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# The influence of electron beam irradiation on colour stability and hardness of aesthetic brackets

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SUMMARY Electron beam irradiation can be used to improve the mechanical properties of polymers. The aim of this study was to investigate the influence of electron beam irradiation with an energy dose of 100 kGy on the mechanical properties and colour stability of conventional polymer brackets and experimental filled composite brackets.

The conventional brackets tested were Aesthetik-Line, Brillant, and Envision. The experimental brackets contained urethane dimethacrylate, as a monomer matrix and functional silane-treated $SiO_2$ fillers with a filler content of either 10 (Exper 1) or 40 (Exper 2) vol per cent. The influence of electron beam post-curing on Vickers hardness (VH) of the polymer brackets was investigated. Additionally, a possible discolouration of the brackets after electron beam irradiation was determined according to the three-dimensional $L^*$ $a^*$ $b^*$ colour space. The irradiated brackets were compared with untreated control groups. Statistical analysis was performed using the Wilcoxon test.

With the exception of Brillant brackets, all investigated brackets showed a significant enhancement of VH after electron beam post-curing. However, the brackets suffered a significant increase in discolouration. Aesthetik-Line brackets showed the highest discolouration, $\Delta E$, and Exper 2 brackets the lowest $\Delta E$ values. The discolouration of the examined brackets differed significantly.

These results demonstrate that the mechanical properties of polymer brackets could be modified by electron beam irradiation. Nevertheless, clinical use of electron beam post-curing might be restricted because of unacceptable colour changes.

## Introduction

Polymer brackets still present some disadvantages because of decreased hardness and wear resistance. A modern method to improve the properties of polymers and composites is high-energy dose irradiation. Electron beam irradiation is widely used in industry to advance the mechanical properties of some polymers, especially machine bodies, cars, and insulators (Barlow *et al.*, 1981). Polyethylene, polystyrene, and polycarbonate demonstrate enhanced mechanical behaviour after electron beam post-curing (Charlesby and Pinner, 1959; Tada, 1983).

While the mechanism of crosslinking polymers by irradiation has been extensively studied, the exact mechanism is still unknown. The mechanism involves the splitting-off of a hydrogen atom from a C–H bond (Behr *et al.*, 2005b). After separation of a second hydrogen atom, molecular hydrogen is formed. Consequently, the two bordering polymeric radicals merge to form a crosslink (Behr *et al.*, 2006). The described effect of electron beam induced crosslinking is that the molecular mass of the polymer increases, which leads to branched chains until ultimately a three-dimensional (3D) network is formed (Behr *et al.*, 2006). This appears when each polymer chain is linked to another chain (Seguchi *et al.*, 2002; Behr *et al.*, 2005c, 2006). In contrast, chain breakage can also occur. This phenomenon happens when using a high-energy dose and specific resins. During chain breakage, the C–C bonds split off and the polymeric structure is broken down (Behr *et al.*, 2005a). Whether additional crosslinking or chain breakage dominates in a polymer is difficult to predict; it depends on different parameters, e.g. the irradiation dose, polymeric structure, temperature and storage during irradiation, and functional groups of the polymer and fillers in the polymeric matrix (Ungar, 1981).

In dentistry, only a few publications can be found concerning electron beam post-curing of polymers or composites. It was reported by Faltermeier *et al.* (2007a) that a significant colour change could be measured for denture-based polymers after electron beam post-curing with an energy dose of 200 kGy. It was concluded that the reason for the discolouration could be colour centres, which occur in crystalline regions consisting of anion defects in the lattice and linked surplus electrons (Behr *et al.*, 2005c). Experimental $SiO_2$ filler reinforced urethane dimethacrylate

(UDMA) brackets revealed an obvious trend for increased hardness, stiffness, and improved wear resistance in comparison with unfilled brackets (Faltermeier *et al.*, 2007b). However, the question arises as to whether increased filler levels in plastic brackets may constrict the crosslinking process of the polymeric part of the brackets during the electron beam post-curing process.

The aim of this study was to investigate the influence of electron beam irradiation with an energy dose of 100 kGy on conventional plastic brackets and experimental-filled composite brackets. The influence of electron beam post-curing on Vickers hardness (VH) of polymer brackets was also investigated. Additionally, a possible discolouration of the brackets after electron beam irradiation was determined according to the three-dimensional (3D) *L* a* b** colour space.

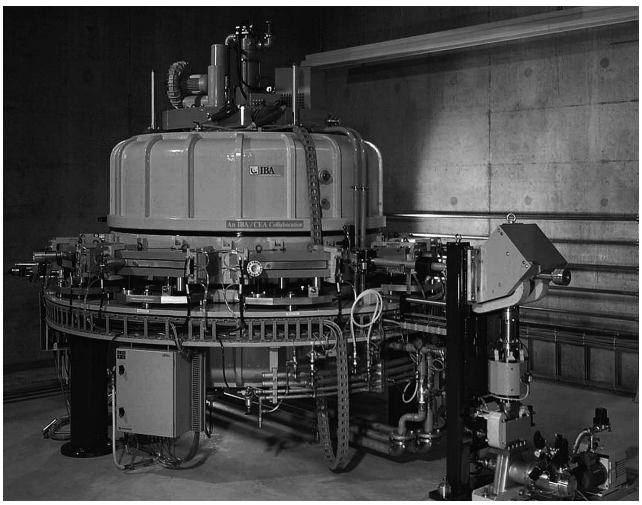


**Figure 1** The Rhodotron electron beam accelerator.

## Material and methods

The conventional brackets chosen were Aesthetik-Line (Forestadent, Pforzheim, Germany) made of a reinforced polycarbonate, Brillant (Forestadent) consisting of polyoxymethylene (POM), and Envision (Ortho Organizers, San Marcos, California, USA) manufactured using a special thermoplastic polyurethane. The experimental brackets contained UDMA as a monomer matrix and functional silane-treated $SiO_2$ fillers with a filler content of 10 (Exper 1) and 40 (Exper 2) vol per cent. All investigated plastic brackets differed in the polymer type and the experimental brackets in the filler content.

### *Manufacture of experimental brackets*

Initially, the composite mixtures were produced by hand-mixing the monomer and filler. In addition, the composite matrix was mixed in a Speed mixer device (Speed Mixer DAC 150FVZ, Hauschild Engineering, Hamm, Germany) for 60 seconds (1800 rpm) to a homogenous mixture. To avoid premature polymerization, the manufactured composites were stored in opaque receptacles.

After preparation, the bracket polymers were carefully placed in a mould made of a silicone impression of an upper central incisor bracket. Polymerization was carried out using a polymerization device (Targis-Power-Lichtofen; Ivoclar-Vivadent AG, Schaan, Lichtenstein) for 25 minutes. After polymerization, the brackets were taken out of the silicone mould and the composite surplus was removed with a scalpel. Twenty brackets per group were produced.

### *Electron beam irradiation*

Ten brackets of each group were electron beam post-cured. This process was carried out using a Rhodotron electron accelerator (Figure 1, BGS beta gamma service, Bruchsal, Germany). The brackets were transported on a conveyor belt ($v$ = 5 m/minute; scan width = 100 cm; scan distance = 90 cm) resulting in an irradiation time of 2 seconds/ specimen. The acceleration voltage of the electron beam device was 10 MeV and the energy dose 100 kGy.

The irradiated specimens were stored before and after electron beam irradiation for 7 days in distilled water at 37°C, prior to measurement. A control group was kept in distilled water at 37°C for 14 days to ensure identical storage conditions for all groups.

### *Vickers hardness*

For measuring hardness, the brackets were placed in a VH measuring device B3212001 (Zwick, Ulm, Germany). This procedure was completed by a pyramid-shaped loading die with a weight of 0.5 kg. The loading time was set to 60 seconds. The pyramid-shaped indention that occurs in the polymer depends on the hardness of the resin. VH, which is proportional to the quotient of applied load and the area of the indention, was determined for each sample.

### *Colour measurement*

Colour measurements were carried out using a spectro-photometer (CM-C3500 Minolta Co. Limited, Tokyo, Japan) with a pin-hole diaphragm diameter of 3 mm according to the CIE *L*a*b**-system (Commission Internationale de l`Eclairage, 1976). A colour graph consisting of *L**, *a**, and *b** coordinates can be produced by means of mathematic transformations. The *L** parameter corresponds to the degree of lightness and darkness and the *a** and *b** values to the chroma, where $+a^*$ is red, $-a^*$ is green, $+b^*$ is yellow, and $-b^*$ is blue. It has been reported that a colour change ($\Delta E^*$) of 3.3 can be visually perceived (Ruyter *et al.*, 1987). Therefore, in this investigation, colour changes of $\Delta E^* \geq 3.3$ were considered not to be clinically acceptable. Calculation of the colour variation $\Delta E^*$ between two colour positions in 3D *L* a* b** colour space were as follows:

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

*Statistic and analysis*

Statistical analysis was performed by the Statistical Package for the Social Sciences (SPSS) for Windows 16.0 (SPSS Inc., Chicago, Illinois, USA) using the Wilcoxon test. Medians and standard deviations were calculated. The significance level was set at $\alpha = 0.05$.

## Results

The median values and standard deviations for the studied brackets are shown in Table 1.

With the exception of the Brillant brackets, all brackets revealed a significant enhancement of VH after electron beam post-curing (Figure 2). The highest VH values were measured for the Exper 2 brackets (Table 1, Figure 2). The hardness increased from 20.80 ± 1.17 (untreated control group) to 22.4 ± 1.03 after electron beam irradiation. Brillant brackets showed a significant decrease of VH after post-curing ($P$ = 0.005, Table 2). The VH of Brillant brackets was reduced from 22.17 ± 1.43 (untreated control group) to 18.47 ± 0.73 after post-curing (Table 1).

The results of discolouration $\Delta E$ are illustrated in Figure 3. All brackets showed a significant increase of $\Delta E$ values. Aesthetik-Line brackets demonstrated the greatest $\Delta E$ and Exper 2 brackets the lowest ΔE values. Discolouration of the brackets differed significantly ($P \leq 0.017$, Table 3).

**Table 1** Median values and standard deviation of Vickers hardness and discolouration, $\Delta E$.

| | Vickers hardness | | Discolouration $\Delta E$ |
|---|---|---|---|
| | Irradiated | Control group | |
| Aesthetik-Line | 14.15 ± 0.38 | 13.61 ± 0.61 | 7.30 ± 0.09 |
| Brillant | 18.47 ± 0.73 | 22.17 ± 1.43 | 5.30 ± 0.26 |
| Envision | 15.26 ± 0.70 | 13.98 ± 0.37 | 6.05 ± 0.18 |
| Exper 1 | 14.90 ± 0.85 | 12.25 ± 0.86 | 7.10 ± 0.17 |
| Exper 2 | 22.4 ± 1.03 | 20.80 ± 1.17 | 2.95 ± 0.10 |

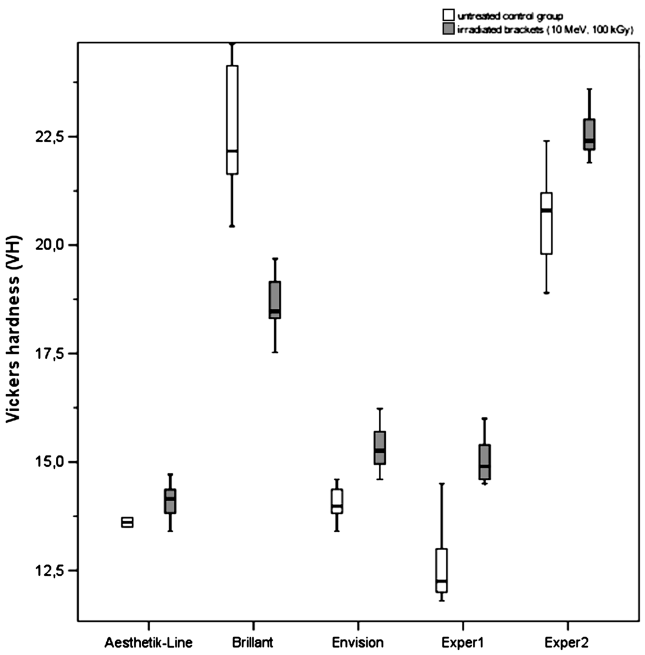


**Figure 2** Vickers hardness of the tested polymer brackets (median, 25 and 75 per cent percentiles).

**Table 2** Statistical analysis of irradiated brackets compared with untreated control groups; Wilcoxon test, $P$ values.

| | Vickers hardness |
|---|---|
| Aesthetik-Line | 0.028 |
| Brillant | 0.005 |
| Envision | 0.005 |
| Exper 1 | 0.005 |
| Exper 2 | 0.005 |

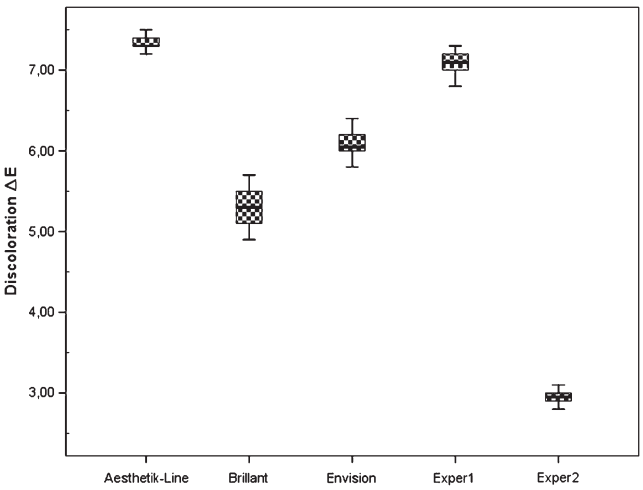


**Figure 3** Discolouration ($\Delta E$) of the tested polymer brackets (median, 25 and 75per cent percentiles).

**Table 3** Statistical analysis of discolouration $\Delta E$ for the different bracket groups.

| | Aesthetik-Line | Brillant | Envision | Exper 1 | Exper 2 |
|---|---|---|---|---|---|
| Aesthetik-Line | — | 0.005 | 0.005 | 0.017 | 0.04 |
| Brillant | | — | 0.005 | 0.005 | 0.005 |
| Envision | | | — | 0.005 | 0.005 |
| Exper 1 | | | | — | 0.005 |
| Exper 2 | | | | | — |

Evaluation of different bracket groups; Wilcoxon test, $P$ values.

## Discussion

Electron beam irradiation is widely used in industrial products such as machine bodies, cars, and insulators. Polyethylene, polystyrene, and polycarbonate are the most commonly irradiated polymers. However, until now, electron beam irradiation of polymers has not been used in dentistry. Electron beam irradiation is reported to increase the stiffness of polymers as well as the links between polymer chains (Behr *et al.*, 2006). Two types of irradiation-initiated reaction can be defined: chain linkage and chain breakage. Which mechanism dominates depends on several parameters, for instance the structure of the polymer, the energy dose, and residual double bonds (Ungar, 1981; Seguchi *et al.*, 2002; Behr *et al.*, 2005a). During chemical reaction, radicals, which induce chain linkage, are initiated from several distinct points. The polymeric chain then increases, but the chain linkage is not equally distributed in the polymer. It has been demonstrated that irradiation initiates the radical build-up of all components of a polymer (Behr *et al.*, 2006). For that reason, the entire polymer may simultaneously be newly arranged and crosslinked when irradiated.

Only a few studies could be found in general dentistry concerning electron beam post-curing of polymers and composites (Haque *et al.*, 2001; Behr *et al.*, 2005a,b,c, 2006; Faltermeier *et al.*, 2007a). It was reported by Haque *et al.* (2001) that electron beam irradiation is able to enhance the mechanical properties of Bis-GMA and UDMA because of an increased degree of crosslinking in the polymeric structure. Nevertheless, polymethyl methacrylate (PMMA) is often described in the literature as a thermoplastic polymer, which tends towards chain breakage during irradiation (Behr *et al.*, 2005b,c). It has been demonstrated that the mechanical properties of mostly PMMA-based denture resins could be improved using electron beam irradiation, although the measured mechanical improvements were low. However, the colour change was not clinically acceptable. Behr *et al.* (2005c) reported that the changes of the mechanical properties of dental PMMA systems appears to be so low that the expenditure of energy and costs do not justify the use of electron beam post-curing for dental PMMA.

Nevertheless, the same authors investigated the influence of electron beam post-curing on dental composites (Behr *et al.*, 2005b). Different composites were examined after electron beam irradiation using increasing energy doses. Those authors found that irradiation caused a significant change in the mechanical properties. In another study, the influence of electron beam irradiation on alloy-to-resin bond strength was examined. The conclusion was that thiol-phosphate primers in combination with electron beam post-curing could considerably enhance the bond between resins and titanium or cobalt–chromium alloys (Behr *et al.*, 2005a).

Analysis of the data in the present study offers some insight into the influence of electron beam post-curing on polymer brackets. Brillant brackets, consisting of POM, showed a significant decrease of VH after electron beam irradiation compared with all other groups. This indicates that not all polymer brackets can be improved using high-energy irradiation. Brillant brackets demonstrated the highest hardness values in comparison with non-irradiated polymer brackets. POM does not seem to benefit from electron beam post-curing. It appears that during irradiation, C–C bonds are split off and the polymeric structure starts to break down. The findings of the present study demonstrate that all the investigated brackets differed in their mechanical properties. Electron beam post-curing caused an improvement of VH of Envision brackets (polymer: polyurethane), Aesthetik-Line brackets (polymer:polycarbonate), and Exper 1 and Exper 2 brackets (polymer: UDMA). With the exception of the Exper 2 brackets, which were highly filled with functional silane-treated $SiO_2$, all brackets showed reduced mechanical properties because of their polymeric structure. Polyurethane, polycarbonate, and UDMA brackets could be improved using electron beam irradiation. It could be assumed that electron beam post-curing results in additional crosslinking and an enhanced molecular mass of polycarbonate, polyurethane, and UDMA based brackets, which cause a newly branched 3D network. The UDMA based bracket, Exper 2, revealed high VH values before and after electron beam irradiation. This was attributed to the functional silane-treated $SiO_2$ fillers with a filler content of 40 vol per cent. (Jaarda *et al.*, 1996; Condon and Ferracane, 1997; Peutzfeldt and Asmussen, 2000).

While the mechanical properties of some polymer brackets may be improved by irradiation, clinical use might be restricted because of the observed colour changes. Nevertheless, the exact process of inducing discolouration during irradiation of polymers is still unknown (Behr *et al.*, 2005b). The reason for the discolouration of the polymer brackets could be that during the irradiation process, chain breakage of the polymers occurs. During chain breakage, C–C bonds are split off and some structureless and unreacted arrangements remain in the lattice that may cause discolouration. Behr *et al.* (2005c) also noted that colour centres occur in crystalline regions. They consist of anion defects in the lattice and linked surplus electrons. The discolouration also depends on the polymeric structure. With the exception of Exper 2, all brackets showed clinically unacceptable colour changes. A colour change of $\Delta E$ of 3.3 was considered visually perceptible according to the descriptions of Ruyter *et al.* (1987) and therefore clinically unacceptable. Exper 2 showed clinically acceptable colour changes. This could be due to the fact that Exper 2 was highly filled with inorganic $SiO_2$ fillers (40 vol%). This inorganic content cannot be influenced by changes of the polymeric structure during irradiation (Khokhar *et al.*,

1991; Dietschi *et al.*, 1994; Leibrock *et al.*, 1997). Therefore, fillers may have a buffering effect on the polymeric structure during electron beam irradiation. The colour changes imply that electron beam irradiation of polymer brackets may result in an unfavourable clinical appearance. Almost all brackets appeared yellower after electron beam irradiation. The cause of this yellow discolouration has been systematically investigated by Ferracane (1995) who identified that yellowing of the polymer is accompanied by a reduction in the quantity of residual unreacted double bonds in the resins. A possible explanation for the yellowing could be oxidation of the unreacted "C=C" to produce coloured peroxide compounds (Ferracane, 1995).

## Conclusions

The findings of the present study demonstrate that the mechanical properties of polymer brackets can be modified by electron beam irradiation. Electron beam post-curing causes an additional crosslinking and enhanced molecular mass in polycarbonate, polyurethane, and UDMA based brackets. However, clinical use of electron beam post-curing might be restricted because of clinically unacceptable colour changes.

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