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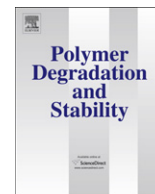
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Electron-beam treatment of poly(lactic acid) to control degradation profiles

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ABSTRACT

Bioresorbable polymers such as polylactide (PLA) and polylactide-co-glycolide (PLGA) have been used successfully as biomaterials in a wide range of medical applications. However, their slow degradation rates and propensity to lose strength before mass have caused problems. A central challenge for the development of these materials is the assurance of consistent and predictable in vivo degradation. Previous work has illustrated the potential to influence polymer degradation using electron beam (e-beam) radiation. The work addressed in this paper investigates further the utilisation of e-beam radiation in order to achieve a more surface specific effect. Variation of e-beam energy was studied as a means to control the effective penetrative depth in poly-L-lactide (PLLA). PLLA samples were exposed to e-beam radiation at individual energies of 0.5 MeV, 0.75 MeV and 1.5 MeV. The near-surface region of the PLLA samples was shown to be affected by e-beam irradiation with induced changes in molecular weight, morphology, flexural strength and degradation profile. Moreover, the depth to which the physical properties of the polymer were affected is dependent on the beam energy used. Computer modelling of the transmission of each e-beam energy level used corresponded well with these findings.

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1. Introduction

Bioresorbable polymers have been used in medicine for decades due to their biodegradable nature and excellent biocompatibility [1–3]. To date, medical implants fabricated from bioresorbable polymers have been applied in a wide range of applications including dissolvable sutures, orthopaedic fixation devices, and replacement tendons, ligaments and cartilage [4]. The key attributes of bioresorbable polymers that have lead to their success include the ability to tailor both their mechanical properties and degradation kinetics. Recent investigations into the control of polymer degradation have lead to the realisation that they also have the potential to have a significant impact in the fields of drug delivery, tissue engineering and regenerative medicine [5–7].

Poly(lactic acid) (PLA), L-lactide/DL-lactide co-polymer (PLDL), poly(glycolic acid) (PGA) and poly(lactic-co-glycolic acid) (PLGA) have generated significant expectation as materials for achieving improved osteosynthesis with regard to bone fixation devices [7,8]. Their potential in this application relies on the ability to engineer

a progressive transfer of mechanical load from device to newly forming bone whilst simultaneously encouraging bone growth. However, there are a number of issues to be addressed in order to achieve this successfully including the precise matching of polymer degradation to the rate of neo-bone formation, assurance of mechanical integrity, and the negation of premature mass loss, all of which are problems currently associated with bioresorbable implant devices. Moreover, control of the degradation rate is also critical to the avoidance of the "acid burst" phenomenon that can occur upon device implantation [9].

A key factor in achieving improved implant performance is the manipulation and control of the polymer degradation profile in a surface-to-core manner. There are two accepted mechanisms of polymer degradation, namely surface erosion or bulk erosion [10]. In many cases "bulk erosion" is observed, whereby water diffuses into the material at a faster rate than the bonds degrade, causing hydrolysis of polymer bonds throughout the entire matrix. The inner core degrades at a faster rate than the surface which not only leads to an early loss of mechanical integrity before any significant mass loss but also the build up of acidic degradation products within the core, that can lead to the 'acid burst' effect causing the inflammation of surrounding tissues. Surface erosion would be the more desirable mode of degradation whereby the rate of

degradation of polymer bonds is faster than the rate at which water can diffuse into the matrix. Thus the device will degrade from surface to core.

A means by which to achieve a level of control over polymer degradation and obtain a preferential modification of the surface in the first instance, i.e. to initiate pseudo-surface erosion, is the utilisation of e-beam radiation. The effects of radiation on polymers are well established and have been exploited in order to manipulate key material properties for specific applications [11,12]. The most common use of radiation treatment for polymers is employed to induce crosslinking of polymer chains (to improve mechanical properties) and for the sterilization of medical devices. Radiation can also cause chain scission to occur within polymers, reducing molecular weight and consequently the mechanical properties of the material. In general, e-beam irradiation of bioresorbable polymers has been primarily used for sterilization purposes, however, due to the high degree of process control and ability to influence the physical properties of polymers, e-beam irradiation may be used as a tool to achieve desired degradation behaviours and rates. E-beam irradiation has therefore the potential to be a major underpinning technology in achieving predictable and controlled degradation of bioresorbable polymers.

Reports in the literature have demonstrated that controlled exposure to e-beam radiation is able to modify polymer degradation predictably by altering the physical properties of polymers through chain scission and crosslinking [13,14]. More specifically, e-beam irradiation can cause a decrease in average molecular weight (through chain scission) advancing the process of hydrolytic degradation [15]. Previous work by the authors has illustrated the potential to influence polymer (PLLA/PLGA) properties, such as molecular weight, strength and corresponding degradation, in a depth dependent manner [16]. This can then allow degradation to proceed in a manner occurring from the outside of the device towards the centre engendering early stage mass loss, maintenance of internal mechanical strength and ultimately the provision of optimum conditions for tissue healing.

The following work investigates further the utilisation of e-beam radiation in order to achieve a more surface specific effect. In this way the effect of varying the e-beam energy was studied as a means to control the effective penetrative depth in polylactide (PLA).

2. Materials and methods

2.1. Materials

The PLLA used in this study was Resomer® L 210S, supplied in pellet form by Boehringer Ingelheim (Ingelheim, Germany). It was manufactured to entirely consist of the poly L-lactide (PLLA) isomer. The material was supplied in a sealed moisture proof container and was stored in a freezer at −20 °C until use.

2.2. Sample preparation

A Collin P200 P computer controlled platen press was used to manufacture polymer sheets. A mould with a thickness of 1.0 mm was used to shape the samples. In practice, this was found to produce sheets with a thickness of 1.1 ± 0.04 mm. A moulding temperature of 200 °C at a pressure of 10 MPa was used. ISO6602 flexural bar samples (80×10 mm) were then cut from the resultant compression moulded sheets. To equilibrate crystallinity and reduce any stressing in the material, all samples were then annealed in a pre-heated air-circulating oven at 120 °C for 2 h.

Acrylic frames were manufactured to support the samples during e-beam irradiation. A set of six samples constituted an energy stack which was placed in an acrylic frame as illustrated in Fig. 1.

2.3. E-Beam irradiation

A Dynamatron Continuous DC e-beam unit (Isotron, UK), with beam energies of 0.5, 0.75 and 1.5 MeV, was used for the irradiation of PLLA samples. Irradiation was performed in the presence of air and samples were treated with delivered surface doses of either 150 kGy or 500 kGy at each energy level. To verify the accuracy of the delivered irradiation dose, thin-film dosimeters (Far West Technology) were used for calculations of dose rates. The discolouration of the dosimeters by the radiation was then quantified using a Thermo Unicam UV2 Spectrophotometer.

2.4. Gel Permeation Chromatography (GPC)

Molecular weight and polydispersity of irradiated samples were determined by GPC. Samples were prepared in chloroform (Sigma lot 7353M) at concentrations of approximately 1 mg/mL and the resultant solutions were filtered through 0.45 µm PTFE syringe filters before analysis. GPC was performed at 30 °C using RID (Reflective Index Detector) as the detector. Column calibration was achieved using narrowly disperse polystyrene standards (Polymer Labs EasiCal PS (1 lot 41) in the range 580 to 750,000 g/mol. All molecular weights quoted are the styrene equivalents.

2.5. Differential Scanning Calorimetry (DSC)

Thermal properties of irradiated samples were evaluated using a Perkin Elmer Diamond DSC. Approximately 0.7 mg of material was removed from the irradiated sample. The samples were heated from room temperature to 200 °C at a rate of 50 °C/min. After a dwell time of 1 min the sample was returned to room temperature at a rate of 100 °C/min. Following a second dwell time of 1 min the sample was re-heated to 200 °C at the same rate. ΔH_{melt} was used to calculate polymer percentage crystallinity relative to the enthalpy of fusion of 100% crystalline PLLA, reported to be 93 J/g.

2.6. Four-point bend analysis

Four-point bend analysis was carried out on samples cut to 26.6 mm × 10 mm using a Lloyds EZL6000R Universal Testing Machine. A specifically designed small scale test rig was used with lower and upper support spans of 20 mm and 10 mm, respectively. Tests were performed at a controlled rate of 5 mm/min and bending strength was calculated in accordance with ISO5833 [17]. The test was stopped at sample failure.

2.7. Accelerated degradation

Prior to hydrolytic degradation, samples were dried under vacuum at room temperature in order to achieve a stable mass. The initial dry mass of each sample was recorded. In accordance with
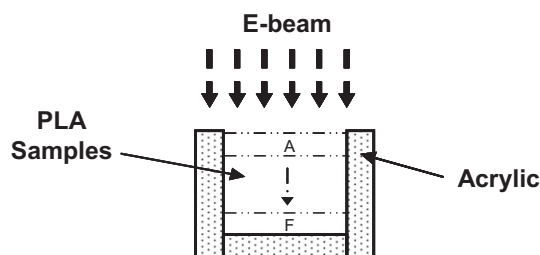

Fig. 1. Schematic representation illustrating sample arrangement during irradiation with Layer A as the most superficial sample through to Layer F at the base of the stack.

ISO15814, samples were placed in glass vials containing 15 ml of phosphate buffered saline (PBS, pH 7.4). For accelerated degradation, a higher temperature of 70 °C was used [18,19]. At defined time points, samples were removed from the PBS, filtered through Grade 1 filter paper and rinsed with distilled water. Samples, including filter paper, were dried in a vacuum oven at 37 °C for 24 h after which final mass was then recorded. The parameters were normalized as percentages of their initial masses.

2.8. Computer modelling

Central to this work is the utilisation of e-beam technology. The ultimate aim is to achieve a high degree of process control to allow a precise prediction of the effects of e-beam radiation on polymeric materials and ultimately their degradation *in vivo*. To validate any possible predications of e-beam irradiation on PLLA, the software program CASINO (Version 2.42), developed and tested by Drouin et al at the University of Sherbrooke (QUEBEC) was used for comparison of active penetration depth of the e-beam [20–22]. CASINO utilizes Monte Carlo simulation to predict electron distribution in materials. For each simulation a PLLA density of 1.25 g/cm^3 was used.

2.9. Statistical analysis

All samples were prepared in triplicate and where statistical analysis of results was required, one-way analysis of variance (ANOVA) using GraphPad Prism version 3.00, (GraphPad Software, San Diego, California, USA) was performed. The Bonferroni *post hoc* test was also performed and a 95% confidence level was considered to be significant.

3. Results

3.1. Gel Permeation Chromatography (GPC)

Fig. 2a and b illustrates the number average molecular weight (Mn) for e-beam irradiated PLLA with delivered surface doses of 150 kGy and 500 kGy, respectively. The molecular weight of the non-irradiated PLLA control sample is highlighted on each graph. A clear variation in Mn through irradiated PLLA sample Layers A–F, i.e. to a surface depth of 6 mm, was observed for all energies studied. As expected all irradiated sample types show a dramatic decrease in Mn within the most superficial layer, i.e. at a surface depth of 1 mm. The reduction in Mn through the PLLA energy stacks beyond the first 1 mm is shown to be different for each energy level. For samples irradiated at 0.5 MeV and 0.75 MeV with a 150 kGy dose (Fig. 2a) the reduction in Mn is only shown to occur at depths of 1 mm and 2 mm, respectively. Samples beyond these depths show a consistent molecular weight similar to that of the non-irradiated control indicating that these deeper samples are unaffected by the e-beam. However, samples irradiated at the higher energy of 1.5 MeV (150 kGy), show a consistent reduction in Mn through to a depth of 6 mm (Fig. 2a). Samples treated with a 500 kGy dose show similar Mn depth profiles for each energy level as illustrated in Fig. 2b. However the higher dose appears to produce a further reduction in Mn. Moreover, the data indicate a gradual increase in molecular weight from the induced lower Mn value (within the uppermost surface layer) to a level similar to the non-irradiated control. In general, all depth profiles for comparative e-beam energies with delivered doses of either 150 kGy or 500 kGy remain similar.

Fig. 3a and b plots the polydispersity indices for e-beam irradiated PLLA with delivered surface doses of 150 kGy and 500 kGy, respectively. The results show a general increase in polydispersity for superficial PLLA sample layers upon e-beam irradiation.
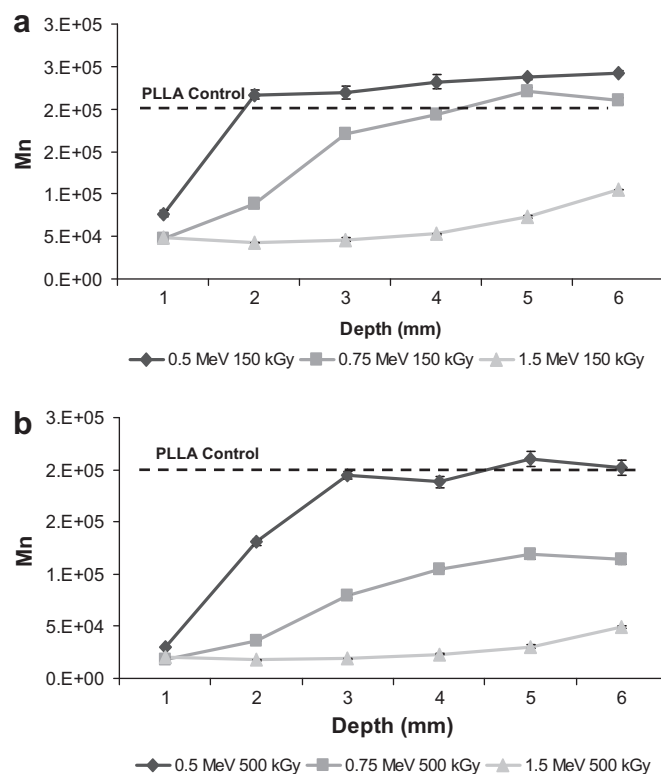
Fig. 2. Number average molecular weight (Mn) for irradiated PLLA at all energy levels with a delivered dose of (a) 150 kGy and (b) 500 kGy.

3.2. Differential Scanning Calorimetry (DSC)

Fig. 4a and b shows melting temperature (Tm) values for the PLLA samples exposed to 150 kGy and 500 kGy surface doses, respectively, at all e-beam energy levels. The value for the non-irradiated control sample (178.8 °C) is indicated on each graph. In general, all irradiated sample types (except 0.5 MeV/150 kGy) show a decrease in Tm within the 1 mm of the sample surface. The depth to which the Tm is further affected beyond this point is again dependent upon the beam energy. For the 0.5 MeV (500 kGy) and 0.75 MeV (150/500 kGy) irradiated samples, Tm values were only decreased within a 1 mm surface depth. At 2 mm or greater, Tm values then increased to a level similar to that of the non-irradiated control. PLLA samples irradiated at 1.5 MeV with 150 and 500 kGy delivered doses showed decreased Tm values to surface depths of 5 mm and 6 mm, respectively. Comparison of Fig. 4a and b demonstrates that the Tm depth profiles for each energy level are similar for both 150 kGy and 500 kGy irradiated samples. However, it should be noted that although the depth profiles at each energy level are similar, Tm values for samples irradiated with a 500 kGy surface dose are significantly lower than those of the corresponding 150 kGy samples ($p < 0.01$).

The calculated percentages of crystallinity for all irradiated samples are shown in Fig. 5a and b for doses of 150 kGy and 500 kGy, respectively. The percentage crystallinity of the non-irradiated PLLA control sample is represented in each graph as a dashed line (33%). For both surface doses there appears to be a relationship between crystallinity and sample depth. The depth to which the irradiation has produced changes in the percentage crystallinity of the samples is dependent upon the e-beam energy. For 0.5 MeV samples treated with doses of 150 kGy and 500 kGy, the percentage crystallinity of PLLA is increased within the first
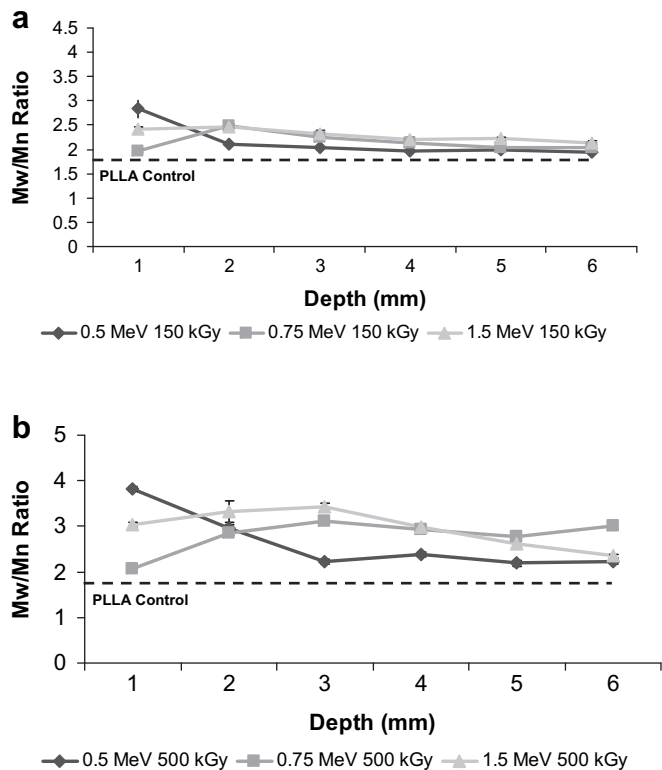
Fig. 3. Polydispersity Index for irradiated PLLA at all energy levels with a delivered dose of (a) 150 kGy and (b) 500 kGy.

Fig. 5. Degree of crystallinity for irradiated PLLA at all energy levels with a delivered dose of (a) 150 kGy and (b) 500 kGy.

1 mm of the surface with obtained values of 55 ± 1.4% and 80 ± 3.2%, respectively. Beyond this depth the percentage crystallinity returns to a consistent value similar to that of the non-irradiated control. 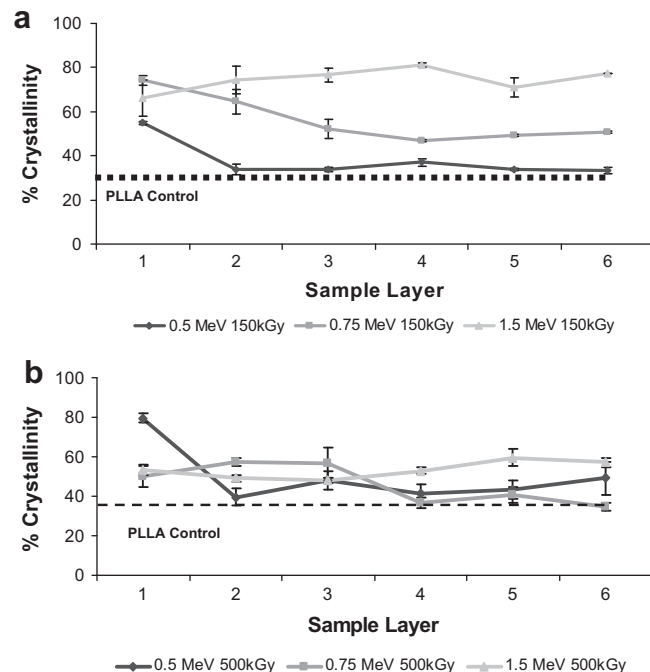Similar induced increases in the percentage crystallinity are observed for samples irradiated at 0.75 MeV with 150 kGy and 500 kGy doses whereas the percentage crystallinity is increased up to sample depths of 3 mm and 4 mm, respectively. At greater depths the crystallinity then returns to a lower consistent level closer to the value associated with the non-irradiated control. For PLLA samples irradiated at 1.5 MeV (150/500 kGy) the percentage crystallinity remains at an increased value through the 6 mm depth studied (74 ± 4.8% and 53 ± 4%, respectively).

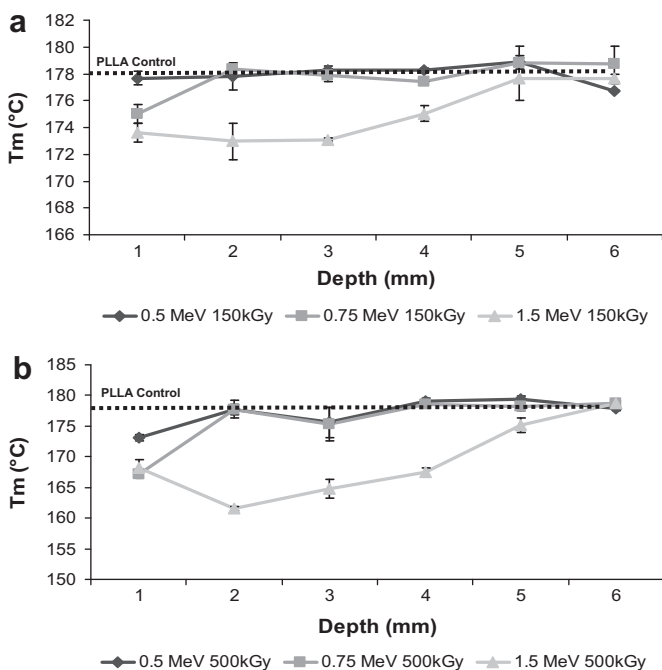### 3.3. Four-point bend analysis

Fig. 6a and b illustrates the maximum bending strengths of irradiated PLLA samples at all energy levels for delivered doses of 150 kGy and 500 kGy, respectively. The non-irradiated PLLA control sample value is represented on the graph as a dashed line. A clear depth-dependent trend in bending strength is observed for each energy level. Again, the depth to which the samples are affected by the e-beam irradiation is dependent on the energy of the beam. For samples irradiated at 0.5 MeV and 0.75 MeV energy levels (150/ 500 kGy), a large change in maximum bending strength can be seen to occur between depths of 1–2 mm and 2–3 mm, respectively. For both surface doses, the irradiation has produced a dramatic decrease in bending strength within these superficial surface regions. Beyond depths of 2 mm and 3 mm there are little differences between the maximum bending stress of the non-irradiated control samples and those of the irradiated samples. Irradiation treatments using 1.5 MeV (150/500 kGy) samples at depths up to 5 mm showed significantly lower bending strength values compared to the non-irradiated control. At a depth of 6 mm, the samples showed an increase in bending strength approaching that of the non-irradiated control. Although beam energy produces similar trends in the depth profiles of bending strength for each dose studied, the higher surface dose of 500 kGy produced a more pronounced effect on bending strength showing significantly lower values than those of 150 kGy sample types ($p < 0.01$).
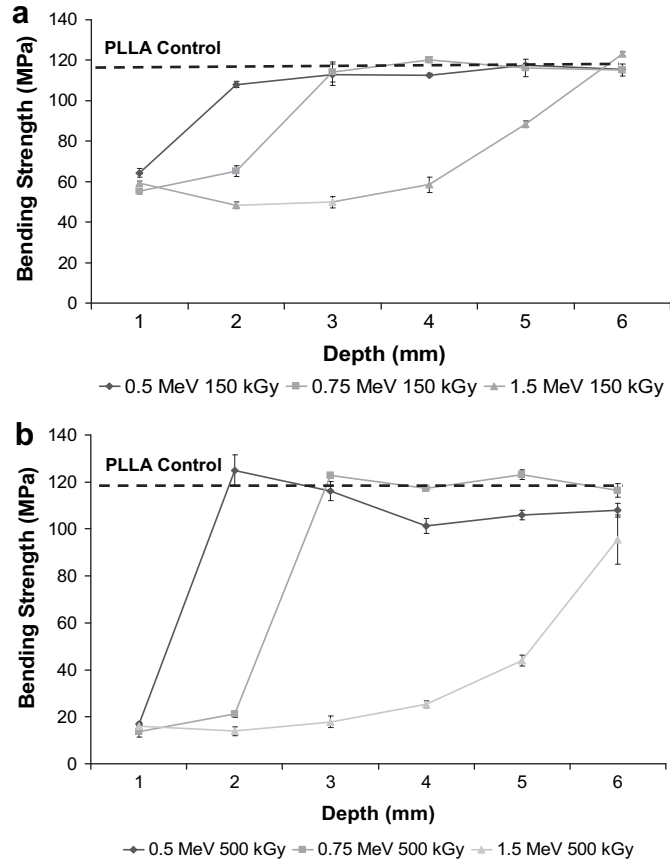

Fig. 4. Tm values for irradiated PLLA at all energy levels with a delivered dose of (a) 150 kGy and (b) 500 kGy.

Fig. 6. Bending Strength of irradiated PLLA at all energy levels with a delivered dose of (a) 150 kGy and (b) 500 kGy.

3.4. Mass loss

The results of the accelerated mass loss studies are shown in Figs. 7 and 8 for all e-beam energies with delivered surface doses of 150 kGy and 500 kGy, respectively. For each individual energy and dose (Figs. 7a–c and 8a–c) the different time points are plotted separately against sample layer depth. In general, the results of the mass-loss study show that, at a given time point, greater mass loss has occurred in the samples nearest the irradiated surface than in the deeper samples. Again, the depth over which the enhanced mass loss occurred was in accordance with the estimated penetration depth of the e-beam, i.e. the affected surface region. Fig. 7a–c illustrates mass loss for all e-beam energies with a delivered surface dose of 150 kGy. At the earliest time point (Day 7) statistical analysis shows that in comparison to the non-irradiated control samples significant increased mass loss occurred in the samples at irradiated of depths of 1, 2 and 4 mm for e-beam energies of 0.5 MeV, 0.75 MeV and 1.5 MeV, respectively. PLLA samples beyond these depths showed little or no mass loss as similar to that of the non-irradiated control samples. This is clear evidence that the samples nearest the treated surface during irradiation are losing mass at an earlier time than the deeper samples. In addition, enhanced mass loss of superficial layers is maintained over all time points studied. Thus the increased mass loss caused by the earlier onset of the process in near-surface samples is maintained well into the degradation process. This pattern in enhanced mass loss of surface layers is also demonstrated for the corresponding energies with a delivered surface dose of 500 kGy as illustrated in Fig. 8.

3.5. Computer modelling-comparison

The CASINO software was successfully run to model the penetration depth of the e-beam in PLLA for beam energies of 0.5, 0.75 and 1.5 MeV. Fig. 9a illustrates the penetration profiles obtained
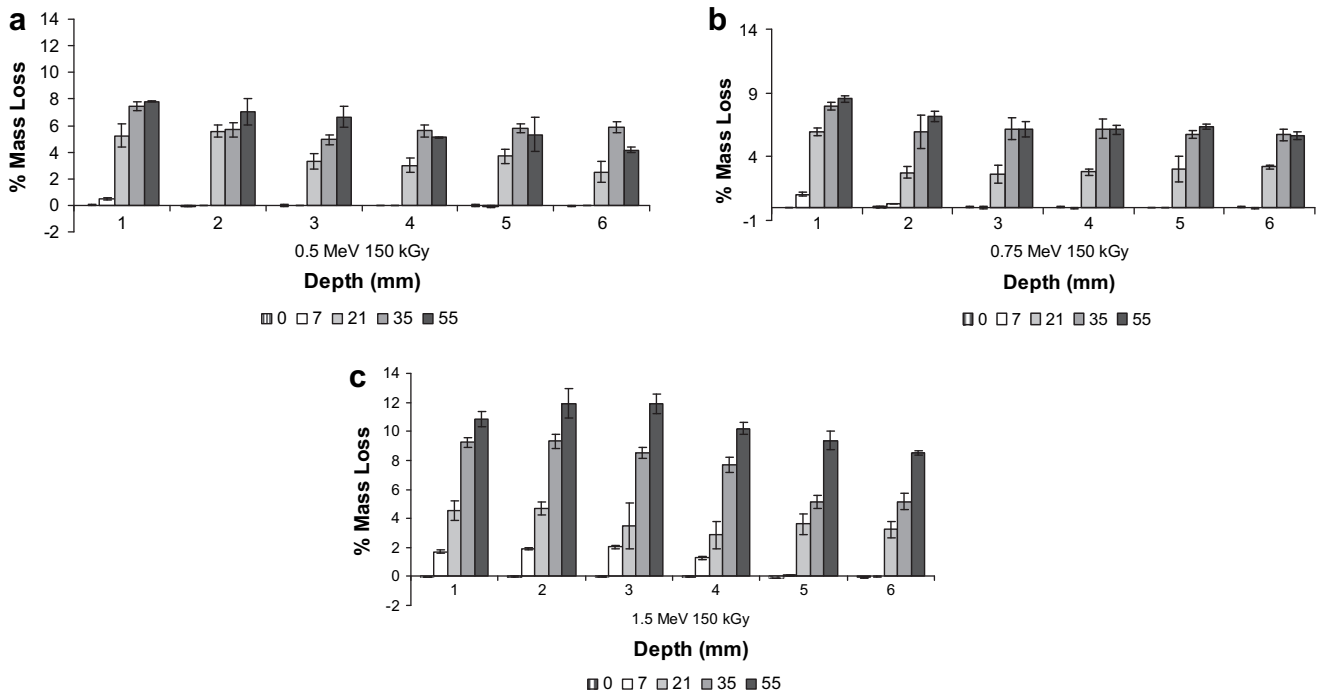

Fig. 7. % Mass Loss for irradiated PLLA with a surface delivered dose of 150 kGy for (a) 0.5 MeV (b) 0.75 MeV and (c) 1.5 MeV.
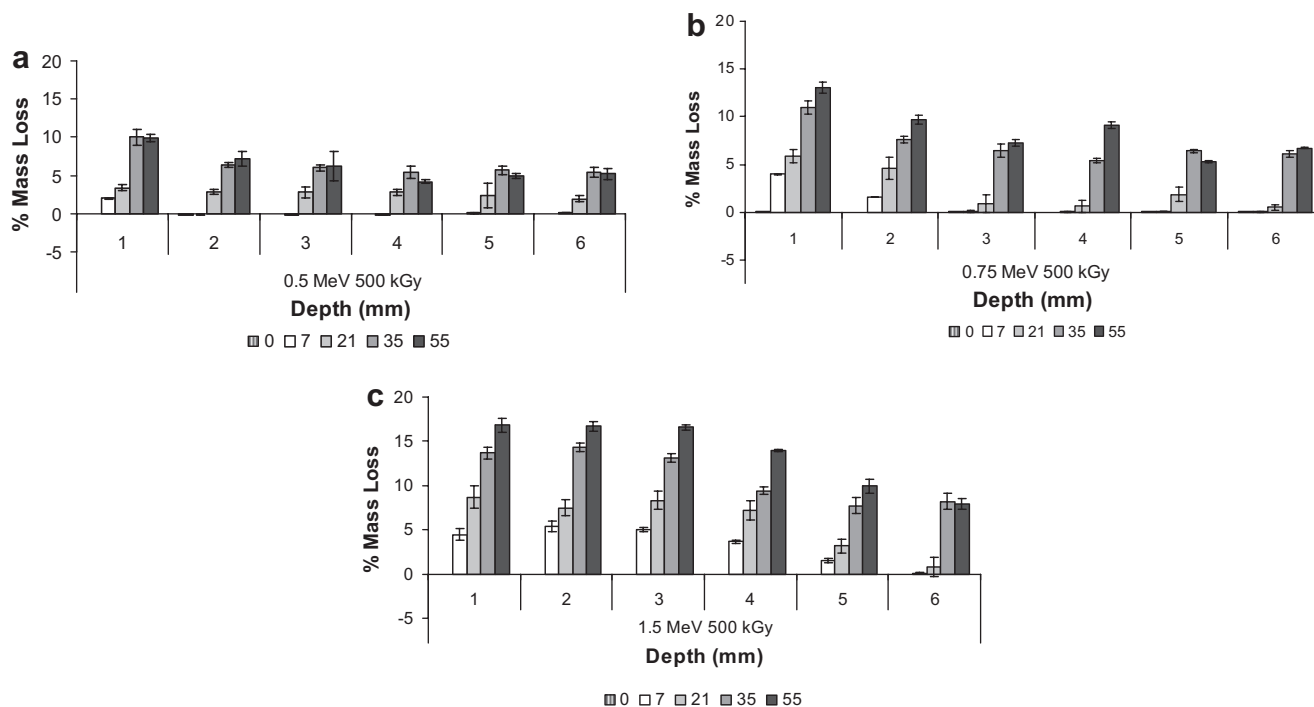
Fig. 8. % Mass Loss for irradiated PLLA with a surface delivered dose of 500 kGy for (a) 0.5 MeV (b) 0.75 MeV and (c) 1.5 MeV.

from the modelling software for the three different energies. The modelling predicts that a 0.5 MeV beam will obtain a maximum penetration depth of 1.5 mm in PLLA. It is also predicted that the 0.75 MeV and 1.5 MeV beams will obtain maximum penetration depths of 2.4 mm and 6.1 mm in PLLA, respectively. To compare the results of the CASINO simulations with empirical evidence of e-beam penetration in PLLA, each predicted penetration profile is overlaid onto the corresponding Mn molecular weight data previously presented. Comparisons are illustrated in Fig. 9b, c and d for e-beam energies of 0.5 MeV, 0.75 MeV and 1.5 MeV, respectively. For all energies there appears to be good correlation between the predicted e-beam penetration profiles and the observed depth dependent reduction in molecular weight. Mn results for the PLLA revealed that samples irradiated at 0.5 MeV, 0.75 MeV and 1.5 MeV showed significantly lower molecular weight than a non-irradiated control within approximate surface depths of 1 mm, 2 mm and 5 mm, respectively. These surface depths are coincident with the predicted penetration depths of the e-beam in the CASINO simulations. Moreover, beyond these depths, where it is predicted that emitted electrons do not reach, the Mn is then similar to the non-irradiated control.

Fig. 9 also illustrates the gradual change in Mn through the most superficial layers as related to the predicted percentage of electrons reaching those depths.

4. Discussion

To further exploit e-beam technology it has been proposed that e-beam irradiation can be used to influence the degradation behaviour and rate of polymers through alterations in their physical properties. Previous work has demonstrated the ability to produce a depth-dependent reduction in the molecular weight and associated effects on the degradation of PLA and PLGA [16,23]. This paper investigates further the ability to provide a degree of control over the depth-dependent radiolytic degradation of PLLA through manipulation of process parameters.

The e-beam irradiation of PLLA sample layers (energy stacks) allowed the investigation of the effect of e-beam energy on the 'active' penetration depth of the beam. Characterisation of polymer molecular weight, morphology and mechanical properties was carried out in order to examine the depth dependent nature of the effects of e-beam radiation on PLLA. GPC analysis demonstrated that e-beam irradiation was found to reduce the number average molecular weight significantly within a near-surface region of the samples. The effective depth within which Mn is reduced by e-beam treatment is influenced by the beam energy, with the lower beam energy producing the most superficial effect on molecular weight. In addition, results demonstrated a molecular weight variation with depth with a particularly marked decrease in Mn in the uppermost layer(s) of all irradiated sample types which then began to increase with depth to an eventual level similar to that of the non-irradiated control. The observed decrease in the Mn weight of irradiated PLLA layers can be attributed to chain scission and is expected as the susceptibility of polymers with ester linkages towards chain scission has been reported [24,25]. E-beam irradiation causes backbone main chain scission due to the high energy of the radiation breaking the attractive forces between the atoms. Active species such as alkyl free radicals and peroxyl free radicals are formed during irradiation as a result of hydrogen abstraction or chain scission at the ester groups of the polymer macromolecule [26]. The propagation of these radicals, in particular the peroxyl free radicals, greatly enhances chain scission whereas their recombination can lead to chain branching [27,28]. Previous work has confirmed that e-beam induced chain scission leads to a decrease in molecular weight of PLLA [16,23]. Moreover, Leonard et al. [16] also illustrated a depth dependent reduction in PLA molecular weight upon e-beam irradiation which was both predictable and repeatable. The variation in Mn from the sample surface towards the bulk was attributed to differences in the received dose as proportional to sample depth. The relationship between molecular weight and received dose has been reported by Loo et al who concluded that at e-beam doses of ≤500 kGy chain
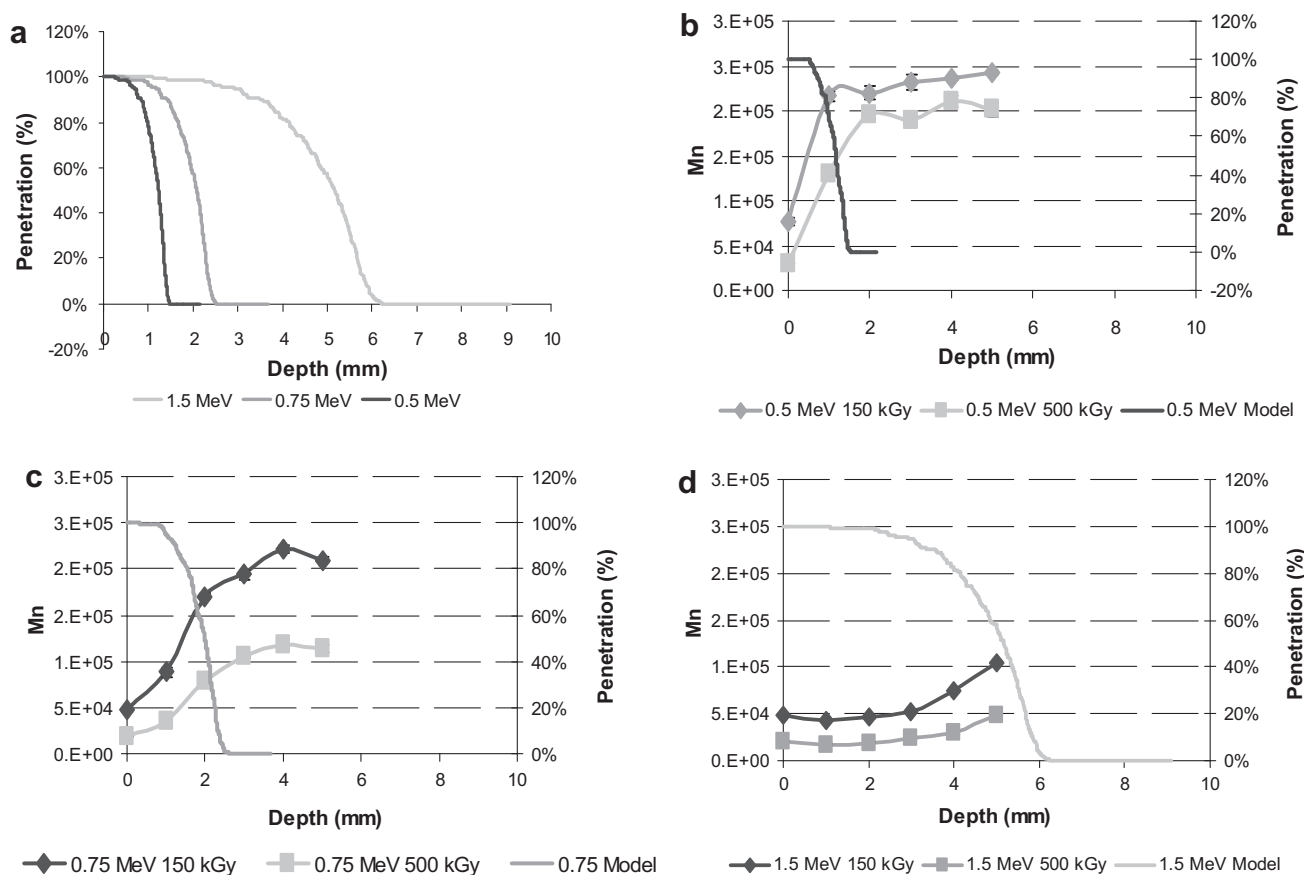
Fig. 9. Computer simulation of electron trajectories within PLLA (a) modeled % penetration for 0.5 MeV, 0.75 MeV and 1.5 MeV (b) comparison of Mn results with predicted 0.5 MeV beam profile (c) comparison of Mn results with predicted 0.75 MeV beam profile and (d) comparison of Mn results with predicted 1.5 MeV beam profile.

scission leads to a reduction in molecular weight proportional to the received dose [14]. Thus, the dose received by each sample layer is decreasing with increasing depth leading to the variation in Mn throughout the PLLA layers. This correlates well with the CASINO simulations of e-beam penetration in PLLA. The software predicts that for any energy, only the uppermost layers will receive 100% of emitted electrons, thereafter the numbers of electrons reaching lower depths decreases with increasing depth. As illustrated in Fig. 9b, for a 0.5 MeV beam the predicted depth to which 100% of electrons will reach is approximately 0.5 mm. Beyond this depth the numbers of penetrating electrons decrease until a depth is reached where they no longer penetrate (1.5 mm). This represents the observed depth dependent variation in molecular weight of PLLA samples irradiated at this energy irrespective of dose. In general, the delivery of a higher dose at each energy level induced a more pronounced affect on the reduction of the Mn.

Polydispersity results showed an increase in PI for superficial layers upon e-beam irradiation for all energies and associated doses. This can suggest the formation of a conglomerate of chains spanning a wide range of molecular weights indicating chain scission [29]. For the 0.5 MeV and 1.5 MeV (150 kGy/500 kGy) samples, PI values show a depth dependent variation similar to that observed for the Mn results with increased PI values obtained for the surface layers which then decrease with depth thereafter. However, for the 0.75 MeV beam energy samples (150 kGy and 500 kGy) the uppermost layer (1 mm) was shown to have a lower PI than those in the immediate lower depths (2–3 mm). The higher PI could suggest a wider range of molecular weights as further induced by a higher degree of chain scission. The phenomenon of

'spiking' has been observed before whereby the dose received by material at the surface is reduced in comparison to material within the bulk, possibly due to the escape of surface electrons [23].

The thermal and morphological properties of a polymer are affected by changes in molecular weight. Therefore chain scission, as induced by e-beam irradiation, can lead to associated alterations in polymer morphology. DSC analysis revealed changes in Tm and percentage crystallinity in the superficial PLLA layers after e-beam irradiation. The depth dependent nature of these differences was synonymous with those observed in the Mn data. The depth to which Tm is affected by the e-beam irradiation within each sample energy stack correlates with the estimated penetration depth of the e-beam as influenced by the beam energy. In general, Tm values are shown to decrease within the affected surface regions of the PLLA stacks until a depth, estimated to be the penetration depth of the beam, where the electrons no longer reach. A decrease in Tm can suggest poor packing capabilities of crystallised chains due to either reduced chain uniformity (attributed to the action of free radicals within crystalline regions) or a decrease in overall crystal size. As percentage crystallinity is observed to increase post-irradiation, the lower Tm values could be indicative of the growth of smaller crystals thus contributing to an overall increase in percentage crystallinity.

A proposed mode of bioresorbable polymer degradation by Hurrell and Cameron involves four distinct stages namely (1) water diffusion into the polymer (2) ester hydrolysis and a gradual decrease in molecular weight (3) a critical molecular weight is reached where degradation products are small enough to diffuse from the sample surface and mass loss is initiated (and a reaction-erosion front is developed) and (4) reaction-erosion fronts that have formed meet

and the sample continues to degrade homogeneously [30,31]. The earlier onset of mass loss in the near-surface layers can therefore be explained by their radiation-induced lower molecular weight prior to the hydrolytic degradation. It has been reported that a lower molecular weight (induced by radiation treatment) leads to higher water uptake during degradation and subsequently an earlier instigation of mass loss [32]. It is suggested that radiation-induced lower molecular weight polymers are rendered more hydrophilic (having a higher percentage of hydroxyl and carboxyl groups) than the corresponding higher molecular weight polymers. This leads to a greater influx of water molecules, initiating the degradation process and subsequent erosion. It is therefore possible that this phenomenon is manifested here. GPC results demonstrated that all irradiated samples had significantly lower molecular weights compared to their non-irradiated controls. Furthermore, the greatest mass loss was observed for those samples with the lowest molecular weight, i.e. PLLA near-surface layers with a delivered surface dose of 500 kGy.

5. Conclusion

The potential of e-beam technology to provide a depth dependent change in polymer properties, and ultimately degradation, has been reported. Examination of polymer characteristics revealed that the near-surface physical properties of the irradiated PLLA samples were affected in a depth dependent manner. The effective range of depth over which the e-beam can induce changes in polymer physical properties can be manipulated by alterations in beam energy. At lower energies (<1.5 MeV) the effective depth gradient is more surface specific producing effects on polymer properties within 1–2 mm of the sample surface. Computer modelling also predicted comparative depths of electron penetration at each energy level studied in pure PLLA. In addition, clear depth variations in PLLA properties, such as molecular weight, crystallinity, and Tm, over the irradiated surface region were also observed. This produced resultant changes in the nature of the hydrolytic degradation of PLLA, as observed for samples throughout each energy stack. The PLLA samples in the uppermost layers of the energy stack were shown to initiate earlier mass losses than those deeper in the stack, i.e. degradation initiated at the surface. The ability to induce pseudo-surface erosion of such polymers could have a significant impact in the design of bioresorbable medical devices. In particular, orthopaedic fixation devices could be treated to degrade in a manner that allows bone tissue ingrowth, until eventual device replacement, whilst maintaining adequate levels of mechanical support. This research has illustrated the potential of e-beam technology in achieving a depth-dependent degradation rate and ultimately improved bioresorbable medical devices.

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