

Hydrolytic Degradation of Composite Resins: Effects on the Microhardness

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The purpose of this investigation was to evaluate the microhardness of two laboratory-processed composites (Artglass; BelleGlass) and two direct placement composites (Filtek Z250; Alert), after aging in distilled water. Twenty cylinders (8 mm diameter; 2 mm height) *per* tested material were prepared and stored in 10 ml of distilled water. Five Knoop hardness measurements were made on the surface of the specimens with a Miniload Hardness Tester under a load of 50 g for 30 s at 10 min, 24 h, 30 and 90 days. Statistical analysis was performed using two-way ANOVA, followed by a SNK multiple comparison test ($p < 0.05$). The analysis showed statistically significant difference among hardness means recorded at the different aging time and the tested materials. It may be concluded that all materials presented hydrolytic degradation due to aging in aqueous environment.

Keywords: *composite resin, hydrolytic degradation, microhardness*

1. Introduction

Composite resins are currently one of the most widely utilized materials in restorative dentistry and the satisfactory clinical performance is largely determined by its resistance to degradation in the oral environment^{1,2}. Mechanical properties of composite resins are vastly influenced not only by their chemical composition, but also by the environment to which they are exposed. The corrosion process promoted by the water and the presence of a constant load on the surface of the resin are responsible for the appearance and propagation of interfacial debonding, matrix cracking, superficial flaws, filler dissolution and filler particle dislodgment³⁻⁵.

The hydrolytic degradation of these materials happens mainly because of accumulation of water between the filler-matrix interface that promotes the displacement of inorganic particles⁶ or due to the slow development of superficial flaws related to preexistent corrosive processes^{7,8}. The dissolution

or elution of leachable components of composite resins, mainly inorganic ions or filler particles, may present, at short or long period, a deleterious effect in the polymeric network of the material, modifying its structure physically and chemically.

The surface microhardness of dental composites may be significantly affected by both water absorption and the contact time with the aqueous media⁹.

A significant reduction of Knoop microhardness in restorative composite resins was observed after storage in distilled water during 30 days¹⁰, 12 months¹¹ and a long period of time¹². However, the different types of restorative composite resins and polymerization method, may yield different performances with respect to the hydrolytic degradation process.

The measurement for hardness of composite resins is an indirect method of evaluating the mechanical strength and

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resistance to intraoral softening^{13,14}.

The aim of this investigation was to assess the surface hardness of four commercial composite resins after aging in water.

2. Material and Methods

Four commercial composite resins were evaluated in this study: two laboratory-processed composite, Artglass (Heraeus Kulzer GmbH, Wehrheim, DE 63450) and belleGlass HP (Kerr Corporation, Orange, CA 92867) an hybrid composite resin, Filtek Z250 (3M Dental Products, St Paul, MN 55144) and an condensable composite resin, Alert (Jeneric-Pentron, Wallingford, CT 06492). Details about the tested materials with their compositions, specifications and manufacturers are listed on Table 1.

Twenty cylindrical specimens of each material were prepared using a split stainless steel mould with 8 mm in diameter by 2 mm in height according to the manufacturer's specifications. The restorative materials Filtek Z250 and Alert were light-cured for 60 s on their top surfaces through clear polyester matrix strip using a visible light-curing unit (KM 100-R, DMC Equipaments, São Carlos, SP) with an intensity of 400 mW/cm² determined with a radiometer (Curing Lightmeter 105, DMC Equipaments, São Carlos, SP).

The laboratory-processed composite resin Artglass were cured with the xenon stroboscopic light curing unit (UniXS, Heraeus Kulzer GmbH, Wehrheim, DE 63450) for 180 s with a polymerization rate between 450-500 nm and strobe frequency of 20 Hz in each 10 ms. The laboratory-processed composite belleGlass HP were cured with a metal halide lamp (Tek Lite, Kerr Corporation, Orange, CA 92867) for 60 s with a wavelength of 400-500 nm, and an addi-

tional polymerization (HP Curing Unit, Kerr Corporation, Orange, CA 92867) was made under 60 psi (29 lb/pol²) nitrogen pressurized at an elevated temperature of 120 to 140 °C for 20 min.

The top surfaces of each specimen were ground with water-lubricated silicon-carbide (SiC) paper and polishing with 2000 grit paper (Wetordry, 3M Dental Products, St Paul, MN 55144) on an automated polisher (Struers A/S, Copenhagen, Denmark) to produce a smooth, uniform surface. Polished specimens were then stored in distilled water at 37 °C.

Five measurements of Knoop surface hardness were recorded from each specimen using a Miniload Hardness Tester (Durimet, Ernst Leitz GmbH, Wetzlar, Germany). A Knoop diamond indenter was applied under a load of 50 g for 30 s and the length of the indentation's long diagonal measured at 400× magnification after the applied load was removed. The surface hardness measurements were recorded at end of the polymerization period (time zero) and at aging times of 24 h, 30 and 90 days of storage in distilled water.

The Knoop hardness number (KHN) for each indentation was determined and means and standard deviation were calculated at each time interval for each group of specimens. The values were compared by factorial analysis of variance (ANOVA) using the SPSS software (SPSS 8.0, SPSS Inc., Chicago, IL 60611). When *F*-tests were significant, *Post-hoc* Student-Newman-Keuls multiple comparison intervals were further performed to identify statistically homogeneous subsets (*p* = 0.05).

Additionally, the surface texture of each two randomly selected specimens and two control samples of the four composite resins were qualitatively evaluated by SEM using a

Table 1. Description of materials.

	Alert	Artglass	belleGlass	Filtek Z250
Manufacturer	Jeneric-Pentron Wallingford CT, USA	Heraeus Kulzer GmbHWehrheim Germany	Kerr Lab Orange CA, USA	3M Dental Products St. Paul MN, USA
Batch	8 609.71	020107	P 900-181	0-EF/1370A2
Presentation	0.15 g/0.30 g/0.45 g	4 g	4 g	4 g
Shade	A2	Dentin A2	Dentin A2	A2
Valid	2003-07	2003-04	2003-10	2003-07
Type	Direct resin	Indirect resin	Indirect resin	Direct resin
Resin matrix	Ethoxylated	Bis-GMA	Bis-GMA	Bis-GMA
Bis-GMA PCDMA	TEGDMA	UDMA	UDMA, Bis-EMA	
Filler type	Ba-B-Al-silicate	Ba-Al-Si glass	Ba-Si glass	Zirconia/silica
TiO ₂ , Glass fibers				
Filler level (wt.%)	83.5%	69%	74 -78%	82%
Filler level (vol %)	54%	52%	78.7%	60%
Particle size (µm)	0.8 µm	0.7 µm	0.5 µm	0.19-3.3 µm

digital scanning microscope (Zeiss DSM 940A, Carl Zeiss, Oberkochen, Germany)

3. Results

Microhardness means recorded at the different aging times and standard deviation are summarized in Table 2.

An analysis of variance demonstrated that all liquid-stored in an aqueous environment were softened compared to dry samples ($p < 0.05$). Aging in water for 24 h did not significantly change the KHN for any of the tested composites. Continued aging in water beyond 30 d generally caused a significant reduction in the microhardness for each composite ($p < 0.05$). After that, a slow gradual decrease in hardness was observed ($p < 0.05$).

It was observed that the differences in microhardness for Alert and BelleGlass between the unaged and 30 and 90 d aging were not significant ($p > 0.05$). The final hardness values, measured at 90 d, were significantly lower ($p < 0.05$) than the corresponding values measured under dry conditions. A more pronounced decrease of microhardness of the wet-stored samples was found during the final wet storage.

Statistical analysis of the data revealed significant difference ($P < 0.05$) among the experimental groups. Comparing the materials, regardless of the microhardness, BelleGlass HP and Alert showed statistical similarity and yielded the highest means. On the other hand, Artglass and Filtek Z250 presented the lowest microhardness mean.

The SEM examinations of dry-stored controls and specimens kept in an aqueous environment showed few surface alterations. The most evident was the presence of voids and porosity in some areas, there were not apparent loss of fillers or topography alterations after aging time (Fig. 1-8).

4. Discussion

The results of this investigation showed that the all four composites stored in distilled water suffered a reduction in surface hardness. All liquid-stored specimens showed a significant drop of Knoop hardness compared to the dry-stored controls.

The fact that composites subjected to the visible light-curing experienced a reduction in properties which closely paralleled the reduction experienced by the laboratory-processed specimens suggests that the reduction has a similar etiology in both cases. Studies have attributed the decrease in hardness of dental composites immersed in water to hydrolysis of ester groups in the resin matrix¹⁵.

The mechanism of hydrolytic degradation is enhanced if the filler particles have metallic ions in their composition^{4,16}. The explanation of this effect is that some ions in the filler particles, such as zinc and barium, are electropositive and tend to react with water. With the loss of these elements into water, the charge balance inside the silica network is changed and reestablished with the penetration of hydrogen ions of the water in the spaces occupied by the zinc and barium. As a result of the increase of the concentration of hydroxy ions, the siloxane (Si-O-Si) bonds of the silica network start to break, and there is formation of an autocatalytic cycle of surface degradation^{4,17,18}. This mechanism would explain the continuity of the superficial softening with aging time.

The short duration of immersion is therefore aimed at investigating surface changes in hardness that will influence mechanical wear. It has been suggested that resistance to initial softening will improve the abrasion resistance of dental composite restorations^{19,20}.

The present study agrees with the results of others studies^{10,11,12}. Decreased in Knoop microhardness was found in the commercially available composites stored in water for 30 days¹⁰, and Helvatjoglou (1991) assumed that the changes in superficial hardness were due to the plasticization by water in the material¹¹. The results of the present study were also consistent with the results of Ferracane *et al.* (1998) for the unaged and aged specimens. Contrary to these findings, Chadwick *et al.* (1990) found that composite resin stored in water did not significantly influence surface microhardness during the 1-year study period.

The laboratory-processed composite BelleGlass and condensable composite resin Alert showed similar results between the unaged and water storage for 30 and 90 days.

Table 2. Microhardness values (KHN) of tested materials after different storage time periods.

Material	aging time			
	T0	24h	30d	90d
belleGlass	18.60(1.51) ^a	18.50(1.27) ^a	21.40(2.01) ^a	23.00(2.58) ^a
Alert	19.70(1.83) ^{ab}	20.70(1.83) ^b	21.80(1.75) ^{ab}	23.20(2.10) ^{ab}
Filtek	22.70(1.42) ^c	23.20(1.14) ^c	24.00(2.16) ^c	25.80(2.66) ^c
Artglass	25.90(2.18) ^d	25.90(2.47) ^d	27.60(1.17) ^d	29.30(1.25) ^d

Means followed by the same superscript letters in the column indicate no significant difference ($p < 0.05$).

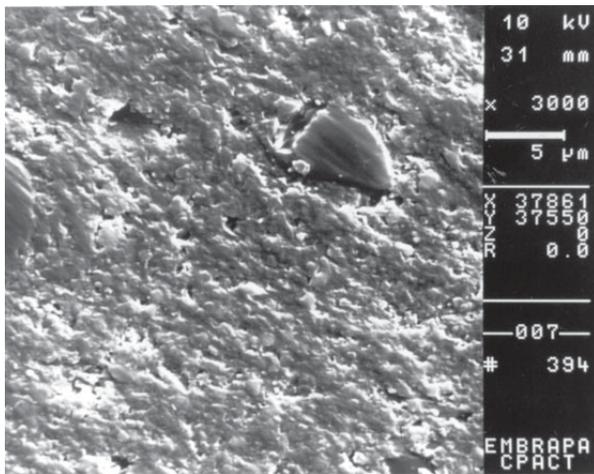


Figure 1. SEM micrograph of Alert surface at aging time 0 (SEM original magnification 10000×).

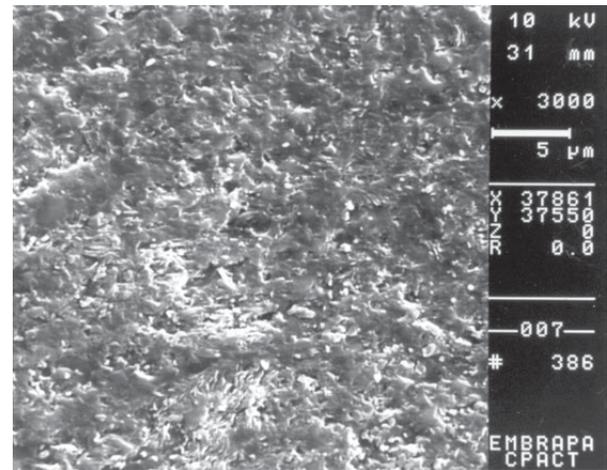


Figure 3. SEM micrograph of Artglass surface at aging time 0 (SEM original magnification 10000×).

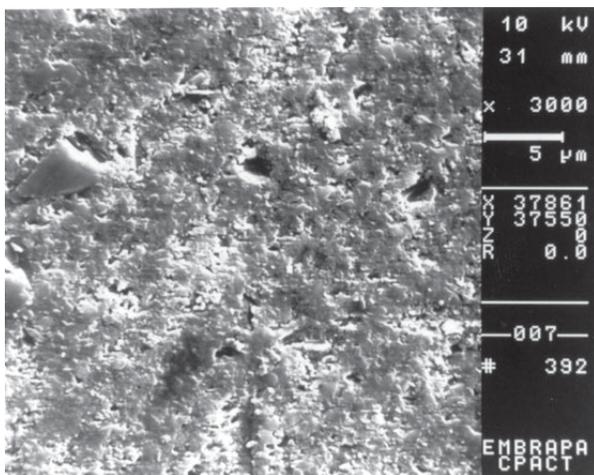


Figure 2. SEM micrograph of Alert surface after 90 days of aging (SEM original magnification 10000×).

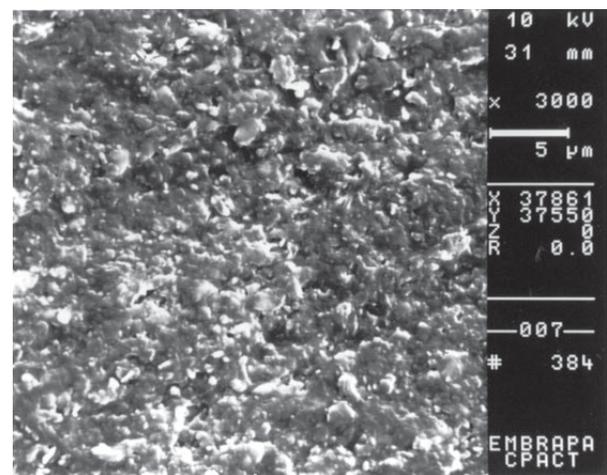


Figure 4. SEM micrograph of Artglass surface after 90 days of aging (SEM original magnification 10000×).

The heat and pressure treatment, alone or in combination with the additional light exposure, was expected to increase the degree of conversion of the polymer. However, no evidence for this was revealed, though this is a technique used in at least one commercial curing system (belleGlass HP).

The lack of a significant difference suggests that the degradative effects of water are independent of cure state. This conclusion supports a clinical study which reported no difference in resistance for inlays that were light-cured only *vs.* those that were exposed to a heat treatment after the initial light-curing²¹ and after aging in water^{12,22}.

In addition, the SEM evaluation of dry-stored controls

and specimens kept in an aqueous environment revealed changes in surface texture. The wet-stored samples were significantly rougher than the dry-stored specimens and showed a fine highly porous structure. This surface roughness appeared to be a discernible loss of material and crack formation. So long as inorganic fillers of the types currently used are present the surface of composite resins will be rough, either because of loss or projection of particles^{23,24}.

Composites containing zinc and barium glasses have been shown to be more susceptible to aqueous attack than those containing quartz^{16,25,26}. From the large softening observed with Filtek Z250 in water, it appears that zirconia

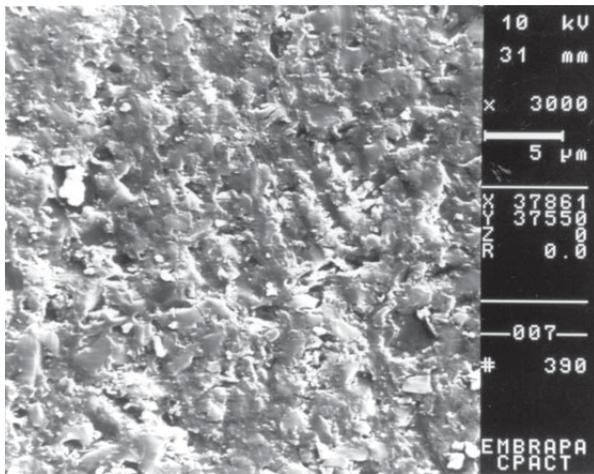


Figure 5. SEM micrograph of Belleglass surface at aging time 0 (SEM original magnification 10000×).

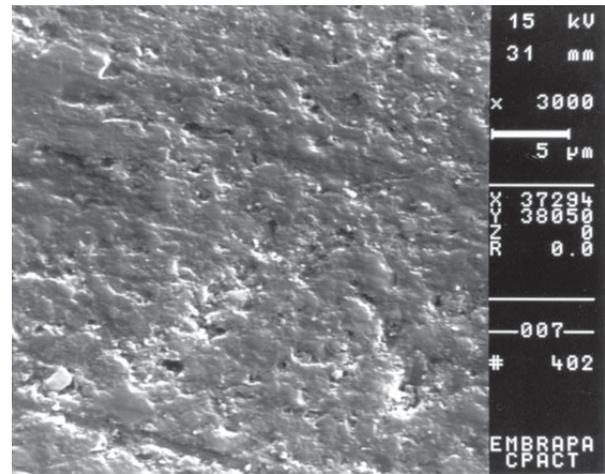


Figure 7. SEM micrograph of Filtek Z250 surface at aging time 0 (SEM original magnification 10000×).

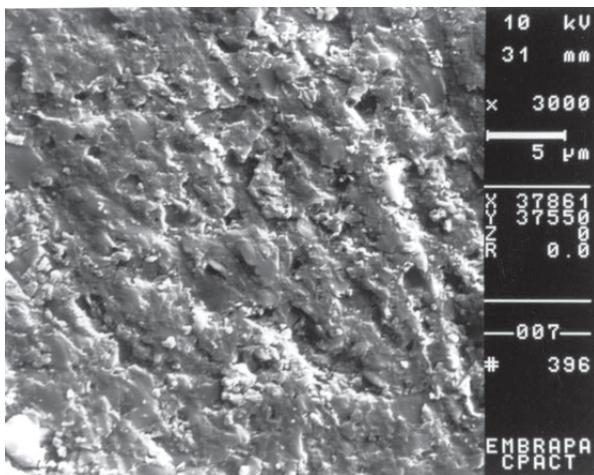


Figure 6. SEM micrograph of Belleglass surface after 90 days of aging (SEM original magnification 10000×).

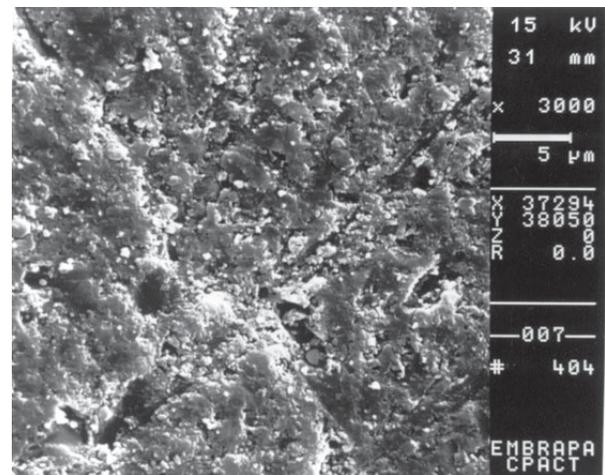


Figure 8. SEM micrograph of Filtek Z250 surface after 90 days of aging (SEM original magnification 10000×).

silicate fillers are also susceptible to aqueous attack. This may be compounded by the smaller filler surface area associated with the spherical shape of zirconia/silica fillers that may decrease bonding of fillers to the resin matrix.

The filler particle dimension and chemistry of the four tested composites did not represent substantial differences among the materials. However, there were statistically significant differences in the hardness results of the various materials. It would appear that the filler is not responsible for the observed differences in properties of the test materials in this study. It may be that the volume percent of the filler content, the amount of residual monomer or matrix polymers is manifest in the different results.

A variety of mechanisms has been suggested in this paper to explain the effects of the storage media upon the surface hardness of all four materials. Further investigation is necessary to more completely characterize the hydrolytic degradation of composites that occurs as a result of accelerated aging.

5. Conclusions

Under the simulated conditions of this study, the following conclusions have been drawn.

All the materials presented hydrolytic degradation due to storage time.

Materials stored in an aqueous environment were softened compared to dry samples.

Within the limits of this study, belleGlass HP was the hardest material, and the composites in order of decreasing hardness were Alert, Artglass and Filtek Z250.

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