

THE EFFECT OF PRIMING ETCHED DENTIN WITH SOLVENT ON THE MICROTENSILE BOND STRENGTH OF HYDROPHOBIC DENTIN ADHESIVE

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ABSTRACT

Deterioration of long-term dentin adhesion durability is thought to occur by hydrolytic degradation within hydrophilic domains of the adhesive and hybrid layers. This study investigated the hypothesis that priming the collagen network with an organic solvent displace water without collapse and thereby obtain good bond strength with an adhesive made of hydrophobic monomers and organic solvents. Three experimental adhesives were prepared by dissolving two hydrophobic monomers, bisphenol-A-glycidylmethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA), into acetone, ethanol or methanol. After an etching and rinsing procedure, the adhesives were applied onto either wet dentin surfaces (wet bonding) or dentin surfaces primed with the same solvent (solvent-primed bonding). Microtensile bond strength (MTBS) was measured at 48 hrs, 1 month and after 10,000 times of thermocycles. The bonded interfaces were evaluated using a scanning electron microscope (SEM). Regardless of bonding protocols, well-developed hybrid layers were observed at the bonded interface in most specimens. The highest mean MTBS was observed in the adhesive containing ethanol at 48 hrs. With solvent-primed bonding, increased MTBS tendencies were seen with thermocycling in the adhesives containing ethanol or methanol. However, in the case of wet bonding, no increase in MTBS was observed with aging. [J Kor Acad Cons Dent 34(1):42-50, 2009]

Key words: Dentin adhesive, Durability, Solvent priming, Hydrophobic monomer, Microtensile bond strength

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I . Introduction

The bonding mechanism of dentin adhesives currently available is partly based on the micromechanical retention through formation of a hybrid layer¹⁾. In order to obtain consistent hybrid layers, the three-dimensional structure of a collagen network should be exposed by etchant or acidic monomers. Water is required to obtain the appropriate acidity of etchants

or acidic monomers. During infiltration of resin monomers, the interfibrillar space of the collagen network should be maintained by being floated in water. Therefore, as an essential component, hydrophilic monomers are incorporated into adhesives applied on dentin. From the view point of 'long-term durability', the bonding procedure itself involves several inherent risk factors. These factors include collagen fibers denatured by strong acid, water used to float the collagen network, phase separation between the hydrophilic and hydrophobic monomers, and the resulting exposure of hydrophilic resin monomers and collagens which are weak to hydrolytic attack.

During wet bonding, the hydrophobic and hydrophilic monomers dissolved in solvents such as

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acetone, alcohol, water and/or their mixture presented different diffusivities into the narrow interfibrillar spaces of the exposed collagen network²⁻⁴. Phase separation between the hydrophobic and hydrophilic monomers made the matrix of the hybrid layer mostly hydrophilic and susceptible to hydrolytic breakdown³⁻⁶. Denatured collagen fibers were also exposed against water attack, because they were intermingled with a porous resin matrix characterized by hydrophobic monomer-rich particles distributed in a hydrophilic monomer-rich matrix⁵. Therefore, within the hybrid layer and even in the overlying adhesive layer, there are abundant hydrophilic domains, such as the essential hydrophilic monomers and denatured collagen. There are several sources of water involving in degradation of the hydrophilic domains. These include water as a constituent of dentin, as a solvent included in the primers and adhesives, and as a remnant after the drying procedure of primed dentin. In the case of total-etch single-bottle adhesives and self-etch one-step adhesive systems that contain more hydrophilic monomers than the adhesives of total-etch three-step adhesive systems, dentinal fluid can also permeate through the hybrid layer and adhesive layer even after polymerization^{7,8}. The hydrolytic degradation of the hydrophilic domains within the adhesive layer and the hybrid layer was suggested to contribute to the deterioration of long-term durability of adhesion⁹⁻¹³.

However, there were few trials for improving the durability of current bonding systems, except a dentin primer containing N-methylolacrylamide, a fluoride-containing self-etching adhesive and an EDTA pretreatment¹⁴⁻¹⁶. In order to improve the durability of dentin adhesives, there may be two approaches for reducing hydrophilic domains: complete removal of water from the exposed collagen network without deteriorating the integrity of its three-dimensional structure and substitution of hydrophilic monomers in the adhesives with more hydrophobic monomers which can resist hydrolysis. Some organic substances and solvents including HEMA and monohydric alcohols are known to stiffen collagen^{17,18}. An aqueous solution of HEMA applied to the dentin improved the substrate's penetrability, substantiated apparent hybrid layer, and improved bond strength,

when the dentin was pretreated with an aqueous solution of 10% citric acid and 3% ferric chloride, rinsed with water and air-dried¹⁹. Like HEMA, alcohols at higher concentration also significantly stabilized collagen¹⁸. High vapor pressure solvents such as acetone and ethanol have been used to compete with and displace water and to facilitate the permeation of monomers²⁰. Although hydrophobic bisphenol-A-glycidylmethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) are not chemically compatible with wet dentin², the chain length-dependent surface tension of alcohols may affect the stability of collagen and control the permeation of the adhesives through the fibers¹⁸.

In order to increase the durability of dentin adhesives, by priming the collagen network exposed after etching and rinsing procedures with organic solvents, we tried to remove water from the collagen network without collapse. We also tried to penetrate the experimental adhesives containing relatively hydrophobic monomers into the collagen network floating in the solvent. For comparison, after etching and rinsing procedures, the adhesives were applied using two bonding protocols: on wet dentin surfaces (wet bonding) or on dentin primed with the same solvent included in the adhesive (solvent-primed bonding). The hypothesis tested was that priming the collagen network with organic solvents might displace water from it without collapse and thereby obtain good bond strength with the adhesives made of relatively hydrophobic monomers and organic solvents. Their microtensile bond strength (MTBS) was measured at 48 hrs, 1 month and after 10,000 times of thermocycling. The bonded interfaces were evaluated using a scanning electron microscope (SEM).

II . Materials and Methods

Preparing experimental adhesives

Three experimental adhesives were prepared by dissolving a mixture (1:1) of two hydrophobic monomers, Bis-GMA and TEGDMA, into an equal amount of an organic solvent (50 wt%), one of acetone, ethanol and methanol each. Camphoroquinone

and Ethyl 4-dimethylaminobenzoate were added each to the mixture by 1.0 wt% of resin monomers (Table 1).

Bonding procedures

Human molar teeth with no caries or fillings were used within six months of extraction. After removal of the soft tissue debris, the teeth were immersed in 0.5 mass fraction % of chloramine-T solution for one week and then stored in distilled water at 4°C. After mounting on a cubic stainless-steel mold with direct resin, each tooth was cut at the occlusal third of the crown to remove the coronal enamel, using a low speed diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA). The exposed dentin surface was then polished with a 500-grit silicon carbide paper under running water using an automatic polishing machine (Rotopol-V, Struers Ltd, Glasgow, UK). The polished dentin surface was etched with a 32% phosphoric acid etching gel (Bisco Inc., Schaumburg, IL, USA) for 15 sec and rinsed with distilled water for 15 sec. Immediately after rinsing, the tooth was covered with blotting paper moistened with distilled water. In the wet bonding protocol, the assigned adhesive was applied with two successive coats and agitated for 10 seconds. Remaining water and solvent were then dried with oil-free air for 10 sec. In the solvent-primed bonding protocol, after removing the blotting paper, the wet dentin was additionally primed with copious amounts of the assigned solvent using pipette for 15 sec. Experimental adhesives containing the same solvent as the priming solvent were then applied on the solvent-primed dentin with two successive coats and agitated for 10 sec. Remaining solvent was dried using the same method as in the wet bonding protocol. The adhesive was cured for 20 sec using a dental light-curing unit (Hilux™ Ultra+, Benlioglu Dental Inc., Ankara, Turkey; power density: > 500 mW/cm²). Z-250 hybrid composite resin (A3 shade, 3M ESPE Dental Products, St. Paul, MN, USA) was built-up in three increments on the adhesive-treated surface to 3.5 mm thick. Each increment was light-cured for 20 sec according to the manufacturer's instructions. After bonding, the specimen was stored in distilled water at room temperature.

Measuring MTBS

MTBS were measured at 48 hrs, 1 month, and after 10,000 times of thermocycling. For the 48 hr measurement, at 24 hrs from bonding, the specimen was trimmed to a rectangular shape with a low speed diamond saw (Isomet, Buehler Ltd., USA). At both sides of the rectangular specimen, two grooves were cut along the bonded interface under water irrigation with a diamond bur (DIA-BURS SF-13, MANI Inc., Tochigi-ken, Japan) mounted in a low speed press drill (SAG-280, Samchully machinery Co., Ltd., Seoul, Korea) to give the section an hourglass shape. The tooth was then serially sectioned with a 0.15 mm thin diamond wheel (Buehler® Diamond Wafering Blade, Buehler Ltd., USA), so that the dimension of the bonded surface area of the hourglass-shaped slab sections were 1.0 mm wide and 0.6 mm thick. At 48 hrs from bonding, the section was attached to a measuring device using cyanoacrylate cement (Super Glue Gel, 3M, St. Paul, MN, USA), and the MTBS was measured with a universal testing machine (Instron Model 4466, Instron Corp., Canton, MA, USA) at a crosshead speed of 1 mm/min²¹). For measuring the MTBS at 1 month, the specimens were immersed in distilled water for 1 month and then sectioned into hourglass-shaped slabs. Their MTBS were measured as described above. To measure the MTBS after thermocycling, the specimens were subjected to 10,000 thermal cycles between a 5°C water bath and a 55°C water bath with a dwell time of 24 seconds and a transferring time of 6 seconds between two baths. After thermocycling, the specimens were sectioned into hourglass-shaped slabs and their MTBS were measured. The MTBS were analyzed by three-way ANOVA. Bonferroni test was performed *post hoc* at a 5% level of significance. All statistical analyses were done using SPSS (version 12.0; SPSS Inc., Chicago, IL, USA).

Examining the bonded interface and fracture modes using SEM

From each tooth prepared for measuring the MTBS, two neighboring sections were selected for

SEM examination. In order to remove smear layer and to expose the bonded interface, each section was treated with 6N HCl for 5 sec and 5% NaOCl for 5 min. One section was desiccated in a vacuum jar overnight, coated with gold under a vacuum and examined directly using a SEM (JSM-840A, JEOL Ltd., Tokyo, Japan). The other section was duplicated to an epoxy resin replica by taking a silicon rubber impression (Examix, GC Co., Tokyo, Japan). The replica was also desiccated, coated with gold, and examined by SEM.

In order to evaluate the fracture modes, both dentin and resin sides of the fractured specimens were observed under stereomicroscope ($\times 20$ magnification). Fracture modes were determined according to typical appearances, which were classified previously under SEM observation.

III. Results

MTBS of three experimental dentin adhesives are presented according to bonding protocols and measuring times in Table 2 and Figure 1. Based on the three-way ANOVA, adhesive, bonding protocols, and measuring times significantly influenced the bond strength ($P < .05$). There were significant interactions between each pair of independent variables and also among the three independent variables. Regardless of bonding protocol and measuring time, significant differences were observed between each pair of adhesives based on the Bonferroni test ($P < .05$). There were also significant differences between the bond strengths at each measuring time, except between those at 48 hours and 1 month. At 48 hours, the adhesive containing ethanol showed the highest mean MTBSs among experimental adhesives. Although the initial MTBS with solvent-primed bonding were similar to those with wet bonding, the

difference between the MTBSs of the ethanol-containing adhesive applied on ethanol-primed dentin and on wet dentin increased after thermocycling. Although the MTBS of the methanol-containing adhesive applied on methanol-primed dentin was low at 48 hours, after thermocycling it increased the greatest, showing the highest MTBS measurements. However, in the case of wet bonding, there was no increase in the MTBS of any adhesives with aging.

Regardless of whether the experimental adhesives were applied on wet dentin or on solvent-primed dentin, well-developed hybrid layers were observed at the bonded interface of most specimens observed using SEM (Figure 2). The micrographs taken from the replicas did not show apparent interfacial gaps between the hybrid layer and the adhesive layer (Figure 2). However, severe interfacial gap formations were observed in micrographs taken directly from specimens, particularly the specimens bonded on wet dentin (Figures 2c and 2k). Most interfacial gaps were observed between the hybrid layer and the adhesive layer (Figures 2a, 2c, 2g and 2k). Corresponding to the site of interfacial gaps, most failures occurred at the interface (Figure 3a). The ethanol-containing adhesive specimens showed thicker adhesive layers, more resin tags (Figure 2e) and better integrity at the interface than observed with the other adhesives. In this group, most of the specimens showed mixed fracture (Figure 3b). The specimens bonded with the adhesives containing acetone or methanol had thinner adhesive layers (Figures 2a, 2c, 2i and 2j) and had fewer and shorter resin tags when the adhesives were applied on wet dentin. After thermocycling, because the interfacial gaps were observed at the same interface between the hybrid layer and the adhesive layer (Figure 4a), the failure modes looked the same with the specimens taken at 48 hrs. The specimens bonded with wet

Table 1. Materials used for the preparation of the experimental resin adhesives

Compound	Acronym	Supplier	Batch No.
Bisphenol-A-glycidyl dimethacrylate	Bis-GMA	Shin-Nakamura chemical Co., Inc.	13431EA
Triethyleneglycol dimethacrylate	TEGDMA	Shin-Nakamura chemical Co., Inc.	09004BC
Camphoroquinone	CQ	Aldrich chemical Co., Inc.	00703MN
Ethyl 4-dimethylaminobenzoate	4E	Aldrich chemical Co., Inc.	11920PA

* Other ingredients, such as inhibitor or stabilizer were not included in the experimental resin adhesives.

Table 2. Microtensile bond strengths of experimental adhesives with different bonding protocols and measuring times (MTBS, unit: MPa)

Adhesives	Bonding protocol	Measuring time		
		48 hours	1 month	Thermocycling
Ac-containing	Solvent primed bonding	14 ± 4.9(13) *	17.4 ± 8.7(17)	18.1 ± 8.3(15)
	Wet bonding	9.7 ± 4.3(19)	8.8 ± 3.5(9)	12 ± 5.8(8)
Et-containing	Solvent primed bonding	38.9 ± 13(21)	40.4 ± 16.2(17)	50.3 ± 10.2(14)
	Wet bonding	33.1 ± 9.2(15)	27.6 ± 12.3(14)	27.6 ± 11.7(14)
Me-containing	Solvent primed bonding	15.2 ± 6.8(23)	19.1 ± 8.7(12)	60.7 ± 10.6(10)
	Wet bonding	12.8 ± 9.4(19)	22.6 ± 9.7(14)	21.6 ± 4.2(9)

Ac: acetone, Et: ethanol, Me: methanol

* The numbers in parenthesis are the sample number.

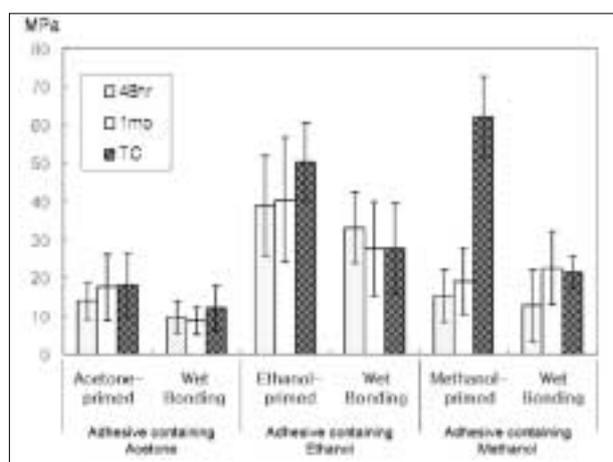


Figure 1. Microtensile bond strength (MPa) of three experimental adhesives according to the bonding protocols and measuring times.

bonding still had considerable interfacial gaps including below and on top of the hybrid layer, as compared to the specimens bonded with solvent-primed bonding protocol (Figures 4b and 4c).

IV. Discussion

From the micrographs, thick hybrid layers were observed when experimental adhesives were applied on solvent-primed dentin. This finding suggests that solvent-priming on etched wet dentin might effectively replace water to solvents, stabilize the three dimensional structure of collagen network, and facilitate penetration of the experimental adhesives into the collagen networks floating in the solvent. After etching and rinsing procedures, water molecules bind to the carbonyl groups protruding from collagen

helices, forming hydrogen bonds and serving to stabilize the ordered triple helix structure^{18,22}. When exposed collagen structure is dried abruptly, loss of unbound water may stabilize the collagen fibrillar structure by increasing the interaction between adjacent collagen molecules. Such dehydration of demineralized dentin by air-drying increases the packing density of collagen molecules and produces loss of volume due to surface tension forces²³. However, dehydration in organic solvents prevented exposure of collagen molecules to the surface tension forces in air, stiffened the interfibrillar spaces with less shrinkage, and improved preservation of the spaces when subsequently exposed to air^{17,18,22}. Both air-drying and dehydration in organic solvents may serve to stiffen demineralized dentin matrix, but their effect on the volume change of the collagen structure differed¹⁷. In this study, because copious amounts of high vapor pressure solvent were used as priming material, the solvents might have competed with water and effectively replaced it²⁰. Therefore, the collagen network was expected to shrink much less and not to collapse^{17,22,24}. Furthermore, because the adhesives were applied before the evaporation of solvents, the solvents occupied the spaces around the collagen fibers during monomer infiltration. As a result, solvents might carry the monomers effectively into the spaces and facilitate the development of a thick apparent hybrid layer.

Among the experimental adhesives, the adhesive containing ethanol showed the highest mean bond strengths, which were comparable to the total-etch three-step adhesives. The alcohols and monomers

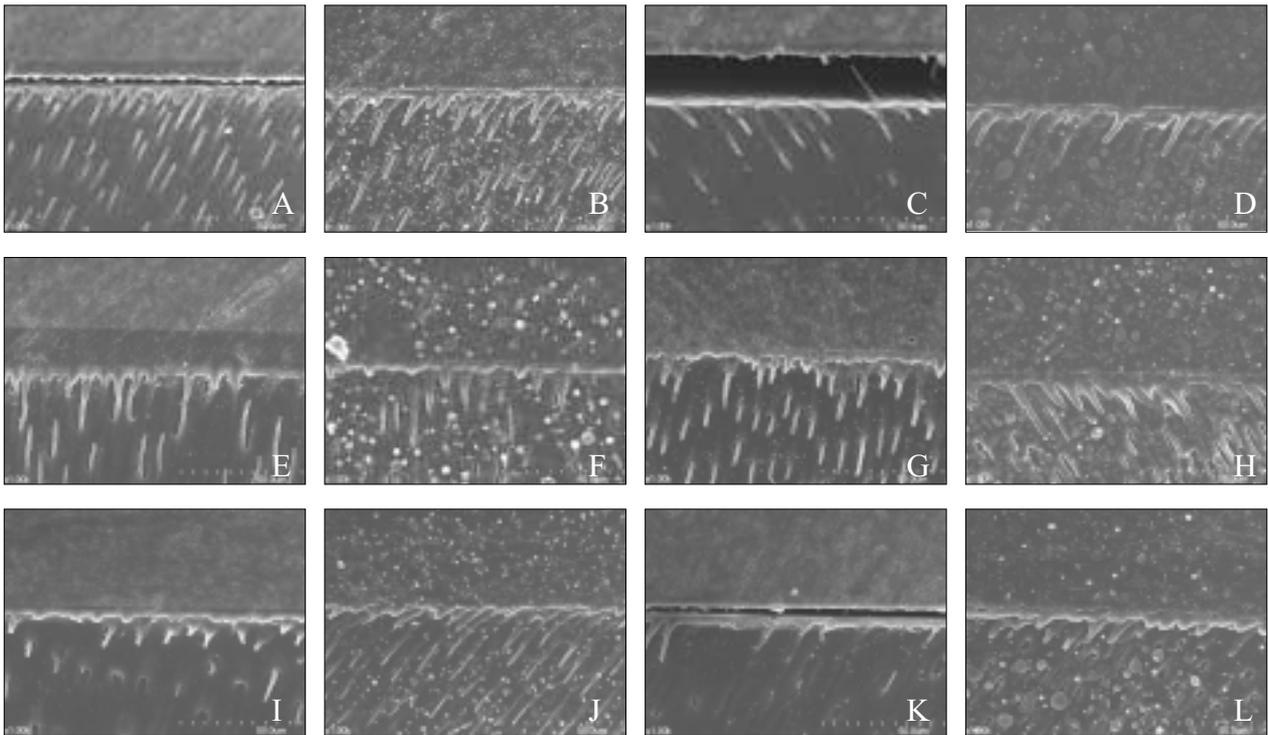


Figure 2. Scanning electron microscopic images of the bonded interfaces. a & b, the adhesive containing acetone was applied on acetone-primed dentin after etching and rinsing procedure; c & d, the adhesive containing acetone was applied with wet bonding protocol; e & f, the adhesive containing ethanol was applied on ethanol-primed dentin after etching and rinsing procedure; g & h, the adhesive containing ethanol was applied with wet bonding protocol; i & j, the adhesive containing methanol was applied on methanol-primed dentin after etching and rinsing procedure; k & l, the adhesive containing methanol was applied with wet bonding protocol. Left column, the micrographs taken directly from the specimens; Right column, those taken from the replica of the specimens.

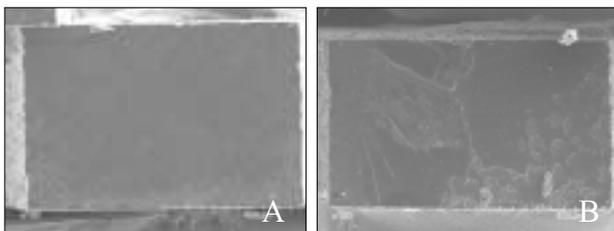


Figure 3. Fractured surfaces of the bonded specimens. a, dentin side of fractured specimen bonded with adhesive containing methanol using wet bonding. Most failures occurred between the hybrid layer and the adhesive layer. b, dentin side of fractured specimen bonded with adhesive containing ethanol using solvent-primed bonding. In this group, most of the specimens showed mixed fracture.

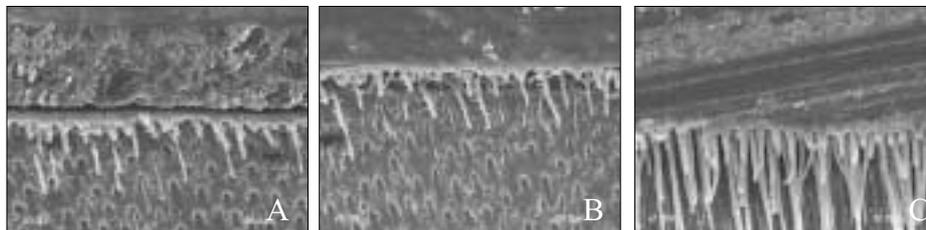


Figure 4. Scanning electron microscopic images of the bonded interfaces after thermocycling. a, the adhesive containing acetone was applied with wet bonding protocol; b, the adhesive containing methanol was applied with wet bonding; c, the adhesive containing methanol was applied on methanol-primed dentin after etching and rinsing procedure. With wet bonding protocol, the interfacial gaps were still observed at the same interface as the specimens observed at 48 hrs. However, with solvent-primed bonding protocol, well-developed hybrid layers and a number of long resin tags were observed without apparent interfacial gap.

used in this study had hydroxyl groups. The hydrogen-bonding between the hydroxyl groups might facilitate their penetration. However, due to lack of hydroxyl group in acetone, the adhesive containing acetone was expected to deliver less additive monomers than those containing alcohols. It might have been the cause of the observed improved integrity of the bonded interface obtained with the ethanol-containing adhesive. This suggests that ethanol and ethanol-containing adhesive may be the most promising candidate among the experimental adhesives for maintaining three-dimensional collagen network structures, infiltrating monomers into the structure, and obtaining reliable bond strength. The higher the concentration of alcohols is and the longer the chain of alcohols is, the more the stabilization of the collagen structure dominates destabilization¹⁸⁾. Surface tension also depends upon the number of CH₂ in homologous alcohols, which in turn controls the permeation of additives through the collagen fibers¹⁸⁾. In this study, because all the solvents used were reagent grade, the collagen structure might be stabilized more efficiently by ethanol than by methanol, and the higher surface tension of ethanol facilitated the permeation of the monomers dissolved in ethanol.

In the case of wet bonding, micrographs also showed relatively well-developed hybrid layers, especially in the ethanol solvent group. During wet bonding procedures, because collagen fibers were not exposed to air, their three-dimensional structure might be maintained relatively well. Two coats of adhesives on the wet dentin surface might supply sufficient amount of solvent to replace most of the unbound water from the floating collagen network. Depending on the solvent, if it was sufficient, the solvent might deliver the relatively hydrophobic monomers into the interfibrillar spaces previously occupied by water, as was seen in our ethanol solvent group. However, the bond strengths obtained using the other experimental adhesives except the ethanol-containing adhesive were still low in wet bonding, as were in solvent-primed bonding. Although Bis-GMA and TEGDMA should be chemically incompatible with wet dentin²⁾, the results suggested that the dentin bond strength depend upon

the solvents used and their resulting penetrability, rather than the chemical interaction between collagen and monomers.

With aging, although the enamel bond strength of self-etching primer systems have been reported to increase in limited studies²⁵⁻²⁷⁾, the dentin bond strength of most current dentin adhesives were generally reported to decrease with wet bonding^{9,25,28-31)}. In this study, the MTBS of the adhesives containing ethanol or methanol increased significantly with thermocycling when applied on the solvent-primed dentin. However, when they were applied on wet dentin, it did not increase. It is well-known that methacrylates continue chain-reaction polymerization at room temperature³²⁾. A temperature of 55°C applied during thermocycling should be sufficient to continue the polymerization reaction of methacrylate monomers of the adhesives. Thus, thermocycling itself might increase the bond strength by improving the properties of the adhesive layer. However, in the case of wet bonding, due to the relatively small amount of solvent, more water might remain within the hybrid layer than in solvent-primed bonding protocol. A small amount of water might remain within the network and act as a risk factor for hydrolytic degradation^{15,33)}. Therefore, in wet bonding, the increasing effect of thermocycling on mechanical properties might be offset by the decreasing effect of the remaining water.

V. Conclusion

Compared to the current dentin bonding systems, in which hydrophilic HEMA is used to enhance penetrability of the adhesive, the priming procedure of collagen network with a copious amount of organic solvents enabled the organic solvents to replace water, stabilize the collagen structure, and permeate its additive monomers through the interfibrillar spaces effectively during the following application of the experimental adhesives. In this study, ethanol was found to be more efficient than acetone or methanol. Compared to wet bonding, the bond strength of the experimental adhesives applied with solvent-primed bonding increased with thermocycling. It might be suggested that the solvent-primed

bonding procedure reduces hydrolytic degradation by replacing water without volumetric loss of the collagen structure while effectively minimizing hydrophilic domains within both the hybrid and adhesive layers.

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국문초록

산 부식된 상아질에 대한 용매를 이용한 프라이밍이 소수성 상아질 접착제의 미세인장접착강도에 미치는 영향

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장기적인 상아질 접착의 내구성 악화는 접착층과 혼성층의 친수성 부위에서의 가수분해에 의해 일어나는 것으로 보고되고 있다. 본 연구의 가설은 콜라겐 망상체를 유기용매로 프라이밍하면 콜라겐 조직을 붕괴시키지 않고 수분을 밀어내고 소수성 단량체와 유기용매로 이루어진 접착제가 침투하여 접착강도를 얻을 수 있다는 것이다. 두 소수성 단량체인 Bisphenol-A-glycidylmethacrylate (Bis-GMA)와 triethyleneglycol dimethacrylate (TEGDMA)를 아세톤, 에탄올 또는 메탄올에 용해시켜 세 가지의 실험용 접착제를 준비하였다. 산 부식과 수세과정 후에, 접착제를 습윤 상아질 표면(습윤 접착)이나 동일한 용매로 프라이밍 된 상아질 표면(용매 프라이밍 접착)에 적용하였다. 48시간 후와 1개월 후, 및 10,000회의 열순환 후에 미세인장결합강도를 측정하였다. 접착계면은 주사전자현미경을 이용하여 관찰하였다. 접착 방법에 무관하게 대부분의 시편의 접착계면에서 잘 발달된 혼성층을 관찰할 수 있었고, 가장 높은 평균 미세인장결합강도는 에탄올을 포함하는 접착제의 48시간 후 시편에서 관찰되었다. 용매를 이용하여 프라이밍하는 접착 방법에서는 에탄올이나 메탄올을 포함하는 접착제에서 열순환 후에 미세인장접착강도가 증가하는 경향을 보였다. 그러나, 습윤 접착의 경우에는 시효처리 후 미세인장결합강도의 증가가 관찰되지 않았다. 본 연구에서 에탄올을 이용한 상아질 프라이밍으로 우수한 접착력을 얻을 수 있었고, 열순환 후 접착력이 더욱 증가하였다.

주요단어 : 상아질 접착제, 내구성, 용매 프라이밍, 소수성 단량체, 미세인장접착강도