Change in adhesive strength and pH of universal adhesive in accordance with varying proportions of 10-MDP

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ABSTRACT

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Objective: This study aimd to investigate the physical properties of dental adhesive according to the composition of 10-MDP, a functional monomer that is a representative component of universal adhesives, by measuring the shear bond strength using direct composite resins, and to determine the optimal proportion of 10-MDP related with pH which can affect compatibility with self-cure composite in universal adhesives for use in restorative dentistry.

Materials and Methods: Experimental adhesive is made through various previous experiments, adhesive ingredients such as Bis-GMA, HEMA, TEGDMA, Ethanol, Water, CQ, EDMAB, and DPPA were performed sensitivity tests and set up the optimize volume to maximize bonding reliability. Bovine and direct resin used for the specimen. Shear bond strength and pH were measured for this test material.

Results: Bonding strength of the experimental universal adhesive increased gradually with increasing amounts of 10-MDP, but showed a tendency to decrease gradually after a certain amount was exceeded. In terms of pH, results showed that as the amount of 10-MDP in the experimental universal adhesive increased, the pH decreased.

Through this study, the universal adhesive used in the experiment showed the highest adhesive strength at 9.710 % 10-MDP content, with a pH of 2.86 for that experimental adhesive group. Based on the results of this study, this composition of 10-MDP can be considered the most ideal.

Keywords; 10-MDP, Dentin adhesive, Incompatibility, pH, Shear bond strength, Universal adhesive

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I. INTRODUCTION

1. Universal adhesive

Dental universal adhesive, also known as universal dental adhesive or all-in-one adhesive, is a type of dental adhesives used in restorative dentistry. It is a versatile adhesive system that is designed to bond various dental materials, such as composite resin, glass resin cement, and ceramics, to tooth structure. Universal adhesives are called so because they are formulated to be compatible with both etch-and-rinse and self-etch techniques. They can be used in both total-etch and self-etch modes, depending on the clinician's preference and the clinical situations (Jang et al., 2016).

Due to variable etching options and the affinity for different substrates, universal adhesives have a much broader application in dentistry than many other adhesive systems. A great amount of confusion exists among clinicians when dental adhesives are brought up for discussion. The actual difference is in the chemistry of universal adhesives. Many contain 10-MDP as the main functional monomer, one with an excellent clinical track record. It can chemically bond to hydroxyapatite and different materials. Some universal adhesives also contain silane, a key chemical for bonding ceramic restorations, which simplified the bonding with glass-based materials and increased the strength bond. The reality is that all the chemistry must be balanced in one bottle, and manufacturers are attempting to combine hydrophilic with hydrophobic monomers (Carrilho et al.,2019).

Universal adhesive for dentin and enamel which are consist of hydroxyapatite as well as restorations made of ceramics, zirconia, and various metals. These restoration materials are applicable for indirect restorations, so the adhesive should exhibit adequate bonding not only with dentin but also between the restoration surface after treatment and the luting cement used between the restoration and dentin.

These adhesives typically consist of a combination of functional monomer, cross-linking monomer, solvents, initiators, and other additives. They often contain hydrophilic and hydrophobic components to improve their bonding properties in different environments. The hydrophilic components help with bonding to dentin, which is a moist and organic substrate. The ideal dental adhesive is hydrophilic during the application to dentin and hydrophobic after application.

The exact composition of dental universal adhesives may vary among manufacturers and product lines. 10-MDP (10-Methacryloyloxydecyl Dihydrogen Phosphate) is a functional monomer commonly used in dental universal adhesives. It is a phosphate-containing monomer that helps to create a strong chemical bond between the adhesive and the tooth structure and also resin to dental zirconia (Valente et al., 2020).

Experimental universal adhesive is made with the ingredients as follows: Bis-GMA (cross-linking monomer), HEMA (hydrophilic monomer), TEGDMA (cross-linking monomer), 10-MDP (functional monomer), ethanol (solvent), water (solvent), CQ (photo initiator), EDMAB, DPPA.

The choice of monomer is important to maintain the strength of the adhesive layer. The Partition coefficient is an indicator of how a chemical substance is distributed between two different phases which are hydrophobic and hydrophilic. When monomers are used in the adhesive layer, a high Partition coefficient for these monomers increases the likelihood of the adhesive layer remaining solid. A high Partition coefficient enables monomers to disperse well within the adhesive layer, enhancing its stability. Monomers that are hydrophobic have a high Partition coefficient. Highly cross-linking monomers can help improve the strength of the adhesive layer. Cross-linking is the process of forming bonds between molecules, creating a network structure within the adhesive layers. Penta or hexa functional monomers, which have multiple bonding points, can be suitable for cross-linking. Using such monomers can lead to the adhesive layer becoming solid, thereby enhancing strength and durability.

In the case of universal adhesive, the functional monomer also plays a very important role. These monomers primarily include bifunctional monomers like 10-MDP, which are often used. A bifunctional monomer refers to a chemical substance that has two chemical reaction sites. It's commonly used in dental adhesives to strengthen the bond between restorative materials and tooth tissue. Bifunctional monomers play a crucial role in forming the molecular structure of the adhesive. Monomers like 10-MDP are commonly used in dental materials and contribute to the formation of a strong chemical bond between the tooth and the restoration.

2. 10-MDP

In dental restorations, the adhesive layer plays a critical role in bonding the restorative material to the tooth structure. The adhesive needs to be able to bond to both tooth structure and restorative material, which have different chemical compositions and surface characteristics. The use of 10-MDP helps to overcome this challenge by providing a strong chemical bond to both types of tooth structure due to its bifunctional characteristic.

10-MDP works by forming a stable chemical bond with the calcium ions present in the tooth structure. This creates a strong adhesion by forming nano-layering in adhesive layer that is resistant to degradation and allows for the long-term stability of the restoration (Yoshida et al., 2012). In addition to its bonding properties, 10-MDP also has improve the wetting and flow of the adhesive, which can help to improve its handling and application.

Overall, the use of 10-MDP as a functional monomer in dental universal adhesives has been shown to provide reliable and long-lasting bonding to both enamel and dentin (Carrilho et al., 2019). However, dental adhesive needs some other components hydrophobic cross-linking monomer like Bis-GMA and solvent. Especially phosphate containing monomer such as 10-MDP mix with water (solvent contains water) than hydrogen ion become activate and adhesive pH will be acidic (Luque-Martinez et al., 2014). Previous study proved that below 3.0 pH generate incompatibility issue when use with self-cure composite despite of lower pH leads decalcification of hydroxyapatite (Yoshida et al., 2001).

The 10-MDP monomer has a proven potential to interact with hydroxyapatite; the bond produced by 10-MDP containing adhesives appears to be very stable, as confirmed by the low dissolution rate of its calcium salts in water. Etching capacities are related to the substrate where it is applied, to the incorporated monomer and to the bonding potential of other commonly used functional monomers (4-META, phenyl-P). At different degrees the bonding potential is substantially low or produces bonds which are not hydrolytically stable. However, adhesion differentials between commercial adhesive systems are noticed depending both on the dental substrate and on other components included in the adhesives formulations. Some universal adhesives were found to produce poor adhesive interfaces by being less 10-MDP concentrated which suggests that an optimal concentration and purity of 10-MDP in self-etch and universal adhesives may exist so the maximum potential of this functional monomer is achieved.

Unlike conventional methyl methacrylate (MMA), the denture base material used to DLP usually consists of several categories of methacrylate or acrylate monomers and oligomers. The 10-MDP monomer has a long and hydrophobic spacer chain and creates a rich MDP-Ca salt adhesive interface, which improves adhesion strength, remaining stable after one year of water-storage. Although all the advantages of this monomer, application protocols are crucial (substrate, time and technique). When using one bottle, self-etching or universal adhesive systems enamel etching may be recommended since these adhesive systems tend to have higher pH values, which lowers the ability to etch the enamel. However, MDP-Ca salts were found to depend on the components that constitute commercial adhesives more strongly than on the concentrations of MDP and water in the adhesive. Water concentration in adhesive systems was found to affect the efficacy of smear layer removal, and dentin bonding performance more strongly than the pH value of the adhesives and ethanol was found to limit the dissociation of phosphate groups from the 10-MDP monomer (Carrilho et al., 2019).

Adhesive systems containing 10-MDP have a proven interest. 10-MDP possesses the ability to form strong bonds between various dental materials. The effective bonding between hydrophilic dentin and hydrophobic resin can contribute to the stability of dental materials, ensuring reliable performance over extended periods of use. These characteristics of 10-MDP can contribute to creating stable bonding during dental treatments, ultimately enhancing the effectiveness of patients' care.

3. pH of Universal Adhesive

A lower pH of universal adhesive is advantageous for etching dentin and enamel however, excessively low pH can lead to compatibility issues with self-cure composite that involves peroxide and amine reaction mechanisms (O'Keefe and Powers, 2001). This issue arises from the acidic monomers remaining in the oxygen-inhibited layer of the bonding, which transform the self-cure composite's 3-valent amines into 4-valent ones. Previous research has shown that the acidity of the bonding must be above 3.0 to resolve this. Therefore, it is necessary to appropriately control the hydrogen ions in phosphate-based monomers like 10-MDP used in universal Adhesive when they contact with solvents like ethanol, as it can affect the adhesive's acidity (Ekambaram et al., 2015).

Generally, the pH levels of universal adhesives may affect their effectiveness when used with self- and dual-cure resin cements, prohibiting the chemical curing necessary for use with self- and dual-cure cements. Risk is increased when relying solely on the self- and dual-cure components without employing a separately applied activator.

4. Objectives

The study will examine immediate bonding strength depend on proportion of the 10-MDP in the experimental universal adhesive. If that the unique characteristics of 10-MDP as a bifunctional monomer, such as its ability to forming nano layering to different characteristics material which are hydrophilic tooth structure and hydrophobic restorative material such as resin monomer as restorative material enhances immediate bonding strength (Dabsie et al., 2012).

pH is an important factor in the adhesion compatibility between dental materials, including universal adhesives and aromatic tertiary amine-containing cements. The pH of a universal adhesive is typically acidic, which is lower than pH 3.0. Phosphate-containing monomers such as 10-MDP mix with ethanol as a solvent result in activate H+ ions in the monomer, leading to increase acidity in the mixture (Chen and Suh, 2013).

This low pH helps with the etching and bonding process by demineralizing the tooth surface and creating micromechanical retention. However, aromatic tertiary amine-containing cements cannot be cured at the interface to bonding layer when its pH is under 3.0. Universal adhesives are commonly used in restorative dentistry to bond composite materials to tooth structures. Aromatic tertiary amine-containing cements, on the other hand, are dental cements that contain chemicals such as benzoyl peroxide and tertiary amines, which are used for cementation purposes.

This study aims to investigate the physical properties of dental adhesive according to the composition of 10-MDP, a functional monomer that is a representative component of universal adhesives, by measuring the shear bond strength using direct composite resins, and to determine the optimal proportion of 10-MDP related with pH which can affect compatibility with self-cure composite in universal adhesives for use in restorative dentistry.

Recently, there has been a significant development in nanotechnology area, and due to this, nanoparticles have received a lot of interest in various fields such as industrial and medical fields. The null hypothesis will test whether increasing the proportion of 10-MDP in universal adhesives leads to an increase in immediate shear bond strength of the adhesion layer and a decrease of pH. This study will contribute to the development of more effective dental adhesives for clinical use.

The null hypotheses were:

1. The proportion of "10-MDP" in a universal Adhesive does not change shear bond strength of the adhesive.

2. The concentration of 10-MDP within a universal adhesive does not affect the pH of the adhesive.

II. MATERIALS AND METHODS

1. Materials

The materials that used to fabricate experimental universal adhesives in this study were on Table 1. Tescera-Direct body A3 (AMCO, Seoul, Korea) and bovine teeth were used as the bonded materials in shear bond strength test.

Table 1. Materials used in this study

	Name	Manufacturer	Lot Number
Bis-GMA	Bisphenol A diglycidyl methacrylate	Sunfine Global	813-320
Bis-EMA	Ethoxylated bisphenol A glycol dimethacrylate	Sunfine Global	813-350
DPPA	Dipentaerythritol pentaacrylate	SIGMA Aldrich	MKCG6054
TEGDMA	Triethylene glycol dimethacrylate	Sunfine Global	813-349
HEMA	2-Hydroxyethyl methacrylate	Samjeon chemical	10820
10-MDP	10-MDP	J.M. Trade	WI20011503
Ethanol	Ethyl alcohol	Samjeon chemical	30420
Water	D.I. water	Samjeon chemical	22720
CQ	Camphorquinone	J.M.Trade	104119-20
EDMAB	Ethyl-4(dimethylamino)benzoate	Sunfine Global	MKCF4294
Oxybenzone	2-Hydroxy-4-methoxybenzophenone	Sunfine Global	WXBD0013
BHT	2,6-di-(tert-butyl)-4-methylphenol	Sunfine Global	BCCC0032
Composite	Tescera-Direct body A3	Amco	2000001717

2. Methods

2.1. Mixing Process

Measure each component and firstly placed Bis-GMA, Bis-EMA, and 10-MDP, which are viscous liquid into the mixing container. Then add the powdered components camphorquinone, EDMAB, oxybenzophenone, and BHT into the viscous liquid mixture. Follow by adding the liquid components ethanol, HEMA, D.I water, and TEG-DMA, place a magnetic stirring bar into the container and mix at 300 RPM with a magnetic stirrer for 2 hours by using jar, magnetic bar, magnetic stirrer (PC-4200, Corning, NY, USA). Figure 1. Represents mixing process.

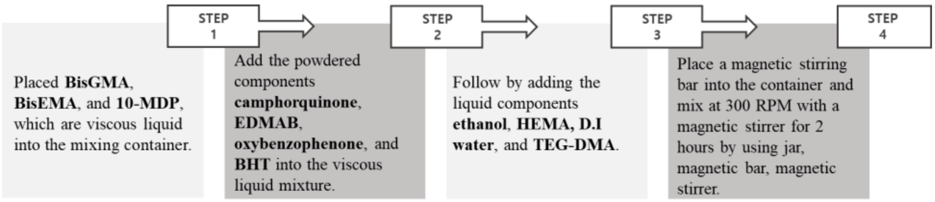

Figure 1. Mixing process flowchart.

2.2. Determining of proportion of 10-MDP

Through various previous experiments, adhesive ingredients such as Bis-GMA, HEMA, TEGDMA, Ethanol, Water, CQ, EDMAB, and DPPA were performed sensitivity tests and set up the optimize volume to maximize bonding reliability. Based on these preliminary experiments, which showed the highest adhesive strength, we aimed to conduct a sensitivity test for the amount of 10-MDP ranging from 9 g to 12 g. Table 2 represents proportion of the ingredients by percentage rate. The weight variation was applied only to 10-MDP.

Consequently, experimental adhesives are prepared with 5 combinations as shown in Table 2.

Table 2. Composition of experimental adhesive by wt % (Unit: wt %)

	MDP-1	MDP-2	MDP-3	MDP-4	MDP-5
Bis-GMA	21.996	21.898	21.801	21.706	21.611
Bis-EMA	8.645	8.607	8.569	8.531	8.494
TEGDMA	1.265	1.259	1.253	1.248	1.242
10-MDP	8.906	9.310	9.710	10.107	10.500
Ethanol	38.334	38.164	37.996	37.829	37.663
HEMA	4.453	4.433	4.414	4.394	4.375
D.I water	0.891	0.887	0.883	0.879	0.875
CQ	0.534	0.532	0.530	0.527	0.525
EDMAB	1.603	1.596	1.589	1.582	1.575
Oxybenzophenone	0.013	0.013	0.013	0.013	0.013
BHT	0.002	0.002	0.002	0.002	0.002
DPPA	13.359	13.300	13.241	13.183	13.125
SUM	100	100	100	100	100

2.3. Specimen preparation for shear bond strength

For the bovine teeth specimens, sound and intact maxillary incisors were selected from slaughtered cattle and cut with a low-speed diamond saw (DIAMO-100S, MTDI, Daejeon, Korea) to obtain tooth specimens without any caries. The tooth surface debris and pulp tissue were removed, and the specimens were stored in distilled water. The dentin exposed tooth specimens were stored at 4 ℃ in distilled water until use. Bonding with experimental adhesive, 5 different 10-MDP volume in them. The prepared tooths were embedded in resin (Vertex Self-Curing, Vertex Dental, Soesterberg, Netherlands), and polished with #320 and #600 SiC paper until the surface was uniform. Figure 2. Represents Specimen preparation flowchart in this study.

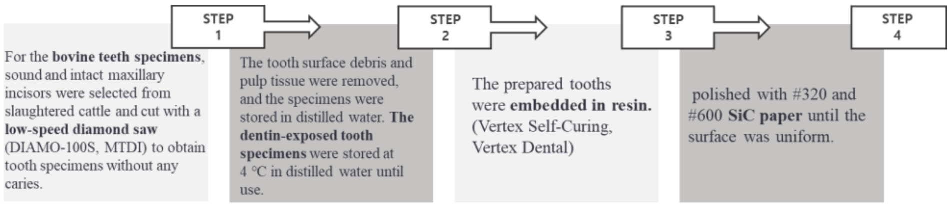

Figure 2. Specimen preparation flowchart.

Apply two separate coats of adhesive to the prepared specimen surface, scrubbing the preparation with a microbrush for 10-15 seconds per coat. Evaporate the solvent using an air blower for 10 seconds, then polymerize the adhesive for 10 seconds using light curing (NOBLESSE, Max Dental, Gyeonggi, Korea). Place a composite resin (TESCERA-Direct, Amco, Seoul, Korea) onto the polymerized adhesive and mold (Φ 2.37 mm × 2.5 mm) it using a bonding mold insert (BOND MOLD A INSERT, Ultradent, UT, U.S.A.). Polymerize for 40 seconds. Store in distilled water at room temperature for 24 hours. Figure 3. Represents Specimen preparation flowchart in this study.

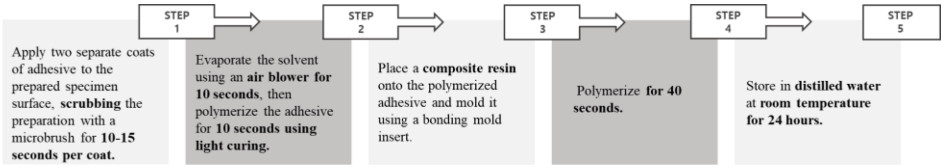

Figure 3. Bonding procedure of Specimen.

2.4. Shear bond strength test

Measure the shear bond strength using a Shear Bond Tester (T-63010k, BISCO, IL, U.S.A.) as shown in Figure 4. The configurations of the test equipment and the specimen were as like Figure 5. The shear bond strength was calculated below equation. Maximum load refers to the maximum force specimen can with stand before breaking.

$$\text{Shear bond strength (MPa)} = \frac{\text{Maximum load (N)}}{\text{Bonded areas (mm}^2\text{)}}$$

After measuring the fracture load, only the occurrence of cohesive and adhesive fracture was observed with naked eye in this study.

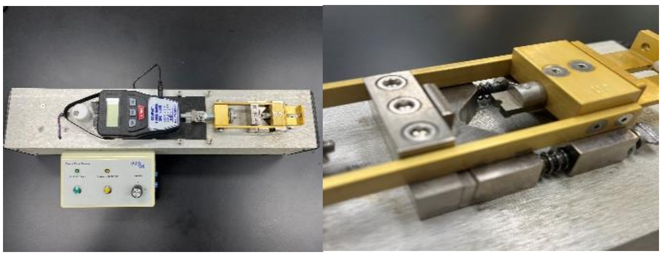

Figure 4. Shear bond strength tester.

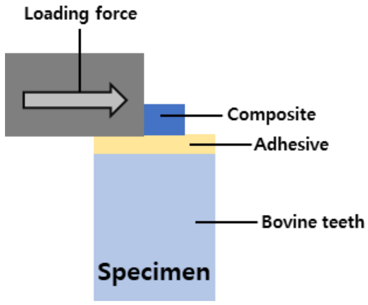

Figure 5. Schematic diagram of shear bond strength test.

2.5. pH measurement

pH meter (Milwaukee MW101 PRO pH Meter, Milwaukee, North Carolina, U.S.A.) is used (Figure 6) to measure the acidity of liquid adhesive after calibration with buffer solution 4.0 and 7.0 at room temperature. Although we attempted to measure the acidity of the adhesive after polymerization using a solid-state pH meter (testo 206 pH2, testo, Lenzkirchj, Germany) (Figure 3), the thickness of the polymerized adhesive was too thin to measure the acidity, so only the liquid adhesive was measured. pH measured 3 times each experimental adhesive. Figure 7. Represents pH measurement flowchart.

Figure 6. pH Meter used in this study.

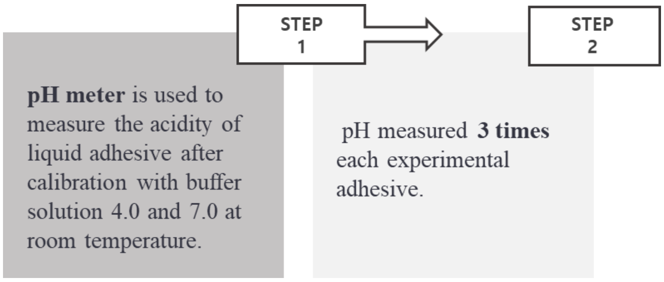

Figure 7. pH measurement flowchart.

2.6. Statistical analysis

The statistical significances of the resulting data were analyzed using one-way ANOVA. The statistical significance was accepted at confidence level of 95 % ($p < 0.05$) by Tukey's test for a multiple comparison procedure. The SPSS program (SPSS Inc., IL, U.S.A.) was used for the statistical analysis.

III. RESULTS

1. Shear bond strength

The results of shear bond strength test were as Table 3 and Figure 8.

Table 3. Shear bond strength (Unit: MPa)

	MDP-1	MDP-2	MDP-3	MDP-4	MDP-5
1	9.949	24.750*	18.747	4.705	12.693*
2	24.211*	31.048	28.818	22.275*	16.487*
3	17.791*	16.713*	29.014	9.312*	16.884
4	18.428	25.388*	20.339	22.814*	19.411
5	17.031	17.252*	34.283*	24.848*	17.641*
6	19.825*	23.770	21.638*	18.624	14.551
7	21.957*	12.326	24.750	13.821	15.149
8	13.600*	20.339	17.889*	13.600*	15.293
9	28.696	18.305*	14.997	15.316	14.357*
10	18.526	25.388	33.621	21.957*	13.154*
11	18.469	19.816*	25.977	15.537	12.761*
12	19.577*	20.143	23.449	18.613*	14.542
13	20.491	18.439	21.003	21.857	14.774
14	17.449	22.507	25.248	19.399	15.294
15	16.248	19.034*	26.471*	15.512	13.546
16	18.019	23.227	24.309	14.143	14.286
17	23.258	22.496	28.166	15.706	16.246
18	21.548*	23.409	27.291*	13.846	17.256
19	18.214	24.579*	22.044	14.629	14.214
20	16.741	21.637	20.148	18.024*	15.010*
Average	**18.966^{b}**	**21.511^{a}**	**24.385^{a}**	**16.944^{c}**	**15.080^{c}**
Standard deviation	**3.819**	**3.950**	**4.882**	**4.725**	**1.677**

Superscript ‘*’ indicates cohesive fractured specimens. Different superscript lowercase letters indicate significantly different shear bond strength ($p<0.05$).

The experimental results showed that there was a significant difference between the groups except for MDP-4 and MDP-5 in table 3. As the amount of 10-MDP increased, the shear bond strength initially increased and then decreased. This demonstrates that while an increase in the amount of functional monomer is beneficial for the reaction with the hydroxyapatite of the tooth surface, its effect on the durability of the bonding layer is limited when measured for immediate bonding strength.

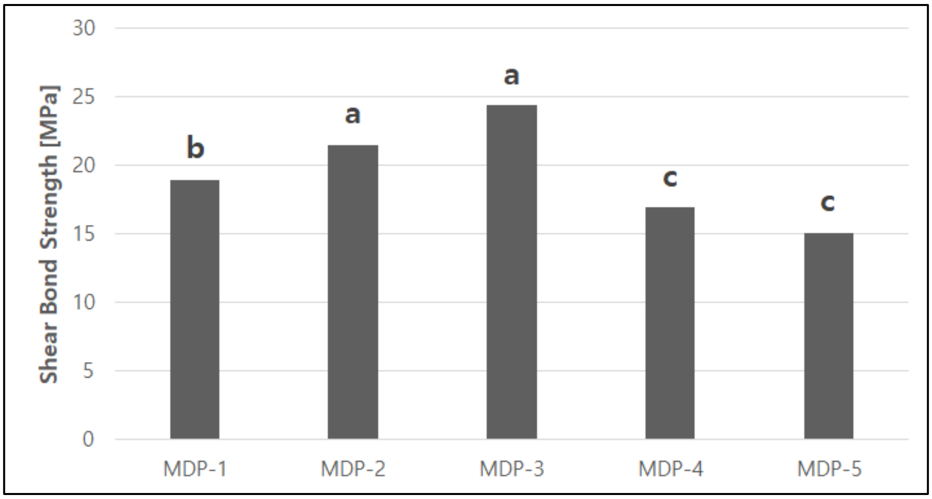

Figure 8. Shear bond strength. Different superscript lowercase letters indicate significantly different shear bond strength ($p<0.05$).

The results of fracture mods were as Figure 9. Observation of the debonded adhesive interface revealed that MDP-3, which had the highest bond strength, had the highest number of specimens exhibiting cohesive fracture with residual resin remaining on the tooth surface. This indicates a positive correlation between the number of specimens exhibiting cohesive fracture and the bond strength.

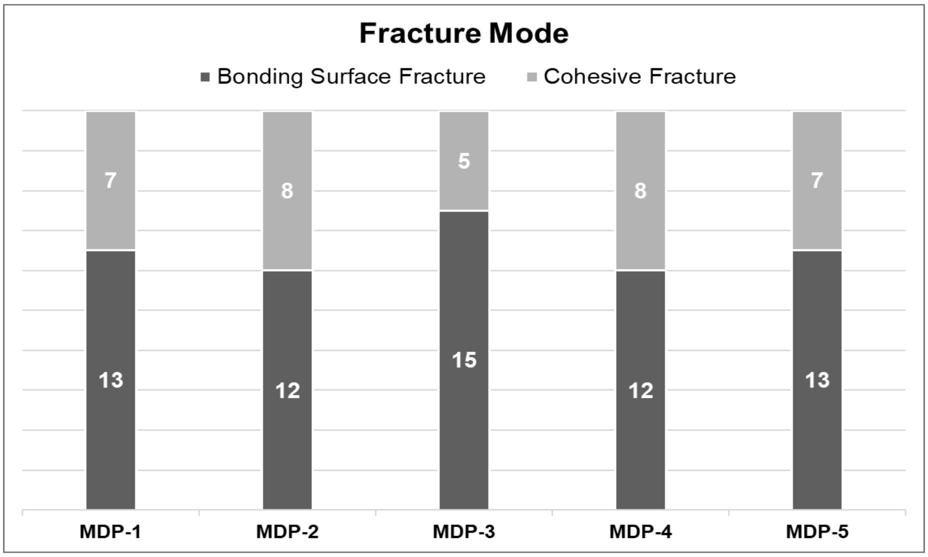

Figure 9. Fracture mode examined after shear bond strength test.

2. pH measurement

The pH of the experimental universal adhesive tended to decrease as the amount of MDP increased (Figure 10). This is presumed to occur because the hydrogen ions in MDP become activated upon contact with water and the solvent, ethanol, thereby lowering the pH of the experimental adhesives.

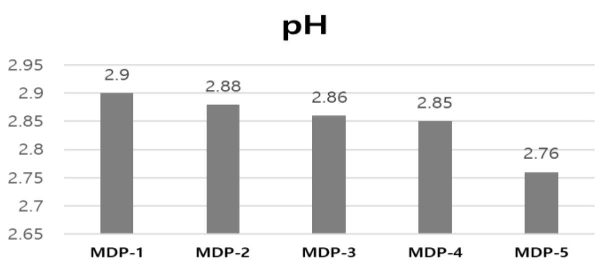

Figure 10. pH of experimental universal adhesives.

IV. DISCUSSION

Universal adhesive refers to an adhesive that can be used with various materials, regardless of the etching method, type of restorative material including zirconia, or type of cement. It is designed to be versatile and compatible with a wide range of applications (Nagaoka et al., 2017). However, depends on the characteristics of substrates as a restorative and luting materials, there are some points to discuss.

1. Bonding Strength, pH and Incompatibility

According to the results of this experiment, there is no correlation between the pH of the universal adhesive and its bonding strength. As the amount of 10-MDP increased, the bonding strength initially increased and then decreased. Meanwhile, the pH consistently decreased as the concentration of hydrogen ions increased.

10-MDP, which exhibits excellent bonding properties with zirconia and enamel, possesses an OH group at one end, which, upon encountering H_2O, activates hydrogen ions, acidifying the entire adhesive solution.

Previous studies have indicated that single-bottle, one-layer adhesives with a pH below 3.0 are incompatible with cements that have a reaction structure consisting of benzoyl peroxide (BPO) and aromatic tertiary amines (Bolhuis et al., 2006).

The theoretical background behind this research suggests that when the adhesive layer has a pH below 3.0, acidic monomers with a pH below 3.0 remaining in the oxygen-inhibited layer hinder the interaction between the amine component of the cement and BPO, preventing their bonding.

Consequently, polymerization of the cement does not occur at the interface between the adhesive layer and the cement, preventing chemical bonding between the two layers (Franco et al., 2005).

Considering two fact, such as mixing silane with 1 bottle universal adhesive and incompatibility with self-cure cement, it is evident that more research is required for single-bottle universal adhesives, to ensure compatibility with all restorative materials including ceramic and self-cure cements.

2. Hydrophilicity of universal adhesive

Universal adhesives containing 10-MDP, when diluted in a solvent, can maintain sufficient hydrophilicity to penetrate dentin tubules and form a hybrid layer. However, after application to the tooth and complete evaporation of the solvent followed by polymerization, the hydrophobic nature of 10-MDP, due to its high partition coefficient, allows for the implementation of a hydrophobic adhesive layer (Feitosa et al., 2014a). In this experiment, contact angle tests conducted on the experimental adhesive, but there is no significant differences between the experimental groups. As the angles measured were consistently 30 degrees or higher, indicating hydrophobic characteristics, contact angle is not measured after 5 data sets. (Feitosa et al., 2014b).

3. Silane and Universal Adhesive

Universal adhesive has limitations when it comes to bonding with ceramics without the addition of silane and compatibility with cements that contain benzoyl peroxide (BPO) and three-component amines in self-curing function due to its fundamental properties.

Silane (3-Methacryloxyproyltrimethoxysilane) is activated through pure acidity and exposure to H_2O. In its activated state, it renders the ceramic surface hydrophobic and prepares it for bonding with the adhesive resin. Silane is crucial for enabling chemical bonding with ceramics (Kim et al., 2021).

However, universal adhesives rely on phosphate-based monomers that have been validated for bonding with zirconia. These monomers, upon contact with water-containing solvents, increase the concentration of hydrogen ions, resulting in acidification. Therefore, if silane is added to universal adhesive, it reacts prematurely in an already activated state before activating the ceramic surface (Yao et al., 2018).

Research has shown that once silane is activated prematurely, it undergoes a self-curing reaction, transforming into silanol, and cannot interact with the ceramic surface. Hence, the claim that a single bottle of universal adhesive can be used for all types of teeth and restorative materials is debatable, and improvements are needed to achieve such capabilities in the future.

4. Zirconia bonding with Universal adhesive

The 10-MDP used in this study is a phosphate-based monomer. Previous research has shown that phosphate-based monomers exhibit higher bonding affinity to zirconia compared to carboxyl-based monomers. Zirconia surfaces do not etch with hydrofluoric acid, unlike traditional ceramics, and they are not affected by silane coupling agents. This is because zirconia surfaces lack silica.

The possible reaction pathway of phosphate monomer with zirconia is, two hydrogen groups (from phosphoric acid group) will react slowly with one oxygen group (from zirconia), liberating a water molecule to from a stable Zr-O-P covalent bond (Suh, 2013).

Based on this theoretical background, several previous studies have investigated adhesion to zirconia surfaces using phosphate monomers. This has been indirectly demonstrated through techniques such as contact angle measurements and SIMS (Secondary Ion Mass Spectrometer). Therefore, inferring from the use of phosphate monomers like 10-MDP as functional monomers, it can be deduced that universal adhesives can achieve bonding to zirconia surfaces as well (Llerena-Icochea et al., 2017).

5. Contact Angle

One of the indirect strength testing methods for dental adhesives, known as Contact Angle, showed no significant differences among the experimental adhesive materials. The results closely approximated those of commercially available products (30 degrees or more), indicating that the overall experimental materials met the necessary and sufficient conditions. Therefore, a comparative analysis among the materials was not conducted (Balkaya and Demirbuğa, 2023).

V. CONCLUSION

The experimental results showed that as the amount of 10-MDP in the experimental Universal Adhesive increased, the pH decreased. In addition, when the experimental Universal Adhesive was applied to the tooth specimen and resin was bonded, the shear bond strength increased gradually with increasing amounts of 10-MDP, but showed a tendency to decrease gradually after a certain amount was exceeded.

Therefore, maximizing adhesive strength and raise the pH as much as possible to address the incompatibility issue, it is necessary to find the optimal amount of 10-MDP that can be used in universal Adhesive. Consequently, the experimental adhesive MDP-3 group exhibited the maximum bond strength when 9.710 % and 11 g were added as weight percentages.

However, despite these efforts, incompatibility still possibly occurred, resulting in a pH below 3.0, which will generate incompatibility issue with amine base self-cure composite. It is necessary to find a way to resolve incompatibility in universal adhesive without adding other substances through additional research following this study.

The null hypotheses were:

1. The proportion of "10-MDP" in a Universal Adhesive does not change shear bond strength of the adhesive. (Rejected)

2. Amount of "10-MDP" in Universal Adhesive does not affect to level of pH. (Rejected)

Through this study, the universal adhesive used in the experiment showed the highest adhesive strength at 9.710 % 10-MDP content, with a pH of 2.86 for that experimental adhesive group. Based on the results of this study, this composition of 10-MDP can be considered the most ideal.

VI. REFERENCES

Balkaya H, Demirbuğa S (2023). Evaluation of six different one-step universal adhesive systems in terms of dentin bond strength, adhesive interface characterization, surface tension, contact angle, degree of conversion and solvent evaporation after immediate and delayed use. *J Esthet Restor Dent* 35(3): 479-492.

Bolhuis PB, de Gee AJ, Kleverlaan CJ, El Zohairy AA, Feilzer AJ (2006). Contraction stress and bond strength to dentinfor compatible and incompatible combinations of bonding systems and chemical and light-cured core build-up resin composites. *Dent Mater* 22(3): 223-233.

Carrilho E, Cardoso M, Marques Ferreira M, Marto CM, Paula A, Coelho AS (2019). 10-MDP based dental adhesives: adhesive interface characterization and adhesive stability—a systematic review. *Materials (Basel)* 12(5): 790.

Chen L, Suh BI (2013). Effect of hydrophilicity on the compatibility between a dual-curing resin cement and one-bottle simplified adhesives. *J Adhes Dent* 15(4).

Dabsie F, Grégoire G, Sharrock P (2012). Critical surface energy of composite cement containing MDP (10-methacryloyloxydecyl dihydrogen phosphate) and chemical bonding to hydroxyapatite. *Journal of Biomaterials Science, Polymer Edition* 23(1-4): 543-554.

Ekambaram M, Yiu CKY, Matinlinna JP (2015). An overview of solvents in resin–dentin bonding. *Int J Adhes Adhes* 57: 22-33.

Feitosa V, Ogliari F, Van Meerbeek B, Watson T, Yoshihara K, Ogliari A, et al. (2014a). Can the hydrophilicity of functional monomers affect chemical interaction? *J Dent Res* 93(2): 201-206.

Feitosa VP, Sauro S, Ogliari FA, Ogliari AO, Yoshihara K, Zanchi CH, et al. (2014b). Impact of hydrophilicity and length of spacer chains on the bonding of functional monomers. *Dent Mater* 30(12): e317-e323.

Franco EB, Lopes LG, D'alpino PHP, Pereira JC (2005). Influence of pH of different adhesive systems on the polymerization of a chemically cured composite resin. *Braz Dent J* 16: 107-111.

Jang J-H, Lee MG, Woo SU, Lee CO, Yi J-K, Kim D-S (2016). Comparative study of the dentin bond strength of a new universal adhesive. *Dent Mater J* 35(4): 606-612.

Kim Y-R, Kim J-H, Son S-A, Park J-K (2021). Effect of silane-containing universal adhesives on the bonding strength of lithium disilicate. *Materials (Basel)* 14(14): 3976.

Llerena-Icochea AE, Costa RMd, Borges AFS, Bombonatti JFS, Furuse AY (2017). Bonding polycrystalline zirconia with 10-MDP–containing adhesives. *Oper Dent* 42(3): 335-341.

Luque-Martinez IV, Perdigão J, Muñoz MA, Sezinando A, Reis A, Loguercio AD (2014). Effects of solvent evaporation time on immediate adhesive properties of universal adhesives to dentin. *Dent Mater* 30(10): 1126-1135.

Nagaoka N, Yoshihara K, Feitosa VP, Tamada Y, Irie M, Yoshida Y, et al. (2017). Chemical interaction mechanism of 10-MDP with zirconia. *Sci Rep* 7(1): 45563.

O'Keefe KL, Powers JM (2001). Adhesion of resin composite core materials to dentin. *Int J Prosthodont* 14(5).

Suh BI (2013). Principles of adhesion dentistry: a theoretical and clinical guide for dentists. AEGIS Communications.

Valente F, Mavriqi L, Traini T (2020). Effects of 10-MDP based primer on shear bond strength between zirconia and new experimental resin cement. *Materials (Basel)* 13(1): 235.

Yao C, Yu J, Wang Y, Tang C, Huang C (2018). Acidic pH weakens the bonding effectiveness of silane contained in universal adhesives. *Dent Mater* 34(5): 809-818.

Yoshida Y, Van Meerbeek B, Nakayama Y, Yoshioka M, Snauwaert J, Abe Y, et al. (2001). Adhesion to and decalcification of hydroxyapatite by carboxylic acids. *J Dent Res* 80(6): 1565-1569.

Yoshida Y, Yoshihara K, Hayakawa S, Nagaoka N, Okihara T, Matsumoto T, et al. (2012). HEMA inhibits interfacial nano-layering of the functional monomer MDP. *J Dent Res* 91(11): 1060-1065.

ABSTRACT (IN KOREAN)

10-MDP의 비율 변화에 따른 유니버셜 접착제의 접착력 및 pH 변화

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서 우 경

목표: 이 연구는 유니버설 접착제의 물리적 특성을 조사하기 위해 10-MDP라는 기능성 단량체의 조성에 따라 직접 복합 레진을 사용하여 전단 결합 강도를 측정하고, 치과 재생수술에 사용되는 유니버설 접착제의 자가중합 composite과의 호환성에 영향을 미칠 수 있는 최적의 10-MDP 함량을 결정하는 것을 목표로 하였습니다.

재료 및 방법: 이전 실험을 기반으로 다양한 접착제 성분인 Bis-GMA, HEMA, TEGDMA, 에탄올, 물, CQ, EDMAB 및 DPPA 등을 사용하여 실험용 접착제를 제조하였으며, 10-MDP의 양을 변화 시킴에 따른 접착강도 실험을 실시하여 접착 신뢰성을 극대화하기 위한 최적 용량을 설정했습니다. 실험에는 우치 및 수복용 레진이 사용되었습니다. 이 실험용 물질에 대해 전단 결합 강도와 pH를 측정하였습니다.

결과: 실험용 유니버설 접착제의 결합 강도는 10-MDP의 양이 증가함에 따라 점진적으로 증가했지만, 일정 양을 초과하면 점진적으로 감소하는 경향을 보였습니다. pH 측면에서는 실험용 유니버설 접착제의 10-MDP 함량이 증가함에 따라 pH가 감소하는 경향을 보였습니다.

이 연구를 통해 실험에서 사용된 유니버설 접착제는 10-MDP 함량이 9.710%이고 pH가 2.86인 경우에 가장 높은 접착 강도를 보였습니다. 이 연구의 결과를 바탕으로 10-MDP 함량이 가장 이상적으로 여겨질 수 있습니다.

핵심되는 말: 10-MDP, pH, 비호환성 유니버셜 접착제, 상아질 접착제, 전단강도