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pH 변화가 복합레진의 굴곡 및 압축성질에 미치는 영향

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Effect of pH variation on flexural and compressive properties of composite resins

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구강내의 pH는 다양한 음식과 음료수에 의해 폭넓은 변화의 폭을 가진다. 본 연구는 pH가 복합레진의 굴곡 및 압축성질에 미치는 영향을 평가한 것이다. 이를 위하여 4종의 복합레진을 시료로 선택하였고, 시료를 광조사한 후 pH가 각각 3, 7.1, 9인 용액에 실온에서 2주 동안 담가두었다. 그리고 만능시험기를 이용하여 굴곡 및 압축성질을 평가하였다. 그 결과 pH에 상관없이 시료는 용액에 담긴 후에 초기 굴곡 및 압축강도가 각각 1.5-30.0%와 0.3-19.6%로 유의하게 변하였고 modulus도 각각 4.4-29.0%와 3.5-21.5%로 유의하게 변했다. 그러나 각기 다른 pH 조건에 대해서 값의 변화는 일관성과 유의성이 없었다.

색인단어 : 복합레진, pH, 굴곡성질, 압축성질

Introduction

Caries is one of the most frequently encountered dental diseases, regardless of nationality, gender, or generation, and thus, many tooth treatments in dental clinics are related to tooth caries. Usually caries forms due to the demineralization of teeth by oral acids formed by oral bacteria that inhabit biofilms on tooth surfaces, and is promoted by acidic foods and beverages. Many soft drinks and fruit juices have low pH values. Generally, the pH of human saliva falls in the range 6-8 (1). However, oral acids, and acidic foods and beverages can result in localized pH values as low as 2. On the other hand, since many vegetables and drinks, such as, milk, coffee,

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and wine, are alkaline, they can sometimes cause oral pH values to increase to near 11 on tooth surface (2,3).

To inhibit or delay the formation of secondary caries after restoration, fluoride-containing functional composite resins were introduced in the mid-1980s (4). In composite resins, fluoride is contained in various forms, such as, inorganic salts, leachable glasses, organic fluoride. Fluoride ions, released from composite resins, can form hydrogen fluoride, if ions encounter acidified plaque or other acidic substances. The cariostatic effect of fluoride ions on teeth had been widely demonstrated in many studies (5-8).

Because the oral cavity and tooth surfaces are always in contact with saliva, restorative materials could interact with saliva and water-based liquids. As an active solvent, water can dissolve and degrade restorative materials via absorptive and softening effects (9-11). As a result, degradation and disintegration of surface structures, and subsequently, instability of the restored structures are possible. In this situation, information is needed regarding the effects of pH variations on restorative materials. Accordingly, the purpose of the present study was to investigate how solutions of different pHs affect the flexural and compressive properties of various composite resins. The hypothesis tested was that the flexural and compressive properties of specimens are significantly and consistently dependent on solution pH.

Materials and Methods

1. Composite resins and test solutions

For the study, four composite resins (all of A3 shade) were selected as outlined in Table1: fluoride containing Charisma Diamond flow (CF) and Tetric N Ceram (TN); non-fluoride-containing AeliteFlo (AF) and Filtek Z350 (ZX). AF and CF are flowable resins and TN and ZX are nanocomposite resins. For light curing, an Optilux 501 (OP, Kerr, Orange, CA, USA) was used as a light-curing unit (LCU) at an intensity of approximately 900 mW/cm^2.

For immersion testing in solutions of different pHs, bottled water (Samdasoo, JPDC, Jeju, Korea) of pH 7.1, as measured with pH meter (720A+, Thermo Electron Corp., Beverly, MA, USA), was used. Solutions of pH 3 and pH 9 were prepared by adding acetic acid and NaOH to bottled water, respectively at a room of 24±1℃ and 60±3% humidity conditions. Specimens were immersed for 2 weeks.

2. Flexural properties

The three-point bending test was performed to determine flexural properties [flexural strength (FS) and modulus (FM)]. To make specimens (n=28 for each resin), a metal mold (25×2×2 mm) was filled with resin according to ISO 4049 guidelines (12). After filling the mold, top and bottom surfaces were covered with glass slides to flatten surfaces. Specimens were irradiated for 40s using a LCU. Since specimens were much wider (25 mm) than the LCU tip size (7 mm), five light exposures were performed on each surface by overlapping curing light beams. After light curing, specimens were removed from molds and aged for 24 h at 37℃ in a dry, dark chamber. After aging, randomly selected specimens (n=7 for each resin product) were loaded into a universal test machine (Instron 3345, Grove City, PA, USA), which was operated at a crosshead speed of 1 mm/min. FS (σ_f in MPa) values were calculated using the following formula

$$\sigma_f = 3DP/(2WH^2)$$

where D is the distance between supports (20 mm), P is the maximum failure load (N), W is the width (2 mm), and H is the height (2 mm) of the tested specimen. FM (E in GPa) was calculated using the following formula

$$E = (P/D) \cdot (D^3/(4WH^3))$$

where P/D is the slope of the linear portion of the load-displacement curve. Remaining specimens were randomly divided into three groups, immersed in test solutions (pH 3, 7.1, or 9), and stored in at 37℃ in a dry, dark chamber for 2 weeks when measurements were repeated. Test solutions were replaced daily throughout the study period.

3. Compressive properties

To measure compressive properties [compressive strength (CS) and modulus (CM)], a hemicylindrical metal mold (outer diameter 10 mm, inner diameter 3 mm, height 6 mm) was prepared. Two identical hemicylinders were combined together to form a cylinder and the inner empty space was filled with resin. After filling the mold, both top and bottom surfaces were covered with glass slides to produce flat surfaces. Since light incident on the top surface did not reach the bottom surface due to poor penetration depth, light was irradiated for 5 s from the top to the bottom. One of the two hemicylinders was removed, and the uncovered lateral surface was exposed to light for 40 s. The remaining hemicylinder was then removed and the uncovered lateral surface was exposed to light in the same manner. The specimens so produced (n=28 for each resin product) were aged for 24 h at 37℃ in a dry, dark chamber, and compression tests were performed on randomly selected specimens (n=7 for each resin product) using the universal test machine at a crosshead speed of 1 mm/min. CS (σ_c in MPa) values were calculated using the following formula

$$\sigma_c = P/A$$

where P is the maximum failure load (N) and A is specimen cross-sectional area. CM (in GPa) of specimens was defined as the slope of the linear portion of the load-displacement curve. Remaining specimens were randomly divided into three groups, immersed in each test solution (pH 3, 7.1, or 9), and stored at 37℃ in a dry, dark chamber for 2 weeks, when measurements were repeated. Test solutions were replaced daily throughout the study period.

Table 1. Materials tested in the present study

Code	Composition	Filler content vol%/wt%[1]/wt%[2]	Manufacturer
CF	EBADMA (=Bis-EMA), UDMA, Ba-Al-F-silicate glass, YbF_3,SiO_2	41/65/58.4	Heraeus Kulzer, Hanau, Germany
TN	Bis-EMA, TEGDMA, UDMA, Barium glass, YbF_3,SiO_2	57/80.5/73.0	Ivoclar Vivadent Schann, Liechtenstein
AF	Bis-EMA, TEGDMA, Barium glass, glass fillers	42/60/56.2	Bisco Inc. Schaumburg, IL, USA
ZX	Bis-EMA, Bis-GMA, TEGDMA, UDMA, Zirconia/silica cluster fillers	63.3/78.5/74.7	3M ESPE St. Paul, MN, USA

CF: Charisma Diamond flow, TN: Tetric N Ceram, AF: AeliteFlo, ZX: Filtek Z350
Bis-EMA: ethoxylated bisphenol A dimethacrylate; Bis-GMA: bisphenol A glycidyl dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; UDMA: urethane dimethacrylate
wt%[1]: weight percent according to the manufacturers
wt%[2]: weight percent according to the ash method

4. Statistical analysis

The obtained results were analyzed using two-way ANOVA. A post-hoc Tukey test was followed at $p<0.05$ level.

Results

Table 2 shows the flexural properties (FS and FM) of the specimens. Specimens showed significant ($p<0.001$) FS decreases (1.5~30.0% depending on condition) after immersion in the pH solutions. However, pH did not affect FS values significantly ($p>0.05$). Of the specimens, TN showed least FS change, which was not dependent on pH value. FM also significantly changed (increased or decreased) after immersion, and CF showed least FM change.

The compressive properties (CS and CM) of the specimens are summarized in Table 3. Initial CS values significantly changed ($p<0.001$) only after immersion in the pH 9 solution. TN showed a minor CS increase (0.3-2.0%) in all pH solutions after immersion. Initial CM decreased significantly after immersion, but CM values obtained from the different solutions were not significantly different at p=0.05 level.

Discussion

Many restorative composite resins contain fluoride to inhibit or delay the occurrence of secondary caries. Since the oral cavity is exposed to wide pH variations, restored restorative materials can be influenced by the oral environment. In the present study, the flexural and compressive properties of four different resins exposed to solutions with different pH values were evaluated. According to the obtained results, the study hypothesis that solution pH variations cause significant and consistent differences in flexural and compressive properties was

Table 2. Three-point flexural properties (FS and FM) of specimens before and after immersion in different pH solutions

		Product				*p*-value
		CF^{A}	TN^{BC}	AF^{B}	ZX^{C}	
FS (MPa)	24 hr^{1}	164.0 (18.3)	128.2 (12.2)	139.9 (16.1)	175.6 (9.3)	$\alpha<0.001$
	pH 3^{2}	147.3 (15.4)	124.9 (9.3)	117.0 (10.7)	123.0 (11.8)	$\beta<0.001$
	pH 7.1^{2}	137.5 (18.2)	123.4 (11.0)	113.9 (17.3)	125.4 (10.7)	$\alpha\times\beta=0.004$
	pH 9^{2}	136.2 (18.7)	126.3 (3.5)	114.8 (22.7)	126.6 (12.5)	
		CF^{A}	TN^{B}	AF^{C}	ZX^{D}	
FM (GPa)	24 hr^{1}	6.60 (0.42)	14.36 (0.91)	5.68 (0.36)	17.54 (1.56)	$\alpha<0.001$
	pH 3^{2}	6.31 (0.39)	10.19 (0.63)	4.87 (0.17)	12.92 (0.67)	$\beta<0.001$
	pH 7.1^{3}	6.58 (0.34)	10.96 (1.10)	4.98 (0.24)	13.51 (1.08)	$\alpha\times\beta<0.001$
	pH 9^{3}	7.05 (0.28)	11.57 (0.84)	5.04 (0.17)	13.60 (0.66)	

* Statistically significant difference on resin product is shown by superscript letters$^{A,B,...}$, on pH condition by superscript numbers$^{1,2,...}$. Same letters or numbers are not significantly different ($p>0.05$).

* On *p*-values, the letters α and β denote resin product and pH condition, respectively.

Table 3. Compressive properties (CS and CM) of specimens before and after immersion in different pH solutions

		Product				*p*-value
		CF[A]	TN[BC]	AF[B]	ZX[C]	
CS (MPa)	24 hr[12]	418.8 (29.0)	337.6 (33.6)	315.3 (35.4)	350.5 (26.0)	α<0.001
	pH 3[23]	377.6 (35.3)	338.5 (29.1)	313.7 (47.4)	347.2 (38.4)	β=0.027
	pH 7.1[23]	354.3 (20.8)	344.2 (19.3)	296.8 (31.5)	353.6 (40.7)	$\alpha\times\beta$=0.195
	pH 9[3]	336.8 (52.8)	340.4 (35.1)	283.0 (29.4)	336.2 (46.9)	
		CF[A]	TN[B]	AF[C]	ZX[D]	
CM (GPa)	24 hr[1]	3.21 (0.17)	4.50 (0.05)	3.17 (0.18)	4.83 (0.09)	α<0.001
	pH 3[2]	2.88 (0.22)	4.25 (0.13)	2.63 (0.20)	4.66 (0.10)	β<0.001
	pH 7.1[3]	2.83 (0.29)	4.30 (0.10)	2.53 (0.18)	4.58 (0.08)	$\alpha\times\beta$=0.051
	pH 9[3]	2.89 (0.16)	4.27 (0.12)	2.49 (0.14)	4.55 (0.33)	

rejected.

Flexural property (strength and modulus) results obtained using the three-point bending test provide measures related to the specimen resistance against external stress. Initial Flexural strengths (FS) of specimens measured after aging for 24 h ranged from 128.2-175.6 MPa, and after immersion, these reduced to 113.9-147.3 MPa. Basically, FS depends more on material volume and internal defects, such as cracks or voids, formed during specimen preparation (13,14). However, after dissolution of fluoride and inorganic fillers, cracks and pores can be more easily generated on surfaces and in subsurface, and since cracks can propagate, they weaken structures. In addition, osmotic pressure can affect subsurface pores, and further weaken structures (11). Of the specimens examined, TN showed least FS decrease (128.2 vs. 123.4-126.3 MPa) after immersion in solutions of different pH values. The highest FS decrease was observed for Z3 and it was probably related to the high water absorption of ZX (15,16). A significant decreases in FS observed for AF and CF (flowable resins) were probably due to low degrees of polymerization and weakening caused by water absorption. Other possible decrease of FS can be owing to the dissolution of inorganic fillers and residual monomers, which were not investigated in the present study. After immersion in pH solutions, FS significantly decreased for all specimens, but the lack of a significant difference between different pH solutions indicates that pH had an insignificant effect on FS regardless of the presence of fluoride. Flexural modulus (FM) is related to the stiffness of a material, the specimens with high strength (or microhardenss) and of flowable resins had high FM values and exhibited less FM change, respectively (17,18). The non-significant FM differences in solutions with different pH values are probably explained in the same manner as the lack of significant changes in FS values.

Compressive properties (strength and modulus) are measures of material's sustained resistance against heavy load such as mastication (2,19). In the present study, initial CS values significantly ($p<0.001$) decreased after immersion in solutions with different pH values, and for

the four resins, flowable resins (AF and CF) showed much lower CS decreases than TN and ZX (nanofiller-containing) after immersion. The reason can be surmised from the fact that composite resins with a high filler content had a higher degree of polymerization than flowable resins with a low filler content, so monomer contents probably affect resultant strengths more than inorganic filler dissolution. The non-significant and inconsistent differences observed for flexural and compressive properties in different pH solutions may suggest an insignificant contribution by inorganic filler dissolution to resultant mechanical properties. FM and CM values of the tested specimens ranged from 4.98 to 17.54 GPa and from 2.49 to 4.83 GPa, respectively, which are lower than those of the FM (17-25 GPa) and CM (11-19 GPa) of dentin (20-22). Since modulus (FM) is related to the stiffness of a material, specimens of high filler content (vol% and wt%) had both high FM and CM values ($R > 0.94$, regardless of pH value). Also, FM and CM were high linearly correlated to each other ($R > 0.99$, regardless of pH value). The results obtained show that modulus of composite resins are not adversely affected by pH variations in the oral cavity, although it should be noted that the resin products tested do not represent all restorative composite resins.

Conclusion

Within the limitations of the present study, the following conclusions could be reached:

1. Flexural and compressive properties of tested specimens decreased significantly after immersion in test solutions regardless of their pH values.
2. However, the strength, and modulus values obtained from different pH solutions had no consistency and statistical significance in their changes in terms of pH variation.

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Original Article

Effect of pH variation on flexural and compressive properties of composite resins

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The pH of the oral cavity can dynamically change due to diverse foods and beverages served. The purpose of the present study was to evaluate flexural and compressive properties of composite resins after immersion in solutions of different pHs. Four composite resins were cured and immersed in test solutions of different pHs (3, 7.1, and 9) for 2 weeks. Flexural and compressive properties (strength and modulus) were evaluated using universal test machine. After immersion, initial flexural and compressive strength significantly changed to 1.5-30.0% and 0.3-19.6%, respectively; flexural and compressive modulus significantly changed to 4.4-29.0% and 3.5-21.5%, respectively. However, the values obtained from solutions of different pHs were not significantly and consistently different to each other.

Key Words : Composite resin, pH, Flexural property, Compressive property