

**Effect of the hydrophilicity of
dentin adhesives on bond strength
after aging in water**

Dong-Hwa Lee

Department of Dental Science

The Graduate School, Yonsei University

**Effect of the hydrophilicity of dentin
adhesives on bond strength after aging
in water**

Directed by Professor Kyoung-Nam Kim

The Master's Thesis

**submitted to the Department of Dental Science,
the Graduate School of Yonsei University
in partial fulfillment of the requirement for the
degree of Master of Dental Science**

Dong-Hwa Lee

June 2005

**This certifies that the Master's Thesis
of Dong-Hwa Lee is approved.**

Thesis Supervisor: Kyoung-Nam Kim

Thesis Committee Member #1: Kwang-Mahn Kim

Thesis Committee Member #2: Sung-Ho Park

The Graduate School

Yonsei University

June 2005

ACKNOWLEDGEMENTS

먼저 자격없는 자에게 만학의 길을 가도록 인도해 주신 하나님께 감사를 드립니다. 그리고 저에게 인격적인 관심과 사랑을 베풀어 주신 고 이사무엘 박사님께 감사를 드립니다. 저를 낳아주시고 길러 주시고 이제까지 돌보아 주시며 힘들 때나 기쁠 때나 묵묵히 저를 위해 기도해 주시며 섬겨주신 부모님께 진심으로 감사를 드립니다. 뿐만 아니라 저에게 학문을 할 수 있도록 배려해 주신 김경남교수님과 본 논문을 꼼꼼히 지도하여 주신 김광만 교수님, 박성호 교수님 그리고 연세대학교 치과대학 치과생체재료공학교실 모든 분들께 진심으로 감사를 드립니다. 피곤하고 힘들 때마다 저를 기도와 사랑으로 격려해 준 사랑하는 아내 영선님께 감사를 드립니다. 새내기 시절부터 저를 사랑으로 섬겨주시고 오늘이 있기까지 도와주신 김다윗 목자님과 김사라 사모님께 감사를 드립니다. 저를 위해 기도해 주신 UBF 모든 동역자들에게 감사를 드립니다. 나의 기쁨과 소망인 사랑하는 마리아, 사무엘, 에스더와도 함께 기쁨을 나누고 싶습니다.

제가 이 논문을 완성하기까지는 많은 어려움이 있었습니다. 때로는 포기하고 싶은 마음이 들 때도 있었습니다. 하지만 “믿음으로 저희가 홍해를 육지같이 건넜으나” 하신 하나님의 말씀과 같이 하나님께서는 신기한 방법으로 저를 도우시며 그 어려움들을 이기게 하시고 여기까지 오게 하셨습니다. 이를 통해 저에게 살아있는 믿음이 무엇인지를 가르쳐 주셨습니다. 앞으로 건너야 할 박사과정의 홍해도 이 믿음으로 건널 수 있기를 기도합니다.

2005년 6월

이동화 드림

CONTENTS

LIST OF FIGURES	6
LIST OF TABLES	8
ABSTRACT	9
I . INTRODUCTION	12
II . MATERIALS AND METHODS	14
1. Hoy's Solubility Parameter (Hoy, 1970)	18
2. Composite block preparation	20
3. Ultimate tensile strength(UTS) evaluation	22
4. Statistical analysis	25
III. RESULT	26
IV. DISCUSSION	30
V . CONCLUSIONS	36
REFERENCES	38
ABSTRACT (in KOREAN)	43

LIST OF FIGURES

Fig. 1. HEMA, TCDM, and 2MP -----	17
Fig. 2. Isomet 1000 -----	21
Fig. 3. Schematic illustration of specimen preparation for microtensile test. (A) composite block; (B) composite-composite block; (C) the first cut slice perpendicular to the adhesive surface; (D) second cut, perpendicular(90 degree) to first cut; (E) bar specimens -----	21
Fig. 4. Bisco Microtensile Tester -----	23
Fig. 5. The specimen placed on the test block key -----	23
Fig. 6. The specimen at the point of UTS -----	24
Fig. 7. The change in UTS of five dentin adhesives after storage in water for 5 weeks. -----	29
Fig. 8. The change in UTS of five dentin adhesives after storage in air for 5 weeks. -----	29

**Fig. 9. Percentage reduction in UTS of the five dentin adhesives after
storage in water for 5 weeks. ----- 30**

**Fig. 10. Percentage reduction in UTS of the five dentin adhesives after
storage in air for 5 weeks. ----- 30**

LIST OF TABLES

Table 1. Composition and Hoy's solubility parameters of the five adhesives	
-----	15
Table 2. Ultimate tensile strengths (MPa) of the five dentin adhesives after	
aging in water -----	27
Table 3. Ultimate tensile strength (MPa) of the five dentin adhesives after	
aging in air -----	28

ABSTRACT

Effect of the hydrophilicity of dentin adhesives on bond strength after aging in water

Dong-Hwa Lee

**Department of Dental Science
The Graduate School Yonsei University**

(Directed by Professor Kyoung-Nam Kim)

Purpose: The objective of this study was to evaluate the effect of the hydrophilicity of dentin adhesives on bond strength after aging in distilled water.

Materials and Methods: Twenty 7x7x5mm composite resin blocks of Renew were prepared and polished to sandpaper and the bonding surfaces were treated with sandblasting. Five different adhesives were applied on the treated surfaces and covered with another composite resin and were divided into five groups (Group 1-5) according to the hydrophilicity of each adhesive. The composite-composite blocks were cut with a diamond saw machine producing sticks (n=550). Ten control specimens were randomly

selected from each group for baseline UTS evaluation. The UTS of the experimental specimens were measured after 1, 2, 3, 4 and 5 weeks of aging in water. The UTS of each group at different storage periods in water were analyzed using the Friedman multiple ANOVA on ranks and Dunn's multiple comparison tests at 95% confidence level.

Results: Significant reduction ($p < 0.01$) in UTS was observed in Group 3, 4 and 5 after five weeks storage in water, while the relatively hydrophobic adhesive group (Group 1 and 2) showed no significant change ($p > 0.05$) in the same period. The percentage reduction in UTS increased with the hydrophilicity of the adhesives.

Conclusion: The bond strengths of the hydrophilic dentin adhesives markedly reduced after aging in water for 5 weeks. It can be assumed that the durability of resin-dentin bonds may be affected by the hydrophilicity of dentin adhesives.

Key words: dentin adhesive, hydrophilicity, ultimate tensile strength, bond strength, composite resin

Effect of the hydrophilicity of dentin adhesives on bond strength after aging in water

Dong-Hwa Lee

**Department of Dental Science
The Graduate School Yonsei University**

(Directed by Professor Kyoung-Nam Kim)

I. INTRODUCTION

II. MATERIALS AND METHODS

III. RESULTS

IV. DISCUSSION

V. CONCLUSIONS

REFERENCES

ABSTRACT (in KOREAN)

I . INTRODUCTION

In order to simplify the bonding procedure, several single bottle primer-adhesive systems have recently been introduced. Early generations of dentin adhesives could not penetrate through smear layers because they were relatively hydrophobic. The bond strengths between dentin and material were very low. To make the adhesives to wet the dentin, the manufacturers reformulated the adhesives by adding 2-hydroxyethyl methacrylate (HEMA). As a result, the adhesives became more tolerant with moisture. This moisture tolerance led the introduction of the "total-etch concept" (simultaneous etching of enamel and dentin) (Fusayama et al., 1979).

With the advent of contemporary self-etching adhesives, greater concentrations of acidic (ionic) resin monomers were incorporated into the adhesives to enable them to etch through the smear layer and demineralize the underlying intact dentin (Van Meerbeek et al., 2003; Perdigão, 2002; Tay et al., 2002). The incorporation of hydrophilic and acidic resin monomers has substantially improved the initial bonding of contemporary total-etch and self-etching adhesives. However, there are some potential problems associated with these increasingly hydrophilic adhesives.

This hydrophilic and acidic nature of the cured adhesive layer introduces new issues of permeability and adhesion compatibility. One research has shown that some of the two-step and all of the one (single)-step adhesives are not compatible with self-cured composite materials because the acidic monomers in the oxygen-inhibited layer on the adhesives effectively neutralize the self-cure mechanism (Swift et al., 2001). Another research also shows that some adhesives, namely one (single)-step and some two-step adhesives, act as a permeable membrane that conducts water from the underlying dentin (Ittahagarun et al., 2004). This property leads to weak adhesive-composite interfaces when the cure of subsequent restorative materials is delayed. Such a delay occurs when

self-cured and dual-cured cements and composites are used. This weak interface can lead to immediate restorative failure. The long-term success of restorations using these semi-permeable adhesives may also be adversely affected due to water sorption within the adhesive layer.

Hashimoto et al. (2002) reported that there was the degradation of resin composite and the depletion of collagen fibrils among the specimens aged in an oral environment (Hashimoto et al., 2002). De Munck et al. (2003) also reported that direct exposure of total-etch adhesives to water for 4 years affected bonds produced by two-step total-etch adhesives (De Munck et al., 2003).

The long-term effects of the hydrophilic components of dentin adhesives on water sorption and the subsequent changes in mechanical properties of the composite resin are not fully elucidated. It has been speculated that the permeability of polymerized dentin adhesives may be related to their hydrophilicity (Burrow et al., 1999), and that hydrophilic dentin adhesives will produce lower mechanical strength after aging in water when compared with relatively hydrophobic adhesives.

The objective of this study was to investigate the influence of the hydrophilicity of dentin adhesives on degradation after their interfaces were exposed to water. Hypothesis tested was that there is no difference in degradation overtime in accordance with the hydrophilicity of dentin adhesive.

II. MATERIALS AND METHODS

Five experimental dentin adhesives with different degrees of hydrophilicity were formulated for this study (Group 1-5). Their compositions and respective Hoy's solubility parameters are shown in Table 1. The hydrophilic and ionic monomers that are used for increasing the hydrophilicity in Group 3, 4 and 5 are shown in Figure 1.

Table 1. Composition and Hoy's solubility parameters of the five adhesives

	Composition	Wt %	Hoy's solubility parameter(J/cm ³) ^{1/2}			
			δ_d	δ_p	δ_h	δ_t
Group 1	Bis-GMA-E	70.00				
	TEGDMA	28.75	14.8	9.8	6.9	19.1
	CQ	0.25				
	EDMAB	1.00				
Group 2	Bis-GMA	70.00				
	TEGDMA	28.75	13.9	12.0	10.3	20.9
	CQ	0.25				
	EDMAB	1.00				
Group 3	Bis-GMA	70.00				
	HEMA	28.75	13.9	12.6	12.2	22.3
	CQ	0.25				
	EDMAB	1.00				
Group 4	Bis-GMA	40.00				
	HEMA	28.75				
	TCDM	30.00	13.6	12.6	11.3	21.9
	CQ	0.25				
	DMABA	1.00				
Group 5	Bis-GMA	40.00				
	HEMA	28.75				
	2MP	30.00	13.9	12.9	12.9	23.0
	CQ	0.25				
	EDMAB	1.00				

Abbreviations

2MP: Bis[2-(methacryloyloxy)ethyl] phosphate

Bis-GMA: bisphenol A diglycidyl ether dimethacrylate

Bis-GMA-E: ethoxylated bisphenol A diglycidyl ether dimethacrylate

CQ: camphorquinone

EDMAB: ethyl N,N-dimethyl-4-aminobenzoate

HEMA: 2-hydroxyethyl methacrylate

DMABA: dimethylaminobenzoic acid

TEGDMA: triethylene-glycol dimethacrylate

TCDM: di(hydroxyethylmethacrylate) ester of

5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride

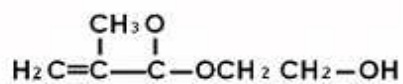
δ_d : dispersion component

δ_p : polar component

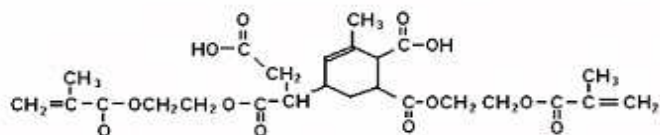
δ_h : hydrogen bonding component

δ_t : total cohesive energy density value

HEMA



TCDM



2MP

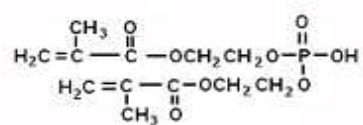


Fig. 1. HEMA, TCDM, and 2MP.

Hoy's Solubility Parameter (Hoy, 1970)

The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporization. What this means will be clarified when we understand the relationship between vaporization, van der Waals forces, and solubility parameter. In 1936, Joel H. Helderbrand (who laid the foundation for solubility theory in his classic work on the solubility of nonelectrolytes in 1916) proposed the square root of the cohesive energy density as a numerical value in indicating the solvency behavior of a specific solvent.

$$\delta = \sqrt{c} = \left[\frac{\Delta H - RT}{V_m} \right]^{1/2}$$

The Hoy's Solubility Parameter method is one of the best and the fastest methods to predict whether an organic material is compatible with another (or soluble in) organic material (solvent, polymer...).

The method is essentially a group contribution method: for each chemical group in the molecule, contributions are added to the total. The Hoy solubility Parameter method is special as it allows to "correct" for structural features like: cis, trans (around double bonds), ortho-, meta-, para-substitution (aromatics), branching (isopropyl, t-butyl) conjugation of double bonds, and rings. The Hoy method for the prediction of the Solubility Parameter is based on three different contributions:

- A dispersive contribution (δ_d): i.e. all non-polar contributions
- A Polar contribution (δ_p): polar contributions
- A hydrogen bond contribution (δ_h): only present when the molecule can form hydrogen bonds. Each of this can be regarded as a vector in three-dimensional space, so the total solubility parameter(δ_t) is defined by:

$$\delta(t)^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

Values for each of these parameters for a particular solvent or solute can be obtained from various literature sources. For organic chemicals not having reported parameters, methods are available in the literature for calculating or estimating the parameters.

This flexibility in using solvent blends to match solubility parameters comes with a price, however. If one was to calculate the optimal blend parameters of a 3-component solvent mixture for each unique combination from a database of, say, 500 'pure' chemical solvents, more than 20 million possible combinations would result. Such an evaluation would clearly require the use of a high-speed computer.

Composite block preparation

Twenty 7x7x5 mm composite blocks were fabricated with Renew(universal hybrid composite, BISCO Inc., Schaumburg, IL, USA). The composite resins were packed into the mold and light-cured at 500 mW/cm² for 80 seconds on each side. After air-drying, the bonding surfaces of composite block were machined flat for surface standardization with No. 600 grit silicon-carbide abrasive paper (Wetordry sandpaper, 3M, St. Paul, MN, USA) in figure-eight motion under continuous coolant water irrigation, washed in water and dried with oil-free compressed air. The flattened surface of each composite block was sand-blasted with 50 μ m aluminum oxide particles for 5 seconds at a distance of 10 mm with a sandblasting device (Microcab Danville Engineering Inc., San Ramon, CA, USA), operating at 35 psi. The blocks were rinsed and dried with oil-free compressed air for 30 seconds.

Then twenty blocks were divided into five groups (Group 1-5). The five different adhesives were applied to the prepared surface of each group of composite block and light-cured at 500 mW/cm² for 20 seconds. Following the adhesive application, composite resin (Renew, universal hybrid composite, BISCO Inc., Schaumburg, IL, USA) was placed on the prepared resin surfaces in three 2-mm-thick layers and each layer was light cured for 40 seconds. Each composite-composite block was attached to an acrylic resin base with sticky wax (Kerr, MI, USA).

The composite-composite block was then mounted in a slow-speed sectioning saw(Isomet 1000, Buehler, Lake Forest, IL) regulated to cut 0.9 mm wide slices with a 0.3 mm diamond-disc under running water(Fig. 2). The first cuts through the composite block produced six slabs of approximately 0.9 mm width. A second set of cuts made perpendicular to the first cuts converted the slabs into 36 bars (bar shaped testing specimens) approximately 0.9 mm x 0.9 mm in transverse cross section (Fig. 3).



Fig. 2. Isomet 1000.

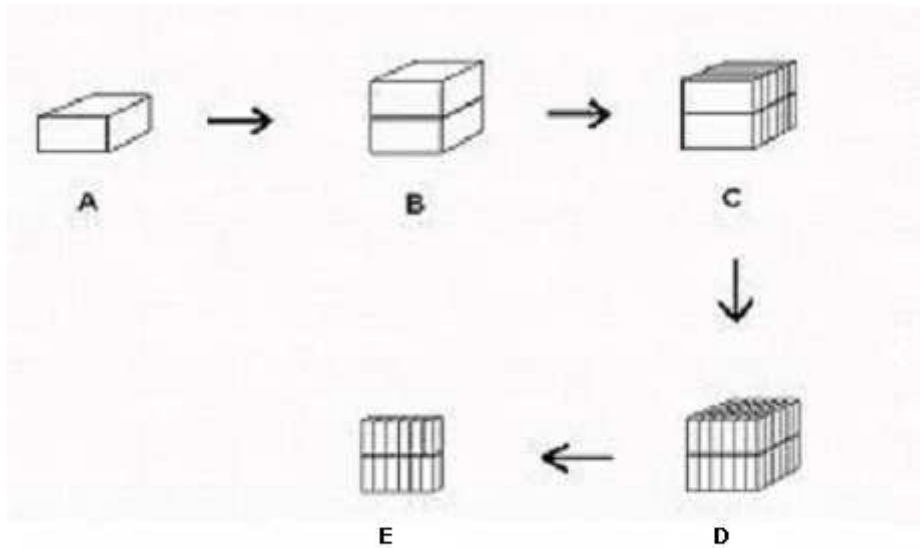


Fig. 3. Schematic illustration of specimen preparation for microtensile test.

(A) composite block; (B) composite-composite block; (C) the first cut slice perpendicular to the adhesive surface; (D) second cut, perpendicular (90 degree) to first cut; (E) bar specimens

Ultimate tensile strength(UTS) evaluation

Ten control specimens were randomly selected from each group for baseline UTS evaluation. Each bar specimen was glued on the test jaw of the Bisco Micro Tensile Tester (MTT, Fig. 4) with cyanoacrylate adhesive (Zapit, Dental Ventures of America, Corona, CA). Specimens were glued as parallel as possible to the direction of the test block keys to avoid the bending forces (Fig. 5). Then the specimens were subjected to tensile forces until failure at a crosshead speed of 0.5 mm/min (Fig. 6). The dimension of each specimen was measured using a digital caliper (Model CD-6BS, Mitutoyo, Tokyo, Japan). The rupture force was gauged in kgs and then divided by the transverse section area of each sample. The UTS of each specimen was calculated and expressed in MegaPascals(MPa).

The 100 specimens from each group were randomly divided into two groups of 50, for aging in water, and 50 for aging in air as a control.

All specimens of test group were then stored in sealed vials containing either 20 mL of unchanged distilled water at 37 °C, in which 1% sodium azide was added to prevent bacterial growth.

At specific time intervals of 1, 2, 3, 4 and 5 weeks, 10 specimens of test group and 10 specimens of control group were randomly removed from water for UTS evaluation.

The dimensions of each tested bars were also measured using a digital caliper (Model CD-6BS, Mitutoyo, Tokyo, Japan) and the bond surface area of the specimen calculated; this surface area was used to calculate the bond strength.

$$\text{UTS (MPa)} = \text{Max. rupture Force (N)} / \text{surface area of cross section (mm}^2\text{)}$$

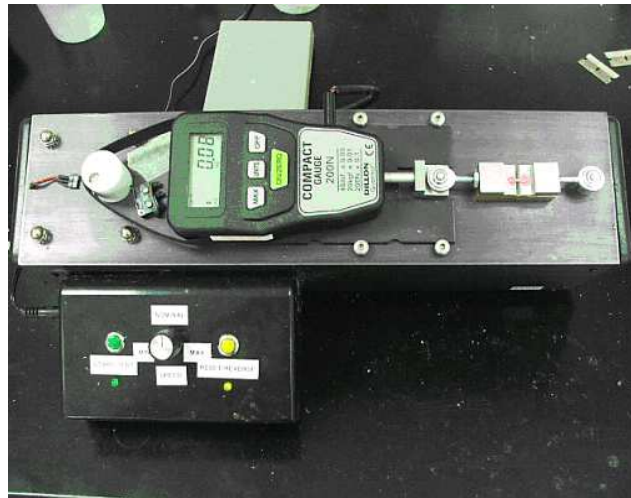


Fig. 4. Bisco Microtensile Tester.

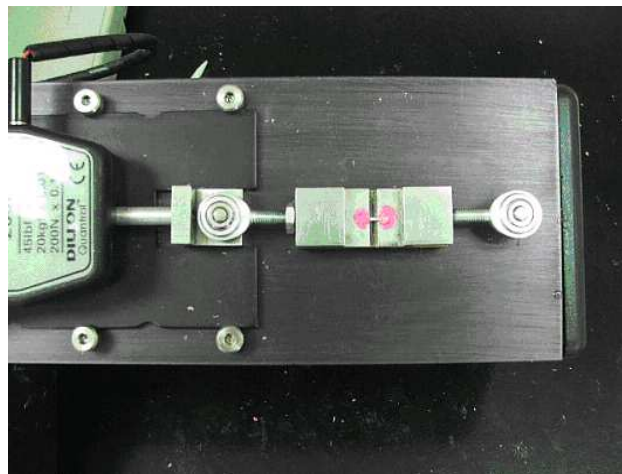


Fig. 5. The specimen placed on the test block key.

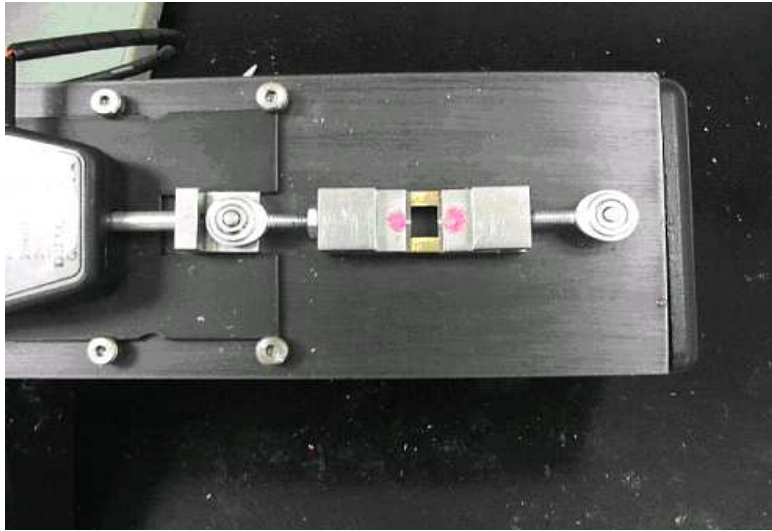


Fig. 6. The specimen at the point of UTS.

Statistical analysis

The collected data were analyzed using a statistical software package (Sigmastat Version 2.03, SPSS, Chicago, IL, USA). The UTS of each group of dentin adhesive at different storage periods in water or air were analyzed using the Friedman multiple ANOVA on ranks and Dunn's multiple comparison tests with statistical significant set at $p = 0.05$.

III. RESULTS

The mean UTS and standard deviations of the five dentin adhesives after aging in water or air over a 5-week period are presented in Tables 2 and 3, respectively. The baseline UTS for the five dentin adhesives ranged from 57.3(7.8) to 67.3(9.3) MPa. Friedman multiple ANOVA and Dunn's multiple comparison tests revealed significant reduction ($p < 0.01$) in UTS in Groups 3 (33.4 %), 4 (31.5 %) and 5 (46.2 %) dentin adhesives after 5-week storage in water. Two-week aging in water caused a drastic decrease in UTS of Group 3, 4 and 5 with no further significant reduction in UTS thereafter (Fig. 7). Conversely, the more hydrophobic Group 1 and 2 dentin adhesives did not show any significant change ($p > 0.05$) in UTS over the 5-week period. Variation in the percentage reduction in UTS of the five dentin adhesives after storage in water for a 5-week period is shown in Fig. 9. Generally, the percentage reduction in UTS increased with the hydrophilicity of the dentin adhesives. Conversely, after 5-week of aging in air, the UTS were preserved ($p > 0.05$) in all groups. (Fig. 8 and 10).

Table 2. Ultimate tensile strengths (MPa) of the five dentin adhesives after aging in water

	Group 1	Group 2	Group 3	Group 4	Group 5
24h	57.3(7.8)	67.3(9.3)	62.4(8.7)	61.8(10.2)	61.1(11.0)
1 week	60.2 (6.5)	57.3(9.4)	46.6(5.8)	42.0(8.4)	32.0(6.3)
2 weeks	63.0(7.7)	53.4(7.2)	43.6(8.0)	32.1(5.9)	31.5(8.5)
3 weeks	60.6(8.6)	69.4(10.2)	53.3(6.3)	40.4(7.2)	35.2(6.2)
4 weeks	55.4(8.4)	53.3(8.0)	48.6(4.5)	44.5(12.3)	38.7(10.4)
5 weeks	61.8(11.1)	65.0(6.5)	41.5(8.5)	42.3(10.3)	32.8(8.0)

Data represents means (standard deviation). Data in each column (i.e. ultimate tensile strengths of each group of dentin adhesive at different aging periods in water) were analyzed using Friedman multiple ANOVA on ranks and Dunn's multiple comparison tests. For each column, values that are indicated by the same superscripts are not statistically significant ($P>0.05$)

Table 3. Ultimate tensile strength (MPa) of the five dentin adhesives after aging in air

	Group 1	Group 2	Group 3	Group 4	Group 5
24 h	57.3(7.8)	67.3(9.3)	62.4(8.7)	61.8(10.2)	61.1(11.0)
1 week	59.6(5.8)	72.4(7.0)	65.8(9.4)	68.4(7.3)	62.1(11.3)
2 weeks	62.8(6.0)	85.1(4.3)	68.8(12.2)	70.3(9.4)	64.7(9.2)
3 weeks	66.7(7.7)	73.3(9.7)	78.5(8.2)	71.7(7.2)	69.4(8.8)
4 weeks	70.5(7.0)	75.2(10.2)	83.7(11.3)	66.9(6.7)	72.3(7.3)
5 weeks	65.8 (8.7)	70.0(6.8)	76.3(12.1)	58.5(6.5)	64.3(7.4)

Data represents means (standard deviation). Data in each column (i.e. ultimate tensile strengths of each group of dentin adhesive at different aging periods in water) were analyzed using Friedman multiple ANOVA on ranks and Dunn's multiple comparison tests. For each column, values that are indicated by the same superscripts are not statistically significant ($P>0.05$)

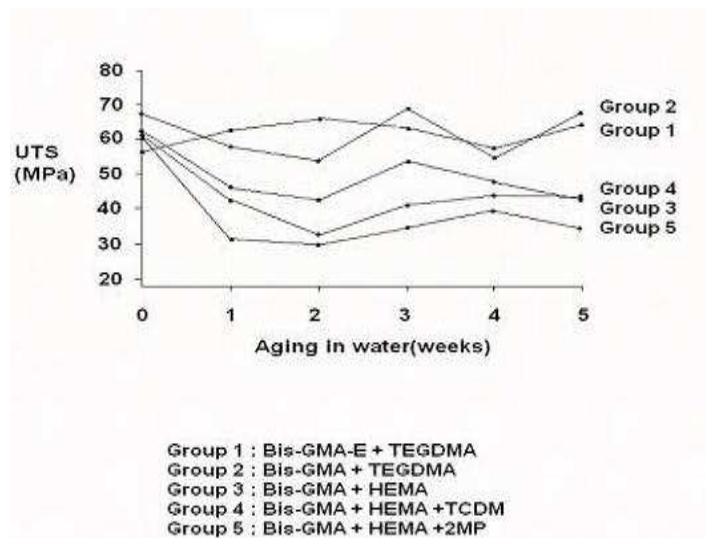


Fig. 7. The change in UTS of five dentin adhesives after storage in water for 5 weeks.

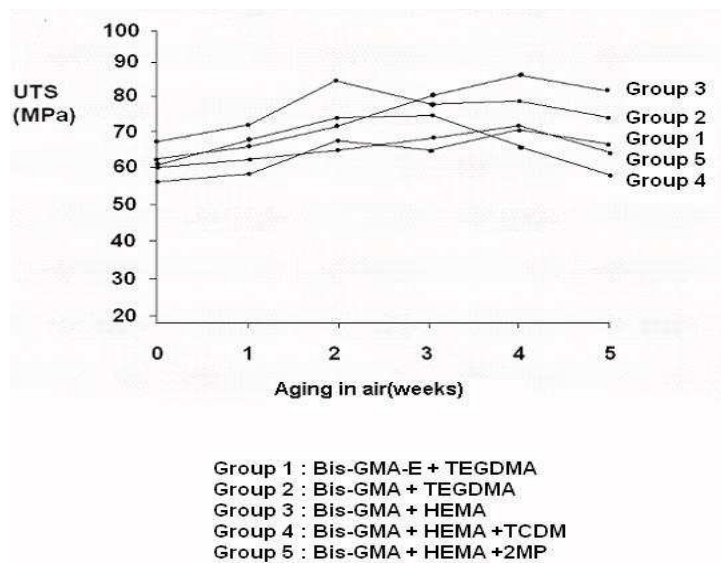


Fig. 8. The change in UTS of five dentin adhesives after storage in air for 5 weeks.

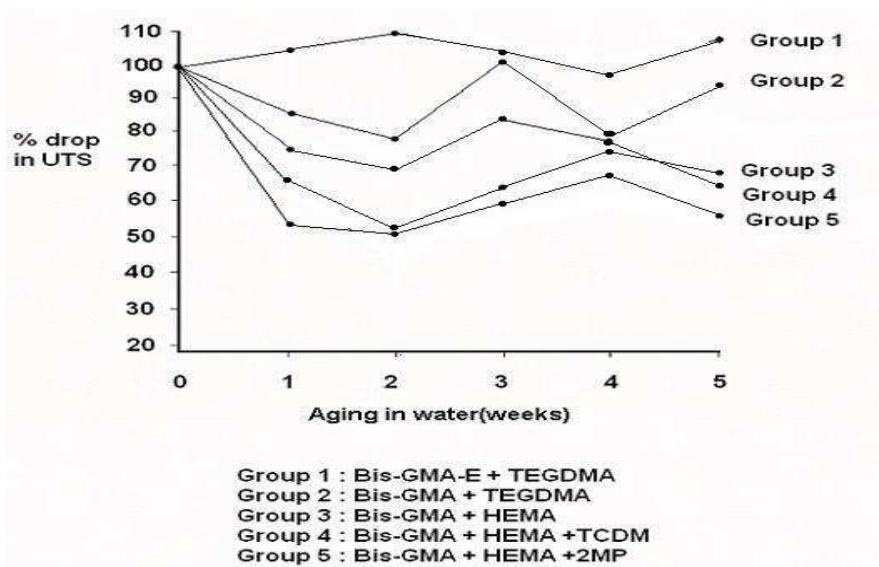


Fig. 9. Percentage reduction in UTS of the five dentin adhesives after storage in water for 5 weeks.

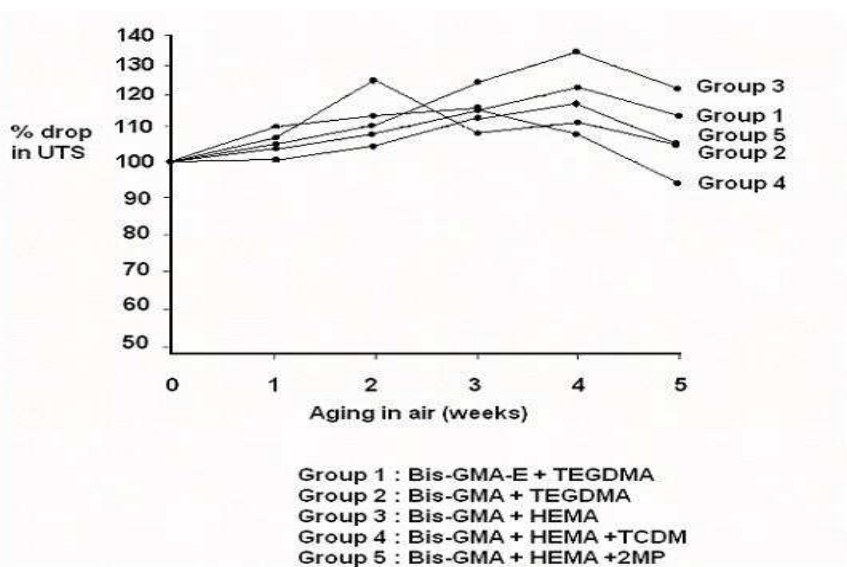


Fig. 10. Percentage reduction in UTS of the five dentin adhesives after storage in air for 5 weeks.

IV. DISCUSSION

It is known that air-drying of acid-etched dentin causes collapse of the collagen fibril matrix and interferes with resin infiltration (Gwinnett, 1994). Thus, the strength of resin-dentin bonds was only half that of resin-enamel bonds. The discovery that water or water-HEMA primers could double the strength of resin-dentin bonds led Kanca to introduce the "wet bonding" technique (Kanka, 1992). However, this new technique raised questions about "how wet is wet dentin" (Tay et al., 1996; Pereira et al., 2001). The optimal amount of surface wetness necessary for wet bonding varies among marketed total-etch adhesive systems, which are acetone-based, ethanol-based or water-based (Asmussen et al., 2001; Perdigão et al., 2001). Also, it is impossible to simultaneously achieve uniform wetness on the axial, pulpal and gingival walls because of differences in hydraulic conductance between superficial and deep dentin (Fogel et al., 1988; Tagami et al., 1989; Ozok et al., 2002) and the presence of caries-affected or sclerotic dentin in which the dentinal tubules are partially or completely obliterated by whitlockite crystals (Daculsi et al., 1987; Yoshiyama et al., 1989; Schpbach et al., 1992).

Another approach to decreasing the technique-sensitivity of wet bonding is to return to dry bonding to smear layers, but using much more acidic monomers dissolved in water-HEMA primers. The materials used with this method are known as self-etching primer adhesives. These water containing adhesives are acidic enough to etch and prime through thick smear layers and into the underlying intact dentin (Tay et al., 2000). Those with a pH between 1.9 and 2.4 incorporate the smear layer into the hybrid layer if the primers are not agitated during etching (Oliveira et al., 2002). If the primers are agitated, the smear layer can be dissolved and dispersed into the hybrid layer and the overlying adhesive.

All self-etching adhesives bond reasonably well to ground enamel, there is a general

consensus that the milder versions of these adhesives do not etch well on unground, aprismatic enamel where there is no resin tag formation and little subsurface demineralization for micromechanical retention (Pashley et al., 2001; Kanemura et al., 1999; Perdigo et al., 2003).

To make self-etching primer systems even simpler, manufacturers have recently introduced single-step self-etching adhesives, which etch, prime and bond tooth surfaces simultaneously. Some of these all-in-one adhesives have been made more acidic and more hydrophilic than the 2-step self-etching primers (Van Meerbeek et al., 2003; Inoue, 2001). One advantage of hydrophilic resin systems is that they attract water (Tanaka et al., 1999). However, it is difficult to evaporate water from these all-in-one adhesive resins. This water sorption plasticize polymers and lowers their mechanical properties (Bastoli et al., 1990). Although hydrophobic dimethacrylates are added to all-in-one adhesives to produce stronger cross-linked polymer networks, the hydrophilic monomers tend to cluster together before polymerization to create hydrophilic domains (Eliades et al., 2001; Spenser et al., 2002) and microscopic water-filled channels called "water-trees" (Tay et al., 2002; Ferrari et al., 2003). These water trees permit movement of water from the underlying dentin through the hybrid and adhesive layers to the adhesive-composite interfaces (Tay et al., 2003).

Through the results of this study, it was found that the percentage reduction in UTS increased with the hydrophilicity of the dentin adhesives after storage in water for a 5-week period. Water uptake in polymer network is related to resin polarity and chain topology (Soles et al., 2000; Soles at al., 2003). Resin polarity influences the number of hydrogen bonding sites and the attraction between the polymer and water molecules, while chain topology determines the spatial configuration of the molecular segments and the availability of nanopores within the polymer structure.

In this study, Hoy's solubility parameter method was used to predict the hydrophilicity

of respective dentin adhesives. There are three kinds of component in the solubility parameter: dispersion component, hydrogen bonding component, and polar component. Based on the result of this study, it was possibly speculated that there was little correlation between the hydrophilicity of dentin adhesives and dispersion component or hydrogen bonding component of solubility parameter. Rather, the percentage reduction of the UTS was closely related to the polar component of the solubility parameter. It can be assumed that the hydrophilicity of dentin adhesives is mainly influenced by the polarity or acidity of the dentin adhesives.

Group 1 dentin adhesive showed no significant change in mechanical behavior after 5 weeks aging in water, as Bis-GMA-E resin is a relatively hydrophobic. Group 2 Bis-GMA resin is comparatively more hydrophilic than Bis-GMA-E as it contains two-OH groups; consequently a 20.6 % reduction in UTS was observed at the end of 2-week aging in water. When the diluent monomer triethyleneglycol dimethacrylate(TEGDMA) was replaced by HEMA, the mechanical behavior of Group 3 adhesive fell significantly (30.1 %) after 2-week of aging in water. This finding is consistent with the result of a previous study, which showed a significant decrease in the UTS of an experimental Bis-GMA-HEMA bonding resin, after only 24h of water immersion (Paul et al., 1999). The UTS of the more hydrophilic Groups 4 (TCDM) and 5 (2MP) adhesives, with carboxyl and phosphate functional groups, fell even more drastically to 50 % of the 24-hour value after 2-week aging in water.

Uptake of water into polymer matrix is controlled by the Fickian (Type I) diffusion process (Braden et al., 1984; Mair, 1999; Hunter, 2003). The patterns of diffusion are governed by either the 'free volume theory', in which water diffuses through nanopores without any mutual relationship to the polar molecules in the material, or the hydrophilic groups (Bellenger et al., 1989). Absorbed water exists in two distinct forms: 'unbound water' that occupies the free volume between the chains and the nanopores created during

polymerization (Sderholm, 1984); and 'bound water' that is attached to the polymer chains via hydrogen bonding (Van Landingham et al., 1999), with the formation of primary and secondary hydration shells around the hydrophilic and ionic domains of the resin matrices (Zaikov et al.). The presence of these domains in Group 3, 4 and 5 resins facilitated water uptake into the resin matrices as 'bound water'. This is similar to a recent study that investigated the effect of a hydrophilic resin monomer, 4-methacryloxyethyl trimellitic anhydride (4-META) on water sorption in polymethyl methacryloxyethyl (PMMA) (Swift et al., 2001). In that study, the "interaction theory" (i.e., hydrogen bonding via polar sites) was found to provide a more mechanism, when increasing concentration of 4-META was incorporated in the PMMA resin (Unemori et al., 2003). Phase separation of the hydrophilic HEMA and hydrophobic domains in the resin matrices may further open up the polymer network, leading to more microvoid formation with increased uptake of 'free' water (Eliades et al., 2001; Spenser, 2002). Water sorption initially caused a softening of the polymer resin component by swelling the network and reducing the frictional forces between the polymer chains (Ferracane et al., 1998). The absorbed moisture also acts as a plasticizer, lowering the glass transition temperature (T_g) of the cured resin. Water sorption may eventually cause irreversible damage to the material by formation of microcracks through repeated sorption/desorption cycles (Musto et al., 2002). This is followed by hydrolytic degradation of the polymer with scission of the ester linkages and gradual deterioration of the infrastructure of the polymer over time. Once the polar sites in the polymer network become saturated with water, equilibrium is reached between bound and free sites, with no further reduction of UTS observed in Group 2, 3, 4 and 5 resins after the second week of aging in water. This agrees with other studies, which demonstrated that water sorption in resin-based composite (Momoi et al., 1994) and fiber-reinforced composite (Vallitu, 2002) stabilized, within one month. The fact that the UTS of control groups were constant or increases after aging support the results of previous studies

(Carrilho et al., in press).

As water storage caused a marked reduction in the tensile strength of the hydrophilic dentin adhesives after 5-week storage in water, we have to reject the hypothesis. The results of this study clearly indicate that the hydrophilicity of dentin adhesive is the prime factor in determining the extent of water sorption. It is speculated that water sorption may enhance plasticizing of the cured dentin adhesives. More effort should be devoted over the next decade to improving the quality of bonding so as to increase their longevity.

V. CONCLUSIONS

Within the limits of the present study, the following results were obtained:

1. The bond strength of hydrophilic dentin adhesives markedly reduced after aging in water.
2. The reduction in bond strength of the hydrophilic dentin adhesives occurred mainly during two-week aging in water.
3. The percentage reduction in the bond strength increased with the hydrophilicity of the dentin adhesives, as measured by their Hoy's solubility parameter for hydrogen bonding.
4. The bond strength of hydrophobic dentin adhesives was generally maintained even after aging in water.

From these results, it can be concluded that excessive hydrophilicity of dentin adhesives may compromise the durability of resin-dentin bonds.

ACKNOWLEDGEMENTS

This study was based on the work performed by Dong-Hwa Lee for fulfillment of Master's degree, the Yonsei University, College of Dentistry. The author would like to express the gratitude to Mr. Byoung In Suh. The resin blends used in this study were generous gifts from Bisco, Inc.

REFERENCES

- Asmussen E, Peutzfeldt A: The influence of relative humidity on the effect of dentin bonding systems. *J Adhes Dent* 3(2):123-127, 2001.
- Bastioli C, Romano G, Migliaresi C: Water sorption and mechanical properties of dental composites. *Biomaterials* 11(3):219-223, 1990.
- Bellenger V, Verdu J: Structure-properties relationship for densely crosslinked epoxy-amine systems based on epoxide or amine mixtures. *J Mater Sci* 24:63-68, 1989.
- Braden M, Clarke RL: Water absorption characteristics of dental microfine composite filling materials. I. Proprietary materials. *Biomaterials* 5:369-372, 1984.
- Burrow MF, Inokoshi S, Tagami J: Water sorption of several bonding resins. *Am J Dent* 12:295-298, 1999.
- Carrilho MRO, Carrilho RM, Tay FR, Pashley DH: Effects of storage media on mechanical properties of adhesive systems. *Am J Dent* 17(2):104-8, 2004.
- Carrilho MRO, Tay FR, Pashley DH, Tjaderhane L, Carvalho RM: Mechanical stability of resin-dentin bond components. *Dent Mater* 21(3): 232-41, 2005.
- Daculsi G, LeGeros RZ, Jean A, Kerebel B: Possible physico-chemical processes in human dentin caries. *J Dent Res* 66(8):1356-1359, 1987.
- De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K et al.: Four-year water degradation of total-etch adhesives bonded to dentin. *J Dent Res* 82(2):136-140, 2003.
- Eliades G, Vougiouklakis G, Palaghias G: Heterogeneous distribution of single-bottle adhesive monomers in the resin-dentin interdiffusion zone. *Dent Mater* 7:277-283, 2001.
- Ferracane JL, Berge HX, Condon JR: In vitro aging of dental composites in water effect of degree of conversion, filler volume, and filler/matrix coupling. *J Biomed Mater Res* 42:465-472, 1998.

- Ferrari M, Tay FR: Technique sensitivity in bonding to vital, acidetched dentin. *Oper Dent* 28(1):38, 2003.
- Fogel HM, Marshall FJ, Pashley DH: Effects of distance from the pulp and thickness on the hydraulic conductance of human radicular dentin. *J Dent Res* 67(11):1381-1385, 1988.
- Fusayama T, Nakamura M, Kurosaki N, Iwaku M: Non-pressure adhesion of a new adhesive restorative resin. *J Dent Res* 58(4):1364-1370, 1979.
- Gwinnett AJ: Chemically conditioned dentin: a comparison of conventional and environmental scanning electron microscopy findings. *Dent Mater* 10(3):150-155, 1994.
- Hashimoto M, Ohno H, Sano H, Tay FR, Kaga M, Kudou Y et al.: Micromorphological changes in resin-dentin bonds after 1 year of water storage. *J Biomed Mater Res* 63(3):306-311, 2002.
- Hoy KL: New values of the solubility parameters from vapor pressure data, *J Paint Techn* 42(541):76, 1970.
- Hunter G, Lane DM, Scrimgeour SN, McDonald PJ, Lloyd CH: Measurement of the diffusion of liquids into dental restorative resins by stray-field nuclear magnetic resonance imaging(STRAFI). *Dent Mater* 19:632-638, 2003.
- Inoue S, Vargas MA, Abe Y et al.: Microtensile bond strength of eleven contemporary adhesives to dentin. *J Adhes Dent* 3(3):237-245, 2001.
- Itthagarun A, Tay FR, Pashley DH, Wefel JS, Garcia-Godoy F, Wei SH: Single-step, self-etch adhesives behave as permeable membranes after polymerization. Part III. Evidence from fluid conductance and artificial caries inhibition. *Am J Dent* 17(6): 394-400, 2004.
- Kanca J 3rd: Resin bonding to wet substrate. 1. Bonding to dentin. *Quintessence Int* 23(1):39-41, 1992.
- Kanemura N, Sano H, Tagami J: Tensile bond strength to and SEM evaluation of ground

- and intact enamel surfaces. *J Dent* 27(7):523-530, 1999.
- Mair LH: The silver sorption layer in dental composites: three-year results. *Dent Mater* 15:408-412, 1999.
- Momoi Y, McCabe JF: Hygroscopic expansion of resin based composites during 6 months of water storage. *Br Dent J* 176:91-96, 1994.
- Musto P, Ragosta G, Scarinza G, Mascia L: Probing the molecular interactions in the diffusion of water through epoxy and epoxy-bismaleimide networks. *J Polym Sci Part B: Polym Phys* 40:922-938, 2002.
- Oliveira SS, Marshall SJ, Hilton JF, Marshall GW: Etching kinetics of a self-etching primer. *Biomaterials* 23(20):4105-4112, 2002.
- Ozok AR, Wu MK, Wesselink PR: Comparison of the in vitro permeability of human dentine according to the dentinal region and the composition of the simulated dentinal fluid. *J Dent* 30(2-3):107-111, 2002.
- Pashley DH, Tay FR: Aggressiveness of contemporary self-etching adhesives. Part II: etching effects on unground enamel. *Dent Mater* 17(5):430-444, 2001.
- Paul SJ, Leach M, Rueggeberg FA, Pashley DH: Effect of water content on the physical properties of model dentin primer and bonding resins. *J Dent* 27:209-214, 1999.
- Perdigo J, Frankenberger R: Effect of solvent and rewetting time on dentin adhesion. *Quintessence Int* 32(5):385-390, 2001.
- Perdigo J: Dentin bonding as a function of dentin structure. *Dent Clin North Am* 46(2):277-301, 2002.
- Perdigo J, Geraldini S: Bonding characteristics of self-etching adhesives to intact versus prepared enamel. *J Esthet Restor Dent* 15(1):32-41, 2003.
- Pereira GD, Paulillo LA, De Goes MF, Dias CT: How wet should dentin be? Comparison of methods to remove excess water during moist bonding. *J Adhes Dent* 3(3):257-264, 2001.

- Schpbach P, Lutz F, Guggenheim B: Human root caries: histopathology of arrested lesions. *Caries Res* 26(3):153-164, 1992.
- Sderholm KJ: Water sorption in a bis(GMA)/ TEGDMA resin. *J Biomed Mater Res* 18:271-279, 1984.
- Soles CL, Chang FT, Gidley DW, Yee AF: Contribution of the nanovoid structure to the kinetics of moisture transport in epoxy resins. *J Poly Sci* 38:776-791, 2000.
- Soles CL, Yee AF: A discussion of the molecular mechanisms of moisture transport in epoxy resins. *J poly Sci* 38:792-802, 2003.
- Spenser P, Wang Y: Adhesive phase separation at the dentin interface under wet bonding conditions. *J Biomed Mater Res* 62:447-456, 2002.
- Swift EJ Jr, Perdigao J, Combe EC, Simpson CH 3rd, Nunes MF: Effects of restorative and adhesive curing methods on dentin bond strengths. *Am J Dent* 14(3):137-40, 2001.
- Tagami J, Tao L, Pashley DH, Horner JA: The permeability of dentine from bovine incisors in vitro. *Arch Oral Biol* 34(10):773-777, 1989.
- Tanaka J, Ishikawa K, Yatani H, Yamashita A, Suzuki K: Correlation of dentin bond durability with water absorption of bonding layer. *Dent Mater* 18(1):118, 1999.
- Tay FR, Gwinnett JA, Wei SH: Micromorphological spectrum from overdrying to overwetting acid - conditioned dentin in water-free acetonebased, single - bottle primer/adhesives. *Dent Mater* 12(4):236-244, 1996.
- Tay FR, Sano H, Carvalho R, Pashley EL, Pashley DH: An ultrastructural study of the influence of acidity of self-etching primers and smear layers thickness on bonding to intact dentin. *J Adhes Dent* 2(2):83-98, 2000.
- Tay FR, Pashley DH: Aggressiveness of ontemporary self-etching systems. I: Depth of penetration beyond dentin smear layers. *Dent Mater* 17(4):296-308, 2001.
- Tay FR, Pashley DH, Yoshiyama M: Two modes of nanoleakage expression in single-step adhesives. *J Dent Res* 81(7):472-476, 2002.

- Tay FR, Pashley DH, Yiu CK, Sanares AM, Wei SH: Factors contributing to the incompatibility between simplified-step adhesives and self - cured or dual - cured composites. Part I. Single-step self-etch adhesive. *J Adhes Dent* 5(1):27-40, 2003.
- Unemori M, Matsuya S, Akashi A, Akamine A: Water absorption of poly (methyl methacrylate) containing 4-methacryloxyethyl trimellitic anhydride. *Biomaterials* 24: 1381-1387, 2003.
- Van Landingham MR, Eduljee RF and Gillespie JW: Moisture diffusion in epoxy systems. *J App Ploy Sci* 71:787-798, 1999.
- Van Meerbeek B, De Munck J, Yoshida Y, et al.: Buonocore memorial lecture. Adhesion to enamel and dentin: current status and future challenges. *Oper Dent* 28(3):215-235, 2003.
- Vallitu PK: Effect of 180-week water storage on the flexural properties of E-glass and fiber acrylic resin composite. *Int J Prosthodont* 13:334-339, 2000.
- Yoshiyama M, Masada J, Uchida A, Ishida H: Scanning electron microscopic characterization of sensitive versus insensitive human radicular dentin. *J Dent Res* 68(11):1498-1502, 1989.
- Zaikov GE, Iordanskii AL, Markin VS: Diffusion of electrolytes in polymers. Utrecht, The Netherlands: *VSP BV* (formerly *VNC Science Press BV*), 48-70.

ABSTRACT(In Korean)

물에 보관한 후 상아질 접착제의 친수성이 접착강도에 미치는 영향

이동화

연세대학교 대학원 치의학과

(지도교수:김경남교수)

상아질에 친화성을 띠게 하고자 하는 목적과 접착과정을 단순화하기 위한 목적으로 최근 개발되고 있는 상아질 접착제들은 더욱 산성화되고 있는 경향이 있다. 그 결과 초기 접착력은 상당히 향상되었다. 그러나 이런 상아질 접착제의 문제점은 강한 친수성으로 인하여 구강 내에서 수분을 흡수하여 시간이 지남에 따라 물리적 강도가 약해지는 경향이 있다. 친수성을 띠는 상아질 접착제는 상대적으로 소수성인 상아질 접착제에 비하여 물속에서 물리적 강도가 약해질 것으로 생각된다.

이 실험의 목적은 친수성인 상아질 접착제가 물에 노출되었을 때 발생할 수 있는 접착력의 변화를 관찰하고자 하는 것이었다. 이 실험을 위해서 각각 다른 친수성을 가진 다섯 가지의 실험적인 상아질 접착제를 특별히 제작하였다. 친수성의 정도는 호이 용해도 변수를 기준으로 그 크기를 정하였다. 20 개의 7x7x5 mm 크기의 콤포지트(Renew, 비스코) 레진블록을 제작하여 접착면을 표면 처리하였다. 5가지 실험적 접착제(BISCO 자체 제조)를 표면에 바르고 다른 콤포지트 레진을 부착하여 각각의 접착제의 친수성에 따라서 친수성이 가장 작은 그룹을 그룹 1로 하고 친수성이

가장 큰 그룹을 그룹 5으로 하여 5가지 그룹으로 분류하였다. 콤포지트 블록을 다이아몬드 톱을 이용하여 단면이 약 1mm² 되고 길이가 약 10 mm 정도 되는 바 형태로 잘랐다 (각 그룹에서 110개씩 총 550개의 시편을 제작함). 그룹1부터 5까지 각각의 그룹에서 열 개씩의 시료를 꺼내어서 Bisco Micro Tensile Tester(MTT)를 이용하여 최종인장강도를 측정하여 기준으로 삼았다. 실험군의 시료는 물속에 숙성시킨 지 1, 2, 3, 4, 5 주 만에 10개 씩 꺼내어 최종인장강도를 측정하여 기준치와 비교하고 시간에 따른 변화를 분석하였다. 공기 중에서 숙성시킨 시료는 대조군으로 이용하여 동일한 방법으로 인장강도를 측정하여 실험군과 비교하였다.

기준으로 삼은 다섯 가지 상아질 접착제의 최종인장강도의 범위는 57.3(7.8)에서 67.3(9.3) MPa였다. 5주간의 물속에서의 숙성 후 측정한 최종인장강도를 분석한 결과 그룹 3에서는 기준보다 33.4%, 그룹 4에서 31.5%, 그룹 5에서 46.2%의 감소가 일어났다. 그룹 3, 4, 5에서는 2주간의 물속에서의 숙성으로 급격한 최종인장강도의 감소가 발생하였고, 비교적 소수성 그룹인 그룹 1과 2에 유의한 변화가 관찰되지 않았다. 실험 결과 상아질 접착제의 친수성이 클수록 시간 경과에 따라서 물속에서 최종인장강도가 감소하는 비율이 크다는 사실을 발견하였고 상아질 접착제의 과도한 친수성은 레진과 상아질 결합의 내구성을 저하시킬 수 있다는 결론을 얻을 수 있었다.

핵심어: 상아질 접착제, 친수성, 최종 인장 강도, 접착 강도, 콤포지트 레진