Effect of Alcoholic Beverages on the Surface Microhardness of Three Restorative Materials

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Abstract
To investigate the titratable acidity and erosive potential of alcoholic beverages on the surface hardness of three restorative materials.

A Zirconia-reinforced glass ionomer cement (Zirconomer), an Alkasite-based material (Cention N) and a bulk fill composite (Filtek Bulk Fill Posterior Restorative) were the restorative materials tested in this study. Beverages tested were deionized water, beer, red wine and whisky. Surface microhardness testing was carried out before and after immersion using a microhardness tester with a diamond Vickers indenter (MMT-X7A, Matsuzawa, Japan).

Data was analysed using two-way ANOVA and post hoc Tukey's test (P < 0.05).

Among the beverages tested, Red wine had the highest erosive potential. Microhardness of all three restorative materials significantly reduced after 7 days of immersion in all the alcoholic beverages tested. Filtek Bulk Fill Posterior Restorative showed the least degradation among the three restorative materials.

Alcoholic beverages, depending on their acidity and alcohol content, could cause degradation in the surface microhardness of restorative materials.


Keywords: Alcoholic beverages, Microhardness, Restorative materials, Titratable acidity.

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Introduction
The resin-based restorations are currently in demand due to their excellent aesthetics, easy handling, and adhesion properties. The durability of any restoration relies upon the nature of material being used and the effect of degradation on its mechanical properties such as resistance to wear, bond strength, tooth-restoration interface, aesthetics, surface hardness and roughness.¹ ² ³

Kent and Wilson developed the conventional GICs back in 1960s, which set by an acid-base reaction. A new generation of GIC (Zirconomer) was developed at SHOFU, Japan by incorporating zirconia particles to improve compressive and flexural strength, reduce the occlusal wear and to fasten the setting reaction.⁴

Centon N (CN) is an “Alkasite” restorative material, which is similar to Compomer or Ormocer. It is composed of an alkaline filler that releases acid-neutralizing ions. CN consists of powder and liquid components in a weight ratio of 4.6–1 that are hand mixed prior to use. The liquid component includes dimethacrylates and initiators, and the powder components include various glass fillers, initiators, and pigments.⁵

Filtek Bulk Fill composite is a light-cure material with excellent strength and wear resistance properties. It comprises of AUDMA, UDMA and 1, 12-dodecane-DMA polymers and fillers are a combination of non-agglomerated/non-aggregated 20 nm silica filler, 4–11 nm Zr filler, aggregated Zr/Si cluster filler (comprised of 20 nm silica and 4–11 nm Zr particles and ytterbium trifluoride filler comprising of agglomerate particles (100nm).

Polymer degradation associated with the erosion of the composite material may occur due to mechanical, thermal or passive hydrolysis. Extrinsic causes of erosion include, intake of acidic food, alcoholic beverages, soft and energy drinks.⁶ ⁷ Intrinsic causes include GI disorders
such as anorexia and bulimia, which cause repeated regurgitation thus reducing the pH of the oral environment. These factors contribute to softening of the material and increased surface irregularities, thus rendering them to wear further.

Due to the increased trend for social drinking in current times, several doubts have been raised regarding the erosive potential of the alcoholic beverages on the tooth structure as well as the restorative materials. The alcohol present in the drink diffuses into the resin, plasticizes the matrix, thus lowering the mechanical properties of the material, by acting on the filler-matrix interface. As a result, there might be retention of microorganisms, faster colonization of the biofilm, thereby promoting caries as well as staining of restorations.

This study examined the erosive potential and titratable acidity of three alcoholic beverages (beer, whisky and red wine) on the surface microhardness of three tooth coloured restorative materials.

The null hypothesis states that there is no change in the surface hardness of the restorative materials post immersion in three alcoholic beverages.

Materials and methods

Table 1 presents the restorative materials and storage media tested in the study.

Sample preparation

With the help of acrylic moulds (6mm in diameter and 3mm in thickness), thirty-six samples of individual material were prepared. Zirconomer and Cention N, supplied in powder/liquid form, were hand mixed (manufacturer’s instructions), packed and condensed into the acrylic mould. Filtek Bulk Fill Posterior Restorative, supplied as single paste, was loaded directly and condensed into the acrylic mould. A Mylar matrix strip and glass slide were placed on the mould with slight pressure to achieve a smooth and flat surface and to extrude excess material. Zirconomer and Cention N samples were left to set in an incubator for 1 hour, whereas Filtek Bulk Fill Posterior Restorative material was polymerized for 40s with a light-curing unit (Elipar DeepCure-S LED, 3M USA). The intensity of curing light was checked with a measuring device (Cure Rite, L.D. Caulk, Milford, DE, USA). No mechanical alterations of the specimens were performed after curing.

Storage media preparation

Deionized water (control), beer, red wine and whisky were the storage media used. The pH values of individual storage media (except the control) were recorded with a digital pH meter (Systronics, India). Three pH readings of each storage media were recorded and a mean value was obtained. The titratable acidity was determined by adding 0.5mL increments of 0.1N sodium hydroxide (NaOH) to 20 ml of each storage media being tested. The quantity of NaOH (mL) necessary to reach pH 5.5, 7.0 and 10.0 was measured. The titrations for individual solutions were repeated thrice for a mean value. A graph of pH versus the quantity (mL) of 0.1N NaOH needed to reach pH 5.5, 7.0 and 10.0 was then plotted.

Alcoholic beverage immersion and microhardness testing

Thirty-six samples of individual material were divided into four groups (9 specimens/group) and placed in 20 mL of the storage media in individual plastic storage cups. The samples in the moulds were maintained at 37°C throughout the experiment. To maintain a stable pH of the beverages, each storage media was replenished every 24hours.

The microhardness values (kg/mm²) of each sample were measured with a microhardness tester with a diamond Vickers indenter (MMT-X7A, Matsuzawa, Japan). The samples were kept on a platform facing the testing surface towards the indenter. A load of 200g was then applied for 10 seconds to the samples. Three indentations, equally spaced on a circle, were made on individual samples for the mean value. The surface microhardness test was done after 1 hour (before immersion) and after 1 day, 3 days and 7 days of immersion in beverages. The continuous variations in the microhardness were measured at specific time intervals as mentioned above.

Statistical analysis

The data obtained was tested for significant difference ($P<0.05$) using a two-way ANOVA with repeated measurement and Tukey’s Honestly Significant Difference (HSD) for multiple comparisons.
Results

All four alcoholic beverages tested were acidic. The mean pH value and standard deviation values of beer was 3.61 (0.04), red wine was 3.49 (0.04), and whisky was 3.81 (0.03). Titratable acidity of the alcoholic beverages with 0.1N NaOH is shown in Figure 1. The microhardness values of the restorative materials post immersion in various storage media over 7 days are presented in Table 2.

Filtek Bulk Fill Posterior Restorative had the highest microhardness value, before immersion (at 1 hour), followed by Cention N and Zirconomer. After immersion in different beverages (from day1 to day7), all materials tested had different surface hardness reduction values. After 7 days of immersion, the surface hardness of all materials significantly reduced after immersion in all the alcoholic beverages tested. For Zirconomer, the surface hardness significantly reduced after 1 day of immersion in beer, in red wine and in whisky, except in deionized water. On the 7th day, the surface hardness of Zirconomer significantly reduced after immersion in all the storage media including deionized water, while immersion in red wine produced the most surface hardness reduction.

For Cention N, the surface hardness significantly reduced after 3 days of immersion in all the three types of alcoholic beverages. The extent of surface hardness reduction of Cention N after 7 days of immersion in beer was lesser, while the result of both red wine and whisky immersion after 7 days were more and comparable.

For Filtek Bulk Fill material, there was a statistically significant reduction in the surface hardness only in red wine immersion after 3 days. On the 7th day, similarly to the result of Cention N, the surface hardness significantly reduced in all the three alcoholic beverages immersion, while immersion in beer produced lesser surface hardness reduction, compared to red wine and whisky immersion.

The effect of the alcoholic beverages on the microhardness values of the restorative materials was tested by Tukey’s HSD multiple comparisons. This showed that both red wine and whisky immersion produced no significant difference in the degree of degradation on any of the materials after 7 days, whereas red wine immersion after 7 days produced the highest reduction in surface hardness value of Zirconomer. The deionized water showed least reduction in hardness value in all three materials, followed by beer.

Based on the extent of degradation in the surface microhardness, the restorative materials could be graded as follows: Zirconomer > Cention N > Filtek Bulk Fill Posterior Restorative.

The grading order of the erosive potential of the alcoholic beverages is as follows: Red wine > Whisky > Beer.

Discussion

One of the most important properties of a restorative material is its surface hardness, which correlates with wear resistance, compressive strength and resistance to intraoral softening. A low surface hardness increases the susceptibility to wear and scratching, and also compromises fatigue strength which can lead to restoration failure. In the constant changing environment of the oral cavity, due to thermal, chemical and mechanical influences, the ability of a restorative material to resist or show minimal changes determines its clinical success and longevity. In this study, three restorative materials were immersed in three alcoholic beverages without any thermal or mechanical influence. Therefore, any degradation in the surface hardness of restorative materials tested was solely due to a chemical process.

Several studies reported that acidic drinks could induce erosive wear to restorative materials. Titratable acidity measures the total acid concentration contained within a solution and is a better indicator of erosive potential than the pH value. Despite the minor difference in pH between the beer, red wine and whisky tested, their titratable acidity indicated differently. From the results obtained, red wine had a much higher titratable acidity than beer, whereas whisky had the least. For whisky, the initial pH (3.81) rose to pH 11 when only 0.5mL of 0.1N NaOH was added. This could probably mean that there was very minute amount of undissociated H+ ions present in whisky, compared to beer and red wine, and therefore a lower buffering capacity. Among the three alcoholic beverages tested, beer caused the least reduction in the surface hardness of all
materials even though beer had higher titratable acidity than whisky. Due to the significant lower alcohol content in beer (4.8%) than whisky (42.8%), it could be assumed that alcohol also played a similar role as acidity in the degradation of the materials. Studies have shown that alcohol has the ability to penetrate polymer matrix and causes a plasticizing effect. It can act on the filler-matrix interface, reducing the chemical bond between the filler particles and polymer matrix, and subsequently causing debonding and leaching of the filler particles.\(^{16, 17}\) This in turn causes softening of the material. Therefore, although whisky had a lower titratable acidity, its significantly higher alcohol content was capable to cause considerable degradation in the surface microhardness in all three materials.

Zirconomer, claims to have the strength and durability comparable to amalgam, while exhibiting the benefits of glass ionomer, hence called as white amalgam.\(^{18}\) After 7 days, Zirconomer showed the greatest extent of degradation. The reason could be Zirconomer, being a glass-ionomer based restorative material, is a less hydrolytic stable material because of its more hydrophilic nature of the polymer matrix.\(^{4, 19, 20}\) Sakar reported that corrosive wear begins with water sorption that diffuses internally through the polymer matrix, filler interfaces, voids and other defects, which in turn leads to interfacial debonding, filler dissolution, matrix cracking and subsurface damage.\(^{21}\) This degradation process could be accelerated by an acidic environment and alcohol attack.\(^{22}\) Besides, it could be speculated that the inclusion of zirconium oxide fillers in glass-ionomer contributed only to physical load resistance but did not affect their chemical degradation resistance as their hydrophilic polymer matrix served as the weaker link.

The results of present study also indicated that Filtek Bulk Fill composite had the lowest degradation in microhardness after being exposed to alcoholic beverages. The explanation could be the lower water sorption ability of composite resin.\(^{23}\) Cention N belongs to the materials group of Alkasites.\(^{5}\) Being a resin-based material, it was expected to have comparable degradation resistance as Filtek Bulk Fill Composite. However, Cention N had greater degradation after immersion in all the alcoholic beverages. This difference could possibly be due to the difference in their structural and chemical composition. The water sorption and solubility behavior of restorative materials are dependent on the polarity of the polymer matrix, the degree of cross-linking of the continuous matrix, filler particle type, size and amount.\(^{24, 25}\) The larger inorganic filler particle size (0.1 – 35um) and the lower filler amount in Cention N (57.6 vol%), could be the reason for the greater degradation as compared to Filtek Bulk Fill Composite which had smaller filler particle size (4 – 20nm) incorporated and a higher filler amount (58.4 vol%). This is in accordance with the study of Berger SB, which reported that the solubility of nanofilled composite was lower than those of the minifilled and microfilled composites.\(^{26}\) Eric Mortier also showed in his study that a high filler content could reduce water sorption and solubility.\(^{27}\) Higher the filler content, lower the volume of resin polymer unprotected by filler particles, which is susceptible to hydrolysis by water sorption.\(^{28, 29}\)

Another possible explanation for greater degradation of Zirconomer and Cention N than Filtek Bulk Fill Restorative material could be the presence of voids as a result of trapped air during mixing of the powder and liquid. These voids could act as an entry for water sorption causing hydrolytic degradation.\(^{30}\)

According to the results of this study, we can conclude that alcoholic beverages, depending on their acidity and alcohol content (ABV), could cause degradation in the surface hardness of restorative materials. The resistance to degradation could be related to the structural and chemical composition of restorative materials. Among the three types of restorative materials tested, Filtek Bulk Fill Posterior Restorative composite performed the best in terms of resistance to degradation by alcoholic beverages. It must be observed that there were some limitations to this study. The duration of contact of alcohol with the restorative materials in the oral cavity and the influence of saliva were not considered. Besides, this study assessed the in-vitro effects alone.

**Conclusions**

Within the limitations of this study, the following conclusions were drawn:
The alcoholic beverages examined (beer, red wine and whisky) are acidic and can degrade surface microhardness of restorative materials. Filtek Bulk Fill composite was more resistant to chemical degradation by alcoholic beverages than Cention N and Zirconomer. For clinical decision making, bulk fill packable composite is a better choice than Alkasite and glass-ionomer based materials for restorations in patients who consume alcohol on a regular basis.

Declaration of Interest

The authors report no conflict of interest.

### Restorative materials used

<table>
<thead>
<tr>
<th>Product</th>
<th>Type of material</th>
<th>Composition*</th>
<th>Mixing*</th>
<th>Particle size*</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconomer</td>
<td>Zirconia-reinforced glass ionomer cement</td>
<td>Polyacrylic acid, Tartaric acid, Fluoroaluminosilicate glass, Zirconium oxide</td>
<td>Hand-mixed (3.6:1 P/L)</td>
<td>-</td>
<td>Shofu, Japan</td>
</tr>
<tr>
<td>Cention N</td>
<td>Alkasite</td>
<td>UDMA, DCP, Aromatic aliphatic-UDMA, PEG-400 DMA, Barium aluminium silicate glass, Ytterbium trifluoride, Isolfiller, Calcium barium aluminium fluorosilicate glass, Calcium fluorosilicate glass, 78.4 wt%, 57.6 vol%</td>
<td>Hand-mixed (4.6:1 P/L)</td>
<td>0.1μm - 35μm</td>
<td>Ivoclar Vivaden t, Schaan, Liechtenstein</td>
</tr>
<tr>
<td>Filtek Bulk Fill</td>
<td>Bulk fill resin composite</td>
<td>AUDMA, AFM, DDDMA, UDMA, Silica, Zirconia, Ytterbium trifluoride, 76.5 wt%, 58.4 vol%</td>
<td>One paste</td>
<td>20 nm silica 4 - 11 nm zirconia</td>
<td>3M ESPE, USA</td>
</tr>
</tbody>
</table>

### Storage media used

<table>
<thead>
<tr>
<th>Storage media</th>
<th>Alcohol by volume (ABV %)</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kingfisher Premium beer</td>
<td>4.8</td>
<td>United Breweries Group, India</td>
</tr>
<tr>
<td>Big Banyan Merlot red wine</td>
<td>14</td>
<td>Big Banyan, India</td>
</tr>
<tr>
<td>Signature Rare Aged whisky</td>
<td>42.8</td>
<td>United Spirits Ltd, India</td>
</tr>
</tbody>
</table>

Table 1. Restorative materials and storage media used in this study.

UDMA: Urethane dimethacrylate; DCP: Tricyclocdecan-dimethanol; PEG-400 DMA: Polyethylene glycol 400 dimethacrylate; AUDMA: Aromatic urethane dimethacrylate; AFM: Addition-fragmentation monomers; DDDMA: 1, 12-Dodecanediol dimethacrylate.

*Information given by the manufacturer.
**Table 2.** Mean surface hardness value (kg/mm²) of restorative materials after immersion in various storage media over a period of 7 days.

<table>
<thead>
<tr>
<th>Restorative material</th>
<th>Mean surface hardness (kg/mm²)</th>
<th>Storage media</th>
<th>Before immersion</th>
<th>1 day</th>
<th>3 days</th>
<th>7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Zirconomer</td>
<td></td>
<td>Deionized water</td>
<td>44.433 (0.792)</td>
<td>45.056 (0.831)</td>
<td>43.800 (1.242)</td>
<td>42.167 (1.662)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beer</td>
<td>43.444 (1.337)</td>
<td>42.067 (0.880)*</td>
<td>35.978 (0.890)*</td>
<td>29.944 (0.904)*b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Red wine</td>
<td>44.289 (1.302)</td>
<td>39.600 (0.954)*</td>
<td>29.833 (1.170)*</td>
<td>19.344 (1.474)*d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Whisky</td>
<td>45.067 (1.751)</td>
<td>41.344 (0.816)*</td>
<td>32.978 (1.220)*</td>
<td>22.000 (1.385)*c</td>
</tr>
<tr>
<td>2. Cention N</td>
<td></td>
<td>Deionized water</td>
<td>58.244 (2.910)</td>
<td>59.156 (3.134)</td>
<td>58.233 (3.380)</td>
<td>57.456 (3.158)*a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beer</td>
<td>57.456 (2.120)</td>
<td>57.544 (2.149)</td>
<td>54.667 (1.963)*</td>
<td>51.833 (1.958)*b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Red wine</td>
<td>55.378 (1.739)</td>
<td>55.033 (2.534)</td>
<td>50.433 (2.101)*</td>
<td>41.056 (2.578)*c</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Whisky</td>
<td>56.633 (2.223)</td>
<td>56.200 (2.445)</td>
<td>50.289 (2.267)</td>
<td>41.878 (2.643)*c</td>
</tr>
<tr>
<td>3. Filtek Bulk Fill Posterior Restorative</td>
<td></td>
<td>Deionized water</td>
<td>63.889 (2.152)</td>
<td>64.467 (1.806)</td>
<td>64.989 (1.948)</td>
<td>64.133 (1.725)*a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beer</td>
<td>64.444 (2.498)</td>
<td>64.456 (2.321)</td>
<td>62.333 (2.215)</td>
<td>59.856 (2.392)*b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Red wine</td>
<td>63.978 (2.014)</td>
<td>62.333 (2.030)</td>
<td>59.556 (2.469)*</td>
<td>56.344 (2.222)*c</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Whisky</td>
<td>62.878 (3.234)</td>
<td>63.011 (2.834)</td>
<td>60.556 (3.390)</td>
<td>55.444 (2.905)*c</td>
</tr>
</tbody>
</table>

*indicates significant difference compared to before immersion for each storage media (in rows) according to Tukey HSD test (P<0.05).

a, b, c, d indicate significant differences among 4 storage media for each restorative material (in columns) according to Tukey HSD test (P<0.05).

**Figure 1.** The graph of titration for three alcoholic beverages showed the amount of 0.1N NaOH solution required to raise the pH of each solution up to pH 5.5, 7.0 and 10.0.
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