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다양한 pH를 가지는 Universal adhesives와 이원 중합 레진 세멘트 간의 전단결합강도

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Shear bond strength between universal adhesives with various pH and dual-cured resin cements

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이 연구의 목적은 현재 쓰임이 증가하고 있는 여러 종류의 범용 상아질 접착제와 삼차 아민을 포함 혹은 포함하지 않는 레진 시멘트 간의 호환성을 평가하기 위함이다. 총 80개의 사람 대구치를 선정해 레진 블럭에 매몰하여 상아질을 노출시키고 600-grit SiC paper로 연마한 후 3종류의 범용 상아질 접착제 Scotchbond universal (3M ESPE, pH 2.6), G-premio bond (GC, pH 1.5), All bond universal (Bisco, pH 3.2) 및 대조군으로 3-step etch and rinse system인 Scotchbond multipurpose (3M ESPE)를 제조사의 지시대로 적용한 후 광중합 시행하였다. 그 위에 직경 2 mm, 높이 3 mm의 몰드를 이용해 삼차아민을 포함한 레진 시멘트인 Calibra (Dentsply) 혹은 삼차 아민을 포함하지 않는 레진시멘트인 RelyX Ultimate (3M ESPE)를 적용하고 20초간 광중합하였다. 그 후 37℃ 증류수에 7일간 보관 후 미세전단강도를 측정하였다. 각 결과값을 ANOVA와 Tukey test로 분석하였다. 실험 결과 Calibra를 사용한 경우 Scotchbond Multipurpose와 All bond Universal adhesive 적용시 G-premio bond 및 Scotchbond universal adhesive를 적용했을 때에 비해 유의하게 높은 미세전단강도를 나타냈다($p<0.05$) RelyX Ultimate를 사용한 경우 adhesive간의 유의한 차이가 관찰되지 않았다($p>0.05$).

색인단어 : 레진 시멘트; Universal adhesive; pH

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INTRODUCTION

Recently, there is an increasing demand for tooth-colored indirect restorations because they offer many advantages such as enhanced mechanical, esthetic, and functional properties when compared with direct restorations. Usually, luting cements are used in the dental procedure for indirect restorations such as inlays, onlays, crowns, endodontic posts (1, 2). There are lots of products for cementation, and it is very common clinical situations using dental adhesive systems and resin cements from different manufacturers together. To prevent adverse reaction between products, it is necessary to have knowledge of bonding agents.

The dental adhesive systems may be classified as etch-and-rinse and self-etch adhesives on the basis of enamel and dentin conditioning with phosphoric acid (3). Depending on the number of procedures, the self-etch adhesive systems can be also divided into two steps and one step systems. These adhesives can also be classified into three categories based on their initial pH-value as mild (pH>2.5), moderate (pH of approximately 1), and strong (pH<1), depending on their acidic monomer (4). Acidic functional monomers play an essential role in the bonding performance of self-etch adhesives, as they may be capable of conditioning enamel and/or dentine substrates. Currently, new and simplified adhesive systems, namely, the universal adhesives or multi-mode adhesives are available in the market (5, 6). These systems can be used with the etch-and-rinse, self-etch, or selective-etch strategies. However, these universal adhesives also contain an acidic functional monomer that affects pH of universal adhesives. Although no adverse reaction will occur with the majority of the clinical situation, some self-etch adhesives are recently found to be incompatible with some resin cements (7-9).

Resin cements are classified as light-cured, chemical-cured, or dual-cured according to the curing mechanism. Dual curing stands for both light curing and chemically curing, and due to limitations of curing depth, many of resin cements are released as dual-cured resin cement. For chemical curing, dual-cured resin cements contain benzoyl peroxide (BPO) as initiator and the tertiary amine catalytic component as a catalyst. The interaction between acidic adhesive monomers and the tertiary amines of the resin cements results in acid-base reactions, leaving unreacted layers (10, 11). This will result in slow or no polymerization, depending upon the acidity and concentration of the acidic resin monomers and decrease bonding performance. To overcome these phenomena, using adhesives with high pH or resin cements without the tertiary amine could be used. Among the universal adhesives that have recently been released, there is All-Bond Universal (Bisco Inc.) that has the pH of 3.2. According to the manufacturer, it is reported that incompatibility does not appear when used with resin cement containing the tertiary amine because the pH is ultra-mild. In the current commercial market, resin cements not containing the tertiary amine such as RelyX ultimate (3M ESPE) and NX3 Nexus™ (Kerr) have been introduced.

Many previous papers have reported the incompatibility between simplified adhesive and dual-cure resin cement, however there are few reports about incompatibility between universal adhesives and resin cements without the tertiary amine. Therefore, the aim of this study was to assess the bonding performance of three universal adhesives with different pH, with two dual-cured resin cements, containing the tertiary amine or not.

MATERIALS AND METHODS

1. Tooth Selection and Preparation

Eighty extracted, caries-free, human third molars were used. This study was approved by the Institutional Review

Board of Pusan National University Dental Hospital (IRB, PNUDH-2018-031). Teeth were disinfected with 0.5% chloramine solution and stored in a distilled water at 4℃ until needed. The teeth were embedded in self-curing acrylic resin (Tokuso Curefast, Tokuyama, Tokyo, Japan) and were sectioned horizontally at the mid-coronal level with a water-cooled diamond saw (Accutom-50, Struers, Rodovre, Denmark) to obtain flat and sound dentin surfaces. The exposed dentin surfaces were wet-polished with 600-grit SiC paper for 60 seconds to standardize the smear layer.

2. Experimental Design and Specimen Preparation

The teeth were assigned randomly to two groups according to the resin cements (n = 40): Calibra (CB; Dentsply, Konstanz, Germany) which is conventional resin cement, and RelyX Ultimate (RXU; 3M ESPE, St Paul, MN, USA) which is tertiary amine free cement. Each group was subdivided into four groups according to the adhesives (n = 10): All-Bond Universal (ABU; Bisco Inc., Shaumburg IL, USA), Single Bond Universal (SBU; 3M ESPE, St Paul, MN, USA), G-Premio Bond (GP; GC Corp., Tokyo, Japan), and Scotch-bond Multipurpose (SBM; 3M ESPE, St Paul, MN, USA). The adhesives were applied according to the manufacturer's instructions. The resin cements and adhesives used were listed in Table 1 and Table 2. After that, the samples were fixed in ultradent jig (Ultradent Products Inc., South Jordan, UT), which has a cylinder (diameter 2 mm, height 3 mm) coated with Teflon. Then resin cement was applied in the mold; excessive cement was removed and light cured for 20

Table 1. Adhesives used in the study

Adhesive	pH	Composition	Application Mode
All-Bond Universal (ABU)	3.2	10-MDP, phosphoric acid ester monomer, Bis-GMA, HEMA, ethanol, water, initiators	Two separate coats of adhesive are applied, and the preparation is scrubbed with a microbrush for 10–15 s per coat. No light curing between coats; gently air spread and light cured for 10 s
Single-Bond Universal (SBU)	2.7	10-MDP, phosphoric acid ester monomer, HEMA, silane, dimethacrylate, Vitrebond copolymer, filler, ethanol, water, initiators, silane	Adhesive is applied to the dentin with a microbrush and rubbed in for 20 s; gently air spread and light cured for 10 s
G-Premio Bond (GP)	1.5	10-MDP, phosphoric acid ester monomer, dimethacrylate, 4-MET, MEPS, acetone, silicon dioxide, initiators	Adhesive is applied to the dentin with a microbrush without rubbing for 10 s; gently air spread and light cured for 10 s
Scotch-bond Multipurpose (SBM)	Primer: 3.3 Adhesive: 8.2	Scotchbond Multi-Purpose primer: HEMA, polyalkenoic acid polymer, water Scotchbond Multi-Purpose adhesive: Bis-GMA, HEMA, tertiary amines (both for light-cure and self-cure initiators), photo-initiator	Etchant is applied for 15 s; rinsed lightly, dried to a moist surface, primer applied, lightly dried for five seconds, adhesive applied and light-cured for 10 s

Bis-GMA: bisphenol glycidyl methacrylate; HEMA: 2-hydroxyethyl methacrylate; MDP: methacryloyloxydecyl dihydrogen phosphate; 4-MET: 4 methacryloxyethyltrimellitate anhydride; MEPS: Methacryloyloxyalkyl thiophosphate

Table 2. Resin cements used in this study

Cements	Chemical composition	Application procedure
RelyX Ultimate (RXU)	Base: Silane treated glass powder, 2-propenoic acid, 2-methyl-,1,1-[1-(hydroxymethyl)-1, 2-ethanediyl] ester, reaction products with 2-hydroxy-1,3-propanediyl DMA and phosphorus oxide, TEGDMA, silane treated silica, oxide glass chemicals, sodium persulfate, tert-butyl peroxy-3,5,5-trimethylhexanoate, copper (II) acetate monohydrate Catalyst: Silane treated glass powder, substituted DMA, 1,12-dodecane DMA, silane treated silica, 1-benzyl-5-phenylbarbic-acid, calcium salt, sodium p-toluenesulfinate, 2-propenoic acid, 2-methyl-, [(3-metoxypropyl) imino]di-2,1-ethanediyl ester, calcium hydroxide, titanium dioxide	Mix base and catalyst (1:1). Apply and light-cure (40 s)
Calibra (CB)	Base: Barium boron fluoroalumino silicate glass; Bis-phenol A diglycidylmethacrylate; polymerizable dimethacrylate resin; hydrophobic amorphous fumed silica; titanium dioxide; dl-camphoroquinone. Catalyst: Barium boron fluoroalumino silicate glass; Bis-phenol A diglycidylmethacrylate; polymerizable dimethacrylate resin; hydrophobic amorphous fumed silica; titanium dioxide; benzoyl peroxide.	Mix base and catalyst (1:1). Apply and light-cure (40 s)

TEGDMA : Tri-ethylene-glycol-dimethacrylate; DMA : dimethacrylate

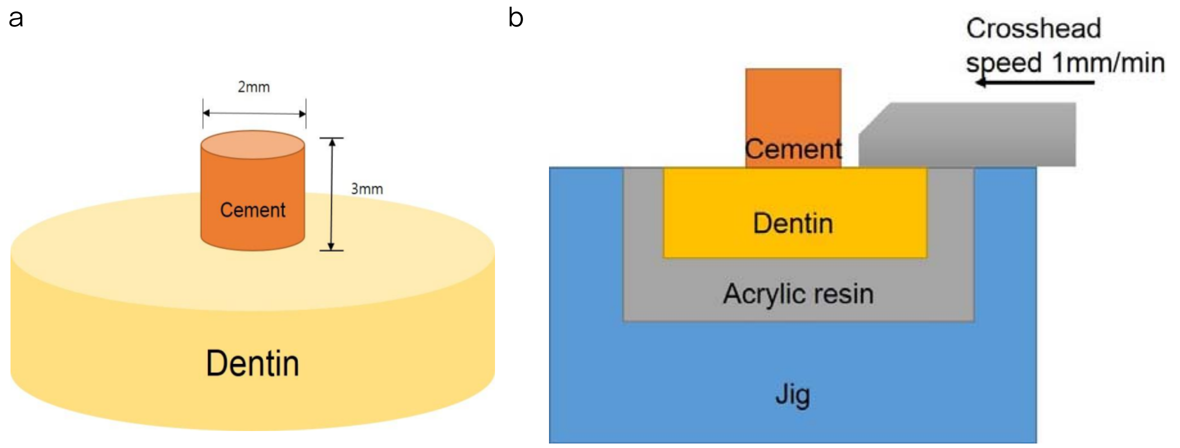

Figure 1. Dimensions of dentin-cement specimen and a shear bond strength test

seconds using a light-emitting diode (LED) light curing unit under 1200 mW/cm^2 (BluephaseG2, Ivoclar Vivadent Inc., Amherst, NY, USA).

3. Shear Bond Strength (SBS)

After storing the specimen in distilled water at 37℃ for 7 days, the specimens were tested in shear mode, using the shear bond testing machine (Bisco, Schaumburg, IL, USA) at a crosshead speed of 1.0 mm/min until failure. Fig. 1 b showed the diagram of a shear bond test. The SBS was calculated by dividing the load at failure by the bonding surface area.

4. Failure Mode Analysis

After the test, all debonded specimens were observed under a stereomicroscope at ×40 magnification (Leica, Heidelberg, Germany) to determine the failure mode. The failure modes were classified as adhesive (A, cement / dentin interface), cohesive (C, exclusively within dentin or resin cement) or mixed (M, resin cement / dentin interface that included cohesive failure of the neighboring substrates).

5. Statistical analysis

The SBS date were analyzed using a two-way ANOVA, followed by a Tukey's post hoc test at 5% level of significance (SPSS 21.0; SPSS Inc., Chicago, IL, USA). Failure modes were evaluated only qualitatively.

RESULTS

Table 3 presents the results. For RXU groups, there were no significant differences among the adhesive systems ($p > 0.05$). For CB groups, ABU, and SBM groups showed significantly higher bond strength than did the GP and SBU groups ($p < 0.05$). Among the adhesives, only GP showed significantly different bond strength between the resin cements.

Table 4 present the results of fracture mode analysis. Adhesive failure was predominant in all groups and there were no significant differences.

DISCUSSION

When universal adhesives that have a lower pH are

Table 3. SBS(MPa) after 7 days' storage

SBS (MPa)	RXU	CB
ABU	10.68 (3.37)^{Aa}	11.07 (2.60)^{Aa}
GP	10.42 (3.29)^{Ab}	5.04 (1.44)^{Ba}
SBU	9.05 (2.23)^{Aa}	7.06 (2.46)^{Ba}
SBM (control)	13.02 (4.44)^{Aa}	11.37 (3.26)^{Aa}

*Within the same column, the same capital letters are not statistically different (P>0.05)
*Within the same row, the same small letters are not statistically different (P>0.05)

Table 4. Failure mode after 7 days' storage

	RXU			CB		
	A	C	M	A	C	M
ABU	80%	10%	10%	90%	0%	10%
GP	90%	0%	10%	100%	0%	0%
SBU	90%	0%	10%	100%	0%	0%
SBM	80%	10%	10%	80%	10%	10%

ABU : All Bond Universal; GP : G-Premio Bond; SBU : Scotchbond Universal; SBM : Scotchbond Multipurpose; RXU : Rely X Ultimate; CB : Calibra; A: adhesive failure; C : cohesive failure; M : mixed failure

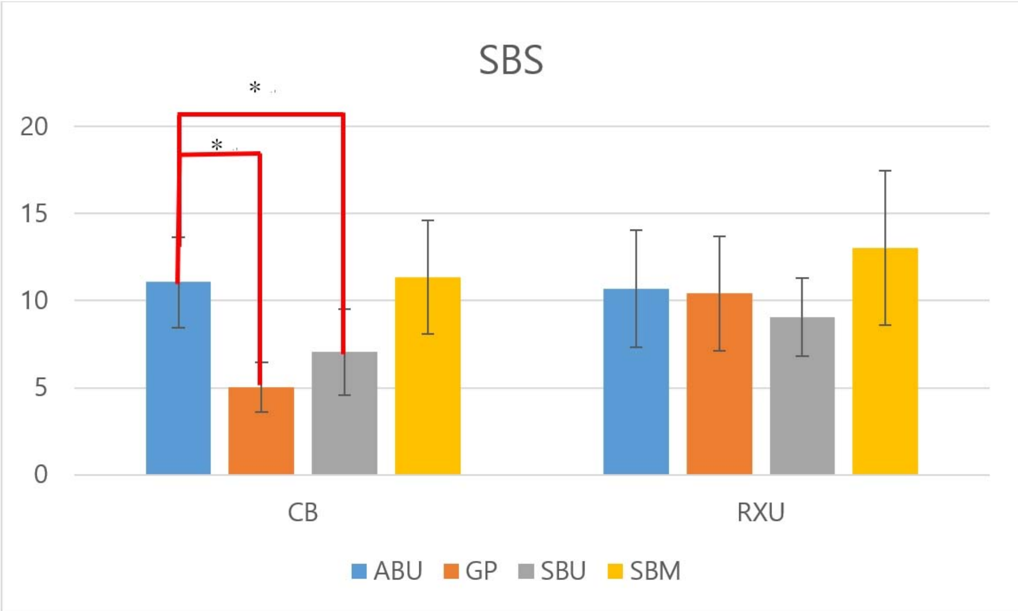

Figure 2. SBS between cements and adhesive

used in association with resin materials containing components responsible for chemical curing like the tertiary amine, there is an interaction of residual acidic monomers, in the adhesive inhibition layer, with the tertiary amine, resulting in unploymerized layer (8, 11, 12). This layer can affect the bonding durability.

Results of the present study showed that different adhesives influenced the shear bond strength when used in association with conventional resin cements with the tertiary amine. SBM was used as a control group, because it's 3-step etch and rinse system and is not affected by resin cements with the tertiary amine. When ABU was used with CB, higher bond strength was observed ($p<0.05$). In contrast, when CB was used with SBU or GP, lower bond strength was observed. This can be explained by the pH of the ABU (pH 3.2), which is higher than that of other adhesives.

Additionally, the hydrophilicity of the adhesive could affect the compatibility with the dual-cured resin cement. Resin cements are basically hydrophobic after cured. When dental adhesives are light cured, hydrophilic nature in adhesive layers becomes hydrophobic. However, even after light curing, unpolymerized acidic monomers in self-etch or universal adhesive can be remained and residual acidic monomers can make adhesive layer hydrophilic. Therefore, when hydrophobic resin cements are applied to the hydrophilic adhesive layer, the wettability of resin cements decrease (13). In this study, ABU group of mild pH presumed that lower residual acidic monomer remained showed higher bond strength.

In addition to using adhesives with mild pH as a method to reduce the incompatibility between self-etch adhesives and dual-cured resin cements, there have been clinical efforts. Sanares et al. predicted that multistep dentin adhesives, requiring the placement of an additional layer of light-curing resin that does not contain acidic functional groups, might be more compatible with self-curing composites (8). Schittly et al. included the application of an intermediate adhesive resin which bonding resin from Clearfil SE bond after pretreatment with Xeno III (pH 1), and this showed better bond strength than did Xeno III alone (9). In this study, resin cements without the tertiary amine have also have been found reducing incompatibility between adhesives with various pH.

In the present study, when using RXU, there was no significant difference between the adhesives. According to the manufacturer, RXU contains another dual-cure activator. This activator was introduced by Yamauch et al. who reported that bond strengths of adhesive systems containing acidic monomers to dentin may be significantly improved by using a ternary initiator system that consists of sulphinic acid or its salts in addition to the existing peroxide-amine systems (14). These components react with acidic resin monomers to produce either phenyl or benzenesulfonyl free radicals that initiate the polymerization reaction via the self-curing mechanism of the adhesive bonding resin (15). Hence, RXU showed reasonable bond strength, regardless of the adhesive. In failure mode analysis, there were no significant differences between adhesives. However, when using RXU with ABU or SBU, there was a mixed or cohesive failure compared to CB with ABU or SBU. These results were consistent with SBS test.

Based on the results of the present study, the clinician can avoid incompatibility between universal adhesives and dual-cured resin cements by using adhesives with mild pH and cements that are tertiary amine-free. Nevertheless, these findings should be interpreted with caution because adhesives and cements used in the present study contain different components that can independently affect the bond strength. Additionally, the long-term performance of the bonded interfaces needs to be evaluated further.

CONCLUSION

Within the limitations of this study, RXU resin cement was compatible with universal adhesives regardless of pH of the adhesives. ABU was compatible with CB resin cement.

Therefore, in dental practice, amine free dual-cured resin can be used with universal adhesives with various pH. And adhesives with mild pH can be used with used with dual-cured resin cements with the tertiary amine.

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Original Article

Shear bond strength between universal adhesives with various pH and dual-cured resin cements

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The purpose of this study is to evaluate the compatibility of universal adhesives with two dual-cured resin cements. Eighty human molars were divided into eight groups. Tooth was embedded in self-curing acrylic resin and sectioned horizontally to exposure dentine surface. After polishing with 600-grit SiC paper, adhesives were applied. All-Bond Universal (Bisco), G-premio bond (GC), Scotch-bond universal (3M ESPE), Scotch-bond Multipurpose (3M ESPE) were used in this study. Calibra (Dentsply) as a conventional dual-curing resin cement and RelyX Ultimate (3M ESPE) as an amine free resin cement were used. The adhesives and the cements were applied according to the manufacturer's instructions. Final specimens were cylinder (diameter 2mm, height 3mm) shape. After storing in distilled water at 37℃ for 7 days the shear bond strength (SBS) test was performed. There was no significant difference in shear bond strength between the adhesives when RelyX Ultimate was used ($p>0.05$). However, when Calibra used with Scotch-bond Multipurpose and All-Bond Universal were used, statistically higher SBS was observed, as compared to the groups which Calibra cements with G-premio bond and Scotch-bond universal adhesive ($p<0.05$) were used. Within the limitations of this study, RelyX Ultimate resin cement was compatible with universal adhesives of various pH. All-Bond Universal adhesive was compatible with a resin cement containing the tertiary amine.

Key Words : Resin cements; Universal adhesives; pH