Effects of a New 4-Acryloxyethyltrimellitic Acid in a Visible Light-Cured Dental Adhesive on Adhesion and Polymerization Reactivity

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ABSTRACT: A new adhesive-promoting monomer, 4-acryloxyethyltrimellitic acid (4-AET), was synthesized. The effects on the adhesion to bovine dentin and the polymerization reactivity [the inclusion varying from 0 to 10 wt % 4-AET of the experimental light-cured dental bonding resins (adhesive), wherein the adhesives were aged artificially at 50°C over 2 weeks] were investigated, using tensile and shear bond testing, a differential scanning calorimeter (DSC), and a scanning electron microscope (SEM). Tensile and shear bond strengths to ground dentin were not significantly decreased in 4-AET content over 2 weeks of aging, and the optimum concentration of 4-AET was found to be 5 wt %. The correlation between the tensile and shear bond strengths to the dentin was highly positive ($r = 0.8517-0.9329$) during the 2 weeks. The maximum temperature (T_{max}) of the polymerization in DSC was affected by the 4-AET content in the positive correlation. The correlation between the T_{max} and the bond strength to dentin was highly positive ($r = 0.8995-0.9644$). The SEM study showed that the bonding resin appeared to adhere strongly to ground dentin without the formation of resin-tags in the dentinal tubules. It was suggested that the bonding strength was attributable to the degree of penetration of the 4-AET/HEMA primer into the dentin and the polymerization reactivity of the bonding resin comprising 4-AET. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1057–1069, 1998

Key words: visible light-cured dental adhesive; 4-acryloxyethyltrimellitic acid; adhesion; polymerization reactivity

INTRODUCTION

Serious consequences encountered in postoperative restorations, that is, pulpal response and secondary caries, are believed to be caused by the invasion of bacteria into the gap formed along the margin of restorations, according to Brännström and Nyborg.[1,2] While effective bonding to etched enamel is now readily achieved, bonding to dentin remains a challenge. The development of an advanced adhesive system that provides good adhesion to dentinal tissues is, therefore, a strong demand in the field of adhesive dentistry. Since Munksgaard and Asmussen,[3] the great majority of studies on bonding to dentin have dealt with an aqueous primer, and, thus, bonding to etched dentin has been much improved. Apart from the enamel, however, pulpal irritation has been more recently noted when strong acid-etching agents

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have been applied to the dentin.[4] Forming a bond to ground (unetched) dentin is more problematic and elusive due to the structure and nature of dentinal tissues with a smear layer on the superficial ground dentin. Much attention has recently been focused on bonding to ground dentin using self-etching primers.[5–7]

Our development of a self-etching primer for ground dentin yielded an advanced primer composition comprising a curing agent, acidic monomers, 2-hydroxyethyl methacrylate (HEMA), and water.[8] A previous work in this series has shown that an aqueous primer solution comprising 4-acryloxyethyltrimellitic acid (4-AET) as a new adhesive-promoting monomer exhibited significant effects on the shear bond strength to ground dentin.[9] Following this, we investigated the effect of 4-AET in a bonding resin on the adhesion to ground dentin. It was expected that 4-AET bearing hydrophilic and hydrophobic structural moieties would provide an effective bonding performance where 4-AET was incorporated into a hydrophobic bonding resin (adhesive) and an aqueous primer. However, the acidic group of 4-AET influenced the polymerization reactivity in the presence of HEMA. While the evaluation of adhesive-promoting monomers applied to dentin is well known, only a few studies have investigated the influence of the polymerization of adhesive monomers on the adhesion to etched dentin,[11,12] and little attention has been paid to the effect of the monomers in a bonding resin on the correlation between the adhesion to ground dentin and the polymerization reactivity. To clarify the role of 4-AET in a dental adhesive system on the adhesion to ground dentin, the present study focused on this correlation and an *in vitro* bonding methodology.

The first objective of this study was to evaluate the effects of the inclusion of 4-AET in a light-cured bonding resin, not only on the tensile and shear bond strength to ground dentin, but also on the correlation between the tensile and shear bond strength. The second objective of this study was to investigate the effects of the inclusion of 4-AET not only on the polymerization reactivity of the bonding resin, but also on the correlation between the adhesion and polymerization. Also, to evaluate the aging effect on utilization, all the light-cured bonding resins used were artificially aged at 50°C during the 2 weeks before testing. In this article, we report on the effects of 4-AET in a light-activated bonding resin on the adhesion and polymerization reactivity, using tensile and shear bond testing, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

EXPERIMENTAL

Syntheses of 4-AETA and 4-AET

The title compounds were synthesized, according to the method previously reported.[9] 4-AET was synthesized by the hydrolysis of 4-acryloxyethyltrimellitate anhydride (4-AETA) synthesized from anhydrous trimellitic acid chloride and 2-hydroxyethyl acrylate by esterification. After hydrolysis of the 4-AETA, the reaction product, recrystallized from *n*-hexane and 4-AET, was obtained in a 61.2% yield. Satisfactory IR spectra (FT-300, Horiba, Ltd., Kyoto, Japan), ^{1}H-NMR spectra [PMX60SI (60 MHz), JEOL Co., Ltd., Tokyo, Japan], and elemental analyses (only for 4-AET), together with the melting points for new compounds, are as follows:

4-AETA: 38.7% yield, a light yellow crystal, mp 43.0–45.0°C, IR spectra (cm^{-1}): 1780, 1855 (C=O, from acid anhydride), 1710, 1720 (C=O, from ester). 4-AET: 61.2% yield, a white needle crystal, mp 119.5–121.0°C, IR spectra (cm^{-1}): 1695 (C=O, from carboxylic acid), ^{1}H-NMR spectra (ppm): 4.53 (4H, —CH_2CH_2—), 5.83, 6.20 (3H, CH_2=CH—), 8.03, 8.53, 8.55 (3H, aromatic).

ANAL: Calcd for $C_{14}H_{12}O_8$: (C, 54.54%; H, 3.90%. Found: C, 54.25%; H, 3.94%.

The syntheses of 4-AETA and 4-AET are given in Figure 1.

Preparation of Reagents

Dimethacryloxyethyl-2,2,4-trimethylhexamethylene diurethane (TMDI–HEMA) as a hydrophobic urethane dimethacrylate was synthesized by an addition reaction of 2,2,4-trimethylh examethylene diisocyanate(TMDI) and HEMA in a 1 : 2 molar ratio, according to the method previously reported.[9] TMDI–HEMA: $\eta_{23°C}$: 5800–5950 cp. The crosslinking agents of triethylene glycol dimethacrylate (TEGDMA) and ethylene glycol dimethacrylate (EGDMA) were purchased from Shin Nakamura Chemical Co. Ltd. (Wakayama, Japan). DL-Camphorquinone (CQ), *N,N*-dimethylaminoethyl methacrylate (DMAMA), and butylated hydroxytoluene (BHT) were all reagent

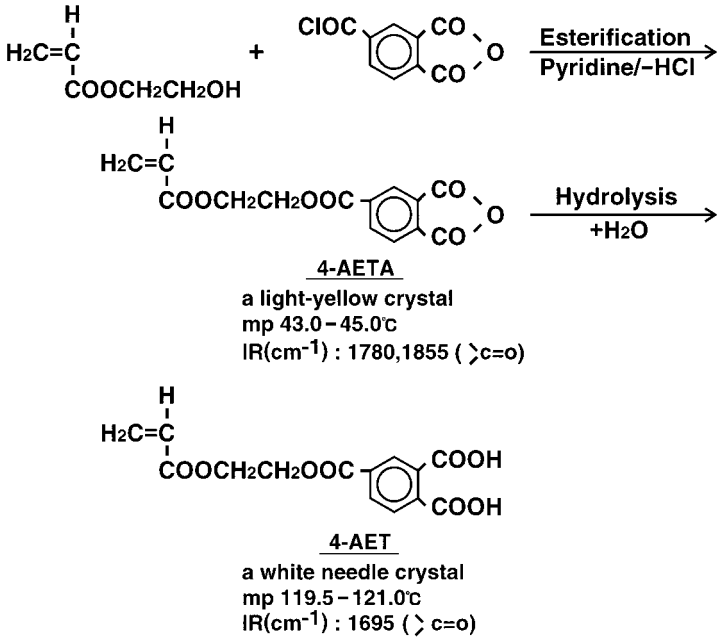

Figure 1 Scheme of the syntheses of 4-AETA and 4-AET.

grade (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and used without further purification.

Preparation of Experimental Primer Solution and Light-Cured Bonding Resins

An experimental self-etching primer and six single-component, light-cured bonding resins were formulated, according to our patent.[8] The primer was prepared from 4-AET, HEMA, distilled water, and photoinitiators (CQ and DMAMA). The composition of the bonding resins used is shown in Table I. The total amount of the 4-AET and TEGDMA contents was 34 wt %. All experimental bonding resins were aged artificially at 50°C in the periods of zero (starting: not aged), 1 week, and 2 weeks, then employed.

Measurement of Bond Strength

Since it is difficult to collect significant quantities of fresh human teeth, bovine teeth were substituted.[12–14] Experimental bonding resins aged artificially at 50°C over 2 weeks were employed.

Tensile Bond Strength to Ground Dentin

Bovine mandibular first incisor teeth with dental pulp were promptly extracted and used within 10 h of slaughtering.[15] The teeth were flat-ground into dentin using a 600-grit SiC abrasive paper under running water and then air-dried. The dentin was then treated with an experimental primer in a rubbing manner for 30 s with a small sponge pellet, then dried with oil-free compressed air for 10 s. After drying, double-faced adhesive tape with a 4.0-mm diameter hole was fixed on the dentin surface, and the experimental bonding

Table I Composition of Experimental Light-Cured Bonding Resins

Material	Ingredients
Bonding resin	0, 1, 3, 5, 7, and 10 wt % 4-AET[a]; 34, 33, 31, 29, 27, and 24 wt % TEGDMA[b]; 54 wt % TMDI–HEMA[c]; 2 wt % EGDMA[d]; 3.5 wt % HEMA[e]; 0.95 wt % CQ[f]; 1.0 wt % DMAMA[g]; and 0.05 wt % BHT[h]

The total amount of 4-AET and TEGDMA is 34 wt %.
[a] 4-Acryloxyethyltrimellitic acid.
[b] Triethylene glycol dimethacrylate.
[c] An adduct of 2,2,4-trimethylhexamethylene diisocyanate and 2-hydroxyethyl methacrylate in a 1 : 2 molar ratio.
[d] Ethylene glycol dimethacrylate.
[e] 2-Hydroxyethyl methacrylate.
[f] DL-Camphorquinone.
[g] *N*,*N*-Dimethylaminoethyl methacrylate.
[h] Butylated hydroxytoluene.

resin was applied and cured with visible light (Shofu Grip Light II, Shofu Inc., Japan) for 30 s. A cylindrical Teflon mold of a 4.0-mm inner diameter and a height of 2.0 mm was then fixed onto the dentin and a light-cured resin composite (LITE-FIL IIA, A2, Shofu Inc.) was placed in the mold and light cured for 30 s. After removal from the mold, the specimens ($N = 7$ in each group) were then immersed in water at 37 ± 1°C. After 20 h, a sandblasted stainless-steel rod (5.0 mm in diameter, 10.0 mm in height) was adhered to the top of the composite using an adhesive resin cement (Imperva Dual, Shofu Inc.) and immersed in water at 37 ± 1°C. After 4 h, the tensile bond strength was measured using a universal testing machine (Instron 5567, Instron Co., USA) at a crosshead speed of 1 mm/min. Schema of the procedure of tensile bond testing on the fresh dentin is shown in Figure 2.

Shear Bond Strength to Ground Dentin

Shear bond testing was carried out in a manner similar to that previously described.[9] Freshly extracted bovine incisors cut off at the roots were embedded in the epoxy resin. The teeth were flat-ground into dentin using a 600-grit SiC abrasive paper under running water and air-dried. Test specimens were prepared according to the manner described above, using a self-etching primer and a light-cured bonding resin. The specimens ($N = 7$ in each group) were then immersed in water at

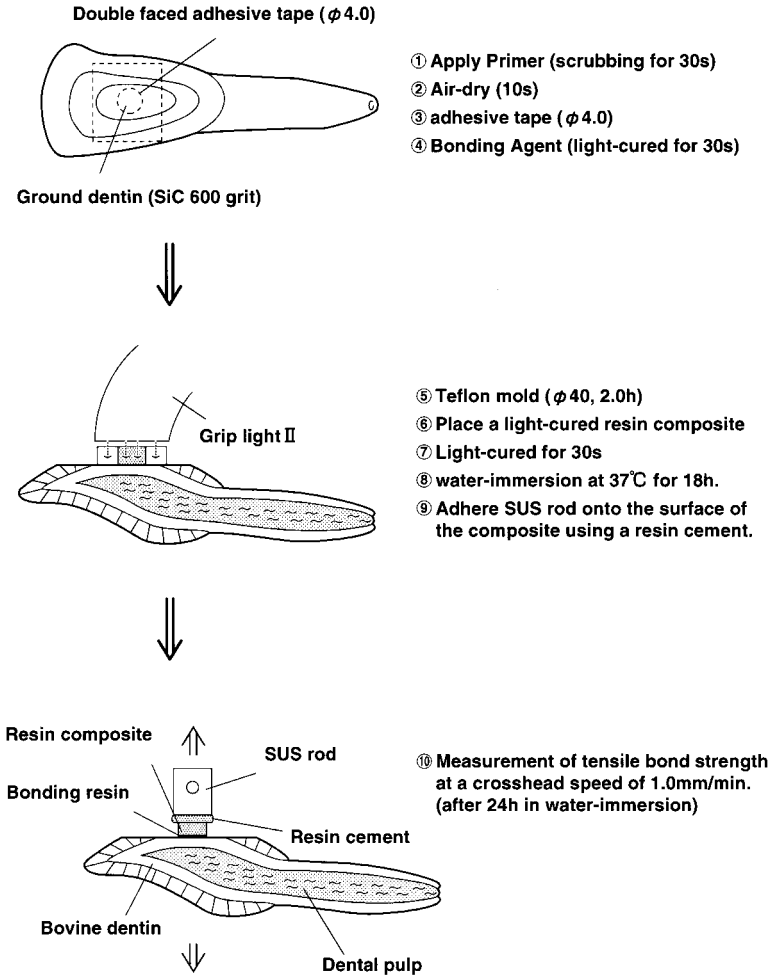

Figure 2 Schema of the procedure of tensile bond testing on the freshly extracted bovine teeth. Bovine mandibular first incisor teeth with dental pulp were promptly extracted and used within 10 h of slaughtering. The cellular tissues of the dental pulp in freshly extracted bovine teeth were vital within 36 h after extraction.[15]

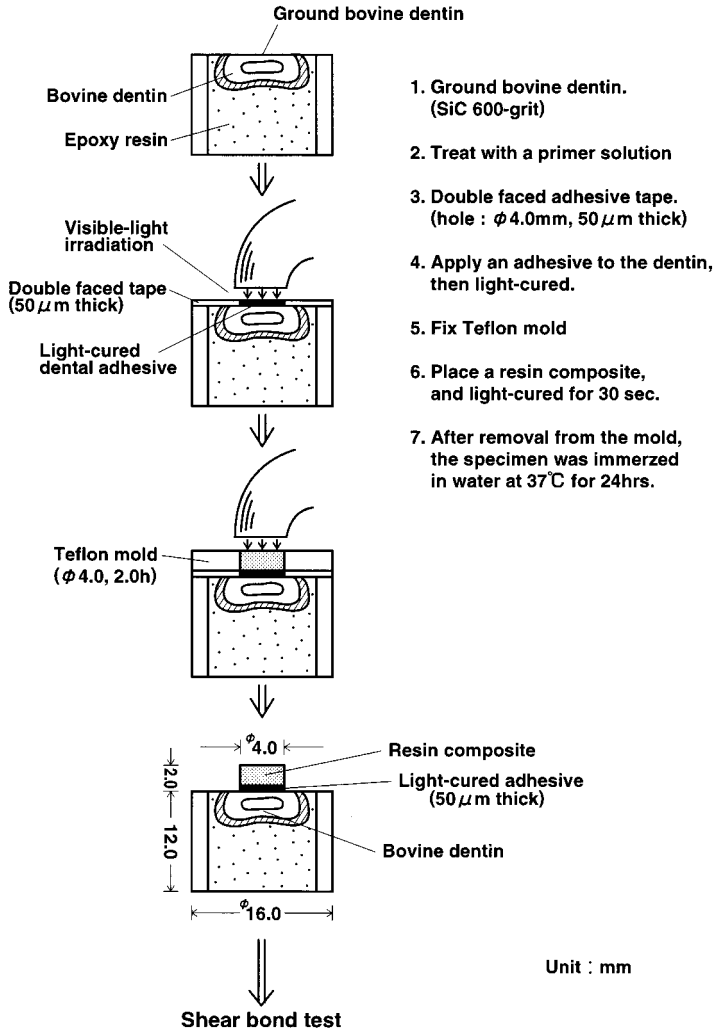

Figure 3 Schema of the procedure of shear bond testing to the ground dentin embedded in the epoxy resin.

37 ± 1°C. After 24 h, the shear bond strength was measured at a crosshead speed of 1 mm/min. Schema of the shear bond testing on the ground dentin is shown in Figure 3.

Schematic diagrams for tensile and shear bond testing are given in Figure 4. All tests described above were carried out at a room temperature (23 ± 1°C). The mean and standard deviation for load at failure were calculated and the results were subjected to a two-way analysis of variance (ANOVA), followed by a Newman–Keuls multiple comparison test. Coefficients of correlation between the 4-AET content and tensile or shear bond strength were further calculated.

Measurement by Differential Scanning Calorimeter

Experimental bonding resins aged artificially at 50°C over 2 weeks and the monomers 4-AET, TMDI–HEMA, TEGDMA, and HEMA were used. A sample of about 10 mg was placed in an aluminum pan, and measurements by a differential scanning calorimeter (DSC, 8230D, Rigaku Co., Tokyo, Japan) were carried out in the thermal range from 23 to 250°C at the rate of 10°C/min. The coefficients of correlations between tensile or shear bond strength and the maximum temperature of polymerization (T_{max}) were further calculated.

Scanning Electron Microscope Observation

After tensile bond testing, the specimens having a typical cohesive failure in dentin with the dentin–resin interface were coated with gold by an ion coater (JEC-1100, JEOL Co. Ltd., Tokyo, Japan) and observed by a scanning electron microscope

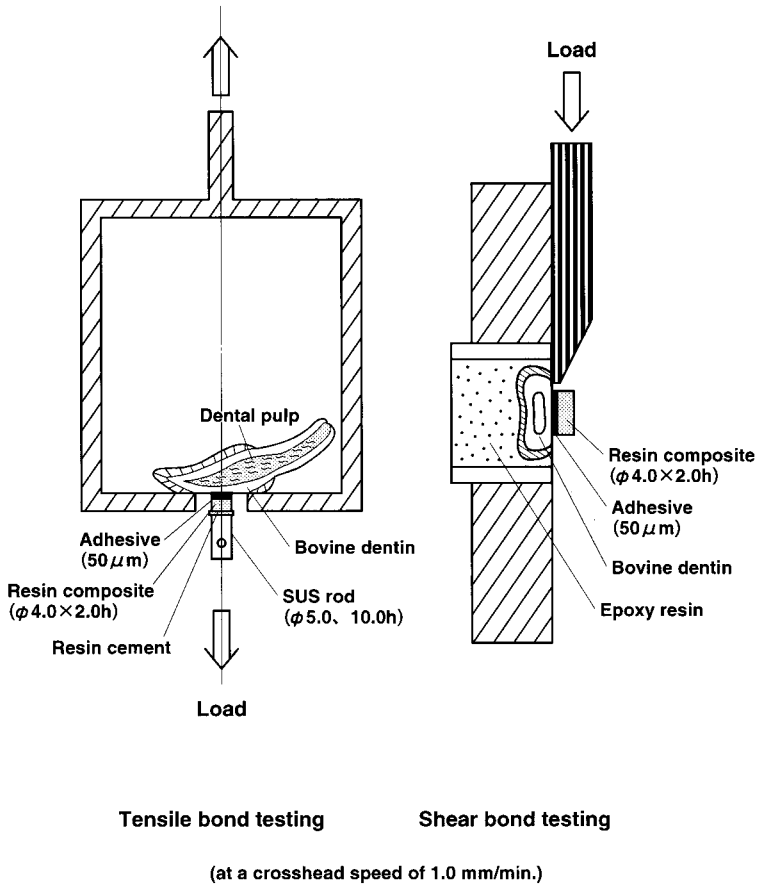

Figure 4 Schematic diagram of tensile and shear bond testing.

(SEM; JSM-5300LV, JEOL). Freshly extracted bovine dentin treated by scrubbing with an experimental primer for 60 s was observed by the SEM. Also, the vertically sectioned surface at the resin–dentin interface of specimen of an experimental bonding resin containing 5 wt % 4-AET, applied to the dentin treated with the self-etching primer, was observed by the SEM.

RESULTS AND DISCUSSION

Measurement of Tensile and Shear Bond Strength

Since occlusal, tensile, and shearing stress are all applied to the adhesive interface during mastication, both tensile and shear bond testing were carried out on bovine dentin. Freshly extracted bovine teeth with dental pulp for tensile bond testing and the bovine dentin embedded in an epoxy resin for shear bond testing to dentin were employed. To evaluate the aging effect on utilization, all experimental light-cured bonding resins used were artificially aged at 50°C during the 2 weeks before the testing.

Figure 5 illustrates the data on tensile bond strength to the fresh dentin achieved with the inclusion of 0–10 wt % 4-AET in the bonding resin. The coefficients of variation calculated indicated ranges of 20.5–35.6% (starting: no aging), 15.3–44.0% (aged for 1 week), and 19.5–39.4% (aged for 2 weeks). Although the ideal number of specimens for the adhesion test is usually 10, seven for each group were used in the present study, while the validity of the data can be confirmed by the ranges of the variation given. It is apparent from Figure 5 that the tensile bond strength to the dentin was maintained in each level of 4-AET content over 2 weeks. Statistical analysis using a two-way ANOVA indicated that where the bonding resin containing 4-AET in the range of 3–10 wt % (starting), 5–10 wt % (1 week), and 5–10 wt % (2 weeks) there was a significant difference in the tensile bond strength to the dentin when compared with the control (0% 4-AET) ($p < 0.01$). Particularly, 5.0 wt % 4-AET

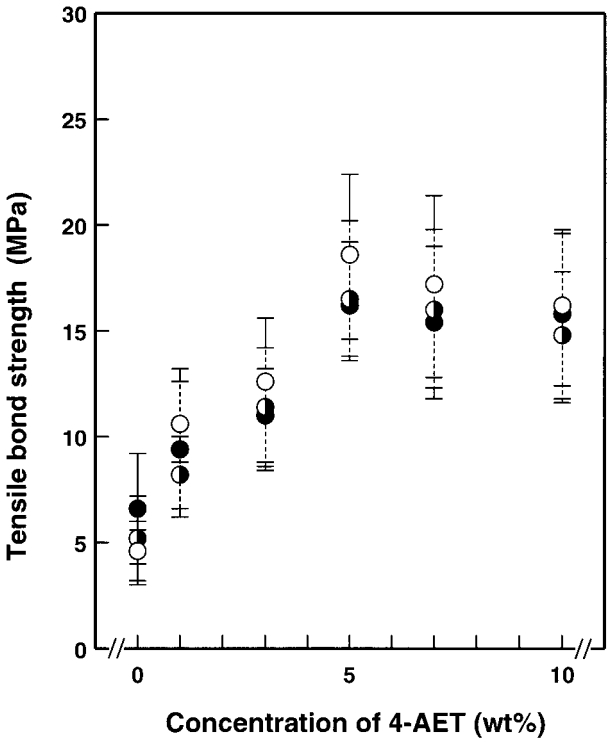

Figure 5 Effect of 4-AET content in the bonding resin on tensile bond strength to the ground dentin of fresh bovine teeth, using the bonding resin aged artificially at 50°C for (○) 0 (starting), (◑) 1, and (●) 2 weeks.

content showed the highest value of tensile bond strength and maintained a tensile bond strength of 18.5 (3.8) MPa (starting), 16.3 (2.5) MPa (1 week), and 16.9 (3.3) MPa (2 weeks). The correlations between the 4-AET content and the tensile bond strength to ground dentin were $r = 0.7895$ (starting), $r = 0.8381$ (1 week), and $r = 0.8596$ (2 weeks).

Figure 6 illustrates the data on the shear bond strength to ground dentin embedded in the epoxy resin achieved with a content of 0–10 wt % 4-AET in the bonding resin. The coefficients of variation indicated the ranges of 19.2–35.6% (starting), 20.8–40.4 (1 week), and 25.3–36.4% (2 weeks). In Figure 6, the shear bond strength to the dentin was maintained at each level of 4-AET content over the 2 weeks. Analysis indicated that where the primer containing 4-AET in the range of 3–10 wt % (starting), 3–10 wt % (1 week), and 3–10 wt % (2 weeks) there was a significant difference in the tensile bond strength to the dentin when compared with the control (0% 4-AET) ($p < 0.01$). Particularly, the highest values of bond strength with corresponding 4-AET content were 7 wt %: 19.8 MPa (starting), 5 wt %: 16.8 MPa (1 week), and 5 wt %: 20.3 MPa (2 weeks). The correlations between the 4-AET content and the shear bond strength to the ground dentin were $r = 0.7871$ (starting), $r = 0.7995$ (1 week), and $r = 0.7557$ (2 weeks).

Tensile and shear bond testing showed the optimum 4-AET concentration to be 5 wt %. The optimum concentration of adhesive monomers reported in previous articles was indicated as 5 wt %, derived from the bonding strength to etched dentin.[14,16,17] While the bonding to ground (unetched) dentin was demonstrated in the present study, the optimum concentration (5 wt %) of 4-AET in the bonding resin agreed with that obtained by the studies.

For tensile bond testing, fresh bovine dentin was employed. Since the cellular tissues of the dental pulp in freshly extracted bovine teeth are vital within 36 h after extraction,[15] it is expected that the fresh bovine tooth with dental pulp is a mimetic adherent as a vital human tooth for an *in vivo* adhesion. Regarding the investigations on *in vitro* bonding methodology, Abe et al.[15] compared freshly extracted bovine teeth which had dental pulp with embedded and thawed teeth for

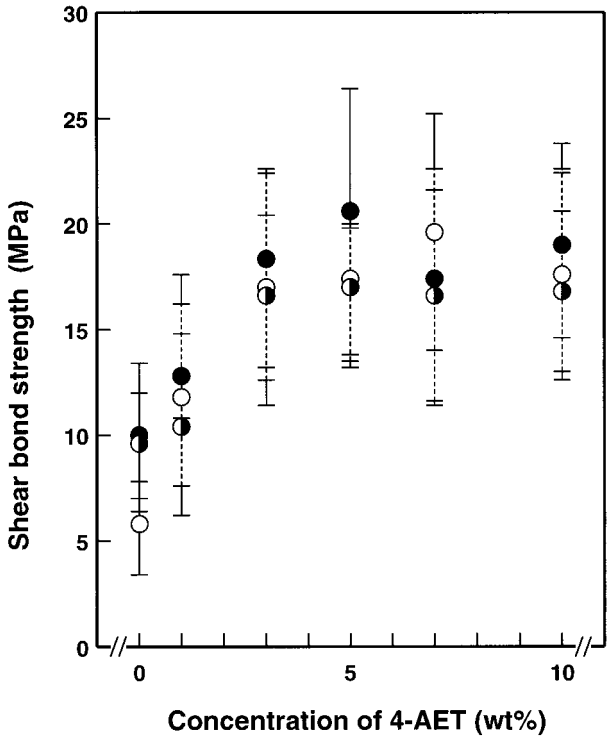

Figure 6 Effect of 4-AET content in the bonding resin on shear bond strength to the ground dentin embedded in epoxy resin, using the bonding resin aged artificially at 50°C for (○) 0 (starting), (◑) 1, and (●) 2 weeks.

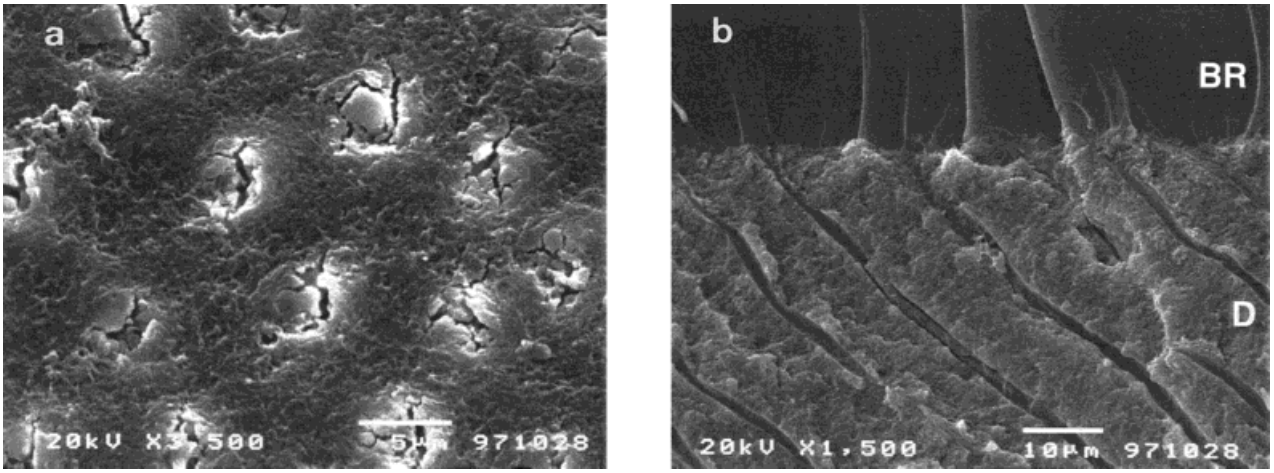

Figure 7 SEM micrographs of (a) the surface of the dentin treated with an experimental primer in a scrubbing manner and (b) the sectioned surface of the adhesive interface between the bonding resin and the dentin. Smear remains can be seen in the dentinal tubules (a) and the bonding resin appears to adhere strongly to the dentin without the formation of resin-tags in the dentinal tubules (b).

the tensile bond strength of a resin composite to these dentin and reported that an influence was observed on the tensile bond strength to the dentin by using bovine teeth under various storing conditions or various pretreating conditions. Since the cellular tissues remain vital, it seemed reasonable that the dentinal tubules were still filled with pulpal fluid in the fresh dentin. We thought that where the dentin was pretreated with a strong acid-etching agent (pH 0.2–0.8) dental fluid leaking through the exposed dentinal tubules influenced the bonding strength.[19] Figure 7(a) shows an SEM micrograph of the surface of the dentin treated by scrubbing with an experimental primer (pH 3.0). Smear remains could be seen in the dentinal tubules. Since a strong acid-etching agent was not applied to the dentin in the present study, a dentinal smear was physically removed with the primer by scrubbing. Apart from the etched dentin, we thought that the tensile bond strength to the ground dentin was slightly affected by the pulpal fluid, consequently achieving good adhesion without the formation of resin-tags in the dentinal tubules [Fig. 7(b)].

Correlation Between Tensile and Shear Bond Strength

Figure 8 illustrates the correlation between the tensile and shear bond strength to the ground dentin. It is apparent that the behavior of both the tensile and shear bond strengths to the dentin show similar tendencies from the highly positive correlations: $r = 0.9329$ (starting), $r = 0.9251$ (1 week), and $r = 0.8517$ (2 weeks) over 2 weeks (Fig. 8). The correlation between the tensile bond strength to the fresh dentin and the shear bond strength to the embedded dentin was positive

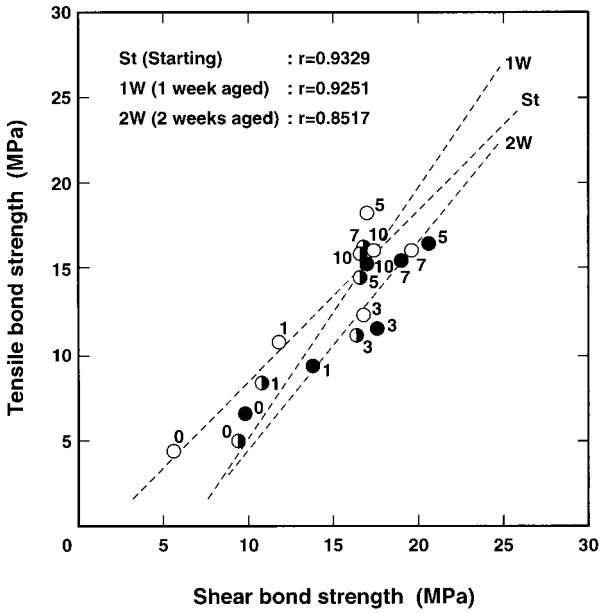

Figure 8 The correlation between tensile and shear bond strength to ground dentin, using the bonding resin aged artifically at 50°C for (○) 0 (starting), (◑) 1, and (●) 2 weeks. Small letters indicate the content of 4-AET in the bonding resins.

Table II Effect of the 4-AET-Content in Bonding Resin Aged at 50°C During 2 Weeks on Shear Bond Strength to Ground Dentin of Embedded Bovine Teeth

Contents (wt %) of 4-AET	Shear Bond Strength (MPa)								
	Starting LC-BR[a]			1-Week-Aged LC-BR			2-Weeks-Aged LC-BR		
	Mean	SD[b]	D (%)[c]	Mean	SD	D (%)	Mean	SD	D (%)
0	5.6	2.3	0	9.5	2.6	0	9.9	3.6	0
1	11.8	4.2	0	10.4	4.2	0	13.8	3.5	14.3
3	16.8	5.5	42.9	16.3	3.8	42.9	17.8	4.5	42.9
5	17.2	3.3	42.9	16.8	3.5	42.9	20.3	6.5	85.7
7	19.8	5.7	71.4	16.5	5.2	42.9	17.0	5.8	42.9
10	17.5	5.4	42.9	16.6	4.2	28.6	19.2	5.0	42.9

$n = 7$. Bovine teeth embedded in epoxy resin were used. Means connected by the vertical line are not significantly different at the level of 0.01.

[a] Light-cured bonding resin.

[b] Standard deviation.

[c] Percent of cohesive failure in dentin.

with respect to the content of 0–10 wt % 4-AET in the bonding resin aged artificially at 50°C over 2 weeks.

In the present study, a number of cohesive failures in the dentin were observed after tensile and shear bond testing. Since the bonding tests were performed using ground dentin, it was thought that an SEM observation of cohesive failures in the dentin was significant to our work. Figure 9 shows an SEM micrograph of a typical cohesive failure in the dentin after the bonding test, which is revealed under magnification of the interface (white arrow in Fig. 9) between the bovine dentin (D) and the bonding resin (BR). A wavelike fractured mode (black arrow in Fig. 9) in the bonding layer is revealed under magnification, which is evidence of the tensile stress applied. It is clear that the adhesive interface was not fractured, in

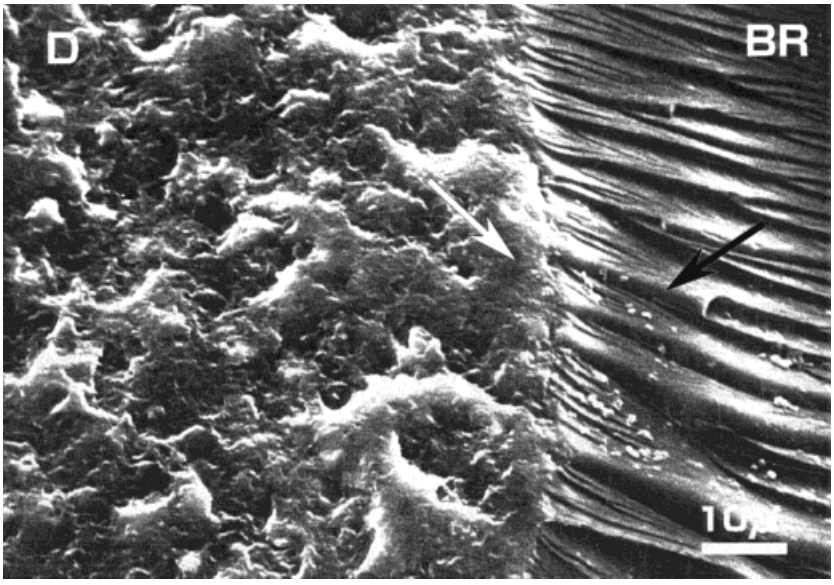

Figure 9 SEM micrographs of a typical cohesive failure in dentin after tensile bond testing. The SEM micrograph shows that the bonding resin (BR) appears to be strongly adhered to the dentin (D), and the dentin–resin interface (white arrow) was not fractured, in spite of the application of the strongly tensile stress (a wavelike fractured mode: black arrow) to the interface.

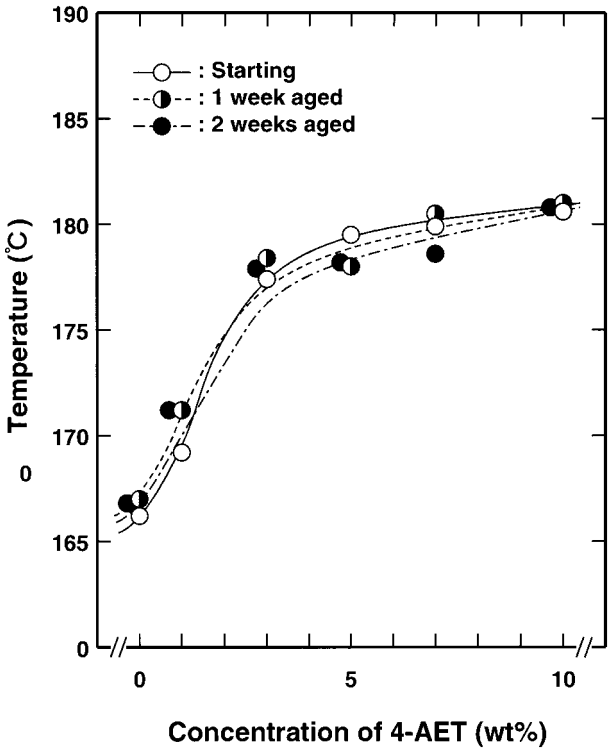

Figure 10 Effect of 4-AET content in the bonding resin on the T_{max} of the DSC measurement, using the bonding resin aged artifically at 50°C for (○) 0 (starting), (◑) 1, and (●) 2 weeks.

spite of the application of strong tensile stress to the interface. Apart from the etched dentin, no resin-tags were formed in the dentinal tubules [Figs. 9 and 7(b)]. A typical cohesive failure in the dentin after the tensile and shear bond testing reveals different fracture modes. Versluis et al.[19] recently developed a failure accumulation simulation program and investigated the cohesive failure in dentin, using a dental bonding system with an etching agent. Yamaguchi et al.[20] introduced theoretical formulas and experimentally clarified the internal stress distribution in the adhesive layer derived from *T*-type shear bond testing under a bending moment. A comparison the two typical cohesive failures in dentin implies that both are attributable to the internal stress distribution at the adhesive interface during tensile and shear bond testing, supporting the findings in these articles.

DSC Measurement

To investigate the effect of 4-AET on the polymerization reactivity of the bonding resin qualitatively, DSC measurement was carried out. Figure 10 illustrates the effect of the 4-AET content on the maximum temperature (T_{max}) of the DSC measurement, using the bonding resin aged artificially at 50°C over 2 weeks. The T_{max} of the polymerization of the bonding resin is affected by the inclusion of 4-AET, and increasing the 4-AET content in the bonding resin results in increasing the T_{max} of the polymerization with the positive correlations of $r = 0.8705$ (starting), $r = 0.8727$ (1 week), and $r = 0.8580$ (2 weeks). The DSC data for several monomers as ingredients of the bonding resin are illustrated in Figure 11. The DSC behavior of 4-AET has an endothermic point as a melting point: 115.6°C, and an exothermic point as a T_{max}: 129.8°C. It is clear that the acrylate monomer of 4-AET shows a higher reactivity (the lowest T_{max}) than that of the other methacrylate monomers; furthermore, 4-AET achieved good copolymerization with these monomers (Fig. 11). In general, it is well known that acrylic ester derivatives have a faster polymerization reactivity than that of methacrylic ester derivatives.[22] However, thus far, the adhesive-promoting monomers have been examined almost exclusively with methacrylic ester derivatives. It was thought the polymerization reactivity of 4-AET was correlated with the bonding performance of 4-AET.

Correlations Between Adhesion and Polymerization Reactivity

Figures 12–14 illustrate the correlations between the T_{max} of bonding resins on the DSC measurement and the tensile bond or shear bond strength

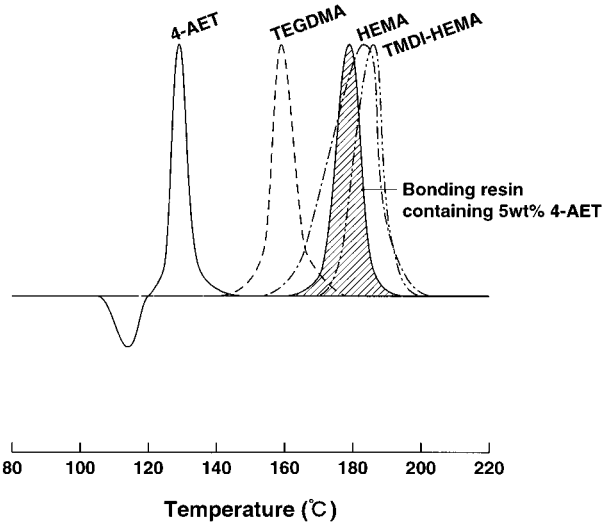

Figure 11 Polymerization behavior of several monomers used for the DSC measurement.

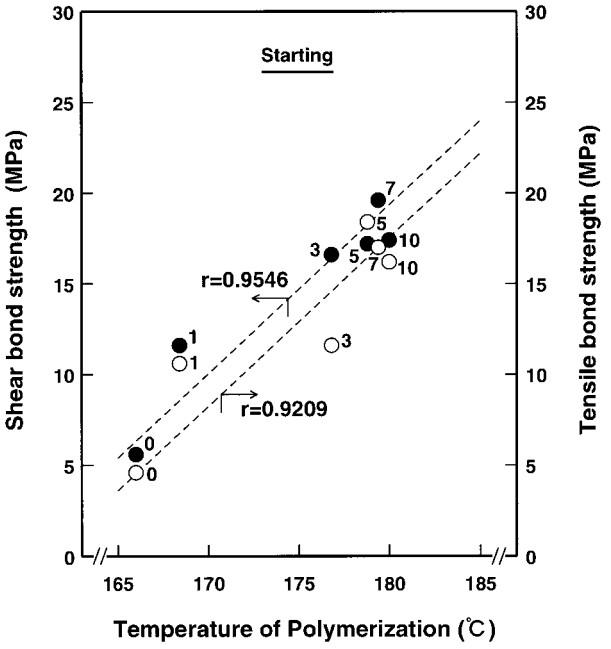

Figure 12 The correlation between the T_{max} of polymerization and the (○) tensile or (●) shear bond strength to the ground dentin, using the bonding resin without aging (starting). Small letters indicate the content of 4-AET in the bonding resins.

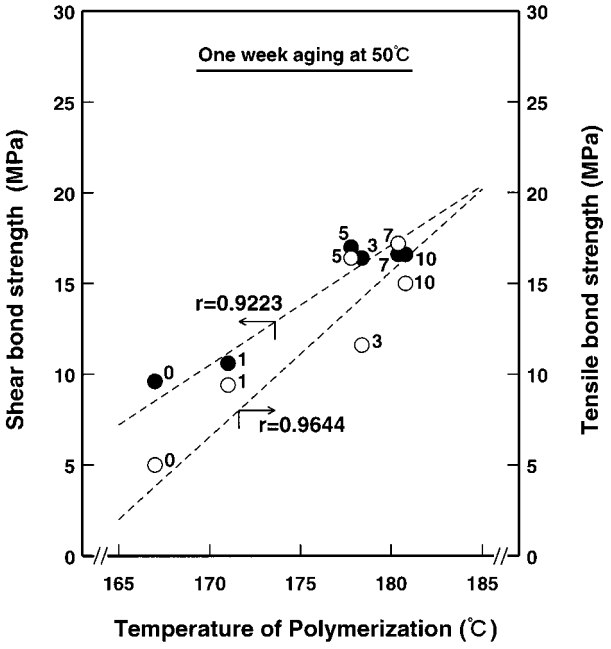

Figure 13 The correlation between the T_{max} of polymerization and the (○) tensile or (●) shear bond strength to the ground dentin, using the bonding resin aged artifically at 50°C for 1 week. Small letters indicate the content of 4-AET in the bonding resins.

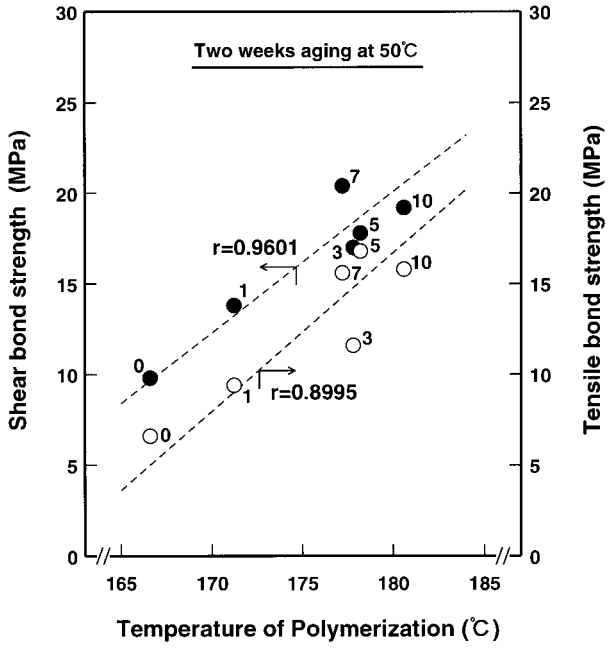

Figure 14 The correlation between the T_{max} of polymerization and the (○) tensile or (●) shear bond strength to the ground dentin, using the bonding resin aged artifically at 50°C for 2 weeks. Small letters indicate the content of 4-AET in the bonding resins.

to ground dentin, using the bonding resin aged artificially at 50°C over 2 weeks. The correlations are highly positive: r = 0.9209 (starting), r = 0.9644 (1 week), and r = 0.8995 (2 weeks) for the tensile bond strength and r = 0.9546 (starting), r = 0.9223 (1 week), and r = 0.9601 (2 weeks) for the shear bond strength (with a content of 0–10 wt % 4-AET in the bonding resin). The correlation between the T_{max} of the DSC data and the bond strength to the dentin was highly positive and we found that decreasing the reactivity of the bonding resin on the copolymerization of 4-AET resulted in increasing the tensile and shear bond strength to the dentin (with a content of 0–10 wt % 4-AET in the bonding resin).

Regarding the influence of polymerization on the bond strength of adhesive monomers to dentin discussed in previous articles,[11] Kasashima et al.[11] reported that the bonding of 4-vinylbenzoic acid (4-VBA) to etched dentin, using tri-*n*-butylborane (TBB)-initiated methyl methacrylate (MMA) (MMA–TBB) resin, indicated significantly higher values than did 3-VBA. The rate of copolymerization with MMA was lower in 4-VBA than that in 3-VBA and suggested that these results were attributed to the polymerization before the diffusion of enough monomers into the etched

dentin. The correlation between adhesion and polymerization of 3-VBA or 4-VBA showed tendencies to those observed in our present study, in spite of the different procedures, wherein the penetration and polymerization of the acidic monomer is achieved at the interface simultaneously (4-VBA) or independently (4-AET). Apart from the MMA–TBB resins, it was suggested that where the penetration of aqueous primers and the polymerization of the bonding resin would occur independently, both adhesion to the dentin and the polymerization of the bonding resin were affected by the inclusion of 4-AET.

Bonding Mechanism to Ground Dentin

To clarify the correlation between the adhesion and polymerization reactivity, it is very important to discuss the bonding mechanism of the 4-AET monomer to the ground dentin. In the SEM study, the 4-AET-bonding resin appeared to strongly adhere to the ground dentin [Fig. 7(b)], suggesting that the penetration or diffusion of 4-AET with HEMA was sufficiently achieved. Since strong acid-etching agents (pH 0.2–0.8) were not applied to the dentin in this study, decalcification of the dentinal surface was minimized. It was suggested that where an aqueous primer (pH 3.0) containing 4-AET was applied to the ground dentin the ionized divalent $—COO^-$ group of 4-AET led to sufficient chemical interaction with the calcium cation (Ca^{2+}) of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, in dentinal tissues. Photoinitiators *in situ* would facilitate photopolymerization at the dentin–resin interface, resulting in increased wettability of the bonding resin (which also contains 4-AET) to the dentin at the adhesive interface. The acrylic ester of 4-AET had a high reactivity of polymerization (Fig. 11) and was highly soluble in the water/HEMA primer.[9] We suggested that this feature of 4-AET provides an effective bonding performance to ground dentin based on its good penetration with HEMA into the dentin substrate.[23,24] HEMA is a key ingredient in dentin primers and can promote penetration into the dentin[4]; however, its polymerization reactivity is significantly low (Fig. 11). However, 4-AET indicates the highest polymerization reactivity and plays an important role in the copolymerization of the bonding resin composition (Fig. 11).

Also, it was suggested that 4-AET–HEMA copolymerization can reduce the internal stress during copolymerization. In view of those findings, we suggested that the increased bonding strength to the ground dentin was attributable to not only the increasing penetration or diffusion of 4-AET from an aqueous primer into the dentin substrate before polymerization, but also to the polymerization reactivity of the bonding resin with a decreased internal stress during copolymerization. To determine the chemical and physical proof for these findings, it is necessary to investigate further the scope for the bonding mechanism and the internal stress during the copolymerization of 4-AET in the bonding resin.

CONCLUSION

Conclusions drawn from the noteworthy aspects of this study are as follows:

1. Tensile and shear bond strengths to ground dentin were not significantly decreased at each level of 4-AET content, using a bonding resin aged artificially at 50°C over 2 weeks. The optimum 4-AET-concentration was found to be 5 wt %.
2. The correlation between the tensile and shear bond strength to ground dentin was positive: $r = 0.8517–0.9329$, where the bonding resin was artificially aged at 50°C over 2 weeks.
3. Increasing the content of 4-AET increases the T_{max} of the polymerization of bonding the resin in positive correlation: $r = 0.8580–0.8727$ over 2 weeks of aging.
4. Increasing the T_{max} of the polymerization of the bonding resin increased the bond strength to dentin (content: 0–10 wt % 4-AET in the bonding resin) with a highly positive correlation: $r = 0.8995–0.9644$ for tensile bond strength and $r = 0.9223–0.9601$ for shear bond strength.
5. The SEM micrograph showed that the bonding resin appeared to strongly adhere to the ground dentin without the formation of resin-tags in the dentinal tubules.
6. We suggested that the increased bonding strength to the ground dentin was attributable to the penetration or diffusion of 4-AET from an aqueous primer into the dentinal tissue before polymerization, together with the polymerization reactivity of the bonding resin and decreased internal stress during copolymerization.

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