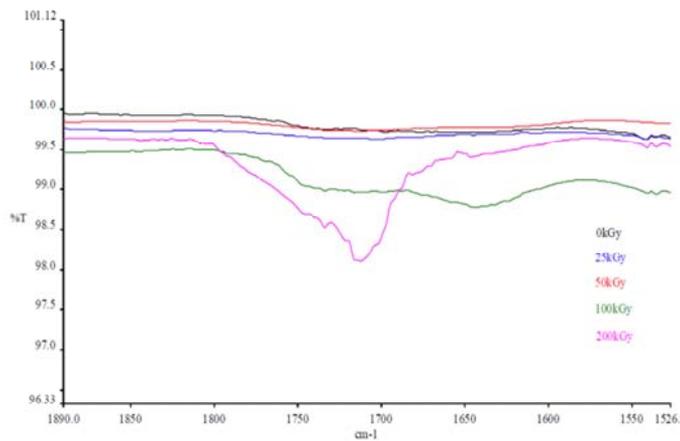


Figure 5: FTIR spectra of the non-irradiated PP

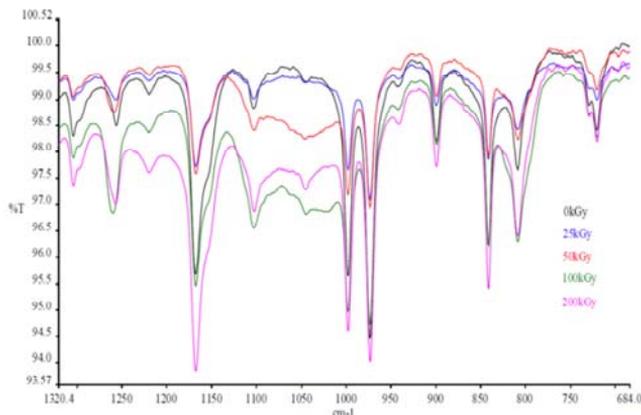


Figure 6: FTIR spectra of the non-irradiated PP

The non-accelerated aged samples illustrated that slight oxidation was occurring due to the formation of peaks between the range of 1720 and 1750cm⁻¹. This is mainly due to post irradiation effects producing free radicals in the molecular chain which in turn interacts with the oxygen molecules such as carbonyl groups [18]. This is more obvious in the accelerated aged samples which are shown in Fig.5. Show in Fig. 6 is the wavelength between 684 and 1320 cm⁻¹ for the accelerated aged samples. It can be seen that a significant amount of changes have occurred within this region. As the irradiation dose increases the greater the intensity for each of the peaks. In the non-accelerated aged sample, the intensity of the peaks remained the same throughout the different irradiation doses. These results prove that degradation occurs after irradiation. However, degradation is more severe after accelerated aging which indicates that further degradation take places as time goes on i.e. 1 year.

Rheological Analysis

The results for the dynamic frequency sweep test conducted on the non-irradiated and irradiated polypropylene samples are illustrated in Fig. 7, 8 and 9. The storage (G') and loss (G'') were plotted as a function of frequency (ω) which was used to measure the controlled and irradiated polypropylene. The two module in Fig. 7 and 8 indicated that the polymer chains were more affected by irradiation in the high frequency regime as opposed to the low frequency regime. In the high frequency regime of Fig. 7 the G' decreased as the irradiation dose increased. This can be attributed to the scission of the macromolecular chains [32] Similar results were reported by reference [33] who focused his analysis between a frequency ranged of 5 and 1000 rad/s. However, between 0.01 and 1.0 rad/s a more complex behaviour occurred where the storage modulus of the non-irradiated sample decreases significantly below the 200kGy sample. This suggests a low crosslinked network formed due to radical reactions [34]. The 200kGy sample in the loss modulus develops a plateau at low frequencies which suggests that long chain branches are present [35]. A shear thinning behaviour is also seen in the loss modulus which is perhaps due to the formation of a gel in the material [33]. Fig. 9 demonstrates the complex viscosity verses the frequency of the non-irradiated and irradiated polypropylene samples. The frequency range between 0.01 and 100 rad/s shows a decrease in complex viscosity as the irradiation dose and frequency is increased which indicates that a fraction of low molecular weight material is formed lubricating the flow. [9] The lower frequencies are not assensitive which could be attributed to the presence of slight crosslinks. Shown in Fig. 10 is a plotted graph for viscosity verses temperature. This experiment provided evidence that the viscosity decreased dramatically as the temperature and irradiation dose is increased. This may be due to radiation induced reactions such as chain scission.

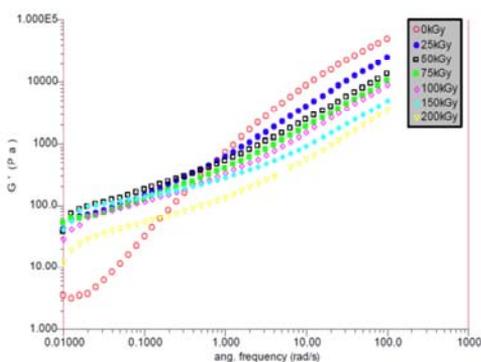


Figure 7: G' verses frequency (ω)

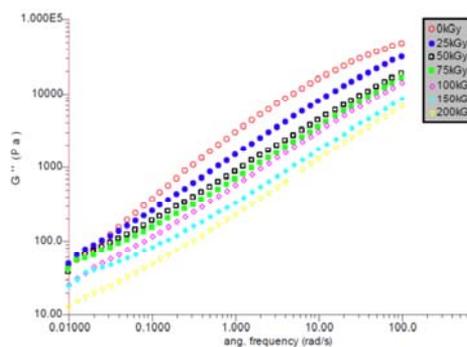


Figure 8: G'' verses frequency (ω)

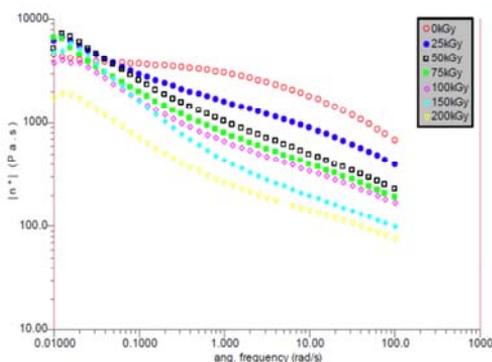


Figure 9: Complex viscosity versus frequency (ω)

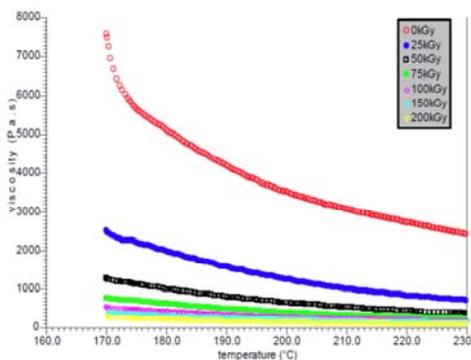


Figure 10: Viscosity versus temperature

X-ray diffraction (XRD)

The XRD spectra for the non-irradiated and electron beam irradiated polypropylene are illustrated in Fig. 11. The six peaks shown in the graph clearly suggest that the material is semi-crystalline in nature. The crystalline peaks (2θ) nearby 14° , 16.8° , 18.5° , 22° , 25.5° and 28.5° are down to the monoclinic structure of α crystal, i.e., (110), (040), (130), (-131), (060) and (220) respectively [36]. It is observed from Fig. 9 that there is a slight growth in the intensity of the peaks. However, the peaks are not increasing according to the increase in irradiation. The intensity of peak (040) remarkably increased which is seen on the 50 and 200kGy curve. This indicates that that the crystalline size has reduced. The Scherrer equation [37] was used to calculate the crystalline size which was reduced from 85 – 82 Å. A new peak at $2\theta = 16.21^\circ$ emerged with sufficient intensity indicating the reorganisation of polymer chains due to chain scissioning and crosslinking. Electron beam irradiation does not affect all regions of the polymers but the amorphous areas are the most vulnerable which contain mostly tie molecules. Chain scissioning of these bonds can cause displacement amongst the crystalline planes which in turn causes depletion of atoms or enrichment of atoms[38]. This maybe the reason for a decrease in plane (110) and the formation of a new peak at 16.21° .

Colorimetry

Colour measurement data for before and after electron beam irradiation are shown in Fig. 12. The Hunter b value illustrated in Fig. 10A showed a significant difference (increased from - 3.88 to 19.72) between the non-irradiated and the irradiated samples, as the b value changed considerably as the irradiation dose increased. As a result the samples became yellowish in colour which was clearly visible to the naked eye as shown on Fig. 13. The Hunter L and a values (Figure 10

B and D) also decreased slightly with increased irradiation dose. The overall colour difference was established by implementing statistical analysis of the E values. E was calculated by using the following formula [29]:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

The Δ is expressed as the difference between the control sample and the irradiated sample colour values. There was a significant increase observed for the ΔE value as the irradiation dose increased. The results correlate well with those of reference [39, 40]. An explanation for such changes after the exposure of irradiation is perhaps due to the formation of conjugated double bonds and/or the entrapment of free radicals [29]. The degree of discolouring is directly related to the nature of stabilising additives used while compounding the polymer material [39].

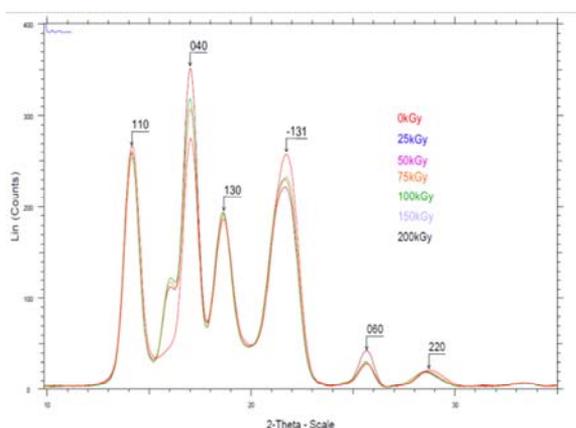


Figure 11: XRD spectra of the non-irradiated and irradiated PP

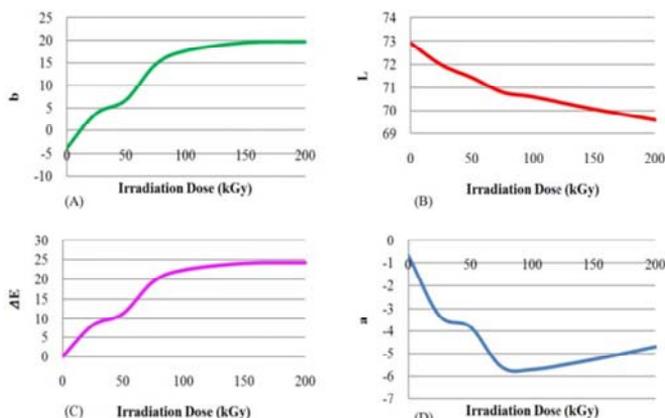


Figure 12: Figure 12. (A) Hunter b value for PP vs. irradiation dose. (B) Hunter L value for PP vs. irradiation dose. (C) Hunter ΔE value for PP vs. irradiation dose. (D) Hunter a value for PP vs. irradiation dose



Figure 13: Visual effect of increased irradiation dose on PP samples

Shore D Hardness

Radiation induced reactions such as cross linking and chain scission can have an effect on the polymer matrix leading to hardness modifications in the sample. The hardness can be classified as the resistance of the material towards local deformation [24]. The results shown in Fig. 14 provide evidence that the irradiated samples remained the same as the non-irradiated samples in terms of resistance towards local deformation. However, the trends obtained for the tensile and impact strength were not in strict agreement with the trends obtained from the Shore D hardness. This is perhaps due to the less sensitivity of the Shore D hardness towards crosslink density of the material [41].

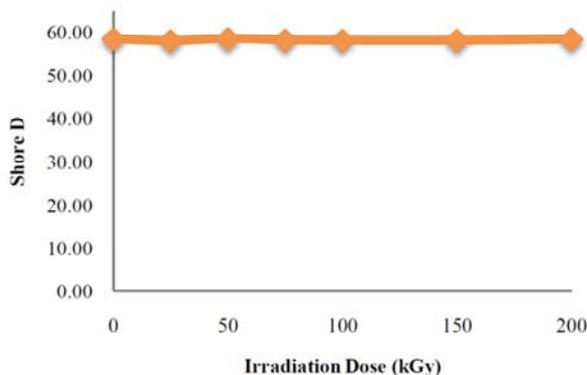


Figure 14: Shore D versus irradiation dose of PP

Oxidative Inductive Time (OIT)

OIT is an important characterisation technique used for identifying the shelf life of medical grade polymers such as polypropylene. The antioxidants within polypropylene dwell mainly in the amorphous phase and it's effectiveness to react

with primary free radicals preferentially decides the overall post irradiation stability of the material [22]. Fig. 15 illustrates the results obtained for OIT on the non-irradiated sample and the 25kGy sample. The non-irradiated sample lasted approximately 14 minutes before it started to failed after the introduction of oxygen into the process. The sample completely failed at approximately 18 minutes due to the antioxidants being entirely used up. The 25kGy sample on the other hand failed straight away when the oxygen was introduced. This outcome is mainly due to a depletion of phenolic antioxidants during the irradiation process. Reference [22] reported similar results in that polypropylene continued to reduce in oxidative stability which agrees with the model of long life free radicals continuously causing oxidation.

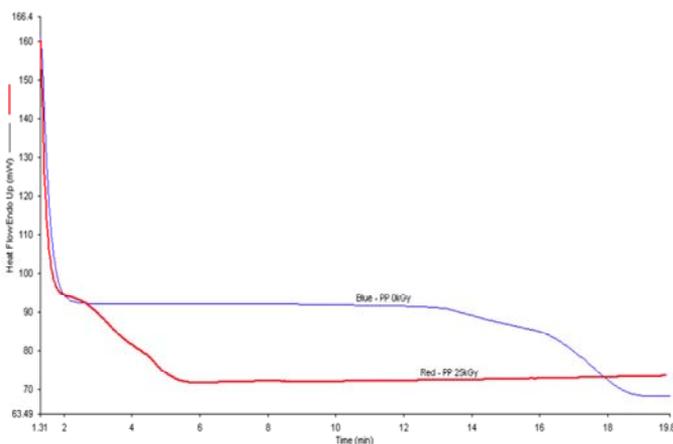


Figure 15: OIT of non-irradiated and 25kGy PP sample

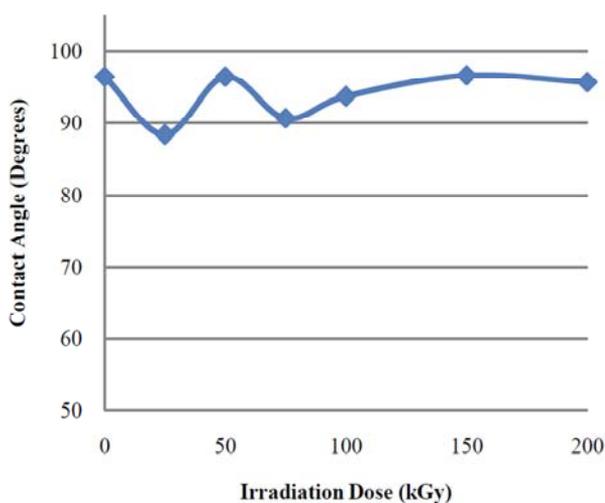


Figure 16: Contact angle of non-irradiated and 25kGy PP sample

Goniometry

Shown in Fig. 16 are the results for the contact angle of the non – irradiated and irradiated polypropylene. The contact angle is generally governed by the degree of roughness and the presence of hydrophilic/hydrophobic chemical species [36]. There are no trends to report here but there are slight changes occurring throughout the different irradiation dose ranges. The slight decreases observed (25 and 75kGy) maybe attributed to the formation of hydrophilic carbonyl groups as well as surface roughening due to irradiation [36]. Where the curve begins to increase i.e. 100 – 150 kGy, this may be due to the material not being as sensitive at that particular irradiation dose.

CONCLUSION

Electron beam irradiation of polypropylene affects the mechanical, thermal, structural and physiochemical properties of the material to a large extent. With regards to the mechanical properties the percent elongation at break and impact resistance decreased dramatically with an increase in irradiation. Thermal properties such as melting temperature and temperature crystallinity decreased as the irradiation dose increased. The melt flow index proved to have similar results. FTIR was implemented to observe structural properties of the material which illustrated that slight changes occurred with an increase in irradiation. However, after accelerated aging more severe changes were observable. The presence of carbonyl groups were identified which proves that oxidative degradation took place. This process leads to the formation of chain scissioning which can attribute for the significant decrease in the mechanical properties. In addition, the physiochemical properties were also modified. Colorimetry provided numeric results which showed that the material turned a yellowish colour as the irradiation dose increased. This could be further proved by visual inspection of the samples. The contact angle of the material did not show any significant changes. Overall, the material was highly affected by the exposure of electron beam irradiation in terms of degradation. This unwanted outcome could be greatly improved by adding various stabilisers to the polypropylene material.

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