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Experimental composites made of electron beam irradiated reinforced fillers

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Abstract This study investigated the influence of electron beam irradiated reinforced fillers on the three body wear and flexural strength of experimental composite blends. Three formulations of reinforced fillers were investigated: (A) high loaded inorganic filler composite with 60 wt.% SiO_2, (B) low loaded inorganic filler composite with 40 wt.% SiO_2, (C) organic filler composite (precipitated Bis-phenol-A-di-methacrylate). The fillers were assigned to two subgroups of unswollen (A, B, C) and monomer swollen (A_s, B_s, C_s) fillers. The experimental blends (matrix: Urethane-dimethacrylate) were mixed using un-treated, annealed (90 °C), or electron beam irradiated fillers with 30 and 90 kGy, respectively. All specimens were heat-cured for 20 min at 140 °C. Three-body abrasion and flexural strength tests were performed. The highest flexural strength was evaluated for composites made of the 30 kGy irradiated type B_s filler. The comparison with annealed fillers showed that the effect was independent of increasing temperatures during the radiation process. Blends with a SiO_2 content of 60 wt.% (type A, A_s) had significantly less wear than blends with 40 wt.% (type B, B_s) or blends with organic fillers (type C, C_s). The flexural strength of the composite could be improved by using pre-irradiated reinforced fillers. However, wear was not affected using this procedure.

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1 Introduction

Composites for fillings, facings, cements or core built-ups are successfully used in dentistry [1]. However, the success rate of composite restoration drops when this material is used in extended occlusal posterior areas [2]. Fractures of facings and occlusal wear have been reported to be one of the key problems with larger composite restorations [3].

The mechanical properties of a composite depend on its main components: fillers and matrix [4]. The filler type, size, filler content and the interaction of filler resin matrix determines properties such as fractures or wear. Further influence is provided by the matrix [5]. Different monomer blends have been chosen and mixed to increase, for example, fracture toughness or wear. Special curing methods using heat, light, pressure or curing under atmospheric N_2 have been developed to enhance the conversion rate of the carbon double bonds in order to strengthen the composites [5].

The clinical experience demonstrates that these efforts do not result in a satisfying fracture or wear behaviour of composite crown or FPD restorations in the long term [1–3]. However, it has been demonstrated that the post-curing of dental composites using electron beam irradiation significantly increased fracture toughness and significantly reduced the wear of facing composites [6]. This method is only economic for plastic parts in mass production and unfortunately all dental restorations are individually fabricated. How can dentistry benefit from the favourable properties of electron beam irradiation on composites? We hypothesize that instead of post-curing, the raw materials of a composite should be irradiated. Then, a new composite blend with improved mechanical properties may be mixed.

Modern composites consist of pre-treated fillers [4, 5]. Because of the high surface area of micro fillers (100–300 m^2/g), only 25% of the initial volume can be added in one step to the monomer matrix. Therefore, the fillers are polymerised with monomers and ground to particles of 10–20 μm in diameter. These reinforced fillers are again added to the monomer and increase the inorganic content up to 40–60% by volume or about 60–70% by weight [4]. The mixing procedure of high-loaded composites works easier if monomer-swollen reinforced fillers are used. It is assumed that in swollen-filler loaded networks the entropy of mixing is reduced or diminished within the boundary layers of the filler particles [7]. These pre-treated fillers (swollen or not) are susceptible to irradiation. Generally, two types of competing reactions occur with electron beam irradiation: chain linkage or breakage [8, 9]. Charlesby and Ross stated in 1953 that “the degree of cross-linking produced in these polymers is proportional to the radiation dose over a wide range of values, so that it is possible to prepare specimens of any required degree of cross-linking without the introduction of foreign atoms or heat treatment” [8, 9]. In order to prove the hypothesis that the irradiation of raw materials of composite blends can improve the fracture toughness and three-body abrasion, experimental composite blends with different types of reinforced fillers were investigated. Two “inorganic reinforced filler types” with high and low content silica and an “organic reinforced filler type” were chosen. As a result of the 80–90 °C heat, which occurs during the irradiation process, a control with tempered fillers and a control with non-irradiated fillers was compared with two groups of irradiated fillers at a dose rate of 30 and 90 kGy, respectively.

2 Material and methods

Three formulations of reinforced fillers were chosen (Table 1a–c):

(A) High loaded inorganic reinforced filler:
  Type A Urethane-dimethacrylate based filler with 60 wt.% of SiO_2
  Type $A_{swollen}$ Urethane-dimethacrylate based filler with 60 wt.% of SiO_2

(B) Low loaded reinforced inorganic filler:
  Type B Urethane-dimethacrylate based filler with 40 wt.% of SiO_2
  Type $B_{swollen}$ Urethane-dimethacrylate based filler with 40 wt.% of SiO_2

(C) Organic reinforced filler:
  Type C precipitated Bis-phenol-A-dimethacrylate
  Type $C_{swollen}$ precipitated Bis-phenol-A-dimethacrylate

Type A_s fillers were allowed to swell in 10% Decanediol-dimethacrylate, type B_s in 10% Butanediol-dimethacrylate and type C_s in 23% Bis-phenol-dimethacrylate for 6 h at 60 °C.

The six different filler groups were assigned to four subgroups each. Group one was the untreated control. Fillers of group two were annealed for 19 days at 90 °C. Group three and four fillers were irradiated at 30 and 90 kGy dose rates, respectively, in intervals of 30 kGy (2 s, 10 MeV, beam current 10 mA, scan width 100 cm, scan distance 90 cm, v = 5 m/min) using a Rhodotron electron beam accelerator (BGS beta gamma service, Saal a.D., G).

Composite blends were mixed in vacuum using a kneader mixer (Ivoclar-Vivadent, Schaan, FL). The monomer was uniformly Urethane-dimethacrylate for all blends (Table 1a–c). The filler weight content was 70%. With these blends, constructed specimens were all heat-cured for 20 min at 140 °C and 5.5 bar N_2 atmosphere (73 psi) in a HiPT-Heat and Pressure device (Ivoclar-Vivadent Technical, Amherst, NY, USA).

2.1 Flexural strength test

Rectangular specimens (n = 10 per group) of 25 mm length, 2 mm width and 2 mm height were constructed using a steel mould. They were stored for 24 h at 37 °C in distilled water. A three-point bending test was conducted using a universal testing machine, Zwick 1446 (Zwick, Ulm, G), following ISO 10477. The rounded supports (diameter: 2 mm) were 20 mm apart. The pressure pane (radius 2 mm) hit the composite beam at a crosshead speed of 1 mm/min.

2.2 Three-body abrasion test

A three-medium wear test device (Willytec, Munich, G) was used according to the description of DeGee [10]. Composite specimens of 3 mm thickness were adhesively mounted on sample wheels. They were reduced using a truing device until the wheel had a diameter of 50 mm. After grinding-in the sample wheel, following the manufacturer’s instructions, it was set at 60 rpm and the

Table 1 Formulation of composite pastes (a) A and A$_s$, (b) B and B$_s$, (c) C and C$_s$

(a) Paste A		
Filler:	4 g	Degussa Hanau, G,
Aerosil 200 silanized by Ivoclar (Batch ZZ3294)		Ivoclar, Schaan, FL
Monomer:	37 g	Ivoclar, Schaan, FL
700 g Urethane-dimethacrylate		Peroxid-Chemie GmbH, G
300 g Decanediol-dimethacrylate		
10 g TBPEH (Tert-butylperoxy-2-ethylhexanoate) (Batch E 07617)		
Reinforced filler (prepolymer):	79 g	Ivoclar, Schaan, FL
Polymerized and grinded polymer based on 120 g Decanediol-dimethacrylate		
474 g Urethane-dimethacrylate		
6 g Benzpinacol and inorganic filler: pyrogenic SiO_2 (60 wt. %)		
Paste A$_s$		
Filler:	4 g	Degussa Hanau, G,
Aerosil 200 silanized by Ivoclar (Batch ZZ3294)		Ivoclar, Schaan, FL
Monomer:	28 g	Ivoclar, Schaan, FL
700 g Urethane-dimethacrylate		Peroxid-Chemie GmbH, G
300 g Decanediol-dimethacrylate		
10 g TBPEH (Tert-butylperoxy-2-ethylhexanoate) (Batch E 07617)		
Reinforced filler (prepolymer):	88 g	Ivoclar, Schaan, FL
Polymerized and grinded polymer based on 120 g Decanediol-dimethacrylate		
474 g Urethane-dimethacrylate		
6 g Benzpinaccol and inorganic filler: pyogenic SiO_2 (60 wt %) swollen with Decanediol-dimethacrylate		
(b) Paste B		
Filler:	4 g	Degussa Hanau, G,
Aerosil 200 silanized by Ivoclar (Batch ZZ3294)		Ivoclar, Schaan, FL
Monomer:	37 g	Ivoclar, Schaan, FL
700 g Urethane-dimethacrylate		Peroxid-Chemie GmbH, G
300 g Decanediol-dimethacrylate		
10 g TBPEH (Tert-butylperoxy-2-ethylhexanoate) (Batch E 07617)		
Reinforced filler (prepolymer):	79 g	Ivoclar, Schaan, FL
Polymerized and grinded polymer based on 120 g Decanediol-dimethacrylate		
474 g Urethane-dimethacrylate		
6 g Benzpinacol and inorganic filler: pyogenic SiO_2 (40 wt %)		
Paste B$_s$ (PD 468–471)		
Filler:	4 g	Degussa Hanau, G,
Aerosil 200 silanized by Ivoclar (Batch ZZ3294)		Ivoclar, Schaan, FL
Monomer:	28 g	Ivoclar, Schaan, FL
700 g Urethane-dimethacrylate		Peroxid-Chemie GmbH, G
300 g Decanediol-dimethacrylate		
10 g TBPEH (Tert-butylperoxy-2-ethylhexanoate) (Batch E 07617)		
Reinforced filler (prepolymer):	88 g	Ivoclar, Schaan, FL
Polymerized and grinded polymer based on 120 g Decanediol-dimethacrylate		
474 g Urethane-dimethacrylate		
6 g Benzpinacol and inorganic filler pyogenic SiO_2 (40 wt %) swollen with Butanediol-dimethacrylate		
(c) Paste C		
Filler:	3 g	Degussa Hanau, G,
Aerosil 200 silanized by Ivoclar (Batch ZZ3294)		Ivoclar, Schaan, FL

Table 1 continued

Monomer:	69 g	Ivoclar, Schaan, FL
700 g Urethane-dimethacrylate		Peroxid-Chemie GmbH, G
300 g Decanediol-dimethacrylate		
10 g TBPEH (Tert-butylperoxy-2-ethylhexanoate) (Batch E 07617)		
Reinforced filler (prepolymer):	17 g	Ivoclar, Schaan, FL
Precipitated Bis-phenol-A-di-methacrylate		
Paste C_s		
Filler:	3 g	Degussa Hanau, G,
Aerosil 200 silanized by Ivoclar (Batch ZZ3294)		Ivoclar, Schaan, FL
Monomer:	69 g	Ivoclar, Schaan, FL
700 g Urethane-dimethacrylate		Peroxid-Chemie GmbH, G
300 g Decanediol-dimethacrylate		
10 g TBPEH (Tert-butylperoxy-2-ethylhexanoate) (Batch E 07617)		
Reinforced filler (prepolymer):	24 g	Ivoclar, Schaan, FL
Precipitated Bis-phenol-A-di-methacrylate swollen with Bis-phenol-dimethacrylate		

Table 2 Mean and standard deviation of flexural strength values (Mpa)

Groups	Control	Annealed	30 kGy	90 kGy	↔
A	105.5 ± 8	96.3 ± 2.9	107.6 ± 6	87.9 ± 7	n.s.
A_s	109.2 ± 8	46.3 ± 7	104.6 ± 3	–	$p < 0.000$
B	116.8 ± 13	86.2 ± 8	119.3 ± 15	96.9 ± 6	$p = 0.008$
B_s	99.5 ± 18	55.4 ± 4	133.7 ± 9	93.0 ± 15	p < 0.000
C	101.1 ± 8	102.2 ± 14	97.9 ± 11	100.5 ± 15	n.s.
C_s	84.9 ± 24	110.5 ± 13	106.2 ± 11	96.1 ± 17	n.s.
↕	n.s	$p < 0.000$	$p = 0.008$	n.s.	

p-values ANOVA. Row 6: horizontal comparison inside a group (e.g. A or A_s). Line 7: vertical comparison between different treatment methods of the fillers

antagonist wheel was set at 130 rpm. The antagonist wheel moved counterclockwise and had a press-on load of 15 N. The abrasion medium was mixed with 275 mL of distilled water, 120 g of rice and 30 g of millet sheets, which were cut for 60 s in a Moulinette-cutter (Moulinex, Alencon, F). A total of 200,000 cycles were carried out. The abrasion medium was replaced every 50,000 cycles [10]. The smaller antagonist wheel provided a wear track on the sample wheel. The depth of this wear track (μm) was determined using the Profilometer Perthen S6P (Perthen-Mahr, Göttingen, G).

2.3 Statistics

Mean and standard deviation were calculated. Statistical differences were investigated using the ANOVA and Tukey tests. The level of significance was set at $\alpha = 0.05$.

3 Results

The highest flexural strength showed blends made of filler type B_s, which were irradiated at 30 kGy (Table 2). Blends with annealed fillers had the lowest flexural strength. This effect was significantly lower for blends mixed with swollen annealed fillers.

The highest amount of wear was observed for composites mixed with annealed fillers (Table 3). However, only the swollen fillers type A_s showed a statistically higher wear rate relative to other filler treatment methods.

The results demonstrated that the amount of three-body abrasion increased with decreasing amounts of inorganic SiO_2 filler. Blends with a SiO_2 content of 60 wt.% (type A, A_s) had significantly less wear than blends with 40 wt.% (type B, B_s) or blends with organic fillers (type C, C_s).

Table 3 Mean and standard deviation of three-body abrasion values (μm)

Groups	Control	Annealed	30 kGy	90 kGy	↔
A	72.5 ± 20	72.3 ± 20	73.5 ± 20	73.1 ± 21	n.s.
A_s	70.9 ± 26	96.4 ± 28	78.5 ± 26	–	$p = 0.005$
B	107.3 ± 36	114.4 ± 34	113.1 ± 36	113.8 ± 32	n.s.
B_s	114.8 ± 33	122.7 ± 49	109.9 ± 47	113.3 ± 44	n.s.
C	136.8 ± 57	145.2 ± 59	144.3 ± 57	139.8 ± 56	n.s.
C_s	134.9 ± 55	140.6 ± 55	110.2 ± 47	157.1 ± 71	n.s.
↕	$p = 0.01$	$p = 0.013$	$p = 0.025$	$p = 0.019$	

p-values ANOVA. Row 6: horizontal: comparison inside a group (e.g. A or A_s). Line 7 vertical: comparison between different treatment methods of the fillers

4 Discussion

The filler/matrix interaction of a composite determines its clinical behaviour. The more efficient the bond works between filler and matrix, the greater the constraint of the matrix, the higher the net modulus, and the higher the strength of the entire composite [5]. This filler/matrix bond can be enhanced using silane coupling agents [11]. Silanes are able to form durable bonds between organic and inorganic materials [11]. A silane coupling agent typically displays two classes of functionality. One side is hydrolysable. Following hydrolysis, a reactive silanol group is formed, which condenses with other silanol groups on the surface of siliceous fillers, to form siloxane linkages. The other side of the coupling agent is a non-hydrolysable organic group that reacts with the matrix [11]. The silane coupling agent should coat the entire filler surface with a monolayer. However, the image of a single inorganic particle surrounded by a thin silane layer is far from reality. Agglomeration of the fillers occurs and multi layers of the coupling agent frequently exist.

Another problem with composites is the mixing procedure of matrix and fillers. Because of the high surface area of micro fillers, reinforced fillers are added to the monomer again and therefore increase the inorganic content [4]. The powder of these reinforced fillers will have multiple flaws: (i) agglomerated fillers, which are not coated by the matrix, (ii) the conversion rate of the carbon double bonds in the matrix may be poor, and (iii) only few bonds between the inorganic particles, coupling agents and oligomers are existing. Therefore, a procedure that reduces these flaws is important.

During electron beam irradiation, reinforced fillers achieve a high energy dose for a few seconds. We hypothesize that this energy alters the reinforced fillers. The changes may hit the polymer matrix or the interface of fillers and matrix. The applied electrons are able to convert residual non-reacted carbon double bonds and enhance the conversion rate of polymers. Furthermore, radiation alters polymerized polymers. Seguchi et al. [12] has mentioned that amorphous polymers contain chain entanglements. If chain breakage occurs during irradiation at the entanglement, a molecular arrangement induces more dense packing and therefore changes the resin properties.

Ray and Bhowmick [13] has demonstrated using atomic force micrographs and dynamic mechanical analysis that irradiation of silanized silica fillers improves their hydrophobicity and reduces their surface polarity, which reduces the tendency of silica fillers to form agglomerates. The investigation of Ray and Bhowmick [13] shows that the storage modulus was lower in electron beam irradiated and silanized silica filled compounds as compared to non-irradiated controls with identical filler content.

This phenomenon is attributed to the breakdown of the filler network under dynamic strain. The high storage modulus of the untreated controls at very low strain implies the presence of a highly aggregated filler network, which breaks down with increasing strain. The phenomenon of filler structure breakdown depends on two factors: (i) filler content, (ii) applied strain level. At high filler contents, the applied strain may not be sufficient enough to break down the filler structure to the same extent that it does at very low filler contents. In this investigation, all blends had a comparable filler content of 70 wt.%. This high filler content may explain why there were (with one exception) no significant differences in flexural strength values observed between controls and the irradiated groups. A recent investigation using a lower filler content of 20 and 30%, respectively, demonstrated substantial flexural strength differences between irradiated and non-irradiated specimens [14].

When the temperature of fillers was measured immediately after the radiation process, they had a temperature of 80–90 °C. It was therefore assumed that the changes observed with irradiation depend only on the heat, which is released during radiation. However, blends of annealed fillers (90 °C) demonstrated the lowest flexural strength values. Particular swollen annealed fillers had significant lower strength values than the 30 kGy irradiated specimens, which indicates that radiation itself had an effect, which is independent of the applied heat. However, swollen type B fillers only benefit from irradiation. All other blends showed no significant difference after irradiation.

Due to the high filler content, the fillers support each other during the bending test, while the influence of the filler/matrix interaction remains negligible.

The influence of the filler content was also demonstrated in the three body abrasion test. Blends of type A with 60 wt.% of silica had substantially lower wear rates than the blends of type B with 40 wt.% of the identical filler or blends with the organic filler type C. Even under the assumption that the filler/matrix interaction may be improved by irradiation, this effect did not contribute to a lower wear rates. This study indicates that the content of inorganic reinforced fillers had a superior influence on three body abrasion than the effect of radiation or tempering. As a result, we reject the hypothesis that composite blends of electron beam irradiated raw materials have reduced three body abrasion.

5 Conclusion

(i) Pre-irradiation (30 kGy) of swollen inorganic reinforced fillers with 40 wt.% SiO_2 can enhance the flexural strength of composites.
(ii) The irradiation effect is independent of the heat applied during the radiation process.
(iii) In this study, the filler content was more important on the wear behaviour of experimental composites relative to the radiation effect.

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