

Diametral tensile strength and Vickers hardness of a composite after storage in different solutions

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Abstract: This study evaluated the Vickers hardness (VHN) and diametral tensile strength (DTS) of the composite Z100 (3M ESPE) cured with: Quartz-Tungsten-Halogen light curing unit (QTH) (700mW/cm² - 40 s) and Argon laser (1,000mW/cm² - 10 s). Specimens of 2 mm depth and 8 mm diameter were immersed for 30 days at 37°C in different storage means: water, alcohol, acetic acid, propionic acid and dry (control). The DTS (n = 8) was determined with a crosshead speed of 0.5 mm/min. The VHN (n = 8) test was carried out using a 50 g load for 60 s. Statistical analysis was performed by two-way ANOVA and Tukey's test ($\alpha = 0.05$). The relationship between VHN and DTS was observed by Pearson correlation. The light source was not significant in both tests (VHN: $P < 0.18$; DTS: $P < 0.92$), but the factor storage showed significance ($P < .001$). Mechanical properties of the control group were statistically superior to those of the other storage groups (VHN = 102.2; DTS = 42.3 MPa). The alcohol group showed the lowest VHN (93.3) and DTS (33.8 MPa) values, which were similar to values for propionic (VHN = 97.5; DTS = 35.9 MPa) and acetic acids (VHN = 97.8; DTS = 36.1 MPa), but different from that of water (VHN = 102.2; DTS = 42.3 MPa). The relationship between VHN and DTS values presented a positive correlation ($r^2 = 0.90$; $P < 0.01$). (J. Oral Sci. 49, 61-66, 2007)

Keywords: dental materials; composite resins; hardness.

Introduction

The most commonly used mode of cure in resin composites is photopolymerization (1). Ideally, the dental restorative resin should have all of its monomer converted to polymer during the polymerization reaction. However, all of the dimethacrylate-based materials exhibit numerous residual carbon double bonds in the final product, with a degree of conversion ranging from 55 to 75% under standard irradiation conditions (2).

The use of curing devices with high light intensities results in a higher degree of monomer conversion, and is associated with improvements in the mechanical properties of the resin composite (3). For the sake of convenience and for economic reasons, practicing dentists would prefer to minimize the clinical exposure time of resin-based restorations. However, the use of high light curing devices (light intensity > 500-600 mW/cm²) induces a more rapid monomer to polymer conversion, possibly increasing the polymerization shrinkage stresses (4,5).

Modified light-curing protocols involving lower initial irradiance, pulsed light applications or ramped light applications have all been suggested to reduce contraction stress in dental composite restorations (6). However, these methods have shown some problems, as they may produce alterations in the nature of the polymer network formed (7,8). It was recently demonstrated that the use of low light intensities can form a more linear polymer, which is likely more susceptible to effects of food substances that can soften the material, or to an enzymatic attack (9-12), and thus reduce the long-term stability of the composite. So

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far, no studies have attempted to address the long-term stability of resin composites polymerized with different light-intensities.

Studies determining the effect of storage conditions on the stability of dental polymer networks have exposed materials to water, artificial saliva, alcohol, and acidic or basic solvents in an attempt to study the aging process (6). The effect of these chemicals is varied, but typically involves an elution of unreacted components and some degradation of the polymer network.

Bis-GMA based polymers are exposed to different substances containing distinct solubility parameters such as dietary components, bacterial plaque and mouthrinses (6,13-16). Solutions of 50-75% ethyl alcohol in water have been shown to be among the best solvents for dental composite networks (17). Some in vitro studies showed sub superficial degradation (18), expansion (19) and inferior physical properties when Bis-GMA based-composites were exposed to ethanol solvent (20).

Although a lot of organic acids are produced by oral microorganisms, little information is currently available regarding their effect on composites (6). In vitro studies have shown that bacteria can colonize resin surfaces, increasing material surface roughness after incubation, suggesting some surface degradation (21). It is likely that this degradation is the effect of acids produced by bacteria. The predominant acids involved in bacterial colonization are acetic, propionic and lactic acids (14,22). Acetic and propionic acids have a greater potential to produce expansion of Bis-GMA based-composite. Additionally, Lee et al. showed that mechanical properties of composites were significantly reduced after 30-day storage in these acids, but it was influenced by the composition of composite (20).

Thus, the objectives of this study were: a) to examine the polymerization efficacy of two light curing devices by evaluating two different physical properties (Vickers hardness and diametral tensile strength); b) to investigate whether storage of composite in five different solutions would result in decreased physical properties, and c) to test the correlation between hardness and diametral tensile strength.

The null hypotheses tested were: 1) there is no difference in polymerization efficacy between the two light curing devices (QTH and laser); 2) storage of the composite in different solutions decreases its physical properties; and 3) there is no correlation between Vickers hardness and diametral tensile strength.

Material and Methods

A commercially available light-cured composite resin restorative material (Z100, 3M ESPE, St. Paul, MN, USA),

shade A3, was used. The material was light-cured with two visible light-curing units: an argon laser (INNOVA 100, Coherent, Santa Paula, CA, USA) with a power density of 1000 mW/cm² and a quartz-tungsten-halogen lamp (QTH, model 200R, K&M Ltda, São Carlos, SP, Brazil) with a power density of 700 mW/cm². Power density was measured using a dental radiometer (model 100, Demetron/Kerr, Danbury, CT, USA) and a power meter (Fieldmaster, Coherent, USA) (QTH and laser, respectively).

Metal split molds 2 mm deep and 8 mm in diameter were used to prepare cylindrical specimens, which were built up in one layer. Unpolymerized composite material was placed inside the molds, covered with a Mylar Strip (Jon, São Paulo, Brazil) and then cured for 10 s (argon laser) or for 40 s (QTH). All specimens were randomly assigned to one of the five media, and stored at 37 ± 0.5°C for 30 days in light-proof containers (n = 8). The storage solutions tested were: 1) dry/without solution; 2) distilled water; 3) 50% alcohol; 4) 95% acetic acid and; 5) 95% propionic acid. Specimens were submitted to Vickers hardness test (VHN) and diametral tensile strength (DTS) test.

Immediately before testing, each specimen was rinsed with running water for 30 s and air-dried. The Vickers hardness number was determined using a load of 50 g and a dwell time of 30 s in a Microhardness Instrument (model mhp 160, Zeiss, Oberkochen, Germany). Three indentations were made in each specimen and these values were averaged for statistical purposes.

The diametral tensile strength (DTS) test was performed using a Universal Testing Machine (Test System 810, MTS, Eden Prairie, MN, USA) at a crosshead speed of 0.5 mm/min. Specimens were positioned vertically on the testing machine base and subjected to compressive load until failure.

Mean VHN and DTS values were expressed in MPa and data were analyzed by two-way ANOVA (light-curing units vs. storage solutions), followed by Tukey's test at a 5% significance level. The correlation between VHT and DTS was analyzed by simple linear regression. The association between these two variables was estimated with the Pearson product-moment correlation statistics ($\alpha = 0.05$).

Results

Vickers hardness

Mean Vickers hardness values for QTH (99.5) and laser (101.2) were not significant ($P < 0.18$). A significant effect was found only for the storage solution factor ($P < 0.001$). The highest value for VHN was observed in the control group (dry), while the lowest value was observed

for alcohol storage that was statistically similar to storage hardness of acetic and propionic acids. The intermediary group, composed of water, acetic and propionic acid presented statistically similar values (Fig. 1). The interaction of two factors (light-curing units vs. storage solutions) was not statistically significant.

Diametral tensile strength

Diametral tensile strength obtained with laser (43.2 MPa) was similar to QTH (39.1 MPa; $P < 0.76$). The effect of the factor storage solution was only significant ($P < 0.001$) as detected by ANOVA. The highest value for DTS was observed for the control group (dry). The lowest value was observed for alcohol storage, but in this case, no statistically significance was observed when compared to storage in acetic and propionic acids (Fig. 1). The interaction of the two factors was not statistically significant.

Correlation between properties

Regression analysis revealed a linear and positive relationship between the Vickers hardness and diametral tensile strength (Fig. 2) ($r^2 = 0.90$, $P < 0.01$).

Discussion

In the present study, no difference could be observed between the light-curing sources tested, so the first hypothesis was accepted. This finding was unexpected, as the energy provided by the two devices was notably different (28 J/cm^2 for QTH and 10 J/cm^2 for Argon laser). Photoactivation with high intensity and short exposure time, like with the argon laser, results in fewer polymer growth centers. Consequently, polymerization propagation will predominantly add one molecule of monomer after the other to a growing polymer chain. This results in a more linear oligomer or polymer structure with relatively few cross-links. The QTH will activate a large part of the remaining camphoroquinone and thus give rise to a multitude of growth centers. The formation of many growth centers increases the tendency to form a branched polymer (9,10).

However, an explanation that could support this finding is related to the characteristics of the argon laser compared to the QTH device, which include monochromaticity (488 nm) and collimation. These aspects are favorable for optimal camphoroquinone activation and a more consistent power density over the distance (23). The capacity of the argon laser to provide light energy concentrated in the 488 nm wavelength could result in a polymerization efficiency equivalent to the QHT unit, which has already been demonstrated (23,24).

In general terms, the decrease in Vickers hardness and

diametral tensile strength after storage in different solutions was observed in comparison to storage in dry condition; thus the second hypothesis was accepted.

The presence of water resulted in significant degradation of the evaluated physical properties of the composite, which is probably associated with chemical degradation. Water or others liquids enter the polymer network through porosities and intermolecular spaces. The uptake of water or solvent by dental composites may cause expansion that can affect the dimensions of the restoration. The solvent diffuses into the network and separates the polymer chains, creating an expansion. In addition, water uptake is

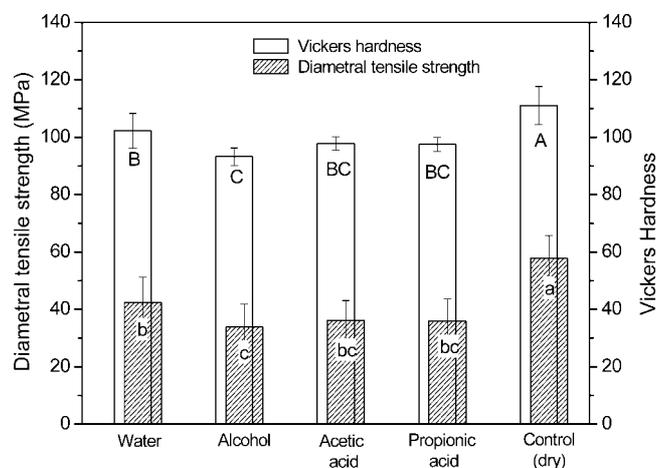


Fig. 1 Means and standard deviations for Vickers hardness and diametral tensile strength for each storage medium using both light cure units (QTH and laser). Identical capital letters indicated no statistical difference between groups in Vickers hardness. Identical small letters indicated no statistical difference between groups in diametral tensile strength.

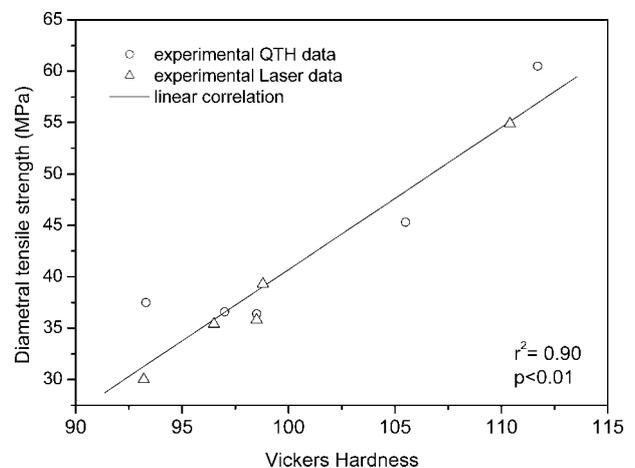


Fig. 2 Regression analysis between mean values of Vickers hardness and diametral tensile strength.

accompanied by a loss of unreacted components, like unreacted monomers, polymerization promoters and oligomers or ions from the filler particles (6,25). The reduction in hardness and other properties, like diametral tensile strength, is a consequence of the separation of the polymer chains by a molecule that does not form primary chemical bonds with the chain, but simply serves as a space occupier (i.e. plastification). Thus, the main effect of the solvent is to reduce interchain interactions, such as entanglements and secondary bonding.

Another possibility could be the chemical degradation occurring via hydrolysis. This process is complex. After water or solvents enter the polymer bulk, the intrusion of water triggers chemical polymer degradation, leading to the creation of oligomers and monomers (26,27). Progressive degradation changes the microstructure of the composite bulk through the formation of pores, via which oligomers, residual monomers, degradation products and additives are released. This process might be responsible for the inferior mechanical properties demonstrated in this study.

With this degradation mechanism, a decrease in the quality of the evaluated properties could be expected when lower pH solutions such as acetic and propionic acids were used, since low pH increases erosion in polymers (28-30). Although no statistically significant difference was observed when comparing the acid solutions to water, the acid solutions showed a tendency to negatively affect mechanical properties of the composite. Additionally, studies on quantification of degradation products of polymers generally show that extraction of the monomers and oligomers is more complete in alcohol or organic solvents compared to water (31-33). However, even studies using water have shown elution of components present in very small concentration, such as photoinitiators (13,34). Unfortunately, due to the few studies using acetic or propionic acid (20), comparisons are difficult.

In the present study, the alcohol-stored group presented the highest material degradation, which can be verified by the decrease in mechanical properties in comparison to the dry condition or water storage group. This could be related to the alcohol solubility parameter, which is similar to the Bis-GMA molecules (17,19).

Lee et al. indicated that there is a similarity between acetic acid and alcohol solubility parameters (20). Besides a close solubility parameter, the molecular weight of these solutions is smaller than that of propionic acid, which implies a greater permeability and enables diffusion 'far' into the specimen, resulting in more expansive and rapid degradation. However, alcohol caused the highest degradation. Alcohol causes softening of the resin

composite surface by removing the polymer compounds such as unreacted monomer, oligomers and linear polymers (9,10), or imparts an open structure to the polymer, decreasing its physical properties and increasing wear (17,19,32). In a resin composite with the same degree of monomer conversion, it is possible that ethanol exerts a more selective dissolution for a relatively linear polymer than for a more cross-linked structure. Cracking within the resin matrix and at the filler/matrix interface was observed by Scanning Electron Microscope after exposure to alcohol (19,31,35,36). Such gaps could also lead to leaching (35) and act as stress concentration regions that could reduce the mechanical strength of composites.

Furthermore, in Fig. 2 it was possible to establish a linear regression between mean values of Vickers hardness and diametral tensile strength for each storage medium ($r^2 = 0.90$), so the third hypothesis was rejected. Hardness evaluation is a widely used test to assess composite resin polymerization and consequently, the efficiency of the light source (37). Hardness has been an indicator of double bonds conversion (38-40) and was therefore used as an indirect measurement of degree of cure in the present study. Likewise, surface hardness may also be related to its wear resistance and ability to maintain form stability (41). On the other hand, diametral tensile strength provides an indication of resistance of a restoration to the lateral forces generated during function (42). The fact that VHN and DTS correlated well is due to both being affected by the surface, and DTS failure probably is initiated by surface conditions.

Despite the fact that this study showed a positive correlation between the two variables tested, a recent study has shown contrary results (33). This difference may be explained by the lower storage time (24 h) used in the previous study, which possibly affected the bulk of composite less and, consequently, improved the mechanical properties. Further studies should be carried out to confirm this hypothesis.

In summary, the two light curing devices tested showed similar mechanical properties. Alcohol caused the highest degradation among the storage solutions tested. Also, a linear and positive correlation could be observed between Vickers hardness and diametral tensile strength.

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