Effects of filler size, water, and alcohol on hardness and laboratory wear of dental composites

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Schwartz JI, Söderholm KJM. Effects of filler size, water, and alcohol on hardness and laboratory wear of dental composites. Acta Odontol Scand 2004;62:102–106. Oslo. ISSN 0001-6357.

Three UEDMA/TEGDMA (50:50 by weight) based dental composites were made, each with filler loadings of 53 vol.%. The three composites contained silane-treated filler particles with average particle diameters of 1.5, 3.0, or 10.0 μm. Twelve specimens per composite were mounted on wear wheels and run through 200,000 cycles in an ACTA wear machine. Six of these specimens per material were worn in slurries consisting of 30 g ground Millet seed shells and 120 g ground rice mixed with 275 mL water. The remaining six specimens were worn in similar 25% ethanol-water slurries. The composite wear profiles were recorded with a profilometer and used to calculate the wear. Hardness values of the composites were also measured both before and after storage for 2 weeks in either water or in a 25% ethanol–water solution. The wear and hardness values from the measurements were analyzed using ANOVA. The wear analysis showed that the finer composites (1.5 μm filler diameter) wore the least and the coarsest composites (10 μm filler diameter) the most. The wear was significantly higher in the ethanol–water slurry than in the water slurry. The hardness value of the coarsest composite decreased more than the finest composite during storage in water or 25% ethanol–water. The hardness decrease was most pronounced in the alcohol solution. ☐ *Dental materials; diffusion; particle size; plasticizers*

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In 1979, Jørgensen et al. (1) claimed that decreased interparticle spacing improved clinical wear resistance of filled resins. They showed how the addition of pyrogenic silica to a sealant improved the clinical wear resistance of the sealant, making the filled sealant more wear-resistant than commercial dental composites available at that time. The explanation advocated by Jørgensen et al. (1) was that smaller filler particles produced composites with shorter interparticle spacing than composites with larger particles. Their explanation for the wear reduction was that shorter interparticle spacing provided better matrix protection, which explained the improved wear resistance.

Another important study dealing with wear of composites was published in 1981, when Wu et al. (2) found that ethanol plasticizes the surface of dental composites and that the plasticizing effect of ethanol accelerated the wear of composites. These are fundamental studies when it comes to understanding the wear mechanism of dental composites.

Clinical wear has long been considered one of the key problems with dental composites, but during the past 20 years there have been substantial improvements in the wear performance of composites. These can be related to increased use of smaller filler particles. Another reason for these improvements relates to better laboratory wear-testing methods that are more capable of simulating in vivo wear performance. One of the first successful laboratory wear-testing machines was the ACTA Wear Machine developed at the Academic Center for Dentistry, Amsterdam in The Netherlands (3). Extensive research conducted by the Dutch research team at ACTA (3) has shown that it is possible to closely simulate the three-body wear that occurs in vivo with the ACTA Wear Machine. These laboratory test methods have made it possible to accelerate the development of newer composites rather than relying on expensive and time-consuming clinical trials. The Dutch studies found that wear decreased when a larger fraction of finer filler particles was added to a composite (4). The Dutch team also found that different media and particular enzymes affected the wear (5).

Based on the above findings, we assumed that a decrease in the interparticle spacing would improve wear resistance by providing better matrix protection, as proposed by Jørgensen et al. (1). By storing the composites in 25% ethanol, we also expected that the matrix would plasticize and decrease the hardness of the composites. Wear particles in the food, as well as dislodged filler particles, abrade composite surfaces; the forces produced by chewing indent and drag these particles across the composite surface. The plowing action of these particles results in material removal and leaves defects in the composite surface. A decrease in hardness facilitates the deeper penetration of wear particles and, therefore, produces greater surface defects than would occur in harder, less plasticized surfaces. Consequently, a plasticizer like ethanol would increase the wear of the composite, particularly for the material with inferior matrix protection caused by longer interparticle spacing.

Against the background presented in the previous paragraph we decided to test the hypothesis that dental composites containing smaller filler particles are more wear-resistant than composites containing larger filler

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DOI 10.1080/00016350410005555

particles, and that the wear increases as the hardness decreases after the composite has been plasticized in a medium such as ethanol.

Materials and methods

Investigated materials

Three composites, each containing 53 vol.% barium glass particles with different filler sizes, were prepared. The different glass particles (52 wt.% SiO_2, 32 wt.% BaO, 8 wt.% B_2O_3, 8 wt.% Al_2O_3) were purchased from Industrial Corporation (Lionville, Pa., USA) as having average particle sizes of 1.5, 3.0, and 10.0 μm. Before making the composites, the filler particle densities were determined with a Micromeritics Pychnometer (Micromeritics, Norcross, Georgia, USA), and their particle sizes and particle size distributions were determined with a Micromeritics SediGraph 5100. Each measurement was repeated five times.

Following the filler particle characterization, the glass particles were silane-treated. The silane treatment was done by first mixing 3.75 mL γ-methacryloxypropyltrimethoxysilane (lot no. 51H0280; Sigma, St. Louis, Mo., USA) with 185 mL toluene (lot no. 920352; Fisher Scientific, Fair Lawn, N.J., USA). To that mixture, 75 g filler was added and stirred for 23 h at room temperature, whereupon the silane-toluene solution was decanted and the filler was washed for another hour in 200 mL toluene. The slurry was then filtered and the silane-treated filler was dried in an oven at 60°C for 24 h, whereupon it was heated to 110°C under vacuum for 1 h.

The composites were made by mixing 53 vol.% filler with a matrix consisting of UEDMA (lot no. PB 2037; Esschem, Essington, Pa., USA)/TEGDMA (lot no. 307-44-2; Esschem) mixture (50:50 by weight UEDMA and TEGDMA). To make the matrix material light-curable we had added 0.35 wt.% d-2,3-bornanedione (lot no. 8074101297; Eastman Kodak, Rochester, N.Y., USA) and 0.7 vol.% 2-(dimethylamino) ethyl methacrylate (lot no. 06622FF; Aldrich Chemical Company, Milwaukee, Wisc., USA) to the resin mixture before we incorporated the filler.

Wear measurements

Twelve specimens of each composite were made for the wear evaluation. These specimens were made by placing the plastic composite in a brass mold with two polyethylene disks attached on either side. The brass mold and the two polyethylene disks had the same radius and curvature as the specimen-mounted wheels used for the wear evaluations. Each specimen was made by placing two layers, each about 2 mm thick. Before the second layer was added, the specimen surface was cured at 6 evenly dispersed locations for 40 s each using a Visilux lamp (3M Dental Division, St. Paul, Mn., USA) with a light intensity of ~580 mW/cm^2 measured with a hand-held radiometer (Cure Rite; EFOS, Mississauga, Ontario, Canada). After the first layer had been cured, the second layer was inserted and covered with a curved Mylar strip to form a convex surface and cured in the identical manner as the first layer.

All specimens were attached to four similar wear wheels with a self-curing composite (Ti-Core, Esssential Dental Systems Inc., Hackensack, N.J., USA). Three specimens of each filler size were placed on each wheel. The specimen surfaces were then ground down to a circular curvature using a laboratory lathe and smoothened with a milling machine (Craftsman Mini Vertical Mill Model 527–2144, Sears Roebuck and Co., Chicago, Il., USA) and silicone carbide paper (no. 120, 240, and 600, Mark V Laboratory, East Granby, Ct., USA). The final surface smoothing was accomplished in the wear machine under water with four different diamond wheels (BN 1873, RB 4669, RB 4670, and RB 4671 (Ernst Winter and Son, Travelers' Rest, Sc., USA), proceeding from the coarsest to the finest.

The wear evaluation was conducted in an ACTA Wear Testing Machine (ACTA, Amsterdam, The Netherlands) (Fig. 1). The force used in the wear machine was 15 N and the slip between the specimens and the contacting wear wheel was 15%. The rotational speed was set at 1 Hz, simulating average chewing frequency.

The abrasive slurry consisted of a mixture of 120 g rice and 30 g Millet seed shells ground together in a blender for 30 s, to which either 275 mL distilled water or 275 mL ethanol–water (25% ethanol by volume) was added. The slurry was then adjusted to a pH of 7.0 by use of 0.1 M NaOH.

After the first 100,000 wear cycles in the wear machine, the abrasive slurry was replaced with freshly mixed slurry and a second 100,000 wear-cycle period was initiated. The pH of the slurry was checked regularly and retained a pH value of ~3.9 throughout most of the duration of the experiment.

After the ACTA wear cycles were completed, each specimen was attached to a measuring device (Micro-Controle, Evry, Cedex, France) in which the specimen-mounted wear wheels could be rotated with a precision of a fraction of a degree, making it possible to record wear profiles at evenly spaced locations with a profilometer (Surfanalyzer, Federal Products Co., Providence, R.I., USA). Seven profile measurements were collected per specimen (Fig. 2). The wear was determined from each of these profiles by establishing a straight line between the edges of the profile measurement location and calculating the surface area encompassed by that line and the wear profile (Fig. 3).

Hardness measurements

Twelve disks, 20 mm in diameter and 1.0 mm thick, were prepared per experimental material. The specimens were made by inserting the composite into a polyethylene mold sandwiched between two Mylar sheets, each covered

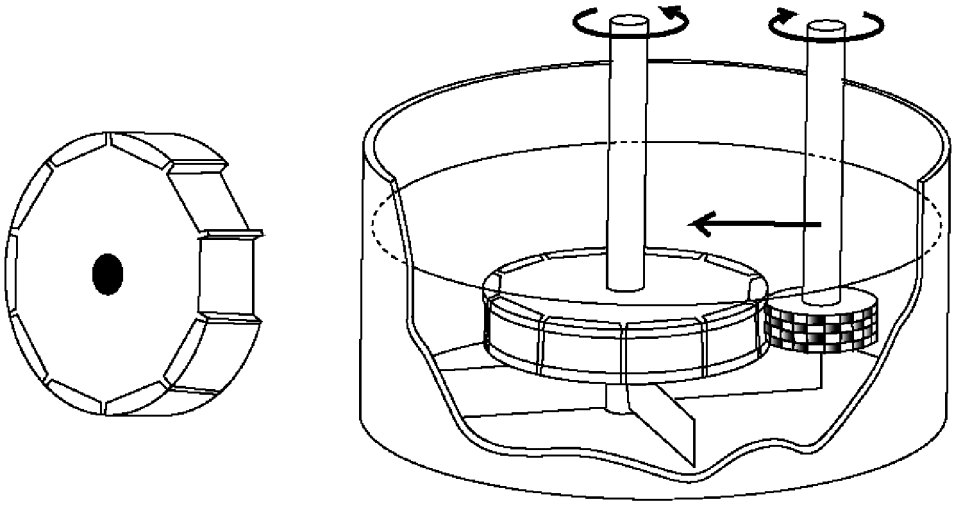

Fig. 1. The specimen wheel shown to the left has 8 specimens attached. On the drawing to the right, the specimen wheel is attached to the rotating axis to the left, while a steel wheel with machined roughness is attached to the rotating axis to the right. The force acting against the specimen wheel was 15 N and the wear process was done inside a bucket filled with the different slurries. (Redrawn after P. Pallav, 1996)

with a glass plate. Curing was conducted by placing the light tip of the light-curing unit in direct contact with the top glass plate. The curing was conducted at 9 different locations for 40 s each using the same light source and light intensity as was used for the wear specimens. These 12 specimens per material were divided into 2 groups of 6 specimens each. One group was assigned to be stored in water, the other to 25% ethanol storage.

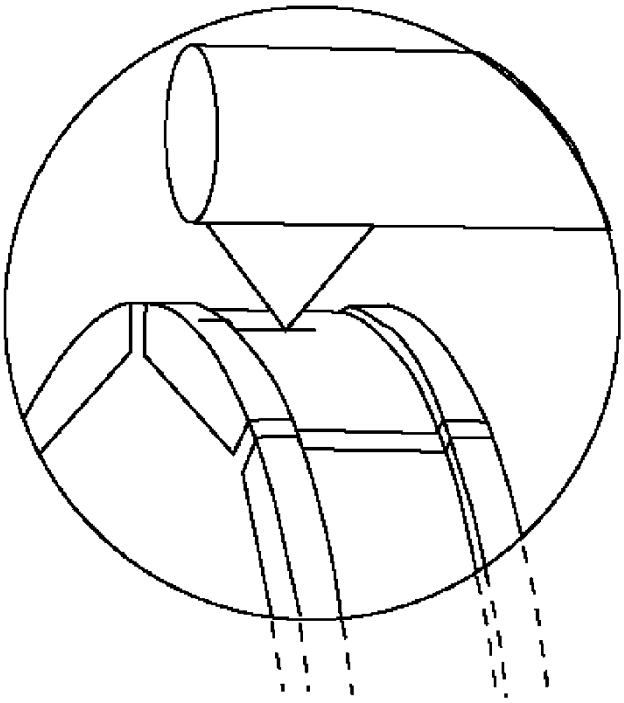

Fig. 2. The worn specimen surface was recorded with a profilometer oriented perpendicularly to the wear direction. (Redrawn after P. Pallav, 1996).

Before any of the 12 specimens per filler group were transferred to water or 25% ethanol, all specimens were first stored for 2 weeks in a desiccator at room temperature before 10 hardness measurements per specimen were done on the dry specimens. The hardness determinations consisted of loading each specimen to 350 g for 90 s using a 136° diamond tip in a Tukon Microhardness Tester (Wilson Instrument, Bridgeport, Ct., USA). The load was released and another 120 s was allowed to pass before the size of the indentation was measured. After determining the Vickers hardness of each of the dry specimens, the mean hardness value was calculated and the assigned specimens were transferred either to distilled water or to the 25% ethanol solution. The specimens were stored for 2 weeks in these 2 solutions before they were removed and 10 more Vickers hardness measurements per specimen were determined a second time in the same manner as used for the dry specimens.

Statistical evaluation

The mean wear and hardness values were compared statistically with a two-way ANOVA (SAS Institute Inc., Cary, N.C., USA) to determine whether there were any significant differences ($P < 0.05$) among the 3 composites and the storage media.

Results

Filler particle characterization

The densities of the investigated filler particles were

Fig. 3. The wear profile was generated and a line was used to join the edges. The surface area formed between the joining line and the wear profile was used to determine the wear.

2.744 ± 0.019 g/cm^3. The average mass particle sizes and the standard deviations of those values were 1.73 ± 0.07, 2.50 ± 0.07, and 7.88 ± 0.41 μm.

Wear measurements

Wear measurements were conducted on 6 specimens per material and storage medium. Seven equally spaced profiles were recorded on each specimen and the mean value of these 7 readings was used as the wear value for that specimen.

The ANOVA revealed that wear was significantly different between storage media ($P < 0.05$) and filler size ($P < 0.05$). Of these 2 variables, storage medium was more important (F value = 173.88 compared to F value of 21.45 for the filler size). There was no clear significant storage-filler interaction ($P = 0.0528$).

Hardness measurements

The Vickers hardness values measured on dry specimens, and after these specimens had been stored in water or alcohol, revealed that there were no significant differences between the dry specimens, independent of filler size, but after storage in water or 25% ethanol there were significant differences among the composite groups (Table 1). Both filler size and storage medium had significant effects ($P < 0.05$) on hardness after storage in the 2 media. The composites with the smallest filler particles did not lose as much hardness as the composites with the larger filler sizes did after storage. Both the 3.0 and 10.0 μm filler composites lost significantly more in hardness after storage than the 1.5 μm filler composite did. Comparing the 3.0 μm and the 10.0 μm composites revealed that the 10.0 μm composite had a greater reduction in hardness than the 3.0 μm composite, but that difference was not significant. The hardness values of the composites stored in water were clearly higher than those stored in the 25% ethanol solution ($P < 0.05$). No significant interaction between filler size and storage medium existed ($P > 0.05$).

Discussion

Our results showed that a decrease in filler size resulted in composite materials with lower wear than composites with larger particles, at least when worn in water or 25% ethanol slurries. Of these two slurries, the 25% ethanol slurry caused more wear (Table 1). In addition to the wear results, our hardness results revealed that the surface hardness of the investigated composite specimens decreased faster in alcohol than in water (Table 1). In addition, hardness decrease was least pronounced for the finer composites and most pronounced for the coarsest composites (Table 1).

At first glance our wear results support Jørgensen et al.'s (1) filler protection explanation, while our hardness changes suggest that there are other mechanisms that might explain why finer filler particles decreased wear the most. However, neither Jørgensen et al. (1) nor have we conclusively proved that finer filler particles and improved matrix protection of the filler are the key factors behind the wear reduction, even though both their results and ours may suggest that such an explanation is feasible. Another possibility is that finer filler particles and shorter filler spacing slow down diffusion of plasticizing agents, and that the lower plasticizing effect caused by the finer particles is the key reason why wear decreases as filler size decreases. By looking at the F values (F value = 173.88 for

Table 1. Wear values (in mm^2) and Vicker hardness values (VH) of the three composites. The wear values are after wear in distilled water or 25% ethanol, while the hardness values are both before and after storage in distilled water or 25% ethanol. Differences in hardness values as a result of storage in the 2 media are also shown

Filler (μm)	Wear value (±*s*)	Dry VH value (±*s*)	Storage VH value (±*s*)	Difference in VH (±*s*)
1.5	0.393 (±0.076)*	1102.4 (±83.1)	941.1 (±75.2)*	161.3 (±81.2)
3.0	0.441 (±0.080)*	1236.8 (±232.1)	900.6 (±91.1)*	336.1 (±234.5)
10.0	0.528 (±0.094)*	1049.6 (±141.7)	753.2 (±109.7)*	296.3 (±178.4)
1.5	0.711 (±0.072)**	1028.5 (±128.5)	701.5 (±62.0)**	326.9 (±82.0)
3.0	0.722 (±0.094)**	1199.0 (±145.4)	752.1 (±34.0)**	446.9 (±123.8)
10.0	0.967 (±0.046)**	1197.3 (±236.8)	615.0 (±36.8)**	582.3 (±219.1)

* After storage in water.
**After storage in ethanol.

storage medium compared to F value = 21.45 for the filler size), it is clear that storage condition had stronger impact on wear than the filler size. It is important to realize this, because lower wear of tested composites was related to higher surface hardness values of the different materials after storage in different media (Table 1).

Table 1 shows that the hardness of the different composites was not significantly different when tested dry. Such a finding is expected when it is considered that the indenter of the hardness tester was substantially bigger than the tested filler particles and their interparticle distances. When dry, the rigidity of the matrix material is also the same for the different composites. Thus, during loading, displacement of the indenter should be the same in the dry composites. However, after storage in water or ethanol–water, the hardness values of all composites decreased, most for the composites with the coarsest filler particles and least for the composites with the finest filler particles (Table 1). That change was most pronounced for composites stored in the ethanol–water solution. These decreases in hardness values can be related to the plasticizing effects of both water and ethanol on the matrix material. Of these two media, ethanol has the more pronounced plasticizing effect, explaining why the surface hardness of composites stored in the 25% ethanol solution decreased most.

As mentioned before, the reason the surface hardness of the coarser composite decreased more than that of the finest composite may be related to differences in diffusion properties among the three composites. Both water and ethanol diffuse into the composite over time. It is known that diffusion of molecules into any composite depends on diffusion through the matrix, diffusion at the filler-resin interface, and diffusion through the filler particles (8, 9). In our composites, diffusion through the matrix is most likely the dominating factor. A composite with finer filler particles has shorter interparticle spacing, but also a larger total filler surface area. As a consequence of the shorter interparticle spacing and the larger filler surface area, diffusion occurs more slowly in the finer composites. An analogy here is diffusion of water through coarse sand versus fine clay.

From the above argumentation, diffusion into deeper layers of the finer composite is likely to occur more slowly than into the composite with the coarser filler particles. The slower diffusion would result in a more localized plasticizing effect and explain why the finer composites did not lose surface hardness as quickly as the coarser materials. Thus, by assuming that diffusion of water and ethanol plasticize the matrix and that differences in filler sizes affect the ease with which water and ethanol molecules reach deeper layers (8, 9), the results presented in Table 1 can be explained.

From our discussion, the explanation presented by Jørgensen et al. (1) needs to be supplemented with a theory that considers how differences in interparticle distances also affect diffusion of plasticizing agents. Based on our results, we cannot exclude the possibility that differences in diffusion of plasticizing agents in composites are a key factor in explaining differences in wear among composites. Future studies are therefore needed, and these studies need to focus on how interparticle spacing affects diffusion and plasticity in the interparticle matrix region.

To conclude, our study shows that smaller filler particles result in higher wear resistance. The size of the filler particles does not affect the hardness of dry specimens, but filler size affects the surface hardness measured after storage in plasticizing media such as water and a 25% ethanol solution. This decrease in hardness is more pronounced for the coarser composite than for the finer composite, and is also more pronounced after storage in the ethanol solution. The wear results and the hardness values suggest a reverse relationship between surface hardness and wear of composites. All these findings support our hypothesis that dental composites containing smaller filler particles are more wear-resistant than composites containing larger filler particles, and that the wear increases as the hardness decreases after the composite has been plasticized in a medium such as ethanol.

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Received for publication 7 May 2003
Accepted 23 February 2004