Studies on Adhesion to Tooth Substrate. VI. The Adhesion of Composite Resin to Dentin Mediated by the Dentin Primer Containing MTYA.

Tohru HAYAKAWA, Hiroshi ENDO, Akihisa NAGATSUKA and Kozo HORIE

Department of Dental Materials, Nihon University School of Dentistry at Matsudo, 870-1 Sakaecho, Nishi-2 Matsudo, Chiba 271, Japan

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The influences of the kinds and concentrations of the aldehydes in the primer on dentin adhesion were investigated. Moreover, the durability of the adhesion to the dentin treated with primer was examined by thermal cycling tests.

Among the aldehyde tested here, glutaraldehyde was effective in improving the adhesion to dentin etched with citric acid. When HEMA was substituted with ethanol, the bond strengths decreased. The relationship between the bond strength and the concentration of glutaraldehyde in the primer was studied. In the cases of phosphoric acid or citric acid etching, the bond strengths were affected by the concentration of glutaraldehyde in the primer. The bond strengths decreased after 2000 thermocycles in phosphoric acid etching.

Key words: Adhesion, MTYA, Dentin Primer

INTRODUCTION

It is well known that the adhesion of dental resin to dentin is more difficult than that to enamel, and therefore such adhesion is filled with problems. There are few dentin adhesives which are available to clinics. Bowen *et al.* reported^{1,2)} that treatment with aqueous ferric oxalate, and NPG-GMA (N-phenylglycine glycidyl methacrylate) or NTG-GMA (N-(p-tolyl) glycine glycidyl methacrylate) acetone solution, and PMDM (the adduct of pyromellitic acid dianhydride and 2-hydroxyethyl methacrylate) acetone solution, in that order, can improve the adhesion between composite resin and dentin. Nakabayashi *et al.*^{3,4)} and Shimizu reported⁵⁾ that 4-META (4-methacryloxyethyl trimellitate anhydride) had a high adhesiveness to dentin, and that 4-META/MMA (TBB-O) resin showed a good adhesiveness to dentin etched with 10% citric acid-3% FeCl₃ or with 0.3M EDTA·2Na-0.2M EDTA·Fe·Na solution.

Recently, the application of dentin primer was investigated. The dentin primer was an aqueous solution and was applied to an etched dentin surface. Munksgaard and Asmussen reported^{6,7)} that GLUMA, which is an aqueous solution of glutaraldehyde and HEMA (2-hydroxyethyl methacrylate), was effective in improving the adhesion between composite resin and dentin etched with EDTA. Itoh *et al.* reported⁸⁾ that 35% HEMA solution treatment gave the same adhesiveness to dentin as GLUMA treatment, and that glutaraldehyde in GLUMA had no effect on the dentin adhesion. Tagami *et al.* reported⁹⁾ that the application of 5% NMSA (N-methacryloyl aminosalicyclic acid) in acetone to etched dentin increased the bond strengths of the composite resin and the MMA/TBB-O resin.

We reported that MTYA (*o*-methacryloyl tyrosine amide) had a good adhesiveness to

Table 1 Composition of each part of the primer

A	6% MTYA - 70% HEMA - 24% H ₂ O
A'	6% MTYA - 70% EtOH - 24% H ₂ O
B-1	2% glutaraldehyde - 98% H ₂ O
B-2	10% glutaraldehyde - 90% H ₂ O
B-3	2% o-phthalaldehyde - 98% H ₂ O
B-4	2% formaldehyde - 98% H ₂ O
B-5	10% formaldehyde - 90% H ₂ O

Fig. 1 Structure of the aldehydes.

dentin in the MMA/TBB-O system¹⁰⁾, and we prepared some kinds of dentin primer consisting of MTYA, HEMA, and glutaraldehyde. Endo reported¹¹⁾ that primer made of 3% of MTYA, 35% of HEMA, and 1% of glutaraldehyde was most effective in improving the adhesion of composite resin to dentin. Hayakawa *et al.*¹²⁾ and Hara *et al.*¹³⁾ also reported that this primer improved the adhesion of MMA/TBB-O resin to etched dentin. Chigira *et al.* reported¹⁴⁾ the efficiency of the primer containing MTYA in dentin bonding.

In this report, we investigated the influence of the kinds and concentrations of aldehyde in the primer on dentin adhesion. Moreover, the durability of the adhesion to dentin treated with primer was examined by thermal cycling tests.

MATERIALS AND METHODS

Preparation of the primer

The primer consisted of two parts. One was MTYA aqueous solution, and the other was aldehyde aqueous solution. These two parts were mixed well before application. The compositions of each component in the primer are listed in Table 1. Glutaraldehyde, o-phthalaldehyde, and formaldehyde, whose structures are shown in Fig. 1, were used as aldehydes. Ethanol was used as a substitution of HEMA. Most notably, the concentration of glutaraldehyde varied from 2 to 10%.

Adhesion test

The general procedures for making test samples are shown in Fig. 2. Bovine teeth were stored at -70°C after extraction. Their enamel was removed by an air turbine. A flat surface of dentin was prepared by wet grinding using No. 800 and No. 1000 stones under running water. The dentin was etched either with 10% citric acid, 40% phosphoric acid or 0.5M EDTA (pH 7.4) for 60 s. After washing and drying, the primer was applied for 60 s. Any excess amount of primer was removed by compressed air for 10 s. A silicone ring, whose

Fig. 2 Procedures for making the test samples.

diameter was 3.2 mm and whose depth was 2.0 mm, was placed on the treated surface. Then the bonding agent* and the composite resin** were applied according to the manufacturer's instructions. After curing the resin, the silicone ring was removed, and the test samples were either stored in 37°C water for 1 day, or they were subjected to thermal cycles between 5°C and 55°C with a dwell time of 60 s. Then, the samples were positioned in a tensile testing

* Clearfil New Bond, Kuraray Co., Osaka, Japan

** Clearfil FII, Kuraray Co., Osaka, Japan

Fig. 3 Tensile bond strength to the dentin etched with 10% citric acid after a one day immersion in 37°C water.

machine***, and the tensile bond strength was measured at a crosshead speed of 2.0 mm/min.

The data were analyzed with an analysis of variance, and with the Scheffe's test for multiple comparison between the means at the $p=0.05$ level of significance.

SEM observation

The flat dentin surface was prepared by wet grinding as mentioned above and was etched with the etching agents for 60 s. The specimens were dehydrated in ethanol and were dried in the chamber of the critical point dry apparatus[†]. Then the specimens were sectioned bucco-lingually and the sectioned surfaces were examined with the scanning electron microscope^{††}.

RESULTS

Figure 3 shows the tensile bond strengths to dentin etched with 10% citric acid. The etched dentin was treated with the primer, whose components are listed in Table 1. Without any primer treatment, the test samples could not be prepared. Statistically, the bond strengths to dentin treated with the primer A+B-1, which contained glutaraldehyde, were significantly higher than those which were treated with the primer, A+B-4, A+B-5, and A+B-6. And, there was not a significant difference between the bond strengths treated with the primer A+B-1, which contained glutaraldehyde, and those treated with the primer A+B-3, which contained *o*-phthalaldehyde. It is worth noting that the decrease in the bond strengths was observed when HEMA was substituted by ethanol.

Figure 4 shows the relationship between the bond strengths and the concentration of glutaraldehyde in the primer. One part of the primer was 6% MTYA and 70% HEMA

*** TOM 10000X, Shinkoh Co., Tokyo, Japan

† HCP-1, Hitachi Co., Tokyo, Japan

†† S-550, Hitachi Co., Tokyo, Japan

Fig. 4 Relationship between the bond strengths and the glutaraldehyde concentration in the primer.

Fig. 5 SEM of the etched dentin.

aqueous solution, and the other part contained various concentrations of glutaraldehyde. The X-axis corresponds to the glutaraldehyde concentration in the primer, not that in the glutaraldehyde solution. In the case of phosphoric acid etching, the bond strengths for glutaraldehyde concentrations of 1, 2, and 3% were significantly higher statistically than those for glutaraldehyde at 0 and 0.5%. For citric acid etching, there was a significant difference between the bond strengths at a 0% concentration of glutaraldehyde, and those at a 3% concentration of glutaraldehyde. For EDTA etching, there was a significant difference between the bond strengths at a 0% concentration of glutaraldehyde and those at a 5% concentration of glutaraldehyde, but there was not a significant statistical difference among the bond strengths for glutaraldehyde concentrations between 0.5 and 5.0%.

In Fig. 5, the layer between arrows is identified as the demineralized layer¹¹⁾. It is supposed that the depth of the demineralized layer is about 5~7 μm in phosphoric acid etching, 0.5~1.0 μm in citric acid etching, and less than 0.5 μm in EDTA etching.

The results of the thermal cycling tests are shown in Fig. 6. The primer used was A+

Fig. 6 Tensile bond strength to the etched dentin after thermocycles.

B-1 listed in Table 1. The bond strength at thermocycle 0 means those samples measured after a 1 day immersion in 37°C water. The bond strengths at thermocycle 0 for phosphoric acid etching were significantly higher statistically than those for EDTA etching. Although there was a statistically significant difference between the bond strengths at thermocycle 0 and those at thermocycle 2000 in phosphoric acid etching, there was not a significant difference between the bond strengths at thermocycle 0 and those at 500, 1000, or 2000 thermocycles for citric acid etching or EDTA etching.

DISCUSSION

It is well known that adhesion to dentin is very difficult. In order to improve the adhesion of dental resin to dentin, primer treatment is available. Endo¹¹⁾ reported that the new primer 1-35 (MTYA) can improve adhesion between composite resin and etched dentin. 1-35 (MTYA) consists of two parts. One is 6% MTYA and 70% HEMA aqueous solution, and the other is 2% glutaraldehyde aqueous solution.

The details of the role of the primer treatment in dentin bonding is not known but a possible mechanism is given below¹³⁾. Most of the reaction between aldehyde and collagen is the condensation reaction between the CHO groups in aldehyde and the NH₂ groups in collagen producing CH=N groups. This is complicated by the fact that the adhesive monomers in the bonding agent doesn't penetrate into the collagen which is a hydrophilic protein. The crosslinking reactions of the aldehyde to the collagen make the collagen more hydrophobic, and, as a result, the monomers in the bonding agent easily penetrate into the crosslinked collagen⁵⁾. The aldehyde also reacts with the amino group of MTYA, and it is possible that the MTYA connects with the collagen through the mediation of the aldehyde. The double bonds of MTYA can possibly copolymerize with the HEMA or the adhesive monomers in the bonding agents. Thus high bond strengths can be obtained.

The bond strengths are thought to be affected by the reactivity of aldehyde. Among the aldehydes tested here, glutaraldehyde was effective in improving the dentin adhesion. Mizunuma *et al.* reported¹⁵⁾ that the resistance against the denaturation of collagen was

stronger with glutaraldehyde modification than with formaldehyde modification, because of the difference of the functionality of aldehydes and the degree of cross-linkage. It is thought that in this study the difference between the functionality of aldehydes and the degree of cross-linkage also influences the bond strength to dentin.

Figure 3 also shows the significance of HEMA as a primer components. HEMA is widely used as a biocompatible monomer¹⁶⁾, and it is also reported to have a good adhesiveness to dentin¹⁷⁾.

The bond strengths to etched dentin was affected by the concentration of glutaraldehyde in the primer as shown in Fig. 4. Phosphoric acid etching or citric acid etching was thought to denature the collagen in dentin. It is reported¹⁵⁾ that the denaturation of collagen reduces the bond strengths to dentin, and that the crosslinking reaction of aldehyde with the denatured collagen improves the bond strengths. It was thought that a higher concentration of glutaraldehyde gives the higher bond strength in the cases of phosphoric acid or citric acid etching.

EDTA etching was not thought to denature the collagen, and the role of the primer in dentin etched with EDTA was different from that in dentin etched with phosphoric acid or citric acid. Shimizu pointed out⁵⁾ the significance of the non-collagenous dentin proteins in the case of EDTA etching. In this study, it is possible for residual glutaraldehyde to react with the non-collagenous dentin proteins.

In dentin adhesion, the significance of the penetration of monomers into the etched dentin was supported by the thermal cycling tests. In the comparison of phosphoric acid etching and EDTA etching, the difference between the tensile bond strengths was thought to be due to the thickness of the resin reinforced dentin. Phosphoric acid etching is thought to give thicker resin reinforced dentin than EDTA, because the demineralized layer caused by phosphoric acid etching is deeper than that by EDTA etching. Endo reported¹¹⁾ that the bond strengths between composite resin and dentin were proportional to the thickness of the resin reinforced dentin.

But, it is doubtful that the monomers sufficiently penetrate into the demineralized layer in phosphoric acid etching, because the demineralized layer is too deep. It is possible that the demineralized layer into which the monomers can't penetrate exists between the resin reinforced dentin and the intact dentin¹⁸⁾. The mechanical properties of this demineralized layer are thought to be weak, and thermal stress can damage this layer. As a result the thermal cyclings reduced the bond strengths to dentin etched with phosphoric acid after 2000 thermocycles. In the case of EDTA or citric acid etching, it is suggested that the monomers can penetrate sufficiently into the demineralized layer, and there is no demineralized layer between the resin reinforced dentin and the intact dentin. It means that all of the demineralized layer was substituted by the resin reinforced dentin. As a result, the decrease of the bond strengths by thermal cyclings was small in EDTA or citric acid etching. Further investigation of the analysis of resin reinforced dentin or fractured surfaces would be necessary to reveal this consideration.

CONCLUSION

In this study, the influence of the kinds and concentrations of aldehydes in the primer components to dentin bonding, and the durability of the adhesion to dentin treated with primer were investigated. The primer consisted of two parts. One was MTYA solution and the other was aldehyde solution. Among aldehydes, glutaraldehyde was effective. The bond strengths were significantly affected by the concentration of glutaraldehyde in the phosphoric acid or citric acid etching.

The decrease in the bond strengths after 2000 thermocycles was large in phosphoric acid etching, though the decrease in the bond strengths by thermal cyclings was small in EDTA or citric acid etching.

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後の重量を計測することによって得られる、無機質フィラー含有量との相関を検討した。

その結果、無機質フィラーが75 wt%以下のコンポジットレジンでは、ギャップが0.09%以下と比較的良好な窩洞適合性を示したのに対し、75 wt%以上になると

ギャップが0.01%を示すコンポジットレジンがある反面、0.43%と極めて大きな値を示すものもあった。すなわち、無機質フィラー含有量が多くなるに従い、窩洞適合性が劣化する傾向がみられたものの、両者間には、統計的に有意な相関関係は見い出せなかった。

有機色素を含有する可視光線重合型レジンに関する研究

—— 即時変色性レジンの開発 ——

中里淳一, 伊藤和雄, 和久本貞雄

昭和大学歯学部第二歯科保存学教室

可視光線照射により即時に脱色する、各種有機色素を含有した試作可視光線重合型レジンの物理学的特性の変化を、吸光度計を用いた光吸収特性の分析と、微小硬度計による重合深度の計測によって検討した。

試作レジンには、Bis-GMA および Triethyleneglycol-dimethacrylate を等量混和することによって調製し、重合開始剤および還元剤として Camphorquinone, Dimethyl-*p*-toruidine を添加して作製した。

その結果、Methylene blue, Nile blue A を含有した試作レジンには、色素を加える事によって重合深度がわずかに低下したものの、重合開始直後の脱色性に優れ、充填時に特に辺縁部の過剰充填を容易に識別でき、ひいては過剰溢出の破折による二時ウ蝕を防止する事が容易となるという利点から、臨床応用も可能であると考えられた。

歯質との接着に関する研究 その6 MTYA を含む

プライマーがコンポジットレジンと象牙質との接着に与える影響について

早川 徹, 遠藤 浩, 長塚明久, 堀江港三

日本大学松戸歯学部理工学教室

アルデヒドとしてグルタルアルデヒド, *o*-フタルアルデヒド, ホルムアルデヒドを用いて、それぞれのアルデヒドと MTYA, HEMA からなるプライマーを調整して、象牙質とコンポジットレジンとの接着性を調べたところ、グルタルアルデヒドが接着性を向上させることがわかった。また、HEMA の代わりにエタノールを用いると接着性が低下することも判明した。さらに、グルタル

アルデヒドの濃度を変えてプライマーを調整し接着性を調べたところ、リン酸エッチング、クエン酸エッチングの場合にはグルタルアルデヒドの濃度によって接着強さは影響を受けた。

また、サーマルサイクル試験を行ったところ、リン酸エッチングの場合、2000 回後で接着強さが大きく低下した。