Effect of hydrogen peroxide on microhardness and color change of resin nanocomposites

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ABSTRACT: Purpose: To examine the effect of hydrogen peroxide on the microhardness and color change of resin composites containing nanofillers. **Methods:** Three resin nanocomposites with three different shades and two different tooth whitening agents were used. The specimens were given a 3-week treatment with one of three protocols: (1) 7 hours/day treatment of carbamide peroxide (CP) + 17 hours/day immersion in distilled water (DW); (2) 1 hour/week treatment of hydrogen peroxide (HP) + immersion in DW for the rest of the week; and (3) immersion in DW for 24 hours/day. The microhardness and color changes were measured after treatment**. Results:** After treatment with the whitening agents, there was an 8.1~10.7% decrease in the original microhardness. These values were similar to those obtained from the samples treated with distilled water. In the same resin product, the decrease was similar regardless of the test agents used. In most cases, the color change was only slight (ΔE^*=0.5~1.4). Hydrogen peroxide enhanced the color change but the absolute color change values were similar in the same product and shade, regardless of the test agent used. (*Am J Dent* 2010;23:19-22).

CLINICAL SIGNIFICANCE: Within the limits of this study, carbamide peroxide and hydrogen peroxide had no additional effect on the microhardness and color change of resin nanocomposites compared with the samples treated with distilled water.

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Introduction

Recently the use of tooth whitening agents has become popular due to the increased interest in esthetics of natural dentition. Sodium perborate, carbamide peroxide, and hydrogen peroxide with a wide variety of concentrations are commonly used to whiten teeth. With these agents, hydrogen peroxide is the fundamental agent regardless of whether it exists from the beginning or was formed after decomposition. Hydrogen peroxide decomposes into oxygen free radicals or reactive oxygen molecules after interacting with the materials, depending on the pathway, even though the complete decomposition mechanisms are not completely understood.[1-3] When reactive molecules interact with stain-related molecules in a variety of materials by penetration or direct contact, the structure of the stain-related molecules changes and the materials appear white. Several studies examined the effect of whitening agents on the resin composites with respect to the surface roughness, microhardness, and color stability.[4-9] Generally, the microhardness decreased, the surface roughness increased, and there was some color change observed in the resin composites. However, despite the general trend, there is some controversy regarding these conclusions. Such inconsistent results might be due to the different test materials and test conditions used.

The development of nanotechnology has made it possible to produce functional materials and nanosize structures (0.1~100 nm). Resin composites containing nanosize fillers have a higher filler content due to a decrease in the amount of empty free space within the resin matrix. The improved continuity between the host material (teeth) and restorative material can increase the strength and durability of resin composites.[10-12] Resin nanocomposites exhibit superior translucency and esthetics over conventional resin composites because the nanofillers do not scatter or absorb a significant amount of visible incident light.[13-15]

Since resin nanocomposites have only been introduced recently, there are a limited number of reports on these materials. This study examined the effect of hydrogen peroxide on the microhardness and color change of resin nanocomposites of various shades. For comparison, carbamide peroxide and distilled water were also tested.

Materials and Methods

Three different resin nanocomposites [Ceram X[a] (CX), Grandio[b] (GD), Z350[c] (Z3)] were chosen for the study (Table 1). A QTH lamp-based unit (Optilux 501[d]) was used for light curing. To prepare the specimens, a metal ring mold (2 mm in height with an inner diameter of 8 mm) was filled with resin and light cured for 40 seconds under light intensity of 1000 mW/cm^2. The light-cured specimens were then removed from the mold and aged for 24 hours in a dark chamber at 37°C.

The specimens were treated with hydrogen peroxide using two different agents (1) 15% carbamide peroxide gel (CP), Opalescence F;[e] and (2) 35% hydrogen peroxide[f] (HP). Distilled water (DW) was used to treat the control specimens. The treatment protocols were as follows: (1) 7 hours/day treatment of CP + 17 hours/day immersion in DW; (2) 1 hour/week treatment of HP + immersion in DW for the remainder of the week; and (3) immersion in DW for 24 hours/day. All treatment protocols were repeated for 3 weeks. The CP gel was pasted uniformly over the specimen to a thickness of approximately 3 mm. The treated specimens were kept at 100% humidity. Before immersion in DW, the treated specimens were rinsed with running water without brushing to remove the remaining agent. After 3 weeks in the test agents,

Table 1. Characteristics of the resins tested in this study, according to the manufacturers.

	Composition	Filler type	Filler vol%/wt%
Ceram X	Methacrylate modified polysiloxane,	Dimethacrylate resin, Ba-Al-borosilicate glass, methacrylate functionalized SiO_2 nanofiller	57/76
Grandio	Bis-GMA, TEGDMA, UDMA	Ba-Al-Borosilicate glass filler, SiO_2 nonofillers	71.4/87
Z350	Bis-GMA, UDMA, TEGDMA, Bis-EMA	Non-aggregated silica, zirconia/silica	59.5/78.5

Table 2. Surface microhardness values (HV) and standard deviations (S.D.) of the specimens after treatments with test agents for 3 weeks.

		Before	After	Δ (=Before-After)	P-value
Ceram X	Distilled water	59.9 (1.6)	53.0 (1.6)	6.9 (2.3)	
(M5)	15% carbamide peroxide	58.8 (0.8)	53.3 (0.9)	5.5 (0.8)	0.171
	35% hydrogen peroxide	58.9 (1.4)	52.6 (1.9)	6.3 (2.0)	
Grandio	Distilled water	101.3 (3.3)	92.9 (1.2)	8.4 (2.3)	
(A3)	15% carbamide peroxide	102.1 (3.4)	93.8 (3.0)	8.3 (1.4)	0.497
	35% hydrogen peroxide	101.9 (2.2)	92.8 (2.5)	9.2 (2.3)	
Z350	Distilled water	87.0 (1.6)	77.8 (1.4)	9.2 (2.2)	
(A3)	15% carbamide peroxide	86.2 (1.0)	77.6 (1.6)	8.6 (2.0)	0.724
	35% hydrogen peroxide	86.7 (1.0)	77.9 (1.9)	8.9 (1.8)	

One-way ANOVA (solutions *vs* Δ).

the specimens were removed and rinsed. The remaining water was removed with tissue paper.

After aging for 24 hours, surface macrohardness of the specimens with shade A3 was measured using a Vickers hardness tester (MVK-H1[g]). A 200-gf load was used to make a micro-indentation (n = 12 for each test condition) with a 10-second dwell time. Next, the measured specimens were treated with the agents for 3 weeks using one of the three protocols; then the second measurement was made near the previously measured positions under the same measurement conditions as before.

In order to measure the color change during the hydrogen peroxide treatment, specimens (n=5 for each test solution) with three different shades (M1, M2, M5 for CX; A1, A3, B2 for GD and Z3) were light cured using the same protocols as before, and aged for 24 hours at 37°C. A spectrophotometer (CM-3600d[h]) was used to measure the color of the specimens. Calibration between 360 and 740 nm was performed using the protocol supplied by the system. After calibration, the initial color of the light-cured specimen was measured by placing the specimen at the center of the target mask in %R (reflectance) mode. This target mask has a 7 mm hole in the center. This hole maintains the consistency of specimen placement during the measurements. After the first color measurement, the specimens were treated with the designated test agent for 3 weeks using one of the three protocols. During the treatments, the distilled water was replaced each day. After 3 weeks, the specimens were removed from the test agent and rinsed with running water. The remaining water was removed with tissue paper. The second measurement of the %R was performed immediately under the same conditions. Based on the measured reflectance data, the color values based on the CIEL*a*b* color coordinate system were evaluated using the internal software in the measurement system. The color difference, ΔE*, was obtained using the following equation:

$$\Delta E^* = [\ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\ ]^{1/2}$$

where ΔL*, Δa* and Δb* represent the changes in L*, a*, and b*, respectively. Here, L* represents the degree of gray and corresponds to the lightness. Parameter a* represents the red (for + a* value) - green (for - a* value) axis, and b* is a parameter for the blue (for - b* value) - yellow (for + b* value) axis.

The results of the microhardness tests were analyzed by a one-way ANOVA for the test agent. The results from the color change tests were analyzed by a two-way ANOVA for the shade and test agent. A Tukey's test was then performed for multiple comparisons. All the results were analyzed at a significance level of 5%.

Results

Table 2 shows the microhardness before and after treatment with the test agents. GD showed the highest microhardness among the specimens. After treatment, each resin product showed an 8.1~10.7% decrease from the original microhardness. For the 3-week treatment with distilled water, there was an 8.3~11.5% decrease from the original microhardness. However, the difference in microhardness was not significant ($P< 0.05$). Therefore, the specimens showed a similar microhardness regardless of the test agent used.

Table 3 shows the color change of the specimens with various shades after treatment with the test agents. Among the specimens, GD showed the lowest color change regardless of the shade. GD showed a slight color change (ΔE*=0.5~1.4), whereas CX and Z3 showed a noticeable color change (ΔE*=1.6~2.9). The specimens treated with hydrogen peroxide showed significantly different color change compared with the specimens treated with distilled water, regardless of the resin product. However, their absolute values within the same resin product were similar despite the shade and test agent used.

Discussion

Bleaching, either in dental clinics or at home, has become a popular method of whitening stained teeth. Many agents for whitening teeth have been introduced. Among them, sodium perborate, carbamide peroxide and hydrogen peroxide are used most widely either alone or in combination. Sodium perborate is used in combination with water or hydrogen peroxide, where it can produce hydrogen peroxide. Carbamide peroxide decom-

Table 3. Color changes (ΔE*) and standard deviations (S.D.) in the specimens of various shades after 3-week treatment of test agents.

		DW[1]	CP[2]	HP[3]	P-value
Ceram X	M1[A]	2.0 (0.1)	2.8 (0.1)	2.5 (0.3)	α =0.008
	M5[B]	1.9 (0.1)	2.4 (0.4)	2.2 (0.1)	β < 0.001
	M2[A]	1.9 (0.1)	2.9 (0.3)	2.3 (0.1)	
Grandio	A1[A]	0.5 (0.3)	1.1 (0.1)	0.7 (0.2)	α < 0.001
	A3[B]	0.6 (0.2)	1.6 (0.3)	1.0 (0.3)	β < 0.001
	B2[B]	0.8 (0.2)	1.8 (0.3)	1.1 (0.1)	
Z350	A1[A]	2.3 (0.3)	2.8 (0.1)	2.9 (0.2)	α < 0.001
	A3[B]	2.1 (0.1)	1.6 (0.4)	1.8 (0.2)	β < 0.001
	B2[B]	1.4 (0.2)	2.0 (0.1)	2.4 (0.3)	

* Statistically significant difference on shade is shown by superscript letters [A, B] on concentration of the agent by superscript numbers[1, 2, 3]. Same letters or numbers are not significantly different (P< 0.05).
* On P-values, the letters α and β denote shade and concentration of the agent, respectively.

poses into urea and hydrogen peroxide. Hence, carbamide peroxide is often referred to as urea hydrogen peroxide. For example, 10% carbamide peroxide is equivalent to approximately 3.5% hydrogen peroxide. With these agents, hydrogen peroxide works as the active agent either after decomposition or from the beginning of its introduction.

When hydrogen peroxide interacts with dental materials or teeth, it can form free radicals, reactive oxygen molecules and hydrogen peroxide anions after decomposition. However, the precise decomposition pathways are unclear. Whitening is achieved from these reactive molecules. The reactive molecules interact with stain-related molecules, which are long-chained with a dark color, and split them into smaller and less colored molecules. Stain-related materials consist of conjugated carbon-carbon double bonds. These bonds appear dark when they absorb visible light. However, once these double bonds are split by reactive molecules, they do not absorb visible light and the bleached materials appear white.[3] Generally, the whiteness of bleached materials depends on the concentration of bleaching agent used, contact duration, and number of contacts with the materials. At that time, a direct interaction between stain-related molecules and reactive molecules is the most important factor affecting the outcome. In many cases, the discoloration of teeth originates from extrinsic factors, such as food, drink and smoking. Regions of discoloration are generally confined to the top surface where the stain-related molecules can transmit through defects formed by trauma or mechanical stress and inherent microchannels in the tooth structure. Whitening can be achieved more easily and quickly in teeth. However, the color in resin composites originates from dye and pigment materials. These materials are distributed uniformly within the entire resin matrix. Since specimens are tightly crosslinked with polymerized molecules and fillers, they contain fewer inherent microchannels than human teeth. The degree of whitening will be low and restricted to the top surface.

After the samples were treated with the test agent for 3 weeks, the initial surface microhardness decreased 8.1~11.5% according to the agent used. This decrease may be related to the degradation of the specimen. Degradation can occur either through hydrolysis or a chemical reaction.[13-15] Water in each test protocol can be absorbed through the interface between the filler and matrix, resin matrix, or defects. Such absorbed water slowly dissolves the residual monomers and filler components and creates vacancies within the subsurface. More water or solution can then accumulate in the vacancies through osmotic pressure, which causes the vacancies to grow and expand. This process can result in surface softening. Bis-GMA and TEGDMA, which were contained in the specimens, can absorb water even though Bis-GMA/TEGDMA copolymers form a dense polymer network. Therefore, the specimens may be susceptible to softening.[16] TEGDMA is the main component released from polymerized resin composites into aqueous media as a result of water absorption.[17] However, statistical analysis showed that the decrease in microhardness was not affected by the difference in test agents used. This suggests that the concentration of test agents has no effect on the difference in the measured microhardness. Other factors, such as the contact duration or the number of application times, were not tested in this study. Further studies will be needed to determine their effect on microhardness.

The resin composites tested in this study contain nanofillers. Nanofillers are used to improve the continuity between the host material (tooth) and filler particles. Improved mechanical properties and optical translucency can be expected due to the stable and natural interface between them. The use of nanofillers allows an increase in the filler volume and a decrease in the free space within the resin matrix, which would be expected to improve the mechanical properties.

The tested specimens showed a slight (0.5~1.4) or a noticeable (1.6~2.9) color change depending on the product or test agent used. Two mechanisms can be used to explain the discoloration of resin composites by a test agent: (1) the oxidation of dyes or pigments that are responsible for the shade of the specimens; and (2) the oxidation of residual amine compounds over time.[8] The oxidation of dyes or pigments can occur from the surface as a result of a direct interaction with the test agent. The degree of oxidation may change depending on the penetration depth of the reactive molecules in the specimens. Since polymerized specimens are tightly crosslinked by molecules, hydrogen peroxide requires more time to diffuse into the crosslink than teeth. The color change caused by hydrogen peroxide was significantly greater than that by distilled water regardless of the shade and product used. However, the differences in the absolute color change values were minor. This suggests that the tested resin nanocomposites provide color stability or a slow color change due to hydrogen peroxide. Such color stability has been observed in many resin composites not containing nanofillers.[18,19]

In conclusion, the changes in microhardness and color of resin nanocomposites after treatment with 15% carbamide peroxide and 35% hydrogen peroxide were similar to those observed in specimens immersed in the distilled water. Therefore, the changes in resin nanocomposites may not require any specific attention.

a. Denstply DeTrey, Konstanz, Germany.
b. Voco, Cuxhaven, Germany.
c. 3M ESPE, St. Paul, MN, USA.
d. Kerr, Danbury, CT, USA.
e. Ultradent, South Jordan, UT, USA.
f. Junsei, Tokyo, Japan.
g. Akashi Co., Tokyo, Japan.
h. Konica Minolta, Osaka, Japan.

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