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Influence of nanometer scale particulate fillers on some properties of microfilled composite resin

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Abstract The aim of this study was to evaluate the effect of different weight fractions of nanometer sized particulate filler on properties of microfilled composite resin. Composite resin was prepared by mixing 33 wt% of resin matrix to the 67 wt% of silane treated microfine silica particulate fillers with various fractions of nanometer sized fillers (0, 10, 15, 20, 30 wt%) using a high speed mixing machine. Test specimens made of the composites were tested with a three-point bending test with a speed of 1.0 mm/min until fracture. Surface microhardness (Vicker's microhardness) was also determined. The volumetric shrinkage in percent was calculated as a buoyancy change in distilled water by means of the Archimedes principle. The degree of monomer conversion (DC%) of the experimental composites containing different nanofiller fractions was measured using FTIR spectroscopy. Surface roughness (Ra) was determined using a surface profilometer. Nanowear measurements were carried out using a nanoindentation device. The water uptake of specimens was also measured. Parameters were statistically analysed by ANOVA ($P < 0.05$). The group without nanofillers showed the highest flexural strength and modulus, DC% and Ra value. The group with 30% nanofillers had the highest water uptake and volumetric shrinkage. No significant difference was found in Vicker's microhardness and the nanowear of the composites. The plain microfilled composite demonstrated superior properties compared to the composites loaded with nanofillers with the exception of surface roughness.

1 Introduction

Dental restorative filling composite resins have been introduced to the dental community in the 1960s [1]. Since then, after many significant material improvements, restorative composite resins still suffer from two key shortcomings: deficiencies of mechanical strength and high polymerization shrinkage [2, 3]. Thus, advanced research has been undertaken to evaluate and improve composite resin in order to have a material with high strength and low polymerization shrinkage combined with the advantages of aesthetic properties. Attempts have been made to modify the monomer matrix from the conventional dimethacrylate monomer systems to the recently introduced epoxy-based resin systems [4, 5]. The most significant changes in composite resins in the last decades have been made by far through improvements in the filler systems. Efforts to change the type of fillers or filler size and their surface sizing by silanisation have been made [6, 7]. Reinforcing the resin with glass fibres [8], with a fibre-reinforced composite (FRC) substructure [9], and the optimization of filler content [10] are among the methods that have been studied. Filler particles are added to the resin system to improve the physical and mechanical properties of the matrix. The resin matrix aims to contain at least 50% of filler particles by weight in order to fulfil the ISO standard requirements of mechanical properties for a dental composite material [11]. In recent studies, the filler particle size and quantity have shown themselves to be influential factors in the determination of physical and shrinkage properties [1, 10–12].

Filler technology has led to the development of composite resins characterized by containing zirconia or silica nano-particle fillers of approximately 25 nm in size and nanoaggregates of approximately 75 nm in size. Several

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recent commercial microfilled composite resins contain nano-particle agglomerates in their structure [12]. These materials have been reported to have a superior polish ability and resistance to wear compared to pure microfilled composite resin [13]. Their clinical performance is acceptable after 2 years [14]. However, whether the addition of nanofiller particles improves the properties of these microfilled composite resins still remains unclear. Based on this knowledge, it is important to obtain more detailed information on this new class of resin-based restorative materials. Thus, the purpose of the present study was to evaluate the effect of different nanofiller fractions on certain material properties (flexural strength and modulus, polymerisation shrinkage, degree of monomer conversion, surface microhardness and roughness, nanowear and water uptake) of experimental microfilled composite resin. The null hypothesis which was tested, was that nanofillers do not significantly influence the properties when compared with microfine silica filler.

2 Materials and methods

The dimethacrylate (BisGMA 67% [bisphenol A-glycidyl dimethacrylate] and TEGDMA 33% [triethylenglycol dimethacrylate]) monomer resin system and radiopaque fillers of $BaAlSiO_2$ (3 ± 2 μm in size) (Specialty Glass, USA) were used. Nanofillers (SiO_2, 20 nm in size) with various weight fractions (Hanse Chemie, Germany) were incorporated into the resin system. Before the filler particles were incorporated into the resin matrix, they were silane treated using the previously defined technique [15].

Experimental composite resins were prepared by mixing 33 wt% of resin matrix with 67 wt% of $BaAlSiO_2$ radiopaque fillers containing various weight fractions of nano-fillers (0, 10, 15, 20, 30 wt%). The fillers were added gradually to the mixture. The mixing was carried out by using a high speed mixing machine for 5 min (SpeedMixer, DAC, Germany, 3500 rpm). All groups had the same resin matrix and constant filler fraction (67 wt%) but various nano-fillers fraction. Classification of the test groups according to various filler content is given in Table 1.

Table 1 Classification of the experimental composite resin test groups used in the study according to their nanofiller content

Groups	Micrometer scale fillers (wt%)	Nanometer scale fillers (wt%)	Resin matrix (wt%)
GR1	67	0	33
GR2	57	10	33
GR3	52	15	33
GR4	47	20	33
GR5	37	30	33

2.1 Flexural strength and flexural modulus

Bar-shaped specimens ($2 \times 2 \times 25$ mm^3) were made in a half-split stainless steel mould between transparent Mylar sheets. Polymerisation of the composite was made using a hand light-curing unit (Optilux-501, Kerr, CT, USA) for 40 s from both sides of the metal mould. The wavelength of the light was between 380 and 520 nm with maximal intensity at 470 nm, and the light intensity was 800 mW/cm^2. The specimens from each group ($n = 6$) were either dry or water stored (37°C for 5 months). The dry-stored (room temperature) specimens were tested 24 h after their preparation. A three-point bending test was conducted according to the ISO 4094 (test span: 20 mm, cross-head speed: 1.0 mm/min, indenter: 2 mm diameter). All specimens were loaded in the material testing machine (model LRX, Lloyd Instrument Ltd, Fareham, England) and the load–deflection curves were recorded with PC-computer software (Nexygen 4.0, Lloyd Instruments Ltd, Fareham, England).

The flexural strength (σ_f) and flexural modulus (E_f) were calculated from the following formula [16]:

$$\sigma_f = 3F_m I / \left(2bh^2\right)$$

$$E_f = SI^3 / \left(4bh^3\right)$$

Where F_m is the applied load (N) at the highest point of the load–deflection curve, I is the span length (20 mm), b is the width of the test specimens and h is the thickness of the test specimens. S is the stiffness (N/m) $S = F/d$ and d is the deflection corresponding to load F at a point in the straight-line portion of the trace.

2.2 Degree of monomer conversion

The degree of monomer conversion (DC%) during and after the photoinitiation of the polymerisation was monitored by Fourier transform infrared spectroscopy (FTIR) (Spectrum One, perkin Elmer, Beaconsfield Bucks, UK) with an attenuated total reflectance (ATR) sampling accessory. The materials were placed in 1.8 mm-thick ring moulds with a diameter of 6.5 mm and placed on the ATR-sensor (ZnSe-crystal). The upper surface of the specimen ($n = 5$ per group) was covered with a Mylar sheet and a glass slide of 1 mm thickness and slightly pressed against the ATR to ensure good contact of the specimen. The light source was placed in contact with the glass surface. The substrate was light-polymerised with a QHT standard tip hand-held light–curing unit (Freelight 2, 3 M ESPE, Elipar, Germany) for 40 s. The spectra during the polymerisation process was recorded every 6 s for 5 min. The DC% was calculated from the aliphatic C=C peak at 1638 cm^{-1} and normalised against the aromatic C=C peak at 1608 cm^{-1} according to a formula (1)

$$DC\% = \left[1 - \frac{C_{\text{aliphatic}}/C_{\text{aromatic}}}{U_{\text{aliphatic}}/U_{\text{aromatic}}}\right]100\% \quad (1)$$

where $C_{aliphatic}$ absorption peak at 1638 cm^{-1} of the cured specimen, $C_{aromtic}$ absorption peak at 1608 cm^{-1} of the cured specimen, $U_{aliphatic}$ absorption peak at 1638 cm^{-1} of the uncured specimen, $U_{aromatic}$ absorption peak at 1608 cm^{-1} of the uncured specimen. The fraction of remaining double bonds for each spectrum was determined by standard baseline techniques using the comparison of maximum heights of aliphatic and reference peaks for calculations.

2.3 Volumetric polymerisation shrinkage

The specimens' densities ($n = 5$ per group) were measured to determine polymerisation shrinkage according to the Archimedes' principle with a commercial Density Determination Kit of the analytical balance Mettler Toledo X. The kit provided a special holder for the specimens, a special container to keep the water, a computer, and appropriate software. The specimens were weighed in air and in water, and the density was directly calculated in gram per cubic centimeter by the software of the Mettler Toledo XS balance according to the equation:

$$D = \frac{A}{A - B} \times (D_0 - D_L) + D_L$$

where D density of sample, A weight of sample in air, B weight of sample in water, D_0 Density of water at the exactly measured temperature in °C according to the density table of distilled water, D_L Air density (0.0012 g cm^{-3}). An internal balance correction factor (0.99985) of the Mettler Toledo XS balance software took the air buoyancy of the adjustment weight into account.

The percentage volume change ΔV after polymerisation was calculated from the densities according to the equation:

$$\Delta V\ [\%] = [(m_2/D_2 - m_1/D_1)/(m_1/D_1)] \times 100$$

where m_1 is the mass of the specimen prior to curing, m_2 is the mass of the specimen after curing, D_1 is the density of the specimen prior to curing, and D_2 is the density of the specimen after curing.

2.4 Nanowear

A nanoindentation instrument (UBI 750, Hysitron, Minneapolis, MN) using a three-sided pyramid diamond Berkovich tip at a constant wearing rate of 30 µm/s and a wear force of 20 µN, was used for polished specimens. A wearing area of 10 × 10 μm^2 of composite for 25 cycles was conducted. The morphology and depth of wear scratch were recorded and analysed using the software available on the instrument (TriboScan, version 9.1.1.0, Hysitron) (Fig. 1). Nano-scale surface roughness inside the wear scratch was evaluated and compared with the area around it. The temperature of the testing chamber was the same as room temperature (24.5°C).

2.5 Water uptake

Six test specimens from each group (test specimens for the three-point bending test) were stored in 120 ml of water for 5 months at 37°C. The dry weight (m_d) of the specimens was measured with a balance (Mettler A30, Mettler Instrument Co., Highstone, Nj, USA), with an accuracy of 0.1 mg. During the water immersion, the weights (m_w) of the specimens were measured for up to 150 days (Fig. 2).

$$\text{Water uptake } \% = (m_{wx} - m_d)/m_d \times 100\,(\%)$$

where x is days of water immersion.

2.6 Surface microhardness

Five specimens from each group (2 mm-thick round specimens 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, the specimens were polished (grit up to 4000 FEPA) at 300 rpm under a water cooler using an automatic grinding machine (Struers Rotopol-11, Copenhagen, Denmark). The specimens were water stored for 24 h at 37°C before testing. Microhardness (Vicker's hardness number, VHN) measurements (10 points for each specimen) were carried out with a universal surface microhardness testing device (wsDuramin, Struers, Copenhagem, Denmark). 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:

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

where H is Vickers hardness in kg/mm^2, P is the load in grams and d is the length of the diagonals in µm.

2.7 Measurement of surface roughness

The surface roughness of the polished specimen ($n = 3$) was measured using a surface profilometer (Mitutoyo surftest 301, Mitutoyo Corporation, Kanagawa, Japan), with a standard cutoff of 0.8 mm, a transverse length of 0.8 mm, and a stylus speed of 0.1 mm/s. The specimens were water stored for 24 h at 37°C before testing. The roughness average (Ra) of a specimen was defined as the

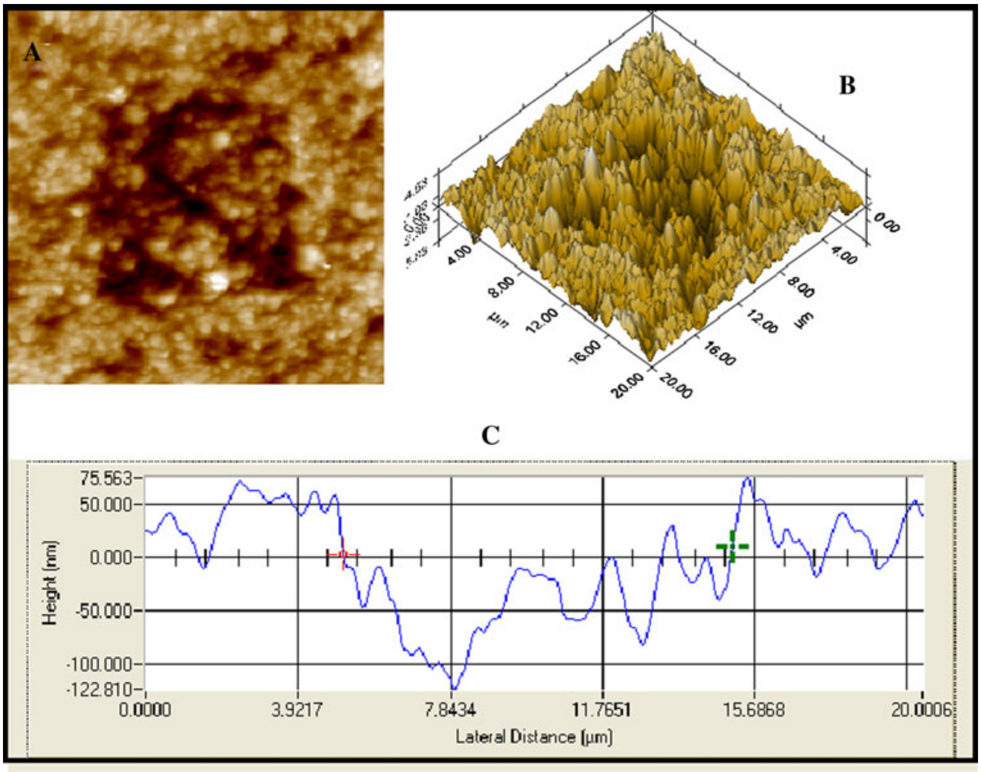

Fig. 1 Nanowear scratch image of 10 × 10 µm^2 of composite for 25 cycles (**a**, **b**), **c** is a typical surface profile of the selected area where nanowear depth is easily measured

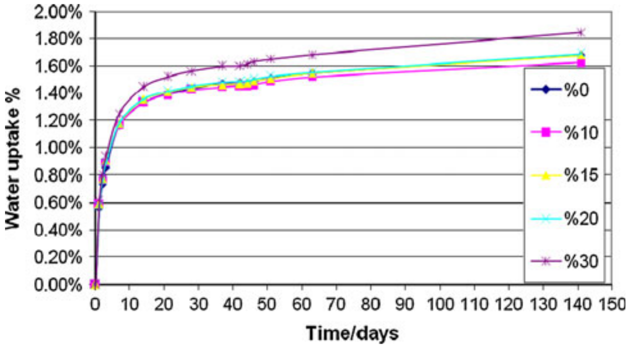

Fig. 2 Water uptake of composites containing various quantities of nano-fillers

arithmetic average height of roughness component irregularities from the mean line measured within the sampling length. Three profilometer tracings were made for each specimen and the numerical average was determined for each group.

2.8 Statistical analysis

The data was statistically analysed with an analysis of variance (ANOVA) at the $P < 0.05$ significance level with SPSS (version 13, Statistical Package for Social Science, SPSS Inc, Chicago, IL, USA), followed by Tukey's post hoc analysis to determine the differences among the groups.

3 Results

The results are shown in Table 2. ANOVA revealed significant differences between the properties of all the groups investigated.

Test specimens of the group without nanofillers before water storage showed the highest ($P < 0.05$) flexural strength (123.7 MPa), modulus (7 GPa), and degree of monomer conversion (60.9%). However, after water storage, no significant difference ($P > 0.05$) between the groups was found. Flexural strength and modulus values drop down except for the modulus in the specimens of groups with 20 and 30% nanofillers, which showed a slight increase of values. The lowest volumetric polymerisation shrinkage (3.62 vol.%) was also found in the group without nanofillers.

Figure 1 shows a typical surface morphology and profile of the exposed surfaces. There were no differences in nanowear values between the tested specimens of various groups (100–150 nm), but the effect of nanofillers was clear in improving the nano sacle roughness inside the wearing scratch.

The specimens in the group with the highest loading of 30% of nanofillers showed the highest water uptake (1.8 wt%) and volumetric polymerisation shrinkage (4.27 vol.%), as well as the lowest degree of monomer conversion (57.4%).

There were no significant differences ($P > 0.05$) in surface microhardness between the tested groups. Among

Table 2 Results, mean and standard deviation

Groups	Flexural strength (MPa)		Flexural modulus (GPa)		DC%	Shrinkage (vol%)	VH%	Water uptake (wt%)	Surface roughness (Ra)
	Dry	wt	Dry	wt					
Gr 1	123.7 (12.1)	67.8 (13.8)	7 (0.5)	4.1 (0.2)	60.9 (0.9)	3.62 (0.27)	43.2 (1.1)	1.68 (0.09)	0.64 (0.005)
Gr 2	84.8 (15.6)	66.7 (11.5)	5 (0.3)	4.4 (0.2)	60.4 (1.1)	3.67 (1.14)	40.9 (1.0)	1.62 (0.09)	0.45 (0.01)
Gr 3	71.1 (17.5)	67.8 (30.0)	4.9 (0.5)	3.5 (0.3)	59.3 (0.6)	4.13 (1.64)	43.8 (1.8)	1.68 (0.02)	0.28 (0.01)
Gr 4	71.2 (10.4)	66.8 (10.4)	3.6 (0.4)	5.1 (0.2)	58.3 (0.3)	3.98 (0.25)	44.4 (1.7)	1.69 (0.03)	0.22 (0.01)
Gr 5	84.4 (9.0)	69.9 (15.1)	3.7 (0.5)	4.3 (0.2)	57.4 (0.3)	4.27 (0.24)	45.6 (1.7)	1.84 (0.12)	0.18 (0.01)

wt water-stored, *vol%* volume percentage, *DC%* degree of conversion, *VH%* vicker's hardness, *wt%* weight percentage, *Ra* average surface roughness

the specimens which were studied, the lowest surface roughness (Ra) was found in the group with 30% nanofillers (0.18) and the roughest surface (Ra) was found in the group without nanofillers (0.64).

4 Discussion

Long term clinical durability of the microfilled composite resin still remains a challenge for researchers. The incorporation of inorganic particles is well established as a reinforcing mechanism of polymer-based materials, as observed in studies where the additions of nanofillers in polymer matrices improve several material properties of the resulting composite [17]. To investigate the influence of adding nanofillers on the properties of microfilled composite resin, five groups of microfilled experimental composite having the same total filler weight content with different quantities of nanofillers were used in this study. The tested parameters were evaluated according to either the dental standard ISO 4094, or other well-proven testing methods [18, 19]. Although the experimental resin-based materials were not optimized, the measurements showed that the chosen formulations met the property range of common trade products [20].

The results showed that the group without nanofillers before water storage had the highest flexural strength (123.7 MPa) and flexural modulus (7 GPa) in comparison to groups with different fractions of nanofillers. This might be due to the agglomerated clusters of nanofillers, which may have enhanced crack propagation through the test specimen. This assumption is supported by investigations which have been done on other technical areas where nanofillers were used. These investigations found that the presence of agglomerates in a nanofiller reinforced polymer can negate the advantages of the nanofillers because, under load, there may be slippage within the agglomerate, the surface area for the interaction between particulate matter and the quantity of polymer is reduced and fracture at the agglomerate sites can be initiated [12, 21]. SEM images of the agglomerated nanofillers reported by Rüttermann et al. showed a very clear porous structure, which supports the assumption of failure running through the agglomerates [12]. After water storage, all the test groups significantly lost flexural strength. Only the microfilled composite lowered significantly the flexural modulus values, whereas groups with 20 and 30 wt% nanofillers showed a slight increase in flexural modulus, although the flexural strength decreased, which has been also demonstrated previously [22, 23].

Water uptake was highest with the specimens of the group with a loading of 30% nanofillers (Table 2). Agglomerated nanofillers themselves were assumed to be the reason for the high water uptake. An analogue finding has been reported with fibre-reinforced composites in which the fibre rich region had not fully been impregnated by the resin matrix, which increased the water uptake [24]. The findings of the present study are in agreement with a study by Ilie and Hickel, which showed that although the incorporation of nanofillers in the resin matrix improved the aesthetics to some extent, the larger surface area to volume ratio of the fillers in the nanofilled materials tended to increase the water uptake. This was supposed to relate to the degradation of the filler/matrix interface, which lowered the mechanical properties when compared to a microfilled composite resin [20].

The wear of dental composites is a complex process involving fatigue, as well as erosive, adhesive, and abrasive components [25]. The three-body wear test with artificial food slurries has been developed to simulate in vivo wear and many authors have used the testing systems, though a high variation in the results have been seen even with the same material and testing technique [26]. Nanoindentation has been successfully used for investigating the hardness and modulus of elasticity of dental composites [27]. However, the nano-scale wear of the dental composite has not been widely evaluated to the authors' knowledge. Thus, the nanowear was evaluated by using a force of 20 µN for the nanofilled composite with filler particles ranging from

20 nm to 4 μm in size. The scratch depth of all tested specimens was in the same range. Thus, nanofillers loading up to 30% were not improving the nanowear of the microfilled composite. In contrast, it was interesting to find that the surface roughness inside the scratch area was observed to decrease linearly with an increasing nanofillers load. A study by Devaprakasam et al. showed that a plain nanocomposite has better nanowear performance compared to a microfilled composite [28].

The addition of nanofillers to the microfilled composite resins decreased the degree of monomer conversion (DC%). The index of refraction increase and the extinction coefficient lower by the propagation of the polymerisation of the monomers [29]. However, the formation of agglomerates of nanofillers could interfere with the light penetration or may act as light scatters, especially those whose size approaches the output wave length of the light curing unit [30, 31]. Thus, with increased scattering, light intensity is decreased. It is also possible that the oxygen in the agglomerates can cause oxygen inhibition of free radical polymerisation inside the specimen, which has been found with some other composites [32]. It was not surprising that were no significant differences between the surface microhardness of the tested groups, because all the groups have a similar polymer matrix, filler weight, and the same filler type material. However, lower surface microhardness values of the same composite after a long water storage time have been reported due to matrix softening by water [33]. On the other hand, if the resin system is modified by glass ionomer, studies have shown higher microhardness values at 6 months than at 24 h of storage in distilled water [34, 35]. They explained the post-hardening reaction of the glass ionomer phase by water after the storage period [36]. Surface roughness can be related to a combination of factors that include the characteristics of the matrix, ratio and size of inorganic particles, exposition of these inorganic particles and formation of air bubbles during material preparation. As apparent in Table 2, there were proportionally significant differences between the Ra values of different nanofiller loading groups. The group with a maximum of 30% nanofiller loading revealed a lower Ra value than other experimental composite resins. This is in accordance with the literature discussing the excellent polishability of nano-particle filled resin-based materials [37, 38]. However, the Ra value of the microfilled composite resin was within the acceptable clinical range [39, 40].

5 Conclusion

Based on the results of the present study, one could conclude that the incorporation of silanised silica nanofillers up to 30 wt% did not improve the properties of the microfilled composite resin.

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