Contact Angle of Dentin Bonding Agents on the Dentin Surface

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Physical changes in the surface characteristics of dentin during bonding procedures were evaluated by measuring the contact angles of three standard liquids, to determine the surface free energy, and that of a commercially available dual cured dentin bonding agent dropped on the primed dentin surface. The commercial dentin bonding agent did not form a hemispherical shape on the ground dentin surface, probably because it penetrated into the smear layer due to the microcapillary effect. Not could the contact angle be measured on the dentin surfaces treated with any of four experimental primers, because the bonding agent rapidly spread over the primed dentin surface. It was concluded that the priming of the dentin surface after removing the smear layer served to increase the surface free energy and to improve the wettability of the bonding agent on the dentin.

Key words : Contact angle, Dentin adhesive, Dentin primer

INTRODUCTION

In 1979, the mechanism of a commercial dentin bonding agent containing methacryloxyethyl hydrogen phenyl phosphate (phenyl-P) was explained in terms of mechanical retention of the resin tag formed in the dentin tubules, which were enlarged by 40% phosphoric acid etching¹⁾. Nakabayashi found that the dentin adhesive of the methyl methacrylate containing 4-methacryloxyethyl trimellitate anhydride (4-META) diffused and polymerized in the superficial intertubular dentin which was etched by 10% citric acid containing 3% ferric chloride²⁾, and that this dentin bonding agent formed a hybrid layer resulting in improved bonding between the resin and the dentin. Sugizaki reported that the dentin primer containing N-methacryloyl 5-amino salicylic acid expanded the dentin collagen which shrank during cleaning with citric acid containing calcium chloride³⁾. Watanabe reported that an aqueous mixture of 2-hydroxyethyl methacrylate (2-HEMA) and phenyl-P exhibited high bonding efficacy as a self-etching dentin primer applied directly on the smear layer. He suggested that the phenyl-P penetrated deep into the sound dentin through the smear layer and consequently improved the bond between the dentin and resin materials⁴⁾.

These speculations about the bonding mechanism relied on observations of the superficial dentin beneath the substrate in the area of the adhesive interface, but no consistent explanation has been advanced. These bonding mechanisms were explained based on measurement of the bond strengths of resin materials to flat dentin surfaces. In bond strength measurement, it is well known that specimens frequently break at the resin composite cylinder or the dentin, which scarcely reflects the bond strength at the adhesive interface.

As suggested by Asmussen in 1975, bonding between the resin composite and the dentin cavity wall is obtained only when the polymerization contraction stress of the resin composite is compensated by the efficacy of the dentin bonding system employed⁵⁾. Contraction gap forms when the contraction stress exceeds the efficacy of the bonding system.

Munksgaard and Asmussen asserted that pretreatment of the dentin surface after dentin cleaning with an aqueous mixture of glutaraldehyde and hydroxyethyl methacrylate (GLUMA) significantly improved the efficacy of dentin adhesives⁶⁾. They explained the bonding mechanism of their dentin primer chemically, suggesting that the nitrogen group of the dentin collagen was activated and made polymerizable by 2-HEMA. In a dentin cavity, the contraction gap is always formed between the resin composite and dentin cavity wall, never inside the resin composite nor in the dentin, which suggests that only the surface characteristics of dentin, not its interior, play a role in the marginal adaptation of resin composite. In a previous study, we restored a tooth scheduled to be extruded mainly for orthodontic reasons and observed the cavity adaptation of the resin composite immediately after the polymerization of the composite⁷⁾. We concluded that the cavity adaptation of resin composite *in vivo* correlated with contraction gap width, measured using the extracted tooth, and not with the tensile bond strength to the flat dentin surface. This finding suggested that neither bond strength measurement nor the fracture type of the specimen are reliable predictors of the clinical performance of a resin composite restoration.

The purpose of the present study is to examine the changes in mechanical interactions between dentin bonding agents and dentin surfaces during priming by measuring the contact angles of dentin bonding agents on flat dentin surfaces.

MATERIALS AND METHODS

The flat dentin surface was prepared with wet 1000 grit carborundum paper. The substrate dentin surface of extracted human molar material was prepared in three groups: ground dentin surface, whose flat dentin surface was prepared by a low speed cutting machine (control group); cleaned dentin surface, which was cleaned with neutralized 0.5 mol/L ethylenediamine tetraacetic acid (EDTA) (pH 7.4) for 60 sec; and primed dentin surface, on which the dentin cleaning with EDTA was followed by priming for 60 sec with one of four experimental dentin primers: aqueous solution of 35 vol% glyceryl methacrylate (GM), 35 vol% hydroxyethyl methacrylate (2-HEMA), 62.5 wt% ethylene glycol, or 45 wt% 1,6-hexanediol (Table 1). In a previous report, these solutions showed complete marginal adaptation when used with EDTA cleaning except 2-HEMA.

The prepared tooth was then mounted on the contact angle measurement apparatus* and approximately 1.5mm of distilled water, 1-bromonaphthalene or diiodomethane was dropped on the substrate through a syringe (Fig. 1). The surface free energy was calculated according to the formula presented in Table 2.

A commercial dual-cured dentin bonding agent** was also dropped on the dentin surface prepared as described above and the contact angle was measured.

* FACE contact angle meter, CA-DT type, Kyowa Interface Science Co. Ltd, Saitama, Japan

** Clearfil Photo Bond, Kuraray, Osaka, Japan

Table 1 Dentin primers tested

	Code	Concentration
Glyceryl methacrylate ¹	GM	35 vol%
Hydroxyethyl methacrylate ²	HEMA	35 vol%
Ethylene glycol ³	EG	62.5 wt%
1,6-hexanediol ⁴	HD	45 wt%

The experimental dentin primers were prepared by diluting the two esterified methacrylates with polyvalent alcohols, and the two diols with distilled water at the above concentrations.

¹ Nihon Oil and Fat, Japan

² Merck, Germany

³ Wako Pure Chemical, Japan

⁴ Wako Pure Chemical, Japan

Fig. 1 Using a syringe, approximately 1.5mm of the tested liquid was dropped on the substrate through the nozzle.

Fig. 2 Hemisphere of commercial dentin bonding agent which was applied after EDTA cleaning.

Fig. 3 The dentin bonding agent spread rapidly on the substrate when the dentin surface was primed with one of four experimental solutions after EDTA cleaning.

Table 2 Formula for calculating surface free energy

$$\gamma = \gamma^d + \gamma^p + \gamma^h$$

γ (Surface free energy)

γ^d (Dispersion force)

γ^p (Dipole force)

γ^h (Hydrogen bond)

Five specimens for each group, 100 in total, were prepared. The free energy of the dentin surface was calculated using the contact angle of the three standard liquids, following

a suggestion by Kitazato and Hata⁸⁾. They speculated that surface free energy is determined by three factors dispersion force, dipole force, and hydrogen bond. Distilled water has all three factors, 1-bromonaphthalene has dispersion force, and diiodomethane exhibits dispersion and dipole forces. The free energy of the dentin surface was calculated with the aid of specialized software[#].

RESULTS

The contact angle and surface free energy data are presented in Tables 3 and 4.

The surface free energy on the ground dentin surface (74.2 mN/m) was reduced by EDTA cleaning (56.9 mN/m), but was restored to 65.1 mN/m by priming with ethylene glycol, and to 76.8 mN/m by 1,6-hexanediol. When the dentin bonding agent was dropped on the ground dentin surface, the contact angle was impossible to measure since the agent rapidly entered the substrate. After EDTA cleaning, the bonding agent formed a hemisphere whose contact angle was $13.2 \pm 1.3^\circ$ (Fig. 2). When the dentin surface was primed by any of the four experimental solutions after cleaning, the dentin bonding agent spread rapidly on the substrate and the contact angle could not be measured (Fig. 3).

DISCUSSION

Light microscopic observation showed clearly that the bonding between a resin composite

Table 3 Contact angles of tested solutions on the dentin surface

	Distilled water	1-Bromonaphthalene	Diiodomethane	Clearfil Photo Bond
Smear layer	22.0 ± 4.9	13.6 ± 1.7	51.6 ± 6.4	Unmeasurable*
EDTA	52.0 ± 5.3	40.4 ± 2.3	76.2 ± 3.2	13.2 ± 1.3
EDTA & GM	10.2 ± 3.2	35.0 ± 4.0	58.0 ± 3.2	Unmeasurable*
EDTA & HEMA	16.0 ± 5.1	32.8 ± 1.3	50.0 ± 2.6	Unmeasurable*
EDTA & Ethylene glycol	29.8 ± 6.1	49.2 ± 6.1	68.4 ± 9.0	Unmeasurable*
EDTA & Hexanediol	7.6 ± 4.4	36.6 ± 8.7	66.4 ± 9.7	Unmeasurable*

* The commercial dentin bonding agent did not form a hemispherical shape because it rapidly spread on the surface

Table 4 Surface free energy

Smear layer	74.2
EDTA	56.9
EDTA & GM	76.2
EDTA & HEMA	72.9
EDTA & Ethylene glycol	65.1
EDTA & Hexanediol	76.8

(mN/m)

After EDTA cleaning, priming with the four aqueous solutions increased the surface free energy.

Surface free energy analysis software EG-2, Kyowa Interface Science Co., LTD, Saitama, Japan

restoration and the dentin cavity margin always fails at the adhesive interface, never inside the dentin cavity wall nor inside the resin composite. This is due to contraction stress on the resin composite during polymerization. The marginal integrity of the resin composite in a dentin cavity was significantly improved by the introduction of the dentin primer initially reported in 1984 by Munksgaard and Asmussen who developed the aqueous mixture of glutaraldehyde and hydroxyethyl methacrylate (GLUMA). We modified their dentin primer by eliminating the glutaraldehyde, though contraction gap formation of the light activated resin composite could not be prevented completely by GLUMA or 2-HEMA priming at room temperature of 24°C⁹. Recently we demonstrated that a polymerizable group in the chemical profile of the dentin primer is not always necessary, because contraction gap formation was prevented completely not only by primers containing methacrylate derivatives such as glyceryl methacrylate¹⁰, erythritol methacrylate¹¹, or xylitol methacrylate¹², but also by the aqueous solution of two diols: ethylene glycol¹³ and 1,6-hexanediol¹⁴.

As discussed above, in investigating improvement of the mechanism of dentin bonding systems using dentin primer, this study focused on physically altering the surface characteristics.

The high surface free energy of the ground dentin surface was explained by microcapillary penetration into the smear layer. The dentin bonding agent penetrated the smear layer, which produced high wettability between the ground dentin and the dentin bonding agent. However, this wettability did not result in tight bonding, because the smear layer disturbs bonding between the dentin and the resin materials¹⁵. The surface free energy on the dentin decreased after EDTA cleaning, and the wettability against the dentin bonding agent also deteriorated. The contact measurement after EDTA cleaning was regarded as representative of the essential characteristics of the dentin substance.

Upon priming with four aqueous solutions, the surface free energy increased and the dentin bonding agent spread rapidly on the primed dentin surface. It is suggested that the bonding between the dentin and resin materials is improved by priming because the dentin bonding agent spreads on the dentin surface and increases the wettability between the resin composite and the dentin cavity wall. We previously reported that the efficacy of glyceryl methacrylate, ethylene glycol, and 1,6-hexanediol priming was definitely superior to that of 2-HEMA priming because contraction gap formation of a light-activated resin composite in a cylindrical dentin cavity could not be prevented completely by 2-HEMA priming, but no gaps were observed in dentin cavities primed with the three experimental primers. Therefore, it may be concluded that improved wettability of the dentin surface is not a reliable indicator of the efficacy of a dentin primer.

CONCLUSIONS

The contact angle measurements may be explained by the effect of dentin priming, which increases the wettability of the dentin surface prior to the application of a dentin bonding agent.

The surface free energy of the dentin surfaces was increased by the experimental dentin primers tested.

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間手指に反復接触させることにより発赤、腫脹を伴う搔痒感に遭遇することを報告しており、さらに多くの研究者らは、この症状が遅延型アレルギーであることを報告している。今回の研究目的は、モルモットを用い、HEMA及び試作デンティンプライマーとして用いられているGlyceryl methacrylate (GM) 水溶液及びメタクリル酸の至適感作濃度、および至適誘発濃度を検討するとともに実際に感作されていると思われる患者に、パッチテス

トによって感作源を確認することである。その結果、至適感作濃度は、HEMA、GMともに0.2から0.5%の濃度でほとんどの動物が感作され、誘発濃度はメタクリル酸以外は100%のみであった。またパッチテストではHEMAとGMに交差反応が認められた。このことにより、ヒトに対する感作濃度は非常に低濃度であることから、臨床的にラバーグラブを装着し、極わずかな接触も回避することが重要であると思われる。

電気化学的析出したリン酸カルシウム塩の形態に及ぼす温度の影響

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NaCl, K₂HPO₄およびCaCl₂・2H₂Oを含む電解液を4°Cから92°Cに保持し、リン酸カルシウム塩をチタン基板上に電気化学的に合成した。走査電顕観察より、4°C, 22°C, 37°Cでの析出物は顆粒状であり、52°Cから92°Cでの析出物は針状であった。針の幅と長さは電解液温度の上昇に伴い大きくなった。電子線回折、フーリエ

赤外分光分析、X線回折を用いた状態分析の結果、顆粒状析出物は結晶性の低いリン酸カルシウム塩であり、針状析出物はc軸方向に配向した炭酸アパタイトであると同定された。結晶性は電解液温度の上昇に伴い高くなったが、002面の配向度は電解液温度の上昇に伴い82°Cまでは増加し92°Cではわずかに減少した。

象牙質面に対するデンティンボンディング材の接触角の計測

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試作デンティンクレンザーおよびプライマーを用いて象牙質処理を行った後の象牙質平面の濡れ性の変化を、象牙質面上に滴下されたボンディング材および標準試薬の接触角を計測し、各々処理平面の表面自由エネルギーを算出することにより検討した。その結果、EDTA処理後のwettabilityは研削面に比較して一旦低下し、その後プライミング処理をおこなうと市販デンティンボンディング材は滴下直後に象牙質面に急激に拡散し、con-

tact angleは計測不可能となった。今回用いた試作デンティンプライマーは、HEMA水溶液を除いて象牙質円柱窩洞内に填塞された市販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形成を完全に阻止しうる、優れた粘性改善効果を示すことが確認されているが、その作用機序は象牙質面の表面活性を効率的に改善することによるものと考えられた。