Effect of Particulate Nanofillers on the Surface Microhardness of Glass-Fibre-Reinforced Filling Composite Resin

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Objective: *To evaluate the effect of different particulate nanofiller fractions on the surface microhardness of short glass-fibre reinforced semi-IPN polymer matrix composite resin.*

Methods: *Experimental composite resin (FC) was prepared by mixing 22.5 wt% of short E-glass fibres (3 mm in length) to 22.5 wt% of resin matrix with various weight fractions of nanofillers (0, 10, 20, 30, 40, 50 wt%) and then 55 wt% of silane-treated silica filler was gradually added using a high-speed mixing machine. Three filling composite resins (Z250, Grandio and Nulite), resin-modified glass ionomers (Fuji II LC), amalgam (ANA 2000), fibre-reinforced composite (FRC; everStick and Ribbond), and prefabricated ceramic filling insert (Cerana class 1) were tested in this study. Enamel and dentine were used as controls. The specimens (n = 3 per group) were polished and water-stored at 37°C for 24 h before testing. A universal testing machine was used for testing Vickers microhardness. All results were analysed statistically with one-way analysis of variance (ANOVA).*

Results: *ANOVA revealed that nanofiller fraction had a significant effect ($P < 0.05$) on the Vickers microhardness of the short-fibre composite resin. No statistically significant difference was found between FC composite resin and conventional filling composite resins (Nulite and Z250) ($P > 0.05$). Ribbond FRC had a lower surface microhardness than everStick FRC ($P < 0.05$).*

Conclusion: *The use of high nanofiller fraction with short-fibre fillers in IPN polymer matrix yielded increased surface microhardness.*

Key words: *surface microhardness, nanofillers, fibre composite resin, filling materials*

Since the first dental resin composites were developed, many efforts to improve their clinical performance have been undertaken[1]. Research on resin matrix is mainly based on the development of new monomers, whereas studies on the filler content focus on loading[2], particle size, and silanation[3]. Such studies are of high importance because the mechanical properties and polymerisation shrinkage depend highly on the concentration and particle size of the filler. However, further significant improvements are still needed in order to use composite resins safely in posterior restorations. Filler technology has led to the development of composite resins characterised by containing zirconia or silica nanoparticle fillers of approximately 25 nm size and nanoaggregates of approximately 75 nm size.

Glass fibres for reinforcing dental polymers have been investigated for over 30 years[4]. They have documented reinforcing efficiency and good aesthetic qualities compared with carbon or aramid fibres[5]. The effectiveness of fibre reinforcement is dependent on many

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variables, including the resins used, the quantity of fibres in the resin matrix[6,7], the length of the fibres[6], the form of the fibres[8], the orientation of the fibres[9], the adhesion of the fibres to the polymer matrix[10], and the impregnation of the fibres with the resin[11]. Short, random fibres provide an isotropic reinforcement effect in multiple directions instead of just one or two directions, as described by Krenchel[12].

Poly(methyl methacrylate) (PMMA) and dimethacrylate-based semi-interpenetrating polymer network (semi-IPN) matrix has been established as a polymer matrix in denture base materials[13]. Also, some products of fibre-reinforced composite (FRC) use semi-IPN polymer in the matrix[14].

Early experiments on the use of experimental semi-IPN matrix in combination with short E-glass fibres in restorative filling composite show enhancement in mechanical properties and load-bearing capacity[15,16]. However, dental restorative composite resins with semi-IPN polymer matrix in combination with short glass fibres and particulate nanofillers have not been evaluated to our knowledge.

One important physical property of a restorative material is surface hardness[17]. The hardness of a material is a relative measure of its resistance to indentation or penetration when a specific, constant load is applied. It has been reported that microhardness is an adequate indicator of the degree of conversion or polymerisation of composite resin. The degree of polymerisation may be related to the clinical performance of resin restorative materials.

Therefore, the objective of the study was to provide an experimental filling material that combines short glass fibre, semi-IPN and nanofiller technologies. Specifically, this study investigates the effect of nanofiller fraction on surface hardness of glass-fibre-reinforced filling material. In addition, the surface hardness of different commercial restorative materials has been evaluated.

Materials and Methods

Materials

Eight commercial restorative materials (three filling composite resins, resin-modified glass ionomers [RMGIs], amalgam, two fibre-reinforced composites and prefabricated ceramic filling insert) were tested in this study. They are listed in Table 1.

Dimethacrylate (bisphenol A-glycidyl dimethacrylate [BisGMA] 67% and triethyleneglycol dimethacrylate [TEGDMA] 33%) resin consisting of nanofillers (SiO_2, 20 nm in size) of various weight fractions (Hanse Chemie, Germany) (Table 2) and E-glass fibres with BisGMA–PMMA (MW 220,000) resin matrix (everStick, StickTech Ltd, Turku, Finland) were used. In addition, radio-opacity fillers of $BaAlSiO_2$ (3 ± 2 μm in size; Specialty Glass, USA) were incorporated in the resin system. Before the $BaAlSiO_2$ filler particles were incorporated into the resin matrix, they were silane treated using a previously defined technique[18]. Enamel and dentine were used as control groups.

Methods

Experimental fibre composite (FC) resins were prepared by mixing 22.5 wt% of short E-glass fibres (3 mm in length and 15 μm in diameter) to 22.5 wt% of resin matrix with various weight fractions of nanofillers (0, 10, 20, 30, 40, 50 wt%) and then 55 wt% of $BaAlSiO_2$ radio-opacity fillers were added gradually to the mixture. The classification of the experimental test groups according to the various filler contents is given in Table 2. The mixing was carried by using a high-speed mixing machine for 5 min (SpeedMixer, DAC, Germany, 3,500 rpm). The dimethacrylate-based resin matrix with PMMA forms a semi-IPN polymer matrix for the composite resin of FC.

Five specimens for each material (2 mm thickness ring with a diameter of 6.5 mm) were photo-polymerised for 40 s using a light source with an irradiance of 800 mW/cm^2 (Optilux-500, Kerr, CT, USA). After polymerisation, specimens were polished (grit up to 4,000 FEPA) at 300 rpm under water cooling using an automatic grinding machine (Struers Rotopol-11, Copenhagen, Denmark). Specimens were water stored for 24 h at 37°C before testing. Microhardness measurements (10 points for each specimen) were carried out with universal Vickers device (wsDuramin, Struers). A load of 1.96 N was applied for 10 s on their surface. The length of the diagonal of each indentation was measured directly using a graduated eye-lens. The Vickers hardness number (VHN) is obtained using the following equation:

$$H = \frac{1854.4P}{d^2}$$

where H (kg/mm^2) is the Vickers hardness, P (g) is the load and d (μm) is the length of the diagonals[17].

The surface microhardness data were analysed statistically using analysis of variance (ANOVA) at the $P < 0.05$ significance level with SPSS (version 13, Statisti-

Table 1 Materials used in the study

Material	Manufacturer	Batch
FC	Experimental short fibre composite	
Z250	3M Dental Products, St Paul, MN, USA	20061003
Grandio	Voco, Cuxhaven, Germany	630615
Nulite	Hornsby NSW, Australia	021703
Fuji II LC	GC Corporation, Japan	540 1042
Amalgam(ANA 2000)	Nordiska Dental AB, Ängelholm, Sweden	95127-3468
everStick	StickTeck Ltd, Turku, Finland	2060727-ES-158
Ribbond	Ribbond Inc, Seattle, WA, USA	9541
Cerana class 1	Nordiska Dental AB, Ängelholm, Sweden	141002-26XL

Table 2 Classification of fibre composite resin test groups used in the study according to their filler content and composition (n = 3, per group)

Group	Fibres (wt%)	Nanofillers (wt%) in the resin matrix/resin mixture (22.5 wt%)	Micrometre-scale fillers (wt% of the resin–nanofiller–fibre mixture)
FC0	22.5	0/22.5	55
FC1	22.5	10/22.5	55
FC2	22.5	20/22.5	55
FC3	22.5	30/22.5	55
FC4	22.5	40/22.5	55
FC5	22.5	50/22.5	55

cal Package for Social Science, SPSS Inc, Chicago, IL, USA), followed by Tukey's post hoc analysis to determine the differences among the groups.

Results

The mean values of microhardness for the groups tested, with standard deviation, are summarised in Figs 1 and 2.

ANOVA revealed that nanofiller fractions had a significant effect ($P < 0.05$) on the microhardness of the short-fibre composite resin. No significant difference in the VHN was found between experimental FC composite resin (77 ± 13) having 50 wt% nanofillers (group FC5) and groups made from Nulite (71 ± 10), everStick (77 ± 16) and Z250 (82 ± 4) composite resins ($P > 0.05$) (Fig 2). The highest VHN value was obtained with specimens made from Cerana class 1 (466 ± 47), and specimens made from Ribbond had the lowest values (25 ± 8).

Discussion

Microhardness testing of materials appears to represent one of the most straightforward tests used for characterisation of restorative dental materials. It gives an indication of the resistance to penetration when indented by a hard asperity[19].

Recently, it has been shown that the use of a semi-IPN matrix in combination with short glass fibres in restorative filling composite resin has given encouraging results[15,16]. The use of semi-IPN matrix lowers the cross-linking density of the resin matrix, which leads to a decrease in the VHN of the composite resin. Incorporating nanofillers into composite resin reduces the fraction of the lower cross-link density monomers, leading to an increase in surface hardness. Thus, we hypothesised that using high-fraction nanofillers with short glass fibres and a semi-IPN resin matrix could improve the surface hardness of composite resins.

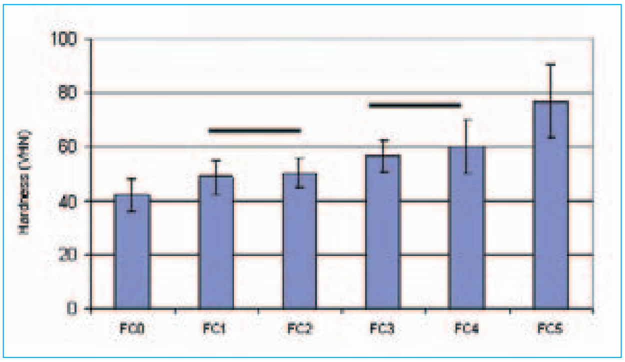

Fig 1 Mean surface microhardness of fibre composite resin tested groups with different weight fractions of nanofillers. Vertical lines represent standard deviations. Horizontal line above the bars indicates groups that do not differ statistically from each other.

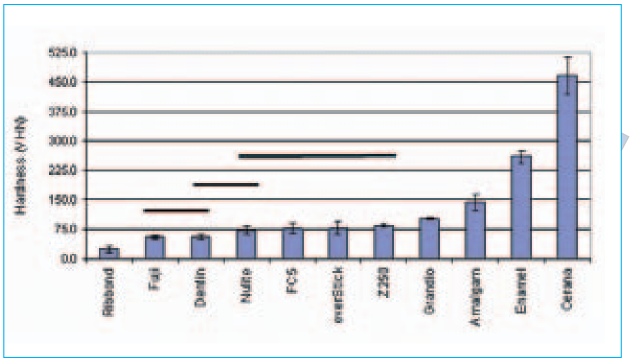

Fig 2 Mean surface microhardness of the materials tested. Vertical lines represent standard deviations. Horizontal line above the bars indicates groups that do not differ statistically from each other.

This study showed that the VHN increased by increasing the quantity of nanofillers (Fig 1). As apparent in Fig 2, there were significant differences between the VHN of different restorative materials. However, microhardness of short-fibre-reinforced composite resin was at the same level as the commercial hybrid composite resins (Nulite and Z250). On the other hand, Grandio showed a higher VHN than other composite resins because of the high filler content. In general, our results are in agreement with previous laboratory studies, which showed that composite materials with high filler loading resul-ted in increased surface hardness of the materials[17]. However, some of the differences could also be explained due to differences in the polymer matrices and the filler type materials we used. It was not a surprise that Cerana (prefabricated ceramic filling insert) had considerably higher VHN values than enamel, because the theoretical density of sintered alumina particles is around 98.8 vol%. Enamel is the hardest substance in the human body and consists of 92–96 vol% of relatively large hydroxyapatite crystals. On the other hand, human dentine is composed of only 45 vol% apatite minerals, distributed in an organic matrix of collagen fibre and fluid.

Ribbond (an ultra-high molecular weight polyethylene FRC) had a lower microhardness than everStick (electrical-glass FRC). It is likely this is due to inadequate interfacial adhesion between the fibres and the polymer matrix. It is also possible that the impregnation of the ultra-high molecular weight polyethylene fibres by the resin was inadequate. Vallittu has discussed these problems previously[20,21]. It is proposed that the combination of inadequate interfacial adhesion and inadequate impregnation may hinder stress transfer from the polymer matrix to the fibre reinforcements.

RMGIs showed lower VHN values than composite resins and was at same level to dentine. Since RMGIs contain a resin component, the surface of the sample will be resin rich due to filler particle migration towards the bulk of the material. This resin-rich layer often remains only partly polymerised due to the oxygen inhibition of polymerisation[22]. Previous studies have shown that RMGIs stored in water reached maximum surface hardness over 1 to 7 days and maintained this value for up to 1 year[22,23].

In order to simulate clinical conditions, aging processes, such as alternate thermal stress, mechanical stress, wear, and water storage, should also be taken into consideration. A clinical study reported by Van Dijken showed that a restorative composite resin (Nulite) with microfibres suffers extensive wear[24], which can be partly explained by the fibre length used being well below the critical fibre length. Using a fibre fragmentation test, it was found that the critical fibre length of E-glass in a BisGMA polymer matrix varies between 0.5 and 1.6 mm[25]. In order for a fibre to act as an effective reinforcement for polymers, stress transfer from the polymer matrix to the fibres is essential[26–28]. This is achieved by having a fibre length equal to or greater than the critical fibre length[26,28]. Therefore, the length of the fibres used as fillers in this study was chosen to be 3 mm, thus exceeding the critical fibre length. It is well known that the hardness of dental material is not useful to predict the abrasiveness of these products against human enamel. Thus, an *in vitro* wear evaluation of short glass-fibre composite resin with high nanofiller fraction and semi-IPN resin matrix will be evaluated in a further study.

Methodologically, one limitation of the present study is related to the testing of water-stored specimens after

1 day only. Several studies have already shown the influence of water saturation on the microhardness of composite resins and other materials[2]. In a previous study, we showed that water sorption of FC composite resin was similar to that of a conventional filling composite[15]. Water storage could decrease the surface hardness of the specimens. In the polymer matrix, water acts as a plasticiser, increasing free volume and decreasing the glass transition temperature of the polymer matrix[29,30]. It has also been reported previously that there is a potential deteriorative effect of water on the interfacial adhesion between the polymer matrix and the glass fibres through rehydrolysis of the silane coupling agent[29].

Based on the results of this study and our previous published data of short-fibre composite resin, it is suggested that experimental FC composite could be used successfully to fulfil the requirements for the ideal posterior restoration. However, it should be emphasised that clinical trials are necessary in order to evaluate the usefulness of FC composite resin in dental restorations.

Conclusion

E-glass FRC composite resin with a semi-IPN polymer matrix and nanofillers has similar microhardness values to conventional particulate filler restorative composite resins.

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