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Efficacy of Glyceryl Methacrylate as a Dentin Primer

Hisashi CHIGIRA*, Atsufumi MANABE*, Kazuo ITOH*, Sadao WAKUMOTO* and Tohru HAYAKAWA**

*Department of Operative Dentistry, School of Dentistry, Showa University, 2-1-1 Kitasenzoku, Ohta-Ku, Tokyo 145, Japan

**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 efficacy of pretreatment on the dentin surface with an aqueous solution of glyceryl methacrylate (GM) was examined by measuring the wall-to-wall polymerization contraction of a light activated composite in a cylindrical dentin cavity, and by measuring the tensile bond strength to a flat dentin surface. All of the tested dentin surfaces were cleaned with neutralized 0.5 M EDTA and treated with experimental primers, followed by a marketed dentin bonding agent and composite. The contraction gap formation of the composite was completely prevented by the application of the GM solution at concentrations of 25 and 35% in water. In contrast, half of the specimens treated with 35% HEMA and 35% HEMA containing 5% glutaraldehyde showed gap formation. Furthermore, a considerably high tensile bond strength of more than 18MPa was observed in the above described dentin bonding system.

Key words: Dentin primer, Dentin bonding, Glyceryl methacrylate

INTRODUCTION

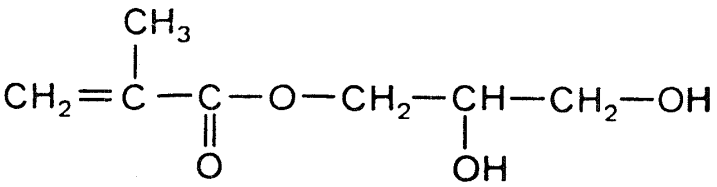
Since Munksgaard and Asmussen[1], in which it was shown that the aqueous mixture of 2-hydroxyethyl methacrylate (HEMA) and glutaraldehyde can significantly improve the bond between dentin and resin materials, the efficacy of some functional monomers as dentin primers has been discussed[2-4]. We have already reported the effectiveness of 35% HEMA solution[5] or that of other monomers diluted in the 35% HEMA solution as dentin primers or as self etching dentin primers[6-8]. In spite of this bonding system development, the complete seal between resin and dentin has not been established, and consequently a contraction gap is often observed, which indicates that the contraction stress of the composite resin can not be overcome by the efficacy of dentin bonding systems. Therefore, the possibility of the use of other monomers as dentin primers should be investigated. The purpose of the present study is to examine the efficacy of the aqueous solution of glyceryl methacrylate (GM) as a dentin primer.

MATERIALS AND METHODS

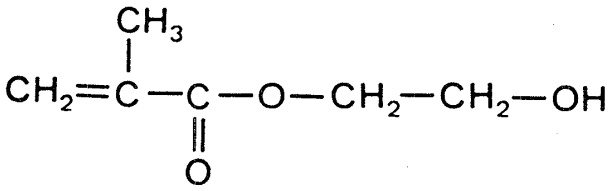
Preparation of GM

Glyceryl methacrylate (GM) was prepared as follows, according to the report of Refojo[9]. In a 500 ml flask, glycidyl methacrylate* (100 ml), distilled water (150 ml), concentrated

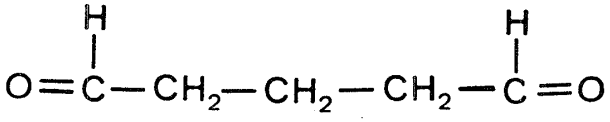
* Glycidyl methacrylate; Wako Pure Chemical Industry Ltd. Osaka, Japan



Glyceryl methacrylate(GM)



Hydroxyethyl methacrylate(HEMA)



Glutaraldehyde(GA)

Fig. 1 The components of the dentin primer

sulfuric acid (0.25 ml), and a small amount of hydroquinone were stirred at 24±1°C for one week. Although the glycidyl methacrylate is immiscible with water, as the reaction proceeded, the reaction mixture became clear during the stirring period.

The reaction mixture was then neutralized with 10% sodium hydroxide solution, and the unreacted glycidyl methacrylate was removed by ether extraction. The residual aqueous reaction medium was saturated with sodium chloride. In the next stage, GM was separated out as an oily layer above the saturated saline solution, and this oily layer was extracted with methylene chloride, then dried with anhydrous sodium sulfate. After the removal of methylene chloride under reduced pressure, the clear liquid, which was mainly composed of GM, and was identified by infrared spectrum and high performance liquid chromatography, was obtained.

Preparation of experimental dentin primers

The components of the dentin primers are listed in Fig. 1. The 35% HEMA** solution and the aqueous mixture of 35% HEMA and 5% glutaraldehyde*** were prepared. The GM was diluted in the distilled water at concentrations of 5, 15, 25, 35 and 45% by volume. The efficacy of these solutions as dentin primers combined with a marketed dentin bonding agent@

** (2-Hydroxyethyl)-methacrylate; E. Merck, Darmstadt, W. Germany
*** Glutardialdehyd; E. Merck, Darmstadt, W. Germany
@ Clearfil New Bond; Kuraray Co., Osaka, Japan

were examined by measuring the wall-to-wall polymerization contraction of a light activated composite@@ in a cylindrical dentin cavity, and by measuring the tensile bond strength to a flat dentin surface.

Measurement of the wall-to-wall polymerization contraction

The proximal enamel of freshly extracted human molars was eliminated by wet silicon carbide paper of grit number 220, and a cylindrical cavity approximately 3 mm in diameter and 1.5 mm in depth was prepared in the exposed dentin. The cavity wall was cleaned with neutralized 0.5 M EDTA for 60 s and rinsed and dried thoroughly. Then the above described dentin primers were applied for 60 s, and the cavity was dried completely. The visible light activated composite was slightly overfilled in the cavity, after the application of the marketed dentin bonding agent. The surface of the composite was covered with a plastic matrix, pressed gently on a glass plate, and irradiated for 40 s by using a lamp unit@@@. After storing the specimens in water at room temperature for 10 min, the excess composite resin was eliminated on the wet silicon carbide paper, and the exposed cavity margin was polished on linen with alumina slurry. The marginal adaptation of the tested dentin bonding systems were inspected using a light microscope#, and the width of the possible polymerization contraction gap was measured by a screw micrometer## mounted on the ocular lens of microscope. The maximum contraction was presented as a percentage of the cavity diameter, as described in our previous paper[10]. All procedures were performed at 24±1°C. Ten specimens were prepared for each primer.

Measurement of the tensile bond strength

The flat dentin surface of the human teeth embedded in an epoxy resin was exposed by using wet silicon carbide paper of grit number 1,000 in the final stage. After cleaning the dentin with EDTA and pretreating it with dentin primer for 60 s, a split teflon mold with an inner diameter of 3.6 mm, an outer diameter of 20 mm, and a height of 8 mm was clamped on the dentin surface. The dentin bonding agent was applied from the top of the mold, and the lower half of the mold was filled with the light activated composite and then irradiated for 40 s. The upper half of the mold was filled with a chemically cured composite###, and a round bar was inserted in the unpolymerized composite to make a grip for a bond strength measurement. After storing the specimens in water for 24 h, the tensile bond strength was measured by using universal testing machine+ at a cross head speed of 5 mm/min. Ten specimens were prepared for each primer at 24±1°C.

RESULTS

The contraction gap of the light activated composite employed in this study was completely prevented in the two groups in which the cavity wall was pretreated by the

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@ Silux; 3 M, St. Paul MN, USA
@@ Quick Light; Morita, Kyoto, Japan
\# Metaloplan; Leitz. Wetzlar, W. Germany
Eyepiece Digital; Leitz. Wetzlar, W. Germany
P-10; 3 M. St Paul. MN. USA
\+ Model 4302; Instron Co. Boston, Mass, USA

Table 1 Wall-to-wall polymerization contraction and tensile bond strength of the light cured composite

Dentin Primer	Contraction Gap* 【GF】	TBS (MPa)**
5% GM	0.120% (0−0.178) 【 1】	16.5±5.6 (6.4−28.1)
15% GM	0.019% (0−0.073) 【 6】	19.6±5.9 (8.9−27.0)
25% GM	0% 【10】	19.6±4.3 (14.3−29.3)
35% GM	0% 【10】	18.7±5.0 (10.4−25.1)
45% GM	0.011% (0−0.079) 【 8】	23.6±7.0 (9.1−30.7)
35% HEMA	0.044% (0−0.109) 【 5】	17.2±7.8 (8.7−32.4)
5%GA, 35%HEMA	0.031% (0−0.108) 【 6】	19.4±6.6 (10.4−32.0)

* : mean (range) n=10
** : tensile bond strength mean±SD (range)
GM : glyceryl methacrylate
GA : glutaraldehyde
HEMA : 2-hydroxyethyl methacrylate
【GF】: number of gap free specimen
The dentin surface was cleaned with EDTA, treated with an experimental dentin primer, and a light activated composite was filled, mediated with a marketed bonding agent.

aqueous solution of GM at the concentrations of 25 and 35%. In the group employing the 35% HEMA solution and the aqueous mixture of HEMA and glutaraldehyde, the gap was observed at the apical margin in nearly half of the ten specimens (Table 1).

In the measurement of the tensile bond strengths of the seven tested groups, a statistically significant difference was observed only between the 5 and 45% GM groups, whereas the differences between all other tested groups were insignificant. Studen's t-test ($p<0.05$) was employed.

DISCUSSION

In order to obtain the complete seal between the composite resin and the dentin cavity wall, the polymerization and the thermal contraction stress of the composite should be overcome by use of an optimum combination of dentin cleanser, primer and bonding agent. Only a few dentin bonding systems, however, have been reported to produce contraction-gap-free specimens. And, it has been already recognized that pretreatment of the dentin surface by a dentin primer is necessary to improve the bond between the resin and dentin, although a clinical procedure of dentin bonding is complicated. In spite of the development of a few functional monomers which had been introduced on the market, it was impossible to avoid a contraction gap in all the specimens tested in our previous reports[6].

It has been recognized that the primary requirement for a dentin bonding system is to completely prevent contraction gap formation, the secondary requirement is to maintain a marginal seal against the thermal and mechanical stresses in the mouth for a long time. And, the possibility of the deterioration of bonding efficacy was examined by measuring the tensile bond strength after storing the specimens for a long period. However, the marginal adaptation of the composite is ensured by water sorption of the composite in the early stage[11], if

the formation of a contraction gap is prevented. Therefore, the tensile bond strength was measured after storing the specimens for 24 h.

The details of the bonding mechanism of dentin primer has not revealed completely, and this includes the new functional monomer reported in this study. Munksgaard[1] speculated that the amino group in the dentin collagen might be activated by the glutaraldehyde and reached with HEMA, although we have revealed that glutaraldehyde in his dentin primer could possibly be eliminated if combined with a dentin bonding agent of high bonding efficacy[5]. We have already reported the efficacy of various dentin primers, and the effectiveness of HEMA not only as a dentin primer, but also as a dilutent of the other primers[6]. Such results indicated that the high permeability of the dentin by HEMA caused the improvement of bonding efficacy.

It has been revealed that the GM is easily gelled compared with HEMA and such a diffence might be responsible for the bonding efficacy of these monomers, although the details of the chemical reaction remain unknown.

For the dentin primer tested in this study, the aqueous solutions of 25 and 35% GM completely prevented the contraction gap formation of the light activated composite in the cylindrical dentin cavity in all cases tested. Therefore, it is possible to conclude that a consistent dentin bonding can be obtained by the combination of cleaning the dentin with neutralized 0.5 M EDTA, pretreatment by the dentin primer of an aqueous solution of GM, application of the marketed dentin bonding agent, and using the composite employed in this study.

Further examination about possible irritation to the pulp or the oral mucous membrane would be required for practical use of this dentin primer.

CONCLUSION

The bonding efficacy of the aqueous solution of GM was tested by measuring the wall-to-wall polymerization contraction of a marketed light activated composite resin in a cylindrical dentin cavity, and by measuring the tensile bond strength to a flat human dentin surface. The marginal gap caused by the contraction stress of the composite was prevented completely by pretreatment of the experimental dentin primer at the concentrations of 25 and 35%. And it is possible to conclude that a consistent bonding between resin and dentin is obtained by the combination of EDTA and GM, a marketed dentin bonding agent, and the light activated composite employed in this study.

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Glyceryl methacrylate 水溶液の dentin primer としての効果について

千木良尚志，真鍋厚史，伊藤和雄，和久本貞雄，早川　徹*

昭和大学歯学部第二歯科保存学教室

*日本大学松戸歯学部歯科理工学教室

Glyceryl methacrylate 水溶液の，dentin primer としての効果を象牙質円柱窩洞内での，可視光線重合型コンポジットレジンのコントラクションギャップの計測と象牙質平面に対する引っ張り接着強さの計測によって評価した。被着象牙質面は，pH 7.4 に調整された 0.5 M 濃度の EDTA によって歯面清掃を行った後，5％から 45％までの Glyceryl methacrylate 水溶液を塗布し，その後市販のリン酸エステル系ボンディング材を併用して市販の光重合型コンポジットレジンを填塞または接着させた。また，コントロールとして 35％HEMA 水溶液と 5％glutaraldehyde を含む 35％HEMA 水溶液を primer として用い，同様の計測を行った。

その結果，25％と 35％の濃度の Glyceryl methacrylate 水溶液を dentin primer として用いた場合に，全試片でギャップが全く認められず，完全な窩洞適合性が得られた。また，24 時間後には，25％および 35％水溶液で，それぞれ平均 19.6 および 18.7 MPa の平均接着力が得られた。

4-META 含有象牙質接着剤に関する研究
―― 接着に対するクレンザーの影響 ――

柳川敏夫，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

著者らは，既に前報にて象牙質窩洞に対しては完全な適合性を有するコンポジットレジンシステムを開発し，報告してきた。本実験においては，このシステムをエナメル質象牙質双方に窩縁を有する窩洞に応用するため，これら 2 種類の窩壁に同時に有効な窩洞清掃法の検討を行なった。窩洞清掃としては，EDTA または 10－3 溶液（3％塩化第 2 鉄を含有する 10％クエン酸水溶液）による一括処理法，さらに，コントロールとして，38％リン酸ゲルと EDTA によるエナメル質，象牙質塗りわけ法を用いた。なお，窩洞清掃法以外は，象牙質窩洞で完全な適合性の得られたシステム，つまり，プライマーとして 35％HEMA 水溶液を用い，4-META を含有する試作ボンディング剤を塗布し，UDMA をベースとする試作コンポジットレジンを填塞硬化させる方法を用いた。なお，これら窩洞清掃法がレジンの接着性に与える影響は，エナメル，象牙質双方に窩縁を有する円柱窩洞内での，maximum contraction gap の測定および平坦な歯面に対する tensile bond strength の測定により評価した。その結果，10－3 溶液で 5 秒間処理した場合に最良の接着性が得られ，窩洞全体を同時に処理しうる清掃法の可能性が示唆された。