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# The Influence Of Electron Beam Irradiation On The Property Behaviour Of Medical Grade Poly (Ether-Block-Amide) (PEBA)

[1]Kieran A. Murray, [1]James E.Kennedy, [2]Brian McEvoy, [2]Olivier Vrain, [2]Damien Ryan, [2]Richard Cowman and [1]Clement L. Higginbotham

[1]Materials Research Institute, Athlone Institute of Technology, Dublin Road, Athlone, Co. Westmeath, Ireland
[2] Synergy Health Applied Sterilisation Technologies, IDA Business & Technology Park, Sragh, Tullamore, Co. Offaly, Ireland

**Abstract:** The aim of this paper is to investigate the potential effects of electron beam, ranging between 5 and 200kGy for unstabilised Poly (ether-*block*-amide) (Pebax) material. The Pebax samples were subjected to a wide range of extensive characterisation techniques in order to identify any modifications to the material properties. The results demonstrated that a series of changes occurred and some of these included a reduction in the mechanical properties and melting strength, an increase in the molecular weight and viscosity and alterations to surface characteristics of the material. Overall, this study provided evidence that electron beam irradiation lead to the development of simultaneous crosslinking and chain scission in the Pebax material, where crosslinking/branching became the dominating factor above 10kGy.

**Key words:** Electron beam irradiation,Poly(ether-*block*-amide), Thermal, mechanical, structural and surface properties, Temperature ramp, Degradation

## INTRODUCTION

Poly (ether-*block*-amide) (Pebax) is a copolymer which consists of linear chains of rigid polyamide blocks covalently linked to flexible polyether blocks via ester groups (Joseph and Flesher, 1986). The polyamide crystalline region provides the mechanical strength while the polyether amorphous region offers high permeability as a result of the high chain mobility of the ether linkage (Joseph and Flesher, 1986; Liu, 2008). Pebax exhibits a semi-crystalline morphology; where the degree of crystallinityis dependent on the polyamide content.There are many types of polyamides that can be used to synthesise Pebax, including nylon 6, nylon 66, nylon 11, nylon 6/11, nylon 12 and nylon 6/12. In terms of polyethers, these include poly(propylene glycol), poly(tetramethylene ether glycol) and poly(ethylene glycol). The content of each segment affects the overall properties of the copolymers. For example, the type and the molecular weight of a polyamide affect the melting point and the chemical resistance whereas the type of polyether influences the glass transition temperature of the copolymer. However, the copolymers retain a high melting temperatureof polyamide, in the range of 120 $^{o}$C to 210 $^{o}$C, and a low glass transition of polyether (-60$^{o}$C to -70$^{o}$C). The ratio of polyamide to polyether determines the hardness and flexibility of the copolymer (Joseph and Flesher, 1986).

Different grades of Pebax polymers are commercially available, and they generally have excellent mechanical strength and good chemical resistance which are ideal for a number of medical applications such as angioplasty balloon technology. Radiation is commonly used to sterilise such applications, however, it is vital that the material properties are not compromised by the treatment. Radiation exposure can result in both chain scission and crosslinking; however, one generally predominates over the other. Chain scission can consequently lead to a reduction in the molar mass whereas crosslinking increases the molar mass leading to a less flexible product (Clayden and Pendlebury, 2001). Chain scission is the predominant factor when polyethylene oxide is irradiated via electron beam (Cholli *et al*., 1988), whilst crosslinking is proposed as the main effect caused by irradiation in polyamides, leading to the loss of crystallinity. The precise physical properties of Pebax after irradiation exposure are dependent on the nature of the polyamide and polyether segments as well as the percentage composition. A general expectation would be a high degree of phase separation between the flexible polyether and rigid polyamide segments (Clayden and Pendlebury, 2001; Goldman and Pruitt, 1998).

This investigation is focused on another strategy, not explored up until now to the best of our knowledge. The main objective of this research was to identify the effects of electron beam irradiation (combined 10/12MeV unit, 20KW) on the properties behaviour of Pebax material by performing a number of analytical techniques. Melt flow index (MFI) was used to identify the change in the flow of the material under heat and pressure and to provide an indirect measure of the molecular weight before and after the irradiation process. Rheological tests were performed via the temperature ramp method in order to identify modifications to the

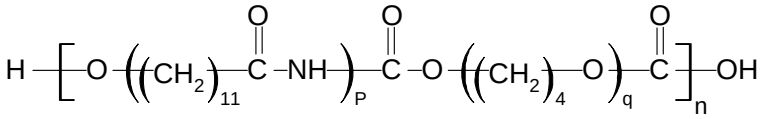
**Corresponding Author:** Clement L. Higginbotham, Materials Research Institute, Athlone Institute of Technology, Dublin Road, Athlone, Co. Westmeath, Ireland

viscosity of the material with a constant shear rate and an increment in temperature. Furthermore, the results of this experiment were compared to that of the MFI to ensure that they followeda similar trend.Since the mechanical properties of a medical grade polymer plays a major role in the final end use application, tensile testing was utilised in examining these properties before and after the exposure of irradiation.Finally, scanning electron microscope (SEM), Atomic force microscopy (AFM) and goniometry were used to determine the surface modifications of the material subsequent to irradiation as the wettability performance of the sample surface is significant in end use medical devices.

## MATERIALS AND METHODS

### *2.1. Materials:*

This study was carried out using Pebax 6333 SA01 material which is a medical grade poly (ether- *block*-amide) virgin polymer manufactured by Arkema. A density of 1.01 g/cm$^3$ was specified for the material with a melting temperature of 169°C. The material was supplied in granular form and used as received. The complex structural formula of this block copolymer is (Murray *et al*., 2013a):



### *2.2. Injection Moulding And Packaging:*

Prior to injection moulding, the Pebax material was dried with a Piovan desiccant dryer in accordance to the manufacturer's specifications (75°C for 6 hours).An Arburg injection moulding machine was utilised in manufacturing type IV ASTM (American society for testing and materials) D638 testing specimens with the use of Pebax material. The machine had a maximum clamping force of 38 tonne with a screw diameter of 25mm. Sample preparation played a significant role in the electron beam process as this controlled the uniformity of the irradiation dose on the samples. Each of the samples i.e. tensile specimens and pellets were placed into sealable low density polyethylene bags in order to contain them in a controlled environment. Sample size, density, weight and orientation remained identical for each bag during the packaging process to facilitate uniform irradiation.

### *2.3. Electron Beam Irradiation:*

Firstly, dose mapping was conducted on the ASTM testing specimens and granules in order to establish the max and min dose zones and reproducibility. A Mevex high energy electron beam irradiator (combined 10/12MeV unit, 20KW) was used to irradiate the samples at doses of 5, 10, 15, 25, 50, 100, and 200kGy. The dose rate was approximately 12.5kGy per pass on each side to accomplish a uniform irradiation dose. All samples were irradiated at room temperature in the presence of air at the Synergy Health 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(Murray *et al*., 2012).

### *2.4. Melt flow index (MFI):*

Melt Flow Index (MFI) values of the non-irradiated and irradiated Pebax granules were measured according to ASTM standard D 1238 (ASTM D638-03, 1994) by means of a CEAST Melt Flow Quick Index. MFI measurements were performed at a temperature of 235°C under a 1kg weight. The melted material flowed through an orifice of 2.00mm diameter during 10mins and the values were reported in g/10min. MFI was used to identify how well the material flowed under heat and pressure while additionally providing an indirect measure of the molecular weight.

### *2.5.Rheology – Temperature Ramp:*

Temperature Ramp tests were carried out on the Pebax material with an AR1000™ rheometer from TA instruments, which is fitted with an environmental test chamber (ETC). This wasperformed by the steady state parallel plate viscometry method. A ramp rate of 2°C/min was applied, with a shear rate of 1 (1/s) and a sample delay time of 10 seconds. Each of the results were analysed to identify the change in viscosity as the irradiation dose increased. The Pebaxmaterial had a temperature ranged between 175°C and 250°C while all samples were tested in a nitrogen atmosphere, to avoid degradation which occurs during the heating stage.

### *2.6. Tensile Test:*

Pebax dumbbell specimens were used to measure the tensile strength, Young's modulus and elongation at break. The experiment was carried out according to ASTM D638-03 (ASTM D638-03, 1994) with the exception of implementing a crosshead speed of 500mm/min. An Instron 3365 universal testing machine was employed to conduct each experiment where a 5kN load cell was applied during the experiments with a gripper distance of 40mm. Five tests were executed for each dose range and the mean was obtained from each of the five results(Murray *et al*., 2013b)

### *2.7.Scanning Electron Microscope (SEM):*

Surface morphologies of the non-irradiated and irradiated Pebax samples were investigated with the aid of a SEM. All test specimens were placed on special sample holders and then sputter coated with gold using a Beltec SCD 005 sputter coater prior to testing. A Mira FE SEM was used in high vacuum mode with an acceleration voltage of 10kV. A resolution of 10μm and a magnification of 3.57 and 3.60kx was used to scan the surface of the samples.

### *2.8. Atomic Force Microscopy (AFM):*

The non-irradiated and irradiated Pebax samples were analysed using a Veeco Explorer AFM, where the samples were mounted onto a metal stub using double-sided adhesive tape. The data acquired from the AFM was the forward and reverse lateral force in contact mode, using the cantilever SCM-PIC tip. Scans were acquired on the surface of the injection moulded test specimens. The PID settings were optimised for each scan in order to ensure accurate data acquisition. The scan range was set to 100 μmX 100 μm. Surface roughness calculations were recorded for each sample.

### *2.9. Goniometry:*

The contact angle for each of the Pebax samples was measured while operating an FTA (First Ten Angstroms) 1000 machine. Each sample was measured three times in the same order to obtain a consistent value while using the sessile drop method. For contact angle measurements, a 0.002ml droplet of distilled water was ejected out of the micrometer syringe (GS-1200) onto the sample 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 result.

## RESULTS AND DISCUSSION

### *3.1. Melt flow index (MFI):*

Melt flow index (MFI) was used to determine the flow behaviour of the non-irradiated and electron beam irradiated Pebax material. This technique was also used to give an indirect measure of the molecular weight before and after the irradiation process. Represented in Fig. 1 is the bar chart of the data collected, where the MFI was plotted as a function of irradiation dose. Initially, the MFI increased between 0 and 10kGy (from 9.4 – 10.6g/10mins), where it then reduced dramatically to 0.0g/10mins at 200kGy. This outcome suggests that the molecular weight of the material had a moderate decline at the low dose rate between 0 and 10kGy which can be attributed to the chain scissioning process. However, from 10 – 200kGy, the melt flow rate reduced significantly which suggests that the molecular weight increased and this resulted in a restriction in the flow properties of the material. Such alterations are perhaps related to the formation of networks between the polymeric chains such as branching/crosslinking, which preferentially materialise in the polyether segment of the Pebax.Based on the aforementioned results, it can be presumed that the dominant process has been crosslinking due to the noteworthy reductions in the MFI value, specifically irradiation doses above 10kGy.

### *3.2. Rheology – Temperature Ramp:*

Rheological analysis via temperature ramp tests were performed on the non-irradiated and irradiated Pebax samples ranging between 0 and 100kGy. In Fig. 2, the viscosity is plotted against temperature as a function of irradiation dose and here it can be observed that the viscosity of the control sample (0kGy) reduced accordingly from approximately 7500 Pa at 175ºC to approximately 1200 Pa at 250ºC. Between 0 and 10kGy the viscosity of the material reduced as the irradiation dose increased. From 10kGy upwards the viscosity of the Pebaxmaterial increased significantly where the 100kGy dose achieved a value of approximately14000 Pa at 175ºC and approximately 5000 Pa at 250ºC. These results are in agreement with the outcome of the MFI test where each of the samples followed the same trend. In the MFI experiment ranging between 10kGy and 200kGy, an increase was exhibited for the molecular weight. This suggests that the viscosity of the material increases correspondingly where Fig. 2 provides evidence for this occurrence.This increase in viscosity is perhaps attributed to radiation induced free radical reactions such as branching/crosslinking. Clayden and Pendlebury(2001), clarified by the use of nuclear magnetic resonance (NMR) spectroscopy that crosslinking

occurred between mobile polyester segments in Pebax 7033 after subjecting it to 46kGy of electron beam irradiation. Temperature ramp tests were also attempted on the 200kGy sample, however, this test was not feasible as the sample did not melt during the heating stage which corresponds to the MFI experiment.

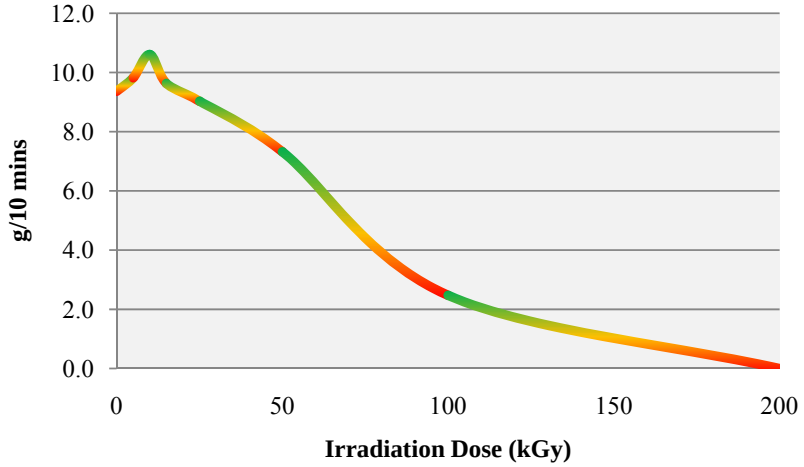



**Fig. 1:** Melt flow index of the non-irradiated and electron beam irradiated Pebax material

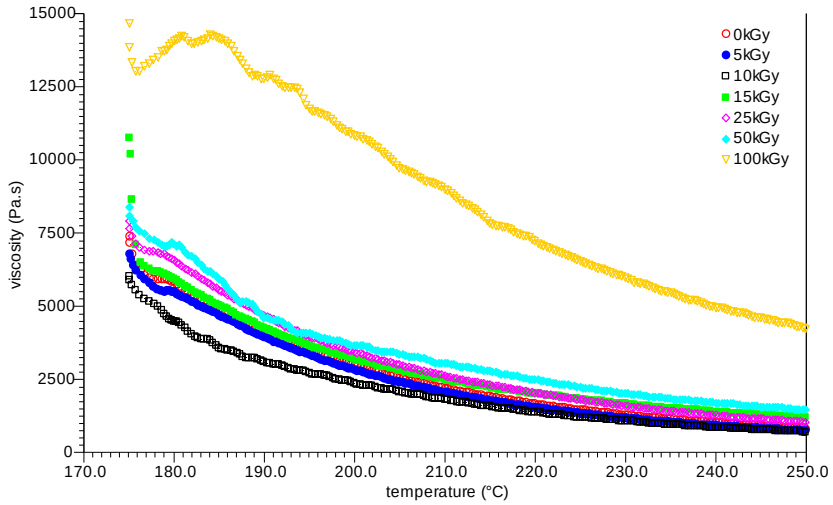



**Fig. 2:** Graphical representation of the viscosity versus temperature of the non-irradiated and electron beam irradiated Pebax material

### *3.3. Tensile Test:*

Fig. 3 represents the data recorded for the tensile strength as a function of irradiation dose. Slight alterations were noticeable between 0 and 25kGy, where the tensile strength increased in a non-linear fashion with irradiation dose. An increase in the tensile strength was perhaps related to the degradation affects caused by the irradiation process.This minor increase in tensile strength could be seen as a positive effect, in that it may have potential use in various applications that require a material with such properties. Above 25kGy, the tensile strength began to decrease according to an increase in irradiation dose. The tensile strength displayed a moderate decline from 53MPa at 25kGy to 47MPa at 200kGy. Similar results were reported for polyamide 610 material where the tensile strength decreased with an increase in irradiation dose (Feng *et al*., 2002). Such alterations could be due to branching and chain scissioning occurring simultaneously. Branching can limit the packing of polymer chains and lead to the formation of free volume in the material, hence causing a reduction in the tensile strength. Based on these results, it is evident that branching was the dominating factor above 25kGy.

Fig. 4 illustrates the influence of electron beam irradiation on the percentage elongation at break. An evaluation of the lower dose range between 0 and 25kGy for the electron beam irradiated samples have shown that the percentage elongation at break was enhanced slightly, which again was perhaps related to the radiation

induced degradation effects.At the higher dose rates between 25 and 200kGy, it was determined that the stretchability of the material reduced in a linear fashion with an increase in irradiation dose. Due to the reduction observed for the percentage elongation at break from 25kGy onwards, it could be assumed that crosslinking and or branching was the source of this imperfection. Crosslinking has possibly initiated stiffness to transpire within the material from the linkage of polymeric chains, which can be seen from the reduction of elongation in the graph (Fig. 4). Branching has perhaps created free volume in the material, therefore causing a decrease in the elongation. This correlates very well with the finding of the tensile strength, where the strength and elongation was greatly reduced.

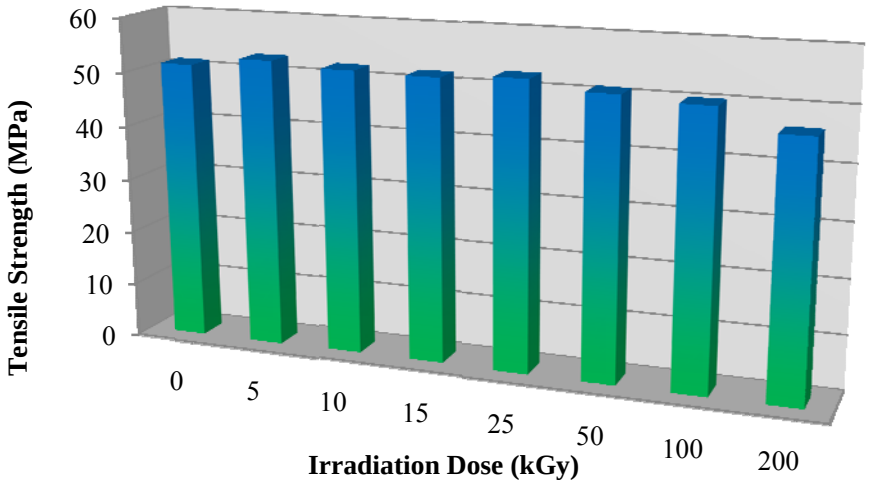



**Fig. 3:**Tensile strength of the non-irradiated and irradiated Pebax material

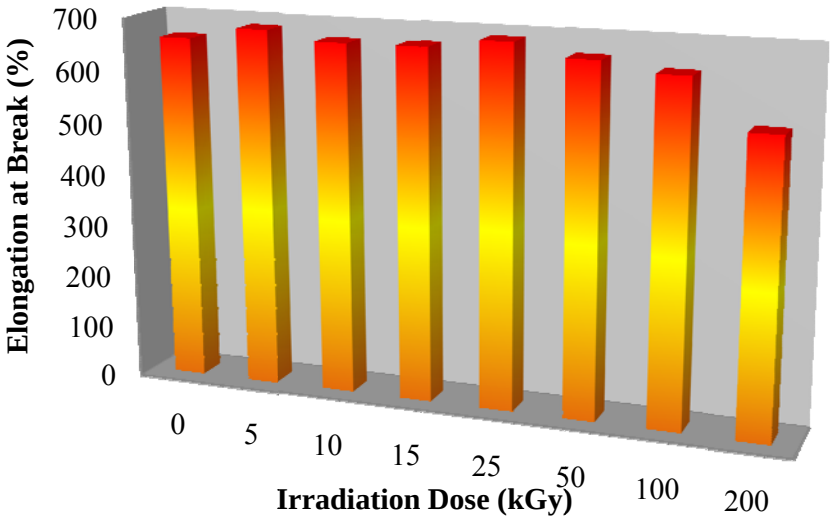



**Fig. 4:** Elongation at break of the non-irradiated and irradiated Pebax material

***3.4. Scanning Electron microscope (SEM):***

Illustrated in Fig. 5 is the images for the surface morphology of the non-irradiated and electron beam irradiated (200kGy) Pebax samples. Based on these results it can be seen that the non-irradiated sample (0kGy) provided an arranged linear pattern on the surface. On the other hand the irradiated sample exhibited a lattice pattern on the surface. These transformation are perhaps related to oxidation occurring on the surface of the material within the thickness of a few microns during the irradiation process. Further analysis was performed on the surface of the material by the use of AFM and goniometry. These methods were additional used to confirm such modifications and are focused on in the next two sections of this study

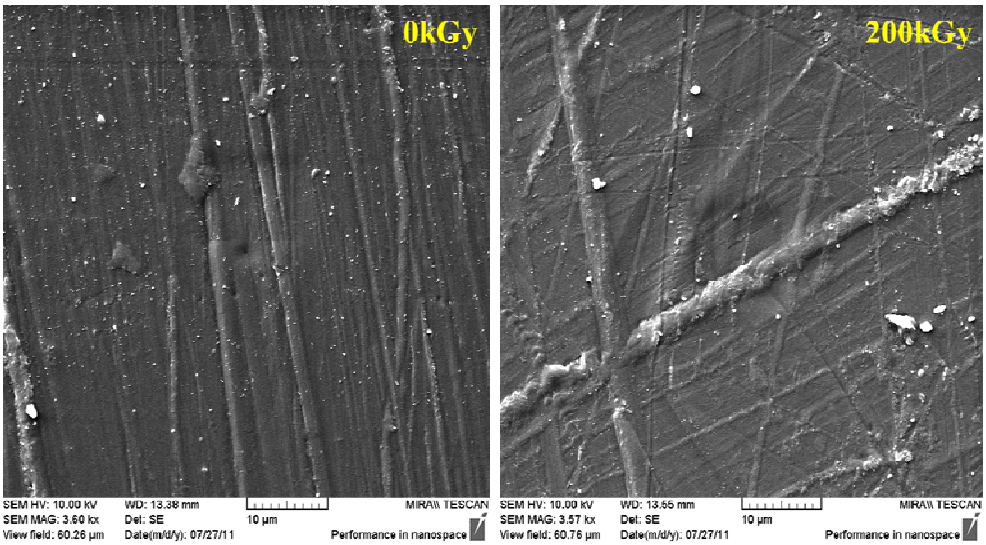



**Fig. 5:** SEM imagery of the non-irradiated and electron beam irradiated (200kGy)Pebax samples

### *3.5. Atomic force microscopy (AFM):*

Illustrated in Fig. 6 is the non-irradiated and the 200kGy electron beam irradiated sample. On investigating the topographies of the two images obtained, it can be observed that the irradiated sample had a smoother surface in contrast to the non-irradiated sample. An average value of 54.8nm was achieved for the height of the non-irradiated sample, however subsequent to irradiation the value declined to 26.6 nm. This indicates that irradiation promoted the transformation of the sample surface which is perhaps due to radiation induced free radical reactions such as chain scission.

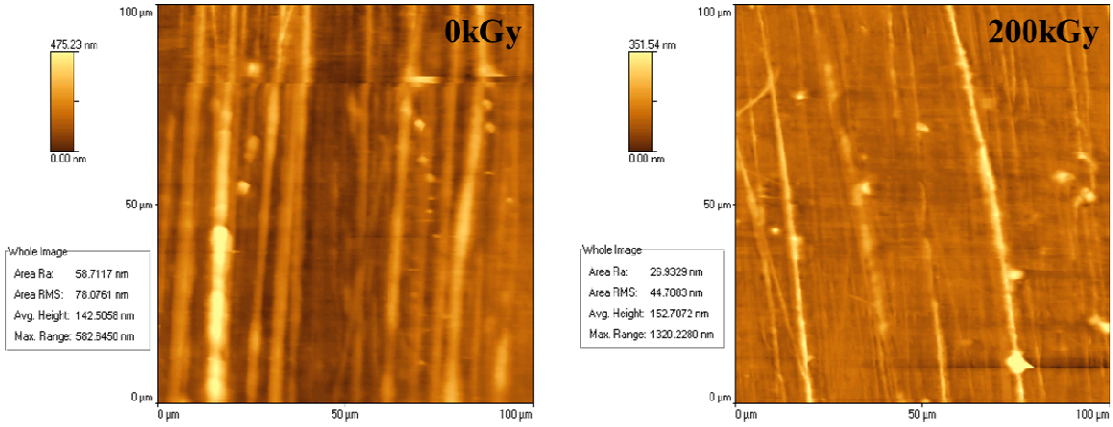



**Fig. 6:** Atomic force microscopy illustrating the surface roughness of the non-irradiated and electron beam irradiated (200kGy) Pebax samples

### *3.6. Goniometry:*

In this experiment the contact angle was determined using the sessile drop method with a goniometer machine. Three tests were carried out on the ASTM tensile specimens for each of the different irradiation dose rates. From this, the average was calculated and the results were plotted on a graph which is displayed in Fig. 7. Fig. 8 demonstrates the contact angle images obtained for each of the irradiation doses. A reduction in the contact angle was observed between 0 and 5kGy, where it then increased from 76.5˚ up to 84.4˚ between 5 and 50kGy. From 50kGy onwards, the contact angle decreased gradually to a minimum of 76.8˚ at 200kGy. Alterations to the contact angle could be attributed to surface degradation and/or oxidation which can result from the process being carried out in an air atmosphere. These alterations can lead to the formation of low molecular weight surfactant like species on the surface (Gorna and Gogolewski, 2003), which is perhaps due to an increase of the C=N and N functionalities onto the surface (Mrad *et al*., 2010). Changes to the wettability of the material could perhaps be a valuablecharacteristic for end use applications such as medical devices.

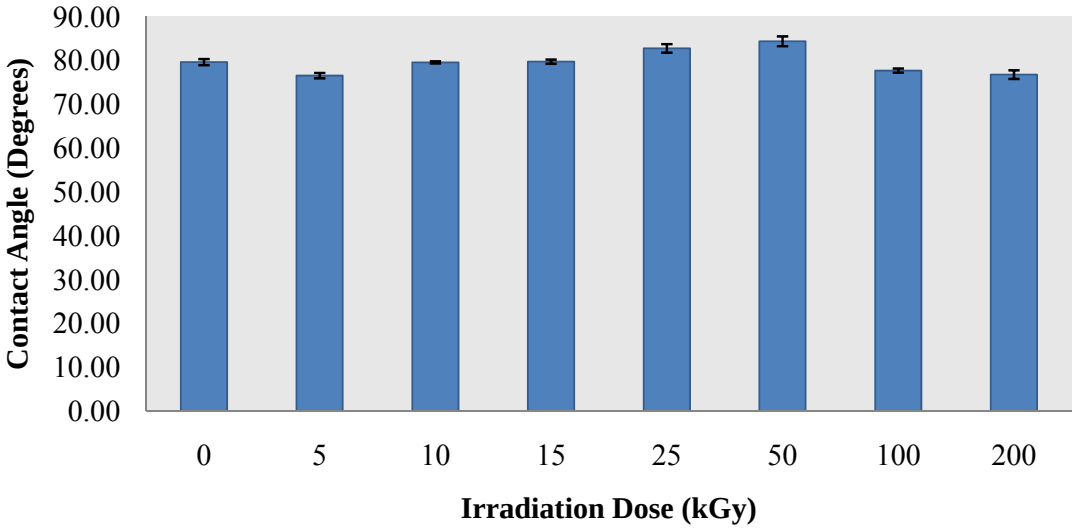



**Fig. 7:** Graphical representation of the contact angle as a function of irradiation dose for the Pebax material


**Fig. 8:** Images of the droplet on the surface of the non-irradiated and irradiated Pebax tensile specimens

***Conclusion:***

An investigation was conducted on the effects of electron beam on Pebax material by implementing a range of analytical techniques. From this study it was determined that the irradiation process strongly affected the properties of the Pebax material.The MFI experiment illustrated a dramatic increase in the melting strength and molecular weight of the material as a result of radiation induced free radical reactions. Temperature ramp tests performed by the rheology machine emphasised the changes to polymer structure which arose after irradiation exposure. It was apparent that the viscosity of the material had a steady increase according to an increase in irradiation dose from 10 to 200kGy. Such modifications observed in the MFI and rheological experiments were

perhaps attributable to branching/crosslinking initiated by the free radicals generated during the radiation process. SEM showed that electron beam irradiation produced a smoother surface morphology on the surface of the Pebax samples. Additional surface characterisation techniques were performed by AFM and goniometry where both techniques exhibited changes in terms of surface roughness and wettability. Evidently, these results prove that simultaneous reactions of chain scission and branching/crosslinking were present during the irradiation process, however, branching/crosslinking was the predominant phenomena.

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## REFERENCES

ASTM D638-03, 1994. Standard test method for tensile properties of plastics. ASTM International, West Conshohocken, PA.

Cholli, A.L., F.C. Schilling, A.E. Tonelli, 1988. Solid state NMR of polymers. Plenum Press, New York.

Clayden, N.J., R. Pendlebury, 2001. NMR study of the effect of electron beam processing on a poly(ether-block-amide). Polymer., 42: 8373-8377.

Feng, W., F.M. Hu, L.H. Yuan, Y. Zhou, Y.Y. Zhou, 2002. Radiation crosslinking of polyamide 610. Radiation Physics and Chemistry, 63: 493-496.

Goldman, M., L. Pruitt, 1998. Comparison of the effects of gamma radiation and low temperature hydrogen peroxide gas plasma sterilization on the molecular structure, fatigue resistance, and wear behavior of UHMWPE. Journal of Biomedical Materials Research, 40: 378-384.

Gorna, K., S. Gogolewski, 2003. Molecular stability, mechanical properties, surface characteristics and sterility of biodegradable polyurethanes treated with low-temperature plasma. Polymer Degradation and Stability, 79: 475-485.

Joseph, R., J.R. Flesher, 1986. PEBA polyether block amide - a new family of engineering thermoplastic elastomers. Elsevier, New York.

Liu, L., 2008. Gas Separation by Poly(Ether Block Amide) Membranes, Engineering. Waterloo, Waterloo, Ontario, Canada, pp: 196.

Mrad, O., J. Saunier, C. Aymes Chodur, V. Rosilio, F. Agnely, P. Aubert, J. Vigneron, A. Etcheberry, N. Yagoubi, 2010. A comparison of plasma and electron beam-sterilization of PU catheters. Radiation Physics and Chemistry, 79: 93-103.

Murray, K.A., J.E. Kennedy, B. McEvoy, O. Vrain, D. Ryan, R. Cowman, C.L. Higginbotham, 2013a. Effects of gamma ray and electron beam irradiation on the mechanical, thermal, structural and physicochemical properties of poly (ether-block-amide) thermoplastic elastomers. Journal of the Mechanical Behavior of Biomedical Materials, 17: 252-268.

Murray, K.A., J.E. Kennedy, B. McEvoy, O. Vrain, D. Ryan, R. Cowman, C.L. Higginbotham, 2013b. The effects of high energy electron beam irradiation in air on accelerated aging and on the structure property relationships of low density polyethylene. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms., 297: 64-74.

Murray, K.A., J.E. Kennedy, B. McEvoy, O. Vrain, D. Ryan, C.L. Higginbotham, 2012. The effects of high energy electron beam irradiation on the thermal, mechanical, structural and physicochemical properties of polypropylene. Journal of Engineering Research and Education., 6: 1-23.