The Effect of Water Absorption on Acrylic Surface Properties

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Purpose: The aim of the present study was to determine whether an increased water content during thermal cycling of hot water-treated acrylic was associated with a reduction in surface hardness and an increased opacity or whitening of the surface.

Materials and Methods: Ten acrylic samples were treated with 30 soak cycles (cycle duration, 24 hours), using warm water (40°C) and an alkaline peroxide tablet (Efferdent® control group); a further ten samples were treated with boiling water (100°C) and one Efferdent® tablet (experimental group). Indentation hardness of the acrylic specimens was measured prior to and immediately following the completion of the warm and hot water treatments, using an automated micro-indentation system. The hydrated acrylic specimens were then allowed to air dry at room temperature (20°C) and were weighed weekly until they had obtained a constant dry weight. The loss in weight of the acrylic specimens represented the maximum water absorption.

Results: The hot water-treated specimens were much whiter than the warm water-treated specimens. The mean reduction in hardness (H_{IT}) of the acrylic specimens following the treatment with hot water and alkaline peroxide tablet was 12.9%. Treatment with warm water and alkaline peroxide resulted in a slight increase in mean hardness (2.63%). There was a significant correlation between the water content of the acrylic specimens after treatment and the percentage of change in indentation hardness ($r = 0.495, p = 0.026$).

Conclusions: The hot water treatment of the acrylic was associated with a significant reduction in hardness. We attribute the whitening and reduction in the hardness of the hot water-treated specimens to absorption of water and a disruption of the acrylic surface structure.

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INDEX WORDS: whitening of acrylic, plasticizing effect, indentation hardness

IT HAS been shown that when patients use hot water to clean their acrylic dentures(usually by immersing them in an alkaline peroxide solution), the dentures take on a bleached appearance. The denture opacity may result from an extensive surface degradation of the acrylic,[1] with measured reductions in the physical properties of the acrylic resulting from the plasticizing effect of absorbed water.

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Methyl methacrylate is also known to have a plasticizing effect on the acrylic, but there is no known mechanism in which hot water immersion could increase the concentration of residual methyl methacrylate in the surface of the denture. The tendency of denture cleansers to produce a color change in the acrylic soft lining materials and a severe deterioration in the physical properties of tissue conditioners is a well-known shortcoming;[2] however, when peroxide cleansers are used in a warm water solution as recommended by the manufacturer, no deleterious effects on correctly processed denture acrylic have been found. These cleansers contain alkaline detergents and oxygen-releasing compounds (such as sodium perborate or percarbonate).[3]

Acrylics cannot withstand the operating temperatures observed in high-temperature applications, such as solar water heating system applications.[4] Von Fraunhofer and Suchatlampong[5] showed that water at room temperature could enter denture acrylic and cause a small change in microhardness of the surface. It has also been suggested that hot water will have a much greater effect when absorbed by the acrylic and will set up a differential expansion of the acrylic surface. Absorption of water is markedly increased at high temperatures, which causes the acrylic surface to be supersaturated with water during cooling of the specimen.[6] The water absorption and thermal effects may combine to cause the acrylic to form zones with different optical properties.[7] This phenomenon may be distinct from crazing of acrylic, where definite cracking occurs.

The aim of the present study was to determine whether an increased water content during thermal cycling of hot water-treated acrylic was associated with a reduction in surface hardness and whitening of the surface.

Materials and Methods

Specimen Preparation

Twenty samples (10 mm × 10 mm × 2.5 mm) of Hy-Pro Lucitone acrylic denture-base material (Dentsply, York, PA) were processed using a curing cycle of 8 hours at 70°C, followed by 2 hours at 100°C. All surfaces of each cut sample were polished using 600 grit silicon carbide paper. Efferdent® (Pfizer Consumer Health Care, Morris Plains, NJ) is a proprietary alkaline peroxide used for cleaning dentures and was added to 250 mL of water in each group. Ten acrylic samples were placed in warm water (40°C) with an alkaline peroxide tablet (Efferdent® control group), and ten were assigned to an experimental group, which involved applying boiling water (100°C) and one Efferdent® tablet to the test specimens. Samples were randomly assigned to each group. The specimens were left in the solutions to cool. The water was changed after 24 hours and the cycle repeated. A total of 30 soak cycles were completed, as this has been previously shown to cause acrylic opacity.

Indentation Methodology

A micro-indentation system (+CSM® Instruments, Peseux, Switzerland) was used to measure the indentation hardness and indentation modulus. A Vibraplane Model 9100/9200 vibration isolation table (Kinetic Systems Inc., Boston, MA) was used to prevent the transmission of extraneous vibration during testing of the specimens. The acrylic specimens were stored in deionized, distilled water at 20°C for 24 hours prior to hardness testing. Each acrylic sample was tested for hardness prior to the beginning of the first soak cycle and at the completion of the final soak cycle (30 days later).

The micro-indentation system was located on a vibration-free workstation (Kinetic Systems, Rosindale, MA). Before each sample was tested, a depth adjustment was performed using a contact load of 0.001 N. Poisson's ratio of 0.25 was used for each sample. A diamond Vickers indenter with a tip radius of 50 nm was used. The indenter applied a maximum load of 0.5 N to the acrylic specimens. The specimens were loaded and unloaded at a rate of 1 N/min, with no dwell time. As the acrylic sample was indented, load (y-axis) was displayed on the computer screen in real time against the indentation depth (x-axis). A total of 12 indentations were recorded for each specimen. The acrylic sample was moved 50 μm in the x-axis between each indentation. Data for each indentation were recorded, processed, and stored using the indentation software (Version 3.04, +CSM® Instruments). After the completion of the hardness measurement, the sample was stored in distilled water.

Water Absorption of Acrylic Specimens

The thermal cycling of the acrylic specimens was completed as previously described. After completion of the hardness testing, the acrylic specimens were then placed in distilled water and weighed weekly until they had attained constant weight at 4 weeks. Prior to weighing, the acrylic specimens were dried of surface water using absorbent tissue paper. They were then allowed to air dry at room temperature (20°C) and were again weighed weekly until they had obtained a constant dry weight at 4 weeks. The loss in weight of the acrylic specimens represented the maximum water absorption.

Students' t-test was used to compare mean indentation hardness values for hot water- and warm water-treated acrylic specimens.

Results

One effect of the hot water was to cause a severe whitening of all the acrylic specimens, whereas those treated with warm water were unaffected (Fig 1).

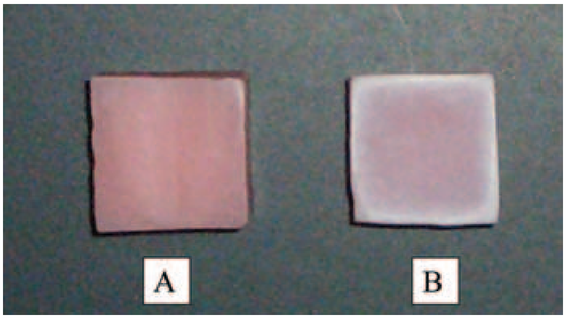

Figure 1. Acrylic specimen A was treated with 30 warm water cycles whereas specimen B was treated with 30 hot water treatment cycles. Acrylic specimen B appeared whiter than specimen A.

Pre- and post-treatment data for indentation hardness (H_{IT}) and Vickers hardness (HV) for all specimens are shown in Tables 1 and 2. The mean reduction in hardness (H_{IT}) of the acrylic specimens following the treatment with the hot water and alkaline peroxide tablet was 12.9%. Treatment with warm water and alkaline peroxide resulted in a slight increase in mean hardness (2.63%). There was a significant difference in the percentage reduction in hardness (H_{IT}) between the acrylic specimens treated with hot water and those treated with warm water ($t = 2.777$, $p = 0.012$).

There were only significant differences between pre-test and post-test indentation hardness (H_{IT}) and Vickers hardness (HV) for the hot water-treated specimens (Table 3). There were no significant differences between the pre- and post-treated specimens immersed in warm water.

Table 1. Warm Water-Treated Specimens. Data for Indentation Hardness (H_{IT}) and Vickers Hardness (HV) for Each Processed Acrylic Specimen Prior to Testing (Pre) and Following Treatment (Post) with Warm Water

Sample	*Pre* H_{IT} *(MPa)*	*Post* H_{IT} *(MPa)*	*Pre HV*	*Post HV*
1	342.800	296.692	32.350	28.004
2	330.540	347.956	31.200	32.842
3	319.020	330.171	30.110	31.163
4	342.010	392.049	32.280	37.004
5	336.750	302.317	31.780	28.534
6	298.181	347.18	28.144	32.77
7	328.600	286.57	31.015	27.05
8	275.638	274.99	26.016	25.96
9	330.941	378.24	31.236	35.70
10	278.243	310.29	26.262	29.29
Mean	318.272	326.645	30.039	30.832

Table 2. Hot Water-Treated Specimens. Data for Indentation Hardness (H_{IT}) and Vickers Hardness (HV) for Each Processed Acrylic Specimen Prior to Testing (Pre) and Following Treatment (Post) with Hot Water

Sample	*Pre* H_{IT} *(MPa)*	*Post* H_{IT} *(MPa)*	*Pre HV*	*Post HV*
11	309.880	291.420	29.250	27.506
12	321.510	263.221	30.350	24.844
13	347.870	307.404	32.830	29.015
14	323.830	278.295	30.570	26.267
15	320.650	307.350	30.210	29.009
16	325.500	292.148	30.723	27.575
17	287.032	252.760	27.092	23.857
18	372.399	281.180	35.149	20.539
19	364.442	242.180	34.398	22.858
20	281.987	319.142	26.616	30.123
Mean	325.510	283.510	30.719	26.159

Following the 30 soak cycle treatments, the specimens were allowed to dry at room temperature to constant weight and the difference in weight was due to the evaporation of previously absorbed water. The acrylic specimens previously treated with hot water reduced in weight by 1.175% (SD = 0.126), whereas the specimens treated with warm water reduced in weight by 1.067% (SD = 0.155). The hot water-treated specimens were softer and absorbed more water (Table 4).

There was a significant correlation between the water content of the hot and warm water-treated specimens (% loss of weight) and the percentage of change in indentation hardness ($r = 0.495$, $p = 0.026$).

Discussion

Previous studies have measured hardness using a variety of shaped indentors (e.g., Rockwell

Table 3. Comparison of Pre-Test vs Post-Test Indentation Hardness (H_{IT}) and Vickers Hardness (HV) for Warm- and Hot Water-Treated Specimens (Using Paired Sample *t*-test)

Pre- vs Postcomparison	*Warm Water Treatment*		*Hot Water Treatment*	
	t-value	*p-value*	*t-value*	*p-value*
H_{IT} (MPa)	0.697	0.503	3.063	0.014
HV	0.700	0.502	2.796	0.021

Table 4. Treatment of the Acrylic Specimens with Hot Water and Efferdent® Resulted in a Reduced Hardness and an Increased Absorption of Water

Treatment 30 Day Cycle	*Mean Vickers Hardness (SD)*	*% Mean Weight Change (SD)*
Warm water and Efferdent®	30.832 (3.703)	1.067 (0.155)
Hot water and Efferdent®	26.159 (3.079)	1.175 (0.126)

and Vickers hardness measurement systems) and loading conditions. In addition, hardness has been traditionally measured using different methodologies, e.g., either a fixed load penetrating a measured depth or an increasing load penetrating to a pre-determined depth. The absence of an accepted, standardized methodology in dental materials testing has complicated comparisons between studies. In the present study, we have presented results for automated indentation (H_{IT}) as well as Vickers hardness (Tables 1–3) to allow comparison with previously published studies that have used the traditional indentation techniques. Our micro-hardness testing equipment provides both traditional and fully automated advanced hardness data.

We have shown that there was a significant reduction in the hardness of acrylic following the treatment with hot water and an alkaline peroxide cleansing tablet, but not with warm water. The percentage reduction in acrylic hardness was significantly correlated with the percentage absorbed water content of the specimens. We conclude that the hot alkaline peroxide solution caused a water supersaturation of the acrylic surface, which resulted in surface whitening and softening. Interestingly, the whitening of the acrylic is not reversible when the specimens were left to dry.

Drying or wetting of denture acrylic at room temperatures causes little dimensional change, but higher temperatures (such as water at 100°C) may lead to increased absorption of water and more significant change. Using self-cure acrylic at room temperature, Heath et al[8] showed that the acrylic saturated with water after 10 weeks immersion gained 1.2% in weight, which agrees with our results. For every 1% increase in weight due to absorbed water at constant temperature, acrylic resin expands linearly by about 0.23%.[9] Similarly, Smith and Schooner[10] showed that denture acrylic resin expanded linearly by 0.38% on immersion in water at 37°C. Using these figures, the absorbed water in our hot water-treated specimens would cause an expected increase in length of specimens in our study of 0.027 to 0.044 mm, which is small. However, immersion of acrylic in boiling water from room temperature has the additional effects of thermal expansion and may involve the absorption of more water. The coefficient of thermal expansion (linear) of acrylic is 76×10^{-6} per °C over the 5 to 37°C range, and 89×10^{-6} per °C over the 37 to 70°C range.[11] Given an 80°C change in temperature of our acrylic specimens on being placed in the boiling water, this would result in a linear thermal expansion (about 0.064 mm), which is greater than that caused by water absorption alone at constant room or body temperatures (0.027 to 0.044 mm). However, we could find no published data that measured the linear expansion of acrylic in contact with water over a wide temperature range.

The dimensional changes following the thermal cycling of acrylic with water at high temperature may cause molecular fracture and cavitation of the acrylic.[12] In support of this, Robinson et al[13] described degradation of the matrix phase of whitened acrylic and formation of voids, while the polymer beads remained unaffected. Absorbed water acts on acrylic as a plasticizer. Von Fraunhofer and Suchatlampong[5] showed that the surface hardness of heat cure acrylic stored in water for 12 days at room temperature was little changed (16.71 kg/mm^2 in the wet condition vs 16.07 kg/mm^2 when stored dry). No reduction in mean hardness was observed in our warm water-treated acrylic control group. Treatment with a hot solution of denture cleanser may cause large amounts of water to be absorbed, which will eventually cause a weakening of intermolecular bonding.[14]

The resemblance between the whitening of acrylic and crazing is, at present, poorly understood. Solvents such as chloroform readily cause crazing of acrylic but not whitening or opacity of the surface. High residual monomer content does affect the mechanical properties of acrylic by acting as a plasticizer,[15] but there is no evidence that it contributes to whitening of the acrylic surface. Arab et al[16] showed that acrylic specimens constructed with either low or high residual monomer did not differ in the whitening effect observed with thermal cycling, and there was a similar percentage reduction in transverse bend strength. Compared with the control specimens at 18°C, the high temperature cycled specimens had a 14.79% reduction in transverse bend strength for the low residual monomer acrylic and 18.5% for the high residual monomer.

From our study, softening of the acrylic may be caused by either hot water alone or a combined effect of the alkaline peroxide and hot water. Those experiments that have used water alone have found that a softening effect is still observed, but extended periods of soaking in water are required. Pavarina et al[17] found that prolonged immersion of denture teeth in water for 120 days at 38°C caused a softening of the acrylic resin.

Absorbed water has been shown to affect the surface properties of all forms of acrylic, e.g. tissue conditioners[18] and autopolymerizing resins.[19] Plasticized acrylic soft lining materials undergo hardening of the surface mainly due to a loss of the plasticizer with time.[20] This is a practical problem because these materials must then be replaced. Autopolymerizing resins are used in the construction of removable orthodontic appliances. Orthodontists usually recommend young patients to remove the appliances from their mouths for cleaning with soap and water and then replace them immediately. They do not usually advise that these appliances be soaked in cleansers for any length of time, because patients may forget to replace them in their mouths. Our future work will investigate the use of alternative methods of cleaning dentures and other oral appliances, e.g. using ultrasound devices which are portable, highly efficient, and do not cause damage to the appliances. Manufacturers of the ultrasound devices claim that they are much more efficient in cleaning oral appliances than using chemical methods alone or mechanical brushing, as only 4 to 8 minutes are required.

Conclusions

The hot water and alkaline peroxide treatment of the acrylic was associated with a significant reduction in hardness. We consider that the absorption of the hot solution by the acrylic caused a disruption of the acrylic surface structure and modification of the surface properties. To definitively determine whether the whitening and surface softening occurred with hot water alone or a combined effect of the Efferdent® and the hot water, future studies will include specimens subjected to only hot water. Pfizer, the manufacturer of Efferdent® denture cleanser, recommends using warm water (not hot) to dissolve the tablet and soak the denture. We would advise that dentists also give clear warnings to patients about the negative effects of using boiling water to clean their dentures.

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