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Electron beam irradiation of denture base materials

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Electron beam irradiation can be used to influence the properties of polymers. It was the aim of this study to investigate whether PMMA denture base materials can benefit from irradiation in order to have increased fracture toughness, work of fracture or hardness. Rectangular specimens of heat-and auto-curing denture base materials were electron beam irradiated (post-cured) with 25, 100 and 200 kGy using an electron acceleration of 10 MeV or 4.5 MeV respectively. Fracture toughness, work of fracture, Vickers hardness and colour changes were measured and compared with not-irradiated specimens.

The toughness, work of fracture and hardness increased using 10 MeV with a dose of 25 kGy and with 100 kGy using 4.5 MeV. However, the clinical use may not benefit from the observed small changes. Higher dosage (200 kGy) decreased the values significantly. The colour changes reached a level which was found to be not clinically acceptable. Conclusion: PMMA denture base materials do not benefit from post-curing with electron beam irradiation.

1. Introduction

Since the basic investigations of Charlesby [1, 2] electron beam irradiation has been used as a method to influence the properties of polymers. It was demonstrated that ionizised irradiation of polyethylene introduced chain linkage which result in an insoluble and more heat-resistant polymer [3–5]. Generally, two types of reactions exist with electron beam irradiation, which compete during radiation: chain linkage or breakage. It depends on the structure of the polymer and the irradiation parameters like dose or acceleration of the electron which reaction type will dominate during irradiation. Beside chain breakage, a disadvantage of irradiation can be colour changes of the resin caused by so called "colour centers" [6]. Colour centres occur in crystalline regions of translucent bodies. They consist of anion defects in the lattice and linked surplus electrons.

While irradiated polyethylene, polystyrene or polycarbonate are widely used in industrial products like cars, machine-bodies or as isolators since years [3, 4, 7], polymer radiation finds little interest in dentistry [8]. Up to now, it was only used to sterilize the powder of PMMA-based bone cements [9].

It was the aim of this study to investigate the influence of electron beam irradiation on the fracture toughness, work of fracture, Vickers hardness and colour changes of dental PMMA (polymethyl methacrylate) denture base materials.

2. Material and methods

Three groups, a heat curing PMMA, a self-curing PMMA and a heat-curing poly-vinyl copolymer/methyl-methacrylate (PVC/MMA) were chosen to represent typical denture base materials and manufacturing methods.

A total of 240 rectangular specimens with the dimension of 36 mm × 8 mm × 4 mm (length, width, thickness) were made. The curing parameters of the resins are described in Table I.

The specimens were randomly divided into a 4.5 MeV and a 10 MeV group. Forty specimens of each group were assigned in four further subgroups of 10 specimens each. The first subgroup remained unirradiated. The second subgroup was electron beam irradiated with 25 kGy in one step, the third group with 100 kGy in steps of 25 kGy and the fourth group was irradiated with 200 kGy using a Rodotron electron accelerator (BGS beta gamma service, Saal a. D., G).

Due to the distance between the place of specimen manufacturing and the place of irradiation, it was not possible to irradiate the samples immediately after manufacturing. The samples were irradiated seven days after manufacturing and the mechanical properties were measured seven days after irradiation. During that time all specimens were stored in distilled water at 37 °C. The control was also stored for 14 days in distilled water before the measurements were carried out in order to have identical storage conditions for all groups.

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TABLE I Manufacturer and polymerization mode of used denture base materials

Brand	Manufacturer	Polymerization mode	Polymer type and initiator system
Probase hot	Ivoclar Schaan, FL	Water bath 100 °C, 45 min	Polymethyl-methacrylate Methyl-methacrylate Benzoyl-peroxide
Probase cold	Ivoclar Schaan, FL	Water bath 40 °C, 4 bar, 15 min	Polymethyl-methacrylate Methyl-methacrylate Benzoyl-peroxide
Luxene	Astron Dental Lake Zurich, USA, Il	Water bath 75 °C, 6 bar 9 h	Polyvinyl-copolymer Methyl-methacrylate Ethyl-methacrylate Triethylene-glycol-dimethacrylate Benzoyl-peroxide

2.1. Colour measurements

The colour is defined in a three-dimensional colour space according the CIE $L^*a^*b^*$-system (Commission Internationale de l'Eclairage 1976) by a value for brightness (ΔL^*), a point on the red-green axis (Δa^*) and a point on the blue-yellow axis (Δb^*). The colour of the specimen was measured before and after irradiation using a spectrophotometer (Minolta CM3500, Osaka, J) with a pin-hole diaphragm of 3mm diameter. The colour difference (ΔE^*) in the three-dimensional colour space was determined according the formula:

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

$$\Delta c^* = [(a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2]^{\frac{1}{2}} \quad c^* = \text{chroma}$$

2.2. Fracture toughness

After grinding the surface with sand paper (grit 800) a 0.5 mm wide and 3 mm deep cut was centrally sawn in the specimens (Fig. 1). This cut was extended to a notch of 0.2 to 0.5 mm length using a razor blade device (Ivoclar, Schaan, FL). A three-point bending test was performed with a Zwick universal testing machine 1446 (Zwick, Ulm G) with a support distance of 32 mm. The load was axially applied with 1 mm/min in the centre of the specimens directly above the notch. A stress/strain curve was recorded. After fracture, the length of the cut and the notch was measured.

The fracture toughness (K_1C) was calculated according to the following formula:

$$K_{1c(\max)} = \frac{(P_{\max} * S)}{B * H^{3/2}} * f(x)$$

$$f(x) = \frac{3x^{\frac{1}{2}}[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{2(1+2x)(1-x)^3/2}$$

$$x = \frac{a}{H}$$

Figure 1 Specimen with saw cut and extended notch.

S: support distance, P: fracture load, B: width, H: height and a: cut + notch length

2.3. Work of fracture

Work of fracture (FW) is defined as the energy necessary to produce two fractured surfaces. The energy fracture (U) is represented by the area under the stress/strain curve and was calculated. The work of fracture could then be determined using the formula:

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

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

2.4. Vickers hardness

The samples were loaded using a pyramid-shaped loading die with a weight of 0.5 kg for 60 sec

TABLE II Mann-Whitney U test: P-values of fracture toughness (K_1C), work of fracture (FW) and Vickers hardness (VH) using 4.5 or 10 MeV and an irradiation dose of 25, 100 or 200 kGy. Comparison between not-irradiated and irradiated specimens

	Probase hot	Probase cold	Luxene
4.5 MeV			
K1C-K1C25	n.s.	n.s.	n.s.
K1C-K1C100	0.08	0.005	0.005
K1C-K1C200	0.008	0.005	0.013
FW-FW25	n.s.	0.007	0.005
FW-FW100	n.s.	0.005	0.074
FW-FW200	0.005	0.005	0.005
VH-VH25	n.s.	0.005	0.007
VH-VH100	n.s.	0.005	0.007
VH-VH200	0.005	0.005	0.051
10 MeV			
K1C-K1C25	0.021	0.05	0.013
K1C-K1C100	0.008	0.005	n.s.
K1C-K1C200	0.008	0.005	n.s.
FW-FW25	n.s.	n.s.	0.005
FW-FW100	0.022	0.005	0.005
FW-FW200	0.005	0.005	0.005
VH-VH25	0.005	0.005	0.005
VH-VH100	0.005	0.005	0.037
VH-VH200	0.005	0.005	0.022

using the Vickers hardness measurement device B 3212001 (Zwick, Ulm, G). This results in a pyramid-shaped indention. Vickers hardness (*VH*) is proportional to the quotient of applied load and the area of the indention and was calculated following the formula:

$$VH = 0{,}102 * \frac{F}{A} = \frac{0{,}102 * F * \sin\frac{136^\circ}{2}}{d^2}$$

F: load and A: area.

2.5. Statistics

Median and 25/75% percentiles were calculated. Statistical differences were investigated using Mann Whitney U test. The level of significance was set at $\alpha = 0.05$.

3. Results

3.1. Colour changes

ΔE values greater than 3 indicate visible colour changes. This was found for all auto-curing and PVC/MMA denture base materials after irradiation with 4.5 as well as 10 MeV (Fig. 2). Using 10 MeV, ΔE values increased with increasing dose (25, 100, 200 kGy) for the PVC/MMA material and showed highest values with 4.5 MeV only at 100 kGy. The auto-curing material had the highest value with 10 MeV and the lowest value with 4.5 MeV using a dose of 100 kGy. Samples irradiated with 25 and 200 kGy doses had lower values.

The heat-curing system showed colour changes of $\Delta E < 3$ independent from the electron beam acceleration. There was a tendency to higher values using 10 MeV.

Chroma (Δc^*) changed for 10 MeV with increasing dose rates. For 4.5 MeV, the greatest changes were

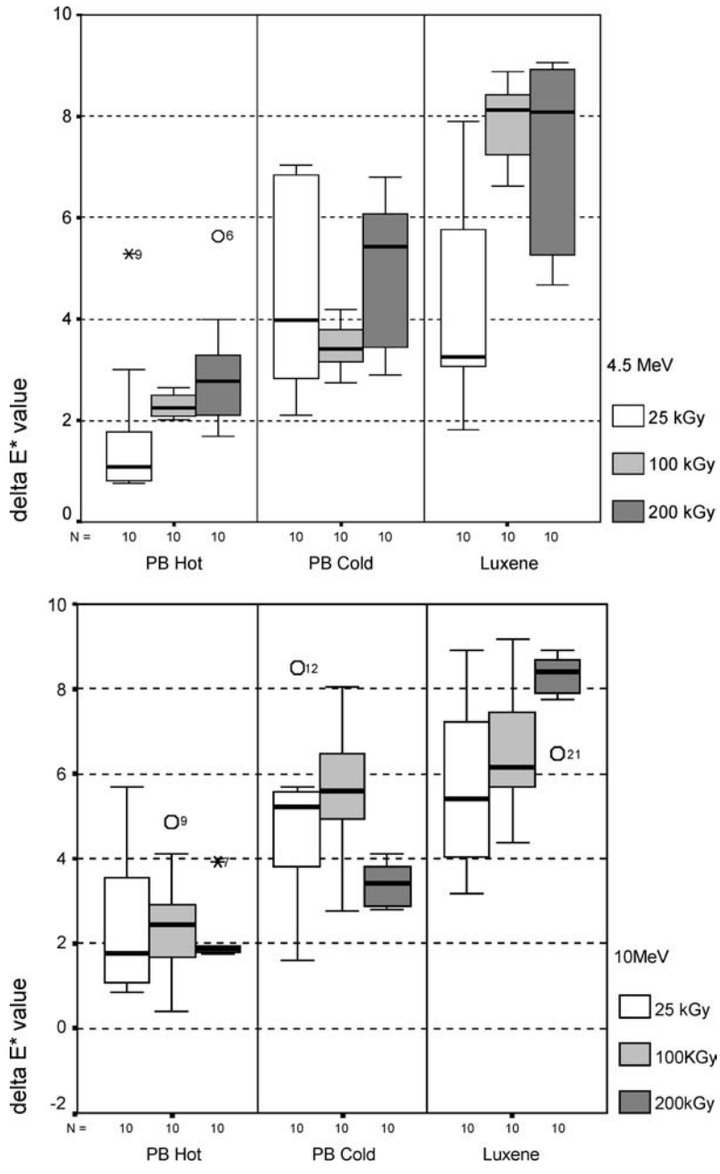

Figure 2 Colour changes of denture base materials after electron beam irradiation with 25, 100 or 200 kGy: delta E^*-values.

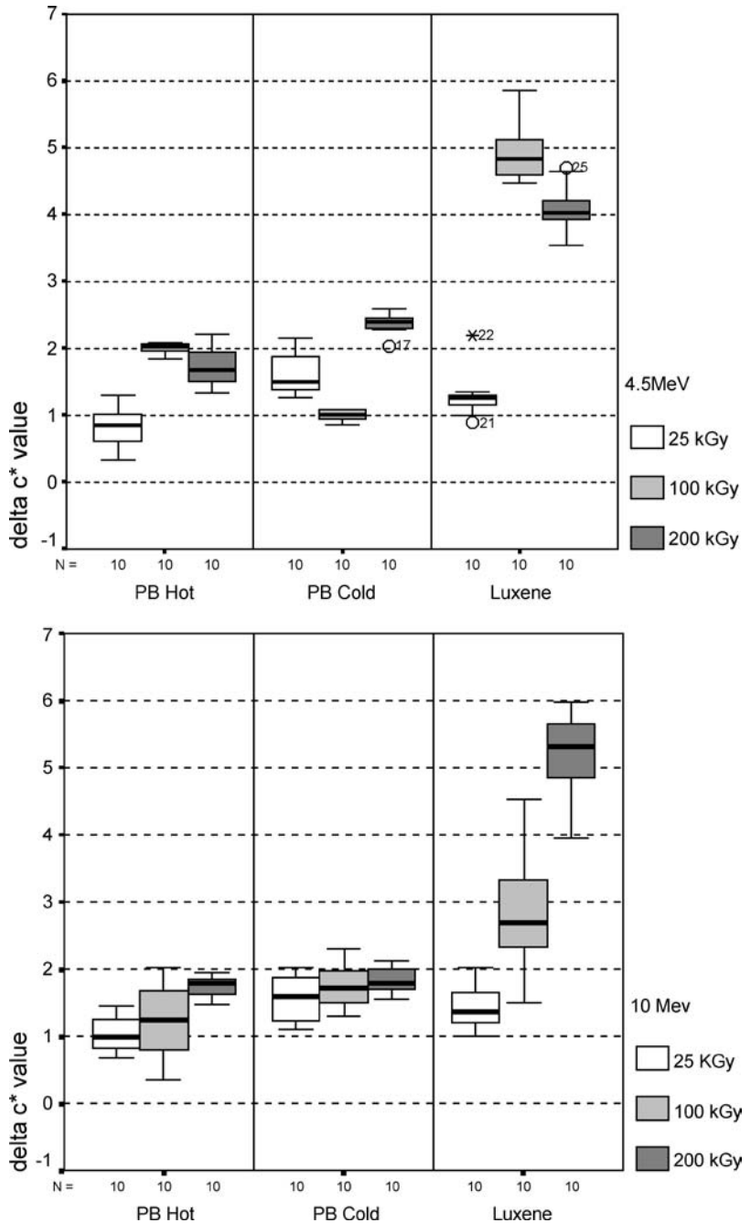

Figure 3 Colour changes of denture base materials after electron beam irradiation with 25, 100 or 200 kGy: delta c^*-values.

observed with 100 kGy (Fig. 3). Generally, the specimens became more yellow. The PVC/MMA material showed considerable changes with Δc^* values up to 5.2 while the heat-curing system had the lowest changes in chroma.

3.2. Fracture toughness

Fracture toughness was influenced by the chosen electron acceleration. With 4.5 MeV, the fracture toughness achieved the highest values for 100 kGy and with 10 MeV at a dose rate of 25 kGy (Fig. 4). The heat- and the auto-curing PMMA had significantly lower fracture toughness after irradiation with 200 kGy. The exception was the PVC/MMA material. It did not show a lower fracture toughness using 200 kGy (Table II).

3.3. Work of fracture

The work of fracture was not influenced by electron acceleration for heat- and auto-curing PMMA material, and was reduced with increasing dose rates (Fig. 5). With 200 kGy the reduction was statistically significant. PVC/MMA material had significantly higher work of fracture. Highest values were found for 4.5 and 10 MeV with 25 kGy (Table II).

3.4. Vickers hardness

Statistically significant lower Vickers hardness was shown for heat- and auto-curing PMMA after irradiation with 200 kGy. The Vickers hardness increased for 4.5 MeV and 100 kGy. Using 10 MeV, this behavior was observed at 25 kGy (Fig. 6).

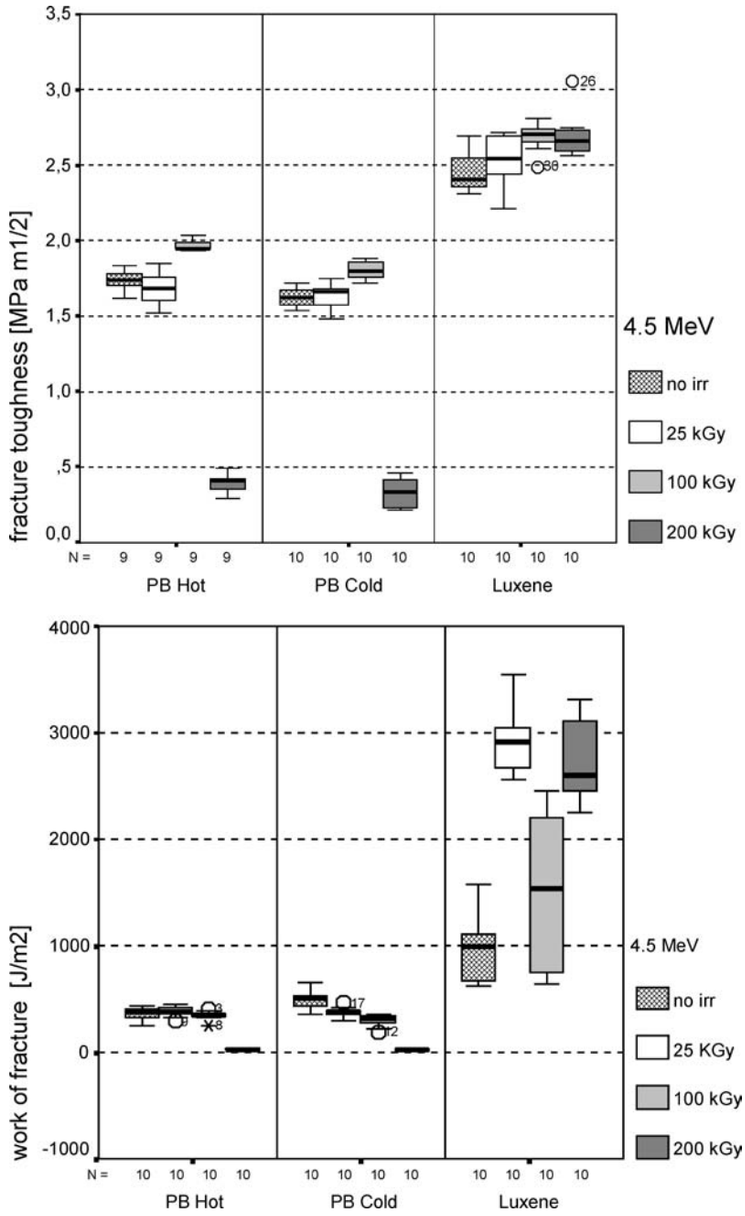

Figure 4 Fracture toughness and work of fracture of denture base materials after electron beam irradiation with 25, 100 or 200 kGy: 4.5 MeV.

The PVC/MMA material had significantly lower hardness for 4.5 MeV (all dose rates). With an electron acceleration of 10 MeV and a dose rate of 25 kGy the Vickers hardness increased significantly, while with 100 and 200 kGy dose the hardness decreased significantly (Table V).

4. Discussion

When irradiated, PMMA is described as a thermoplastic polymer which tends more to chain breakage [2, 5, 10, 11]. At lower dosage (<50 kGy) it stained yellow and at higher dosage it becomes friable and brittle [10].

This behavior could not be generally found for PMMA in this investigation. Depending on the electron acceleration, the chroma increased at 10 MeV with the dose rate (Fig. 2) while the brightness showed a maximum at 100 kGy (exception PVC/MMA (Luxene)), and for 4.5 MeV, the brittleness increased with the dose rate and showed no maximum (Fig. 1). It was stated in the literature that the acceleration influenced only the depth of penetration of the electrons and not the reaction type: chain linkage or breakage [4]. The gentle thickness of the samples made sure that they were completely transmitted by electrons using 4.5 MeV as well as 10 MeV. However, increasing acceleration and dose leads to increasing temperature in the sample. The dominating termination reaction starts with splitting of methyl ester groups resulting in a gas formation: CO, CO_2, H_2 and CH_4 [10]. The trapped gas results in volume expansion. Higher temperature produces more gas and volume expansion. This leads to a shift between the chains or chain-groups and opacifies the polymer. Furthermore, colour centres occur in crystalline regions. They consist of anion defects in the lattice and linked surplus electrons. The existence of anion defects depends on the

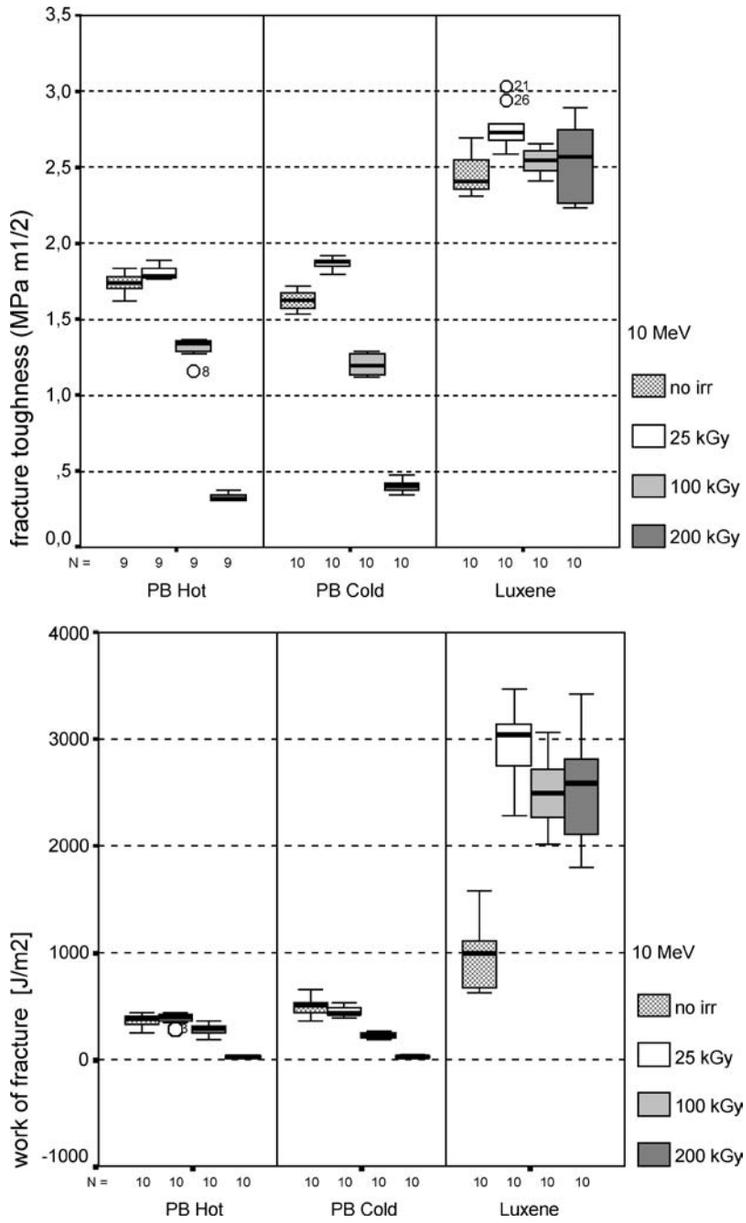

Figure 5 Fracture toughness and work of fracture of denture base materials after electron beam irradiation with 25, 100 or 200 kGy: 10 MeV.

residual initiator system and on halogenic components of the polymer. This could be verified by this investigation. The highest changes of chroma and brightness were shown for the autocuring system, which had a lower convertion rate than the heat-curing system, and for the PVC/MMA system which had clinically unacceptable changes due to halogenic components.

The mechanical properties were also influenced by the electron acceleration used. Using 4.5 MeV a higher dose of 100 kGy seems to be favorable, while with 10 MeV, 25 kGy result in higher fracture toughness (Fig. 3) and Vickers hardness (Fig. 5). The differences between auto-curing and heat-curing system were low. However, this could depend on the auto-curing initiator used in this study. It was shown by Behr [12] that other auto-curing systems with other initiator systems differ significantly from heat-curing systems and increased their fracture toughness by activation of unreacted carbon double bonds. But what induced the improvement or deterioration of fracture toughness and Vickers hardness in PMMA or other resins during irradiation? Seguchi [13] mentioned that amorphous polymers may contain chain entanglements. When chain breakage occurs during irradiation at the entanglement, the molecular arrangement would induce a more dense packing. With increasing dose (and resulting temperature) this effect reached an optimal relationship. Then the increasing dose decreased the molecular weight and the arrangement deviated from the optimal packing.

All in all, the fracture toughness, and particular the work of fracture, increased only moderately after irradiation. Even in cases with statistically significant differences the improvement was less than 0.5 MPa $m^{1/2}$. Furthermore, the Vickers hardness decreased for most

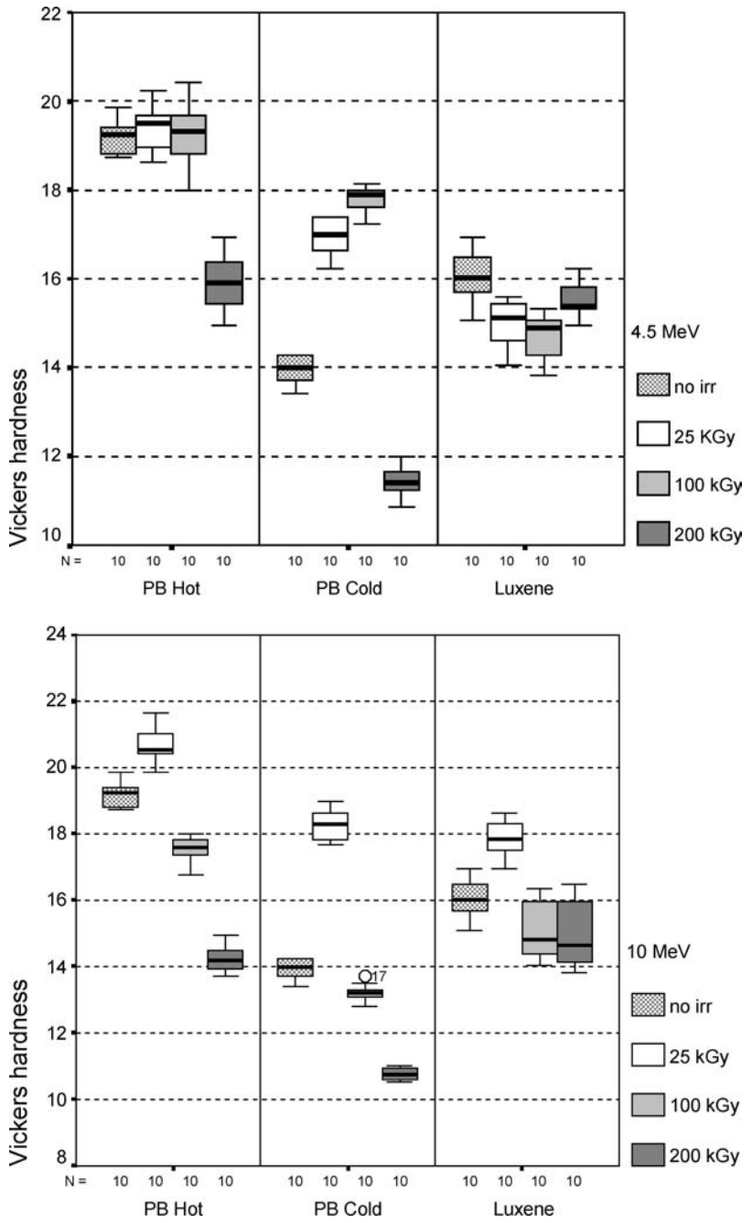

Figure 6 Vickers hardness of denture base materials after electron beam irradiation with 25, 100 or 200 kGy: 4.5 and 10 MeV.

doses and acceleration combinations. The changes of the mechanical properties of dental PMMA systems seems to be so low that the expenditure of energy and costs do not justify the use of electron beam irradiation for dental PMMA.

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