

Effect of immersion into solutions at various pH on the color stability of composite resins with different shades

Ji-Deok Moon¹, Eun-Mi Seon¹, Sung-Ae Son¹, Kyoung-Hwa Jung¹, Yong-Hoon Kwon², Jeong-Kil Park^{1*}

¹Department of Conservative Dentistry, ²Department of Dental Materials, School of Dentistry, Pusan National University, Dental Research Institute, Yangsan, Korea

Objectives: This study examined the color changes of a resin composite with different shades upon exposure to water with different pH. **Materials and Methods:** Nanohybrid resin composites (Filtek Z350XT, 3M ESPE) with four different shades (A2, A3, B1, and B2) were immersed in water with three different pH (pH 3, 6, and 9) for 14 day. The CIE $L^*a^*b^*$ color coordinates of the specimens were evaluated before and after immersion in the solutions. The color difference (ΔE^*) and the translucency parameter (TP) were calculated using the color coordinates. **Results:** ΔE^* ranged from 0.33 to 1.58, and the values were affected significantly by the pH. The specimens immersed in a pH 6 solution showed the highest ΔE^* values (0.87 - 1.58). The specimens with a B1 shade showed the lowest ΔE^* change compared to the other shades. TP ranged from 7.01 to 9.46 depending on the pH and resin shade. The TP difference between before and after immersion in the pH solutions was less than 1.0. **Conclusions:** The resulting change of color of the tested specimens did not appear to be clinically problematic because the color difference was < 1.6 in the acidic, neutral, and alkaline solutions regardless of the resin shade, i.e., the color change was imperceptible. (*Restor Dent Endod* 2015;40(4):270-275)

Key words: Color stability; Composite resin; pH; Resin shade; Translucency parameter

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¹Moon JD; Seon EM; Son SA; Jung KH; Park JK, Department of Conservative Dentistry, School of Dentistry, Pusan National University, Yangsan, Korea
²Kwon YH, Department of Dental Materials, School of Dentistry, Pusan National University, Yangsan, Korea

*Correspondence to

Jeong-Kil Park, DDS, MSD, PhD. Associate Professor, Department of Conservative Dentistry, School of Dentistry, Pusan National University, 20, Geumo-ro, Mulgeum-eup, Yangsan, 50612, Korea
TEL, +82-55-360-5221; FAX, +82-55-360-5214; E-mail, jeongkil@pusan.ac.kr

Introduction

Esthetic dental materials are used widely in modern restorative dentistry because of their excellent harmony with natural teeth. Among them, resin composites are the most popular restorative materials. The advantage of resin composites for restoration would be a color match to the adjacent teeth with a wide range of shade options as well as agreeable mechanical properties that are high enough to sustain a range of mastication loads. On the other hand, previous studies reported that restorative resin composites are discolored when exposed to the diverse oral environment.¹⁻³

The discoloration of resin composites might be mediated by water. Chemical degradation can occur if resin composite absorbs water and other colorants because water is an excellent solvent. Chemical degradation can lead to corrosive wear of the resin surface through softening and hydrolytic processes. As the corroded layer is worn out because of mastication or tooth brushing, a fresh surface is exposed and the corrosion cycle continues. Clinically, this can lead to a loss of restoration contour, as well as an increase in surface roughness, and discoloration.^{2,4} Generally, the optical and physical properties of resin composites are affected by the length of degradation.

A range of factors affect the speed of the degradation reaction. Among them, the filler, matrix, type of chemical bond, pH, copolymer composition and water uptake are important. In particular, pH is an unfavorable factor for hydrophilic resins because it affects the degradation rates through catalysis.⁵ In the oral cavity, pH varies according to the oral environment and tooth surface conditions.⁶ Acids produced by the bacterial metabolism, such as acetic, propionic and lactic acid can change pH.⁷ Alkaline beverages, such as mineral water, ion beverages, green tea, and herbal tea, are also potential sources of pH variations. Ideally, polymers of resin composites should not be degraded in an oral environment, in which the pH changes dynamically in an aqueous medium.⁸ According to previous studies, a lower pH had been shown to have an adverse effect on the wear resistance of resin composites.^{5,7} In addition, highly alkaline solutions have been shown to accelerate hydrolysis and produce surface microstructural damage.⁹

On the other hand, the influence of pH on the color stability of resin composites has not been studied sufficiently. Thus far, previous studies focused mainly on the influence of tea, coffee, and soft drinks on the color stability of glass ionomer cements, resin veneers, indirect composites, provisional resin materials, and compomers.^{3,10-12} However the limitation of their studies was that they did not explain whether color change was caused by the pH or by the colorant in the drink solutions.

In order to exclude the effect of colorant in the solutions, this study examined the effects of water with different pH on the color stability of restorative resin composites with different shades. For the study, the color difference (ΔE^*) and translucency parameter (TP) of one resin composite with four different shades under three pH conditions were evaluated to test the color stability.

Materials and Methods

Specimen preparation

For the study, a resin composite (Filtek Z350XT, 3M ESPE, St. Paul, MN, USA) with four different shades (A2, A3, B1, and B2) was used. An LED light-curing unit (L.E. Demetron, Kerr, Danbury, CT, USA) was used for light curing. To prepare the specimens, a metal ring mold (inner diameter, 8 mm; thickness, 2 mm; $n = 30$ for each shade) was filled with resin and light cured for 40 seconds under a light intensity of 1,000 mW/cm². The light cured specimens were then removed from the mold and aged for 24 hours in a 37°C dark and dry chamber. The specimens ($n = 10$) were then immersed into three pH solutions (pH 3, 6, and 9), respectively, for 14 days. To produce the pH solutions, distilled water was mixed with diluted acetic acid to prepare the solutions at pH 3 and 6. A solution at

pH 9 was prepared by mixing dilute NaOH with distilled water. Mixing with acetic acid or NaOH was performed under slowly stirring condition using a magnetic bar. All the processes were conducted at $23 \pm 1^\circ\text{C}$ under $60 \pm 3\%$ relative humidity.

Evaluation of color

A spectrophotometer (CM-3600d, Konica Minolta, Osaka, Japan) was used to measure the color of the specimens. The stored specimens for 24 hours were selected ($n = 10$) for the first color measurements. The initial color of the light-cured specimens was measured by placing the specimen at the center of the target mask in reflectance (%R) mode with white and black backgrounds, respectively. This target mask had a 6 mm hole at the center. This hole enables consistency in specimen placement during the measurements. After the first color measurement, each specimen was immersed in the designated test solution for 14 days. During immersion, the solution was replaced daily. After 14 days, the specimens were removed from the test solution, rinsed with running water, and spot dried with tissue paper. The second color measurement was performed using the immersed specimens ($n = 10$) under the same measurement conditions as before. From the measured reflectance data, the CIE $L^*a^*b^*$ color coordinates were evaluated using the internal software of the measurement system. The ΔE^* was obtained using the following formula:

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

where Δ is the difference between the first and second measurements. Here, L^* represents the degree of grayness, and corresponds to lightness. The parameter a^* represents the red - green axis, whereas b^* is a parameter for the blue - yellow axis.

The TP values were determined by calculating the color difference between the readings using the following formula:

$$TP = [(L^*_B - L^*_W)^2 + (a^*_B - a^*_W)^2 + (b^*_B - b^*_W)^2]^{1/2}$$

where the subscripts 'B' and 'W' refer to the color coordinates over a black and a white background, respectively. The change in the translucency parameter, ΔTP (TP after immersion minus TP before immersion), was calculated for each specimen.

Statistical analysis

SPSS 15.0 software (SPSS Inc., Chicago, IL, USA) was used for statistical analysis. The results of the color change were analyzed using two-way ANOVA for the resin shade and pH of the solution. A *post hoc* Tukey test was performed

followed by a multiple comparison procedure. All tests were analyzed at $p < 0.05$.

Results

Tables 1 and 2 list the CIE $L^*a^*b^*$ color coordinates and color changes of the specimens before and after immersion in the test solutions. The specimens of A2 and A3 shades

have lower L^* and higher b^* values than those of the B1 and B2 shades. L^* values increased after immersion in test solutions except in pH 3. The ΔL^* , Δa^* , and Δb^* values ranged from -0.30 to 1.40, -0.19 to 0.12, and -0.69 to 0.17, respectively, depending on pH. The difference among each coordinate was less than 1.5. In the pH 6 solution, ΔL^* had higher tendency than in other pH solutions regardless of shade.

Table 1. CIE $L^*a^*b^*$ color coordinate values before and after immersion in test solutions for 14 days

Code		Before immersion (24 hr)			After immersion (14 day)		
		L^*	a^*	b^*	L^*	a^*	b^*
A2	3	53.99 ± 0.45	-1.50 ± 0.07	6.52 ± 0.09	53.83 ± 0.52	-1.60 ± 0.09	6.12 ± 0.15
	6	52.87 ± 0.44	-1.59 ± 0.04	6.50 ± 0.18	54.17 ± 0.26	-1.63 ± 0.06	5.81 ± 0.22
	9	53.65 ± 0.20	-1.65 ± 0.03	6.38 ± 0.18	54.55 ± 0.34	-1.59 ± 0.04	6.42 ± 0.21
A3	3	52.90 ± 0.17	-0.33 ± 0.02	7.91 ± 0.13	52.69 ± 0.23	-0.40 ± 0.03	7.68 ± 0.08
	6	52.07 ± 0.14	-0.27 ± 0.06	8.01 ± 0.28	53.48 ± 0.27	-0.45 ± 0.03	7.32 ± 0.28
	9	52.72 ± 0.14	-0.37 ± 0.01	8.00 ± 0.11	53.31 ± 0.17	-0.33 ± 0.02	7.83 ± 0.11
B1	3	57.98 ± 0.23	-1.31 ± 0.04	1.76 ± 0.11	57.68 ± 0.21	-1.34 ± 0.03	1.57 ± 0.06
	6	57.34 ± 0.19	-1.36 ± 0.01	1.94 ± 0.10	58.12 ± 0.28	-1.33 ± 0.06	1.58 ± 0.17
	9	57.94 ± 0.12	-1.37 ± 0.04	1.80 ± 0.07	58.47 ± 0.39	-1.26 ± 0.02	1.91 ± 0.08
B2	3	55.91 ± 0.14	-1.32 ± 0.04	3.98 ± 0.06	55.61 ± 0.29	-1.40 ± 0.07	3.59 ± 0.15
	6	55.04 ± 0.23	-1.27 ± 0.01	4.11 ± 0.22	56.18 ± 0.25	-1.30 ± 0.04	3.81 ± 0.09
	9	56.03 ± 0.27	-1.29 ± 0.03	4.04 ± 0.16	56.63 ± 0.22	-1.16 ± 0.03	4.21 ± 0.14

Codes: 3, pH 3; 6, pH 6; 9, pH 9.

Table 2. Changes of color coordinates (ΔL^* , Δa^* , Δb^*) after immersion in test solutions for 14 days

Code		ΔL^*	Δa^*	Δb^*
A2	3	-0.16 ± 0.18	-0.05 ± 0.05	-0.40 ± 0.15
	6	1.30 ± 0.66	-0.04 ± 0.05	-0.69 ± 0.19
	9	0.90 ± 0.15	0.06 ± 0.05	0.03 ± 0.09
A3	3	-0.21 ± 0.07	-0.07 ± 0.03	-0.23 ± 0.13
	6	1.40 ± 0.19	-0.19 ± 0.05	-0.69 ± 0.13
	9	0.60 ± 0.09	0.04 ± 0.02	-0.17 ± 0.11
B1	3	-0.29 ± 0.04	-0.02 ± 0.05	-0.19 ± 0.10
	6	0.78 ± 0.28	0.02 ± 0.06	-0.36 ± 0.09
	9	0.52 ± 0.34	0.11 ± 0.04	0.11 ± 0.13
B2	3	-0.30 ± 0.23	-0.09 ± 0.03	-0.39 ± 0.11
	6	1.14 ± 0.31	-0.03 ± 0.03	-0.30 ± 0.21
	9	0.59 ± 0.25	0.12 ± 0.02	0.17 ± 0.18

Codes: 3, pH 3; 6, pH 6; 9, pH 9.

Table 3. Color changes (ΔE^*) in the specimens of various shades after 14 days immersion in the test solutions

	pH 3 ¹	pH 6 ²	pH 9 ³	<i>p</i> value
A2 ^A	0.46 ± 0.16	1.51 ± 0.58	0.91 ± 0.14	$\alpha = 0.003$
A3 ^{AB}	0.33 ± 0.09	1.58 ± 0.16	0.63 ± 0.11	$\beta < 0.001$
B1 ^B	0.36 ± 0.07	0.87 ± 0.25	0.56 ± 0.33	$\alpha \times \beta = 0.03$
B2 ^{AB}	0.53 ± 0.18	1.19 ± 0.30	0.65 ± 0.24	

*Statistically significant difference in shade is shown by superscript letters^{A,B} within the column, and on concentration of the agent by superscript numbers within the row^{1,2,3}. Groups with same letters or numbers are not significantly different ($p < 0.05$).

*On *p* values, the letters α and β denote the main effect of the shade and pH of the agent, respectively.

Table 4. Translucency parameter (*TP*) values before and after immersion in test solutions for 14 days

Code		ΔL^*	Δa^*	Δb^*
A2	3	7.95 ± 0.88	8.07 ± 0.94	0.12 ± 0.07
	6	9.46 ± 0.58	8.65 ± 0.35	-0.81 ± 0.52
	9	9.00 ± 0.35	8.05 ± 0.26	-0.95 ± 0.22
A3	3	7.70 ± 0.44	7.86 ± 0.17	0.16 ± 0.33
	6	8.59 ± 0.43	7.99 ± 0.31	-0.60 ± 0.13
	9	9.00 ± 0.35	7.58 ± 0.36	-0.95 ± 0.22
B1	3	7.10 ± 0.56	7.33 ± 0.53	0.24 ± 0.08
	6	8.31 ± 0.24	7.55 ± 0.28	-0.76 ± 0.18
	9	7.83 ± 0.43	7.18 ± 0.23	-0.66 ± 0.32
B2	3	8.54 ± 0.20	8.91 ± 0.25	0.37 ± 0.07
	6	8.85 ± 0.20	8.08 ± 0.09	-0.77 ± 0.26
	9	8.07 ± 0.22	7.29 ± 0.35	-0.78 ± 0.23

Codes: 3, pH 3; 6, pH 6; 9, pH 9.

ΔTP (*TP* after 14 days immersion minus before immersion) was calculated for each specimen.

Table 3 shows the ΔE^* of the specimens before and after immersion in pH solutions. ΔE^* of the tested specimens were significantly different among three pH solutions ($p < 0.05$). In the pH 6 solution, ΔE^* was significantly higher than others, but the color difference was only slight (ΔE^* , 0.33 - 1.58). For shades of resin composite, ΔE^* of A2 shade was significantly different from B1 shade ($p < 0.05$). Other shades were not significantly different from others.

Table 4 shows the *TP* values and *TP* difference (ΔTP) of the specimens between the values before and after immersion in the pH solutions for 14 days. *TP* after immersion of pH solutions had a decreasing tendency except for pH 3 solution, but the absolute values of ΔTP in all pH solutions were very low (0.12 - 0.95).

Discussion

Tooth-colored restorative dental materials are attractive because of the harmonious match with the host teeth by satisfying the aesthetic requirements of a range of users. The restored dental materials are influenced by the dynamic changes in the environment in the oral cavity. In particular, foods and beverages have a wide range of pH because of their diverse ingredients and have a significant effect on the restored resin composites in the tooth cavity.

Previous studies reported that acidic conditions can degrade resin composites.^{8,11,13} According to Poggio *et al.*, cola had the lowest pH (2.55) and might damage the surface integrity of resin composites.¹⁴ The probable

degradation of resin composite might be due to the acid-related hydrolysis of ester radicals present in the dimethacrylate monomers, such as bisphenol A glycidyl methacrylate (Bis-GMA), ethoxylated bisphenol A dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA) and triethyleneglycol dimethacrylate (TEGDMA).⁸ On the other hand, Buchalla *et al.* reported that storage in acidic solutions had very little effect on resin-based luting cements.¹⁵ Eisenburger *et al.* observed no significant differences between the resin luting cement surface profiles after 7 days immersion in citric acid and saline, respectively.¹⁶

Recently, Cilli *et al.* reported that an alkaline medium appears to be more suitable for accelerating composite hydrolysis and producing microstructural damage than acidic media.⁹ According to their study, the strong influence of the alkaline medium on the composite properties was attributed to their interactions with OH ions during the hydrolysis process. At a pH of 13, an alkaline medium provides a million times as many hydroxyl ions as are present in solutions at neutral pH or low pH. In addition to the possibility of hydrolytic degradation of silane couplers and fillers, it is also possible to induce hydrolysis of the inorganic particles themselves with an excess of OH ions.

From the result of others studies, high color change in acidic (pH 3) or alkaline (pH 9) solution was expected due to hydrolysis of resin composites.^{9,11,13,14} In contrast, the results of this study were the opposite. In this study, ΔE^* of the tested specimens were significantly different among three pH solutions ($p < 0.05$). In the pH 6 solution, ΔE^* was significantly higher than the others due to the higher ΔL^* value. On the other hand, the absolute of ΔE^* was also low (at best 1.58) because the absolute value of ΔL^* was low (at best 1.40).

According to individual ability of the human eye to appreciate differences in color, three different intervals were used to distinguish the changes in color values, that is, $\Delta E^* < 1$, imperceptible by the human eye; $1.0 < \Delta E^* < 3.3$, appreciated only by skilled person, both clinically acceptable; $\Delta E^* > 3.3$, easily observed, these color changes are not clinically acceptable.^{17,18} Overall, the resulting change of color of the specimens immersed in the pH 6 solution cannot be easily perceptible and is clinically acceptable. In the case of resin shade, there was significant difference between A2 and B1, but the absolute value of difference was also very slight. Clinical importance was also negligible. Likewise, TP after immersion of pH solutions had a tendency to decrease except for pH 3 solution but the absolute values of ΔTP in all pH solutions were very low (0.12 - 0.95). These results indicate a similar but imperceptibly low color change to the specimens by different pH solutions that can occur in the oral cavity.

The limitation of this study is the static effect of the pH solutions. The oral cavity is always under dynamic stresses,

such as temperature variations, wear by mastication activity, and pH variations due to the different foods and beverages. Moreover, it is unclear if such minor color changes observed in the present study are relevant. Therefore, further study will be needed to evaluate the color changes under such dynamic environments.

Conclusions

Within the limitation of this study, ΔE^* of the tested specimens were significantly different between the pH solutions. However, from the results of this study, the resulting color change was too low to be perceived by the naked eyes. Therefore, such small color changes can be free of the clinical issues arising from the aesthetic requirements.

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Orcid number

Jeong-Kil Park, 0000-0001-6333-8138

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