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Electron-beam irradiation of experimental denture base polymers

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Abstract

Objective. Since the properties of polymers can be influenced using electron-beam irradiation, the aim of this study was to investigate whether electron-beam post-curing can improve the mechanical properties of experimental denture base polymers. ***Material and methods.*** Rectangular specimens of different experimental polymeric blends were electron-beam irradiated (post-cured) with 25 kGy and 200 kGy using an electron accelerator of 4.5 MeV. Fracture toughness, work of fracture, Vickers hardness and colour changes were measured and compared in non-irradiated specimens. ***Results.*** The mechanical properties of all the investigated polymers seemed to benefit from low-energy electron-beam irradiation (25 kGy). Using an energy dose of 200 kGy, all blends showed deteriorated mechanical properties resulting from chain breakage. Nevertheless, all investigated polymers had undesirable colour changes after electron-beam irradiation. ***Conclusions.*** Mechanical properties of experimental polymethyl-methacrylate could be changed using electron-beam irradiation. Because of discolorations caused by the irradiation levels investigated, these levels cannot be recommended for practical applications.

Key Words: *Electron-beam irradiation, experimental denture base resins*

Introduction

Electron-beam post-curing is widely used to improve the mechanical properties of polymers, especially polyethylene, polystyrene and polycarbonate [1–3]. Electron-beam irradiation of polymers was first done in the 1950s [4], and for decades this method has been used successfully in the industry [5,6]. However, few studies can be found in dentistry publications [7–9].

Generally, there are two reactions to electron-beam irradiation that compete during radiation (chain breakage and chain linkage), and which of them is dominant during irradiation depends on different parameters: irradiation dosage, polymeric structure, temperature and storage during irradiation and functional groups of the polymer. For example, elevated temperature during irradiation leads to increased radical mobility, which raises the conversation rate of polymers [10].

Predicting the result of electron-beam irradiation on different polymers is therefore difficult because of diverse irradiation methods and polymeric systems. Haque et al. [7] described UDMA as a polymer that showed improved hardness and reduced abrasiveness after heavy ion irradiation (640 Gy, 290 MeV). Nevertheless, polymethyl-methacrylate (PMMA) is often described in the literature [11–13] as a thermoplastic polymer which tends more to chain breakage during irradiation. However, Thompson et al. [14] have shown that electron-beam irradiation of Bis-GMA increases the degree of cross-linking of the polymer. They found that the residual double-bond content decreased as dosage increased during irradiation.

The aim of this study was therefore to investigate the influence of electron-beam post-curing on the mechanical properties and colour stability of different experimental denture base polymers. The hypothesis was that irradiation of alternative denture base polymers consisting of ethylglycol-dimethacrylate (EGDMA), butane-diol-dimethacrylate (BDDMA) and monomethyl-methacrylate (MMA) may lead to improved mechanical properties. Hence, fracture toughness, work of fracture, Vickers hardness and colour were measured after

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electron-beam post-curing using different doses of energy (25 kGy and 200 kGy).

Material and methods

Six different blends (Table I) of experimental denture base resins "EDBR" (Ivoclar-Vivadent, Schaan, Liechtenstein) were manufactured using different polymers: EDBR 1 and EDBR 2, consisting of monomethyl-methacrylate (MMA); EDBR 3 and EDBR 4, consisting of monomethyl-methacrylate (MMA) and ethylglycol-dimethacrylate (EGDMA); and EDBR 5 and EDBR 6, consisting of monomethyl-methacrylate (MMA) and butane-diol-dimethacrylate (BDDMA). Polymerization (heat-curing under pressure: water bath 100°C, 30 min, 5.5 bar) was carried out using the Ivomat IP 3 polymerization device (Ivoclar-Vivadent).

After manufacturing a total of 180 rectangular specimens (30 per blend each) of 36 × 8 × 4 mm (length × width × thickness), the surface was ground with sandpaper (grit 800). At the midspan of the specimens, a 3-mm-deep and 0.5-mm-wide notch was sawn. This cut was extended to a notch of 0.2 to 0.5 mm in length using a razor blade device (Ivoclar-Vivadent).

Electron-beam irradiation

Thirty samples were manufactured from each denture base polymer, and all specimens from each group were randomly divided into 3 subgroups of 10 samples each. Ten specimens of every blend served as an untreated control. Ten specimens of each group were irradiated using an electron beam with an energy dose of 25 kGy. The third subgroup was electron-beam irradiated with 200 kGy in steps of 25 kGy. The acceleration voltage of the electron-beam device amounted to 4.5 MeV using a Rhodotron electron accelerator (BGS beta gamma service, Bruchsaal, Germany).

Immediate irradiation of the specimens was not possible because of the distance between place of manufacture and electron-beam accelerator. Before measurement was started, the irradiated specimens were therefore stored before and after electron-beam irradiation for 7 days in distilled water at 37°C. The control group was kept in distilled water at 37°C for 14 days to ensure identical storage conditions for all groups.

Table I. Different blends of polymers used in this investigation (EDBR = experimental denture base resin; MMA = monomethyl-methacrylate; EGDMA = ethylglycol-dimethacrylate, BDDMA = butanediol-dimethacrylate)

Brand	Monomer	Ratio powder:monomer
EDBR 1	MMA	8:5
EDBR 2	MMA	24:10
EDBR 3	MMA/EGDMA	24:10
EDBR 4	MMA/EGDMA	8:5
EDBR 5	MMA/BDDMA	8:5
EDBR 6	MMA/BDDMA	24:10

Fracture toughness

A three-point bending test was performed using the Zwick 1446 universal testing machine (Zwick, Ulm, Germany). The load was applied axially mid-span of the 8-mm-long side of the specimens (Figure 1) and fracture toughness was calculated [15].

Work of fracture

After determining fracture toughness, the work of fracture (FW) was calculated. The FW gives the resistance of the polymer to crack expansion and is dependent on the fracture energy, which is defined by the area under the stress/strain curve and can be calculated using the following formula [15]:

$$FW = \frac{U}{2 \times B(H - a)}$$

where U is energy fracture, B is width, H is height and a is saw kerf length + notch length.

Vickers hardness

The Vickers hardness (VH) measurement device B3212001 (Zwick, Ulm, Germany) was used to load the specimens by a pyramid-shaped loading die (load weight: 0.5 kg). The loading time was set to 60 s. The pyramid-shaped indention in the polymer is dependent on the hardness of the resin. VH is proportional to the quotient of applied load and the area of the indention and was determined for each specimen [15].

Colour measurements

Colour measurements were carried out in accordance with the CIE L* a* b* system (Commission international de l'Eclairage, 1976) using the spectrophotometer Minolta CM-C3500 (Minolta Co. Ltd, Japan) with a pin-hole diaphragm of 3 mm diameter. Discoloration of the samples was distinguished according to differences in brightness (ΔL*), in red-green (Δa*) and in yellow-blue (Δb*). Calculation of the colour variation ΔE* between two colour

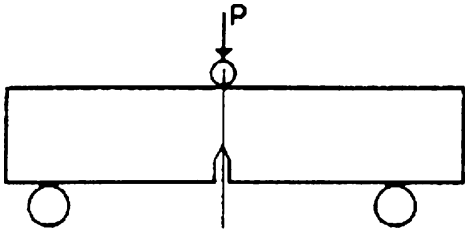

Figure 1. Axially loaded specimen during three-point bending test (P = load).

positions in the three-dimensional L* a* b* colour space is as follows:

$$\Delta E^* = [(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2]^{\frac{1}{2}}$$

Statistics

Means and standard deviations were calculated and univariate analysis of variance (ANOVA) was carried out to determine statistically significant interactions between the groups.

Results

Fracture toughness

With the exception of EDBR 3, based on a monomer mixture of MMA and EGDMA, all the tested experimental denture base polymers showed a significant increase in fracture toughness after electron-beam irradiation using 25 kGy (Figure 2). A distinct enhancement of fracture toughness of EDBR 5 and EDBR 6, consisting of MMA and BDDMA, could be measured after electron-beam post-curing (25 kGy). An energy dose of 200 kGy showed a significant ($p < 0.005$) decrease in fracture toughness and was common for all test groups.

Work of fracture

After electron-beam irradiation with 25 kGy EDBR 1, EDBR 3 and the monomer mixture of MMA and BDDMA (EDBR 5 and EDBR 6) showed a significant enhancement of work of fracture. Using electron-beam post-curing with an energy dose of 200 kGy, a significant decrease in work of fracture could be determined from all tested samples (Figure 3).

Vickers hardness (VH)

A significant increase in VH could be observed for EDBR 3 and the monomer mixture of MMA and BDDMA (EDBR 5 and EDBR 6) after electron-beam irradiation with 200 kGy (Figure 4), while with 25 kGy only a monomer mixture of MMA and BDDMA (EDBR 5) showed a significant increase of VH.

Colour measurements

ΔE^* values >3 indicate visible colour changes. This could be measured for all investigated blends ($p < 0.05$). Regardless of the energy dose, a significant change of colour could be found for all polymer blends (Figure 5). EDBR 2 and EDBR 6 generally showed the greatest colour changes. Discoloration

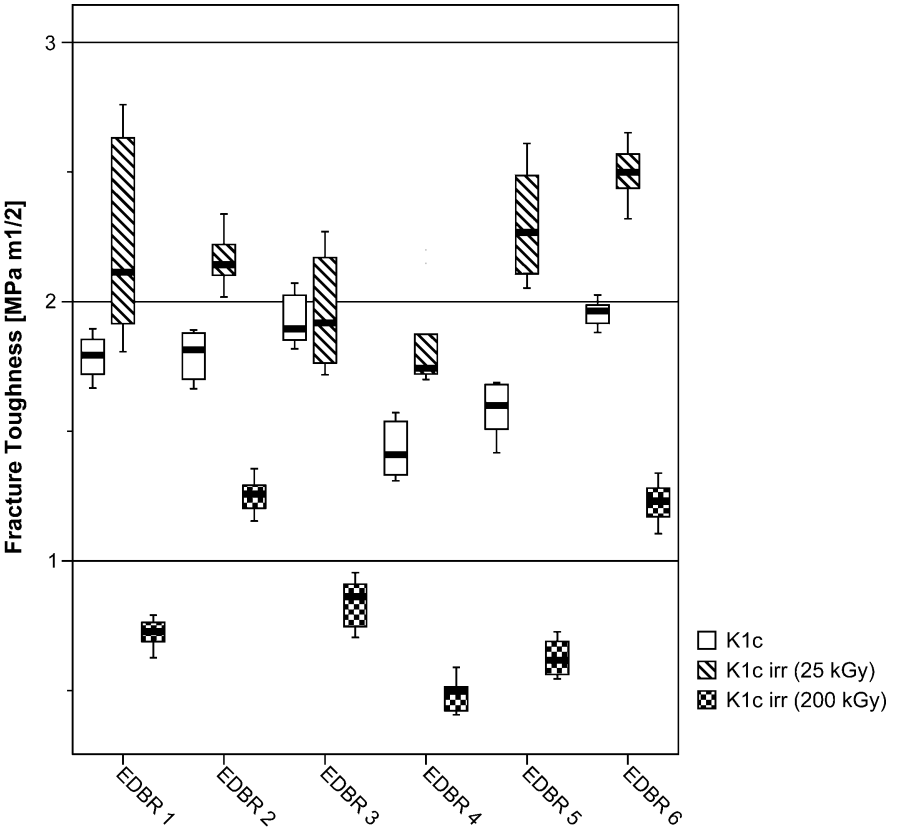

Figure 2. Fracture toughness of experimental denture base polymers after electron-beam irradiation (irr) with 25 kGy and 4.5 MeV (EDBR = experimental denture base resin; K1c = fracture toughness; irr = irradiated).

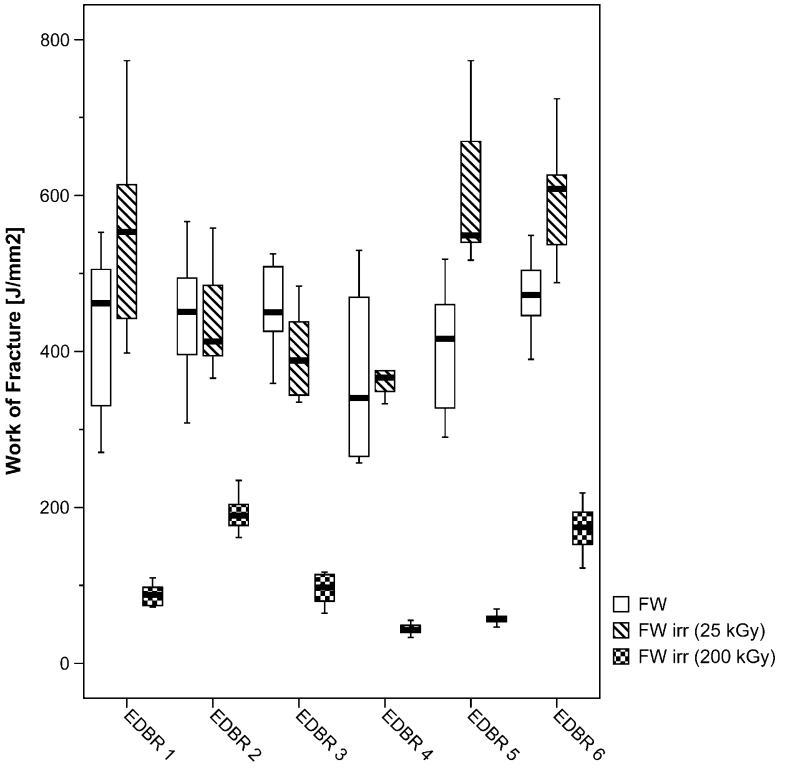

Figure 3. Work of fracture of experimental denture base polymers after electron-beam irradiation (irr) with 25 kGy and 4.5 MeV (EDBR = experimental denture base resin; FW = work of fracture; irr = irradiated).

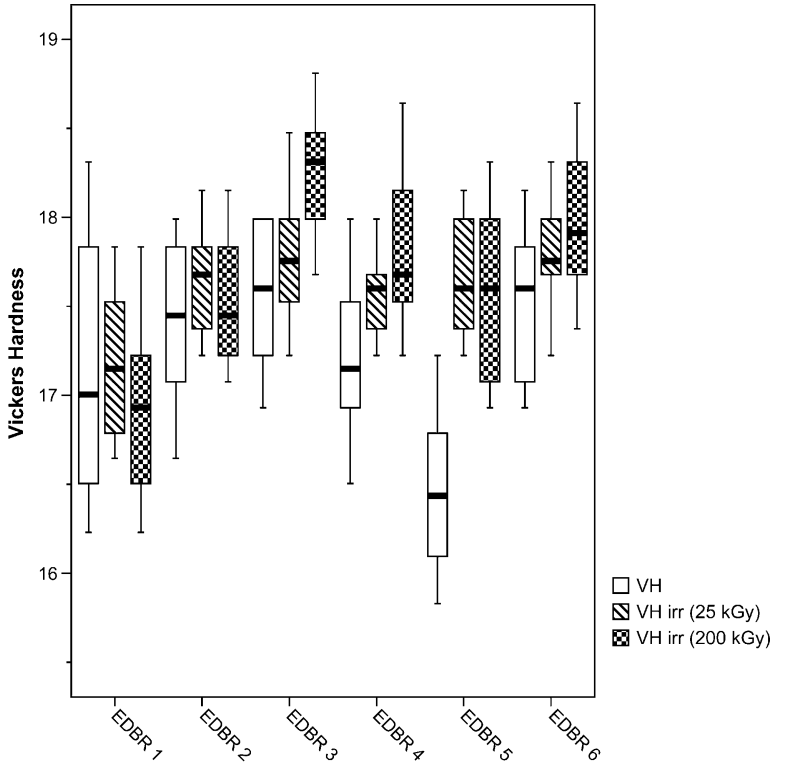

Figure 4. Vickers hardness of experimental denture base polymers after electron-beam irradiation (irr) with 25 kGy and 4.5 MeV (EDBR = experimental denture base resin; VH = Vickers hardness; irr = irradiated).

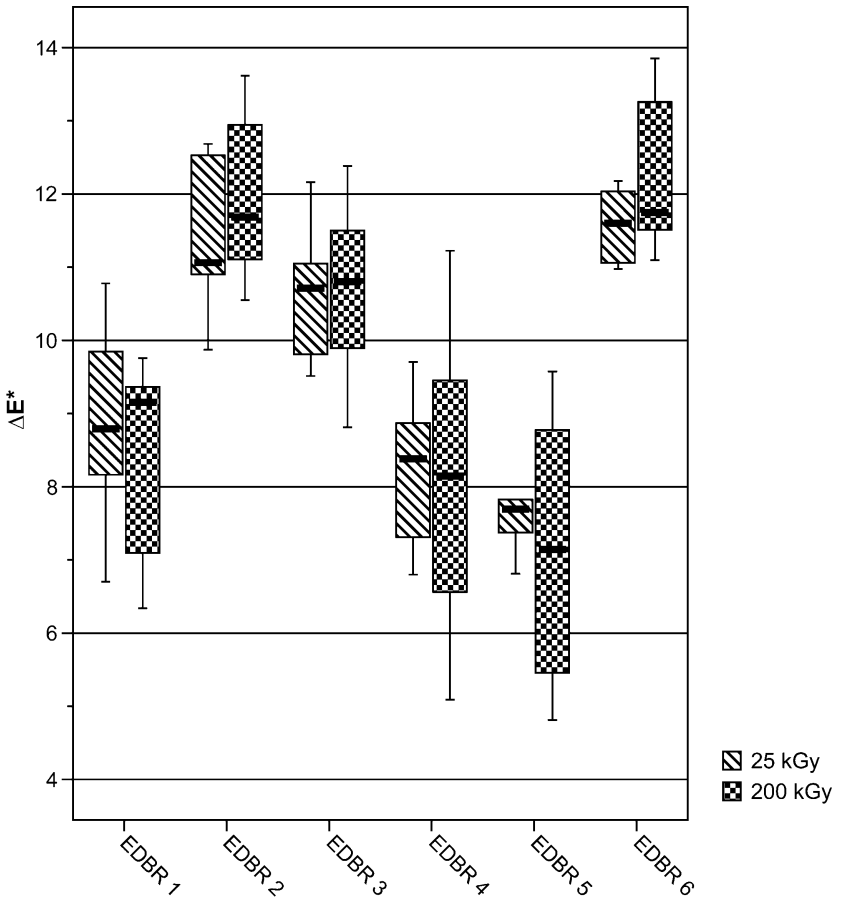

Figure 5. Colour changes of experimental denture base polymers after electron-beam irradiation with 25 kGy and 4.5 MeV (EDBR = experimental denture base resin).

seemed to be independent of the chosen energy dose, because an increase in energy dose to 200 kGy showed no higher colour changes compared to irradiation with 25 kGy.

Discussion

Polymethyl-methacrylate (PMMA) is the most commonly used polymer for denture base resins. Despite its popularity, however, it is still far from ideal in fulfilling the mechanical requirements of a prosthesis. Jagger et al. stated [16] that while on the one hand the fracture of dentures could be due to the poor mechanical properties of the acrylic resin, on the other hand multifold factors could lead to denture base failures. There are three road maps improving the impact properties of PMMA: the reinforcement of PMMA with other materials (metal, fibres), the chemical modification of PMMA and the development of an alternative polymer to PMMA. In this investigation, we tried to combine two of these alternatives. Changing the chemical structure of polymers using electron-beam post-curing, alternative denture base polymers (EGDMA, BDDMA) were examined.

During a chemical reaction, radicals that induce chain linkage are initiated from several distinct points. The polymeric chain increases, but the chain linkage is not equally distributed in the polymer. It has been demonstrated that irradiation initiates the radical building of all components of a polymer in contrast to mere chemical reaction [17]. For that reason the entire polymer may simultaneously be newly arranged and cross-linked when irradiated.

In the literature [11–13], PMMA is often described as a thermoplastic polymer which tends more to chain breakage during irradiation. Behr et al. [18] investigated the influence of electron-beam irradiation on mostly PMMA-based denture base resins. In this study, the mechanical properties of the polymers improved using 10 MeV with a dose of 25 kGy and with 100 kGy using 4.5 MeV. However, the mechanical improvements were low. Moreover, the colour changes reached a level found not to be clinically acceptable. Therefore, Behr et al. [18] stated that the changes in the mechanical properties of dental PMMA systems were so low that the expenditure of energy and costs did not justify the use of electron-beam post-curing for dental PMMA. In this study, we therefore investigated whether alternative denture base polymer, based on different blends of MMA/EGDMA and MMA/BDDMA, differs from these results or not.

In this investigation, all the tested polymeric blends seemed to behave similarly after electron-beam irradiation. Using a low irradiation energy dose of 25 kGy, polymeric chain entanglements seemed to be broken, and therefore the molecular arrangement may have induced a denser packing [10]. All the investigated blends showed a significant enhancement of fracture toughness and VH after electron-beam post-curing with 25 KGy. With increasing energy dose (200 kGy) the molecular arrangement seemed to deviate from the optimal packing because of chain breakage and a reduced molecular weight. All blends showed detoriated mechanical properties using an energy dose of 200 kGy. Regardless of the polymeric structure, all the investigated blends demonstrated the same behaviour.

A significant change of colour could be found for all polymeric blends when energy doses of 25 kGy and 200 kGy were used. Clinically not acceptable ΔE values >3 were measured for all investigated. The reason for the discoloration could have been colour centres, which occur in crystalline regions consisting of anion defects in the lattice and linked surplus electrons. The residual initiator system of the polymer may account for the existence of anion defects [18]. In addition, the dominant termination reaction starts with splitting of the methyl ester groups and results in a gas formation: CO, CO_2, H_2 and CH_4 [19]. Consequently, the trapped gas causes volume expansion and, as a result, a shift between the chain groups occurs and opacifies the polymer.

Fracture toughness and work of fracture of almost all investigated blends benefit from low-energy electron-beam irradiation (25 kGy). However, it is questionable whether the improved mechanical properties of the resins justify the increased cost of an additional irradiation. Besides, all the investigated polymers, MMA, EGDMA and BDDMA, showed undesirable colour changes after electron-beam irradiation (25 kGy and 200 kGy), which might limit the clinical application of this technology.

Acknowledgments

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