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Effectiveness of pretreatment with phosphoric acid, sodium hypochlorite and sulfinic acid sodium salt on root canal dentin resin bonding

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ABSTRACT

Purpose: The purpose of this study was to evaluate the effect of pretreatment using phosphoric acid, sodium hypochlorite and sulfinic acid sodium salt on the bonding of one-step self-etching adhesives to root canal dentin.

Methods: Thirty-six single-rooted sound human premolars were randomly assigned into three groups before applying the one-step self-etching adhesive. These comprised a control group with no pretreatment, an NC group that received phosphoric acid and subsequent sodium hypochlorite gel pretreatments, and an NC + AC group that received an additional treatment with sulfinic acid sodium salt following the same pretreatment applied to the NC group. Microtensile bond strength measurements, bonding interface observations by scanning electron microscopy (SEM), elemental analyses by X-ray photoelectron spectroscopy (XPS) and degree of polymerization (DOP) analyses by Raman spectroscopy were subsequently performed.

Results: The bond strength was significantly higher in the NC + AC group than in the other two groups (Control: $P = 000.1$ and NC: $P = 0.004$). SEM observations showed that resin tags were present in the dentinal tubules in the NC and NC + AC groups. Compared to the control group, the adhesive resin layer had a lower DOP in the NC group, while the DOP for the NC + AC group was higher than that of the NC specimens.

Conclusions: Bonding to root canal dentin was improved by applying sulfinic acid sodium salt in addition to treatment with phosphoric acid followed by sodium hypochlorite. The DOP of the adhesive resin was reduced by sodium hypochlorite and subsequently restored by applying sulfinic acid sodium salt.

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1. Introduction

Since the 1990s, resin core build-up systems have been used with increasing frequency to restore pulpless teeth [1,2]. The major advantage of resin core materials is their elastic moduli, which are similar to that of dentin [1,2]. This similarity results in stress fields equivalent to those associated with natural teeth, leading to fewer incidences of root fracture and subsequent tooth extraction. This is in contrast to cast metal posts and core restorations that exhibit high stress concentrations at the post-dentin interfaces [1–3]. Some clinical studies have also shown that the survival rates of direct resin core restorations using prefabricated posts are significantly higher than those of cast metal cores [4]. However, post de-bonding has emerged as the most frequent failure mode of resin core build-up restorations in the clinical setting. Bonding to root canal dentin can be hampered by limited visibility during application of the bonding material, morphological variations of the dentin, unfavorable conditions with regard to the application of adhesive techniques [5–7], a high configuration factor inside the root canal [8,9] and insufficient irradiation [10,11].

The formation of a thick smear layer during preparation of the post space can also result in inadequate adhesion to the root canal [10]. This occurs because the acidic monomers in self-etching adhesive resins that are meant to condition the substrate are less effective in the presence of a thick smear layer, as this layer prevents sufficient contact of the resin with the root canal dentin

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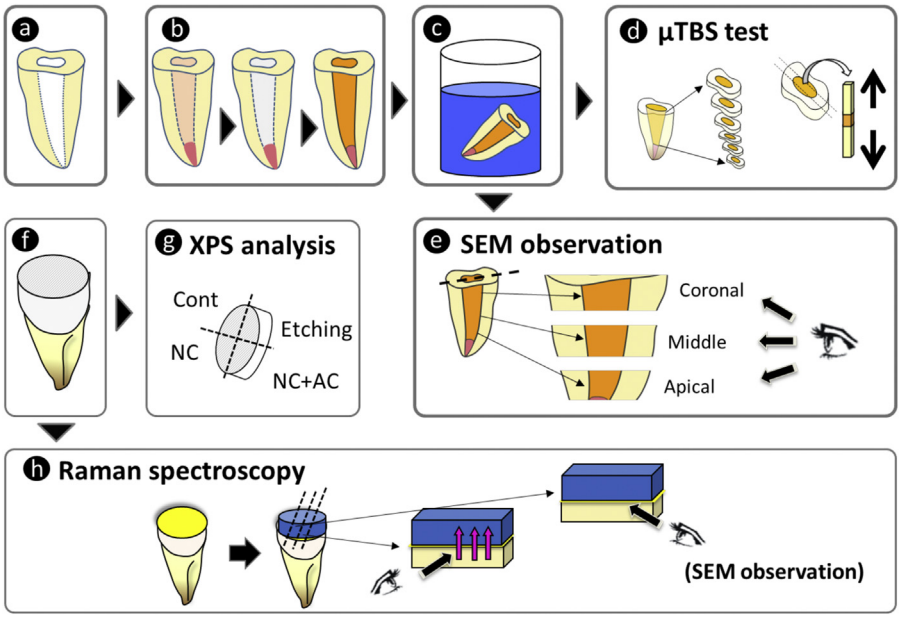

Fig. 1. Schematic illustration of the study design.
(a) Single canal human teeth were cut at the cement-enamel junction and the crown removed. (b) Root canal filling, preparation for post space, pre-treatment for adhesion, filling in post space and light cure. (c) 24-h water storage. (d) Sectioned perpendicular to the long axis into a series of 1-mm-thick slices under water cooling, with six slabs obtained from each tooth and each slice transversely sectioned through the middle part of the post space into approximately 1 × 1-mm-thick beams. Each beam subjected to μTBS testing. (e) Sectioned parallel to the long axis and adhesive interfaces observed using SEM. (f) Third molars mid-coronal dentin surfaces obtained and divided into four sections with each surface then treated. (g) Surfaces qualitatively analyzed by XPS. (h) Application of the one-step self-etching adhesive and aluminum bar on the dentin surface and sectioning parallel to the long axis. Subsequent analysis of one surface by Raman spectroscopy and the other by SEM.

[8,9]. The bonding effectiveness of mild and ultra-mild self-etching adhesives may also be significantly affected by the thickness of the smear layer [12–16], while the complete absence of a smear layer can improve the interactions between such adhesives and the dentin. Other studies have shown that certain single-step adhesive systems may produce lower bond strengths in conjunction with thicker smear layers, suggesting that the smear layer should be removed before applying such resins [12–16]. A phosphoric acidic conditioner can effectively dissolve and remove the smear layer, although collagen fibrils are exposed after this treatment. Incomplete penetration of the resin monomer into this collagen fibril layer could result in decreased resin-dentin adhesion. For this reason, the application of sodium hypochlorite (NaOCl; the so-called NaOCl-cleaning (NC) treatment) as a means of etching dentin while removing surface collagen fibrils was introduced in the early 1990s [17]. Some researchers have reported that the NC treatment results in higher bond strength when it is applied prior to the use of dual-cure resin cements [18–21]. Based on these results, it is possible that the same NC treatment could be helpful if employed before the application of mild one-step self-adhesives, although research into this topic has not yet been reported.

A drawback of sodium hypochlorite is that this compound decomposes to form sodium chlorite and oxygen after application to the dentin surface, following which the oxygen greatly inhibits polymerization of the resin [22,23]. This effect can be mitigated by using an antioxidant/reducing agent prior to the bonding procedure [23–28]. One possible reducing agent is sulfinic acid sodium salt, which is also commonly used as a polymerization catalyst. This chemical has been employed as part of a pretreatment step prior to the application of a 4-methacryloxyethyl trimellitate anhydride/methyl methacrylate-tri-*n*-butyl borane (4META/MMA-TBB) resin bonding system in conjunction with NaOCl-irrigated root canal dentin. However, there is little published information available concerning the effect of pretreatment with reducing agents on the adhesion of other new resin systems.

The purpose of the present study was to evaluate the effects of pretreatment using phosphoric acid, sodium hypochlorite and sulfinic acid sodium salt on the adhesion of a one-step self-etching adhesive to root canal dentin. The null hypotheses were that NC treatment in conjunction with the application of sulfinic acid sodium salt does not affect the bond strength between root canal dentin and one-step self-adhesive, and that NC treatment and sulfinic acid sodium salt do not affect the degree of polymerization (DOP) of one-step self-etching adhesives.

2. Materials and methods

2.1. Bonding effectiveness between post-space dentin and dual-cure resin composite

2.1.1. Tooth preparation

Thirty-six single-rooted sound human premolars were used in the present study. All teeth were extracted due to periodontal or orthodontic reasons and stored in Hank's balanced salt solution (HBSS) at 4 °C. The experimental protocol was approved by the Ethics Committee of the Osaka University Faculty of Dentistry (H26-E6). The crown of each tooth was cut at the cement-enamel junction using a low-speed diamond wheel saw with water cooling (Fig. 1a). Root canals were endodontically instrumented by means of a K-file (MANI, Tochigi, Japan) after which each canal was shaped with a size 80 K-file to the working length and obturated by lateral condensation using gutta-percha points and non-eugenol sealer (Canals N, Showa Yakuhin Kako, Tokyo, Japan). The teeth were then stored in distilled water at 37 °C for 24 h. The root canals were enlarged with low-speed preparation drills (Tokuyama FR drill, Tokuyama Dental, Tokyo, Japan) to a working length of 10 mm from the cement-enamel junction.

2.1.2. Dentin pre-treatment and resin composite filling

All specimens were randomly assigned into three experimental groups (n = 12), followed by the treatments described below (see

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Table 1. Chemical compositions and applications of the materials tested.

		Trade name	Lot	Manufacturer	Composition	Application
Pretreatment	Phosphoric acid	K-Etchant gel	00525A	Kuraray Noritake Dental	40% phosphoric acid, water, thickener, coloring agent	1. Etch for 15 s. 2. Rinse for 15 s. 3. Air dry for 10 s.
	Sodium hypochlorite	AD gel	001023	Kuraray Noritake Dental	10–15% sodium hypochlorite, thickener	1. Apply for 60 s. 2. Rinse for 15 s. 3. Air dry for 10 s.
	Sulfinic acid sodium salt	Accel	FV1	Sun Medical	p-toluenesulfinic acid sodium salt, ethanol, water	1. Apply using a rubbing motion for 15 s. 2. Air dry for 10 s.
Adhesive		Clearfil Bond SE ONE	CE001	Kuraray Noritake Dental	10-MDP, Bis-GMA, HEMA, hydrophobic aliphatic methacrylate, colloidal silica, sodium fluoride, CQ, accelerators, initiators, water	1. Apply bonding and leave for 10 s. 2. Air blow gently for 5 s. 3. Light cure for 20 s.
Composite		Clearfil DC core Automix ONE	270104	Kuraray Noritake Dental	Paste A: Bis-GMA, hydrophobic aliphatic dimethacrylate, hydrophilic aliphatic dimethacrylate, hydrophobic aromatic dimethacrylate, filler, dl-CQ, initiators, pigments Paste B: TEGDMA, hydrophilic aliphatic dimethacrylate, hydrophobic aromatic dimethacrylate, filler, accelerators	1. Filling of the entire cavity. 2. Light cure for 40 s.

Bis-GMA: bisphenol A-glycidyl dimethacrylate, CQ: camphorquinone (photo-initiator), HEMA: 2-hydroxyethyl methacrylate, 10-MDP: 10 methacryloyloxydecyl dihydrogen phosphate, TEGDMA: triethyleneglycol dimethacrylate.

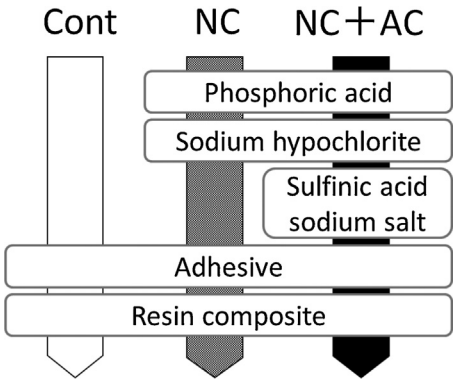

Fig. 2. Experimental groups and treatments.
Cont: Before applying the one-step self-etching adhesive, with no pretreatment of the dentin surface. NC: The dentin surface was etched for 15 s with 37% phosphoric acid, rinsed and air dried. Subsequently, a 10% NaOCl gel was applied for 60 s, rinsed and air dried. NC + AC: The same pretreatment protocol as for the NC group, after which sulfinic acid sodium salt was applied for 15 s with air drying.

Table 1 and Figs. 1a–c and 2). In the case of the control (Cont) group, a photocure adhesive (Clearfil Bond SE ONE, Kuraray Noritake Dental, Tokyo, Japan) and a dual cure resin composite (Clearfil DC core Automix ONE, Kuraray Noritake Dental) were used according to the manufacturers' instructions. After applying the adhesive, each sample was cured by irradiation for 20 s with a cordless light emitting diode (SATELEC Mini LED 3, Acteon, Merignac, France) having a maximum power density of 2200 mW/cm^2. To avoid bubble entrapment, the composite core material was injected carefully without removing the tip from the material and subsequently light-cured for 40 s. According to the manufacturer, this time span is sufficient to completely cure the resin composite.

In the case of the NC group, the dentin surface was etched for 15 s using 37% phosphoric acid (K-Etchant gel, Kuraray Noritake Dental, Tokyo, Japan) and then rinsed, following which a 10% NaOCl gel (AD gel, Kuraray Noritake Dental, Tokyo, Japan) was applied for 60 s and then removed by rinsing. Finally, the adhesive and resin composite were applied in the same manner as employed for the Cont group. The NC + AC group followed the same pretreatment protocol as the NC group. In addition, sulfinic acid sodium salt (Accel, Sun Medical, Moriyama, Japan) was applied for 15 s and air dried. The adhesive and the composite were then applied as described in the details for the Cont group (Fig. 1b).

2.1.3. Micro-tensile bond strength (μTBS) test

All specimens were stored in water for 24 h at 37 °C (Fig. 1c). Nine specimens from each group were sectioned perpendicular to the long axis into a series of 1 mm thick slices, while applying water cooling. Each of these slices was then transversely sectioned through the middle part of the post space into 1 × 1 mm thick beams. These beams were subsequently attached to a jig using cyanoacrylate glue (Dentsply Sankin, Tokyo, Japan) and subjected to tensile force measurement at a crosshead speed of 1 mm/min using a table top apparatus (EZ Test, Shimadzu, Kyoto, Japan) (Fig. 1d). The resulting bond strengths, initially in units of kg-force/mm^2, were converted to MPa. Samples that exhibited pre-testing failure (ptf) are reported herein as having a bond strength of 0 MPa (Fig. 1d).

2.1.4. Statistical analyses

The μTBS data were analyzed using two-way ANOVA and Scheffé's method, and differences were considered to be statistically significant at a level of 5%.

2.1.5. SEM observations

Three specimens from each group were sectioned down the middle, parallel to the long axis. The cutting planes were etched for 15 s using 37% phosphoric acid (K-Etchant gel, Kuraray Noritake Dental, Tokyo, Japan) and then rinsed, after which a 10% NaOCl gel (AD gel, Kuraray Noritake Dental, Tokyo, Japan) was applied for 60 s, then removed by rinsing. The specimens were fixed by overnight immersion in an 8% glutaraldehyde solution followed by immersion in an osmic acid fixative for 2 h. Each sample was subsequently dehydrated by immersion in a graded ethanol series and then freeze dried in a graded *t*-butyl alcohol series. Finally, the specimens were coated with evaporated gold and the post space dentin-resin composite surfaces were observed by scanning electron microscopy (SEM; JSM-6390, JEOL, Tokyo, Japan) at a magnification of ×1000 (Fig. 1e).

2.2. Surface analysis

2.2.1. Tooth preparation

Three extracted human molars free of caries that had been stored in HBSS for less than 6 months were employed in these trials. Mid-coronal dentin surfaces were obtained by removing the occlusal third of the molar crowns using a low-speed diamond saw under water cooling and a standard smear layer was prepared with #600 grit SiC paper (Fig. 1f). The dentin surface was divided into

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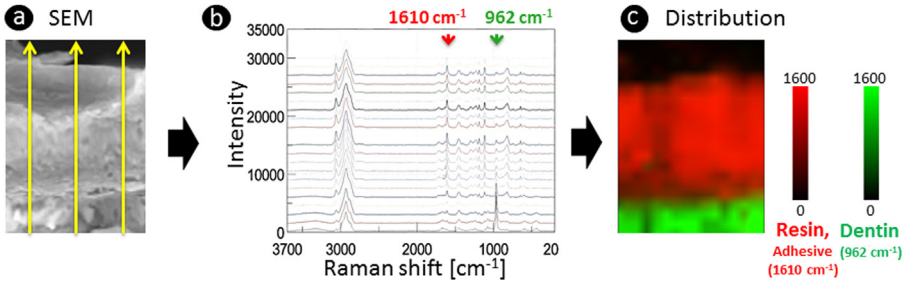

Fig. 3. Distribution maps of the resin and dentin.
(a) The region to be assessed by Raman spectroscopy is determined from SEM images. (b) The Raman spectrum. (c) The resin and dentin distribution maps. The phosphate peak intensity at 962 cm^{-1}, which is characteristic of dentin, is indicated by the green bar. The C=C peak intensity at 1610 cm^{-1}, which is characteristic of the adhesive resin, is indicated by the red bar.

four sections and each surface was subjected to a different treatment. These included no treatment (the Cont group), etching of the dentin surface for 15 s using 37% phosphoric acid (K-Etchant gel, Kuraray Noritake Dental, Tokyo, Japan), followed by rinsing and air drying (the Etching group), etching of the dentin surface using phosphoric acid, followed by rinsing, air drying and the application of a 10% NaOCl gel (AD gel, Kuraray Noritake Dental, Tokyo, Japan) for 60 s (the NC group), and etching of the dentin surface using phosphoric acid, followed by the application of a NaOCl gel and sulfinic acid sodium salt (Accel, Sun Medical, Tokyo, Japan) for 15 s, with subsequent air drying (the NC + AC group).

2.2.2. Elemental analysis of the dentin surface by XPS

The tooth surfaces were analyzed by X-ray photoelectron spectroscopy (XPS; AXIS 165x, Shimadzu, Kyoto, Japan) (Fig. 1g). The XPS analysis conditions included a pressure of 9×10^{-6} Pa, an Al Kα X-ray source, a potential of 15 kV, a current of 12 mA, a wide scanning interval of 1 eV and a sampling time of 100 s (Fig. 1g).

2.2.3. DOP analysis by Raman spectroscopy

Nine dentin surfaces were prepared using the same procedure as described in Section 2.1 and randomly divided into three groups. These surfaces were then treated using the procedure outlined in Section 2.1. The adhesive was applied to the dentin surfaces, following which an aluminum bar was placed on the adhesive surface and light-cured for 20 s. The specimens were subsequently sectioned parallel to the long axis to generate two sample surfaces, one of which was analyzed by Raman spectroscopy (NRS-5100, Nihon Bunko, Tokyo, Japan) (n = 3), while the other was observed using SEM (n = 3). The Raman spectroscopy conditions comprised an exposure time of 5 s and a laser power at the specimen of 5.5 mW with an excitation wavelength of 532 nm. Data were acquired over the spectral region from 200 to 3700 cm^{-1}. The points on the sample surfaces assessed by Raman spectroscopy were determined by SEM examinations.

A Raman spectrum was collected at each of 25 points at 1 μm intervals along the dentine-adhesive interface region, using a computer-controlled motorized x–y–z stage. Each assay was repeated 15 times, for a total of $25 \times 15 = 375$ spectra for each specimen (Fig. 1h and 3). The micro-Raman spectrum of mineralized dentin has been found to exhibit a band associated with PO_4^{3-} ions at 962 cm^{-1}, while the adhesive resin generates a peak associated with phenyl C=C bonds at 1610 cm^{-1}, and the distributions of the dentin and resin were mapped using these peaks. The Raman spectra of uncured adhesives were also acquired to identify peaks related to the raw and the reacted adhesive, so as to calculate the extents of conversion. The phenyl C=C peak at 1610 cm^{-1} was found not to change during polymerization, and so was selected as a reference peak, while the vinyl C=C peak at 1640 cm^{-1} was employed to monitor the extent of the polymerization reaction (Fig. 4). The DOP for each sample was calculated using the ratio between these peak areas.

3. Results

3.1. Bonding effectiveness between post-space dentin and dual cure resin composite

Two-way repeated-measures ANOVA demonstrated the significant effect of pretreatment ($P = 0.001$, $F = 7.03$), while the Scheffé's multiple comparison test showed that the bond strength was significantly higher in the NC + AC group than in the other two groups (Cont: $P = 0.001$ and NC: $P = 0.004$; Table 2 and Fig. 5). The μTBS values for surface 1, which was at the edge of the coronal side, were highest in all groups, and these values gradually decreased on moving from the coronal to the apical side of the root canal. Although two-way ANOVA did not show any significant effect of the root region ($P = 0.61$, $F = 2.17$), the incidence of ptf was greater on the apical side of the root canal in all groups. SEM observations revealed that resin tags were not present in the dentinal tubules in the Cont group. However, in the case of the NC and NC + AC groups, resin tags were observed and the length of these tabs gradually decreased on going from the coronal to the apical side (Fig. 6). No correlations were identified between the individual factors (that is, between pretreatments and root regions) ($P = 0.907$).

3.2. Surface analysis

Wide-scan XPS analyses were performed to determine the elements present on the dentin surfaces (Fig. 7). The Cont group showed the presence of C, N, O, P and Ca, while P and Ca were not detected in the Etching group. The NC group surfaces showed the same elements as those of the Cont group, along with Na and Cl, while the NC + AC group was found to have Na and S in addition to the same elements as determined for the Cont group. A distribution map was generated for the Cont group using the Raman spectral data to assess the coverage of the adhesive resin and dentin (Fig. 8d). In contrast, SEM images of the NC and NC + AC groups in the vicinities of the resin tags (Fig. 8b and c) and the distribution maps for these same groups found indistinct boundaries between the adhesive and resin (Fig. 8e and f). Compared to the Cont group, the adhesive resin layers in the NC group evidently had a lower DOP (Fig. 8g and h). In addition, the DOP values for the samples in the NC + AC group were higher than those for the NC group (Fig. 8h and i) but slightly lower than the values for the Cont group (Fig. 8g and i).

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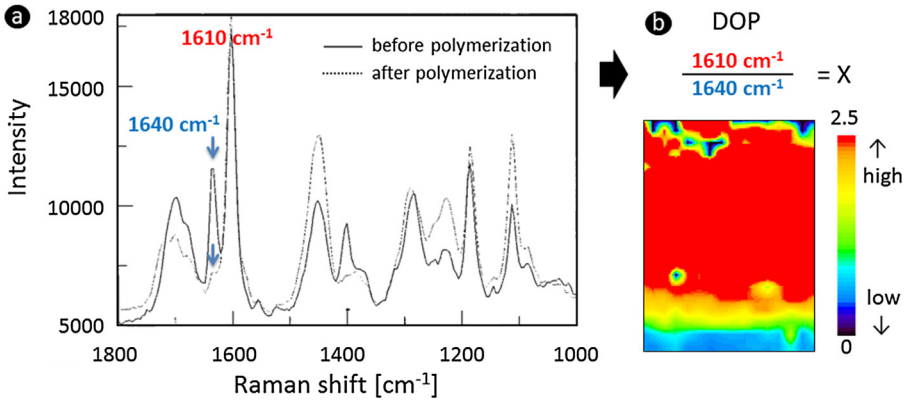

Fig. 4. Degree of polymerization mapping of the adhesive resin.
(a) Peaks before and after polymerization of the adhesive resin. The aromatic carbon-carbon double bonds represented by the 1610 cm^{-1} peak are unchanged before and after polymerization. The aliphatic carbon-carbon double bonds at 1640 cm^{-1} are reduced after polymerization. (b) Mapping of the degree of polymerization.

Table 2. Microtensile bond strength values (MPa).

	Coronal 1	2	3	4	5	Apical 6
Cont[b]	12.8 (11.2)	8.1 (8.0)	6.4 (5.1)	9.7 (12.3)	3.8 (4.2)	7.9 (8.2)
ptf	0	1	2	1	1	1
NC[b]	12.3 (8.3)	10.3 (4.1)	7.7 (6.6)	7.7 (8.2)	7.0 (7.9)	6.1 (7.3)
ptf	0	0	1	3	2	2
NC + AC[a]	16.3 (14.0)	16.3 (9.6)	14.6 (10.2)	14.3 (9.5)	14.9 (11.0)	9.7 (6.1)
ptf	0	0	0	0	1	1

Numbers in parentheses are one standard deviation. Identical superscript upper letters indicate that the values are not statistically different ($P > 0.05$).

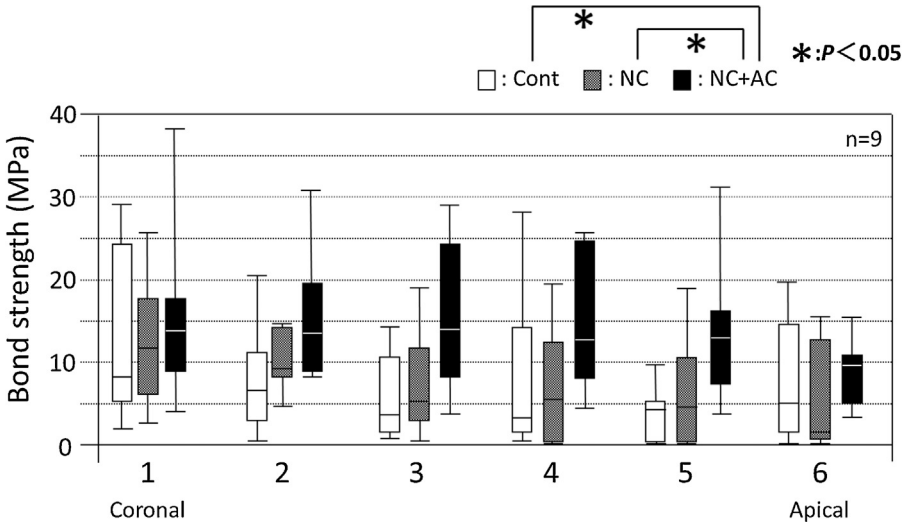

Fig. 5. Micro-tensile bond strength data.
Box plot. From above: maximum, 75th percentile, median, 25th percentile, minimum.
The edge of the coronal side is labeled as no. 1, while the edge of the apical side is indicated by no. 6.

4. Discussion

The bond strengths of the specimens in the NC + AC group were significantly higher than those of the other two groups, while there was no significant difference between the Cont and NC groups. Therefore, the first null hypothesis, that NC treatment and sulfinic acid sodium salt application do not affect the bond strength between root canal dentin and one-step self-adhesives, was rejected in the case of using sulfinic acid sodium salt followed by NC treatment but accepted for NC treatment alone. Surprisingly, there were no significant differences between the locations (from coronal to apical) within each condition group in this work. This is in contrast to previous reports that the location associated with the root canal post affects the μTBS value [29,30]. This discrepancy can be explained by considering that the adhesive resin used in this research polymerizes beginning at the site at which it contacts the core resin. Consequently, the adhesive can undergo polymerization even in locations that receive insufficient irradiation. It should also be noted that the pretreatment of the adhesive surface in this work was different from that applied during previous studies (such as

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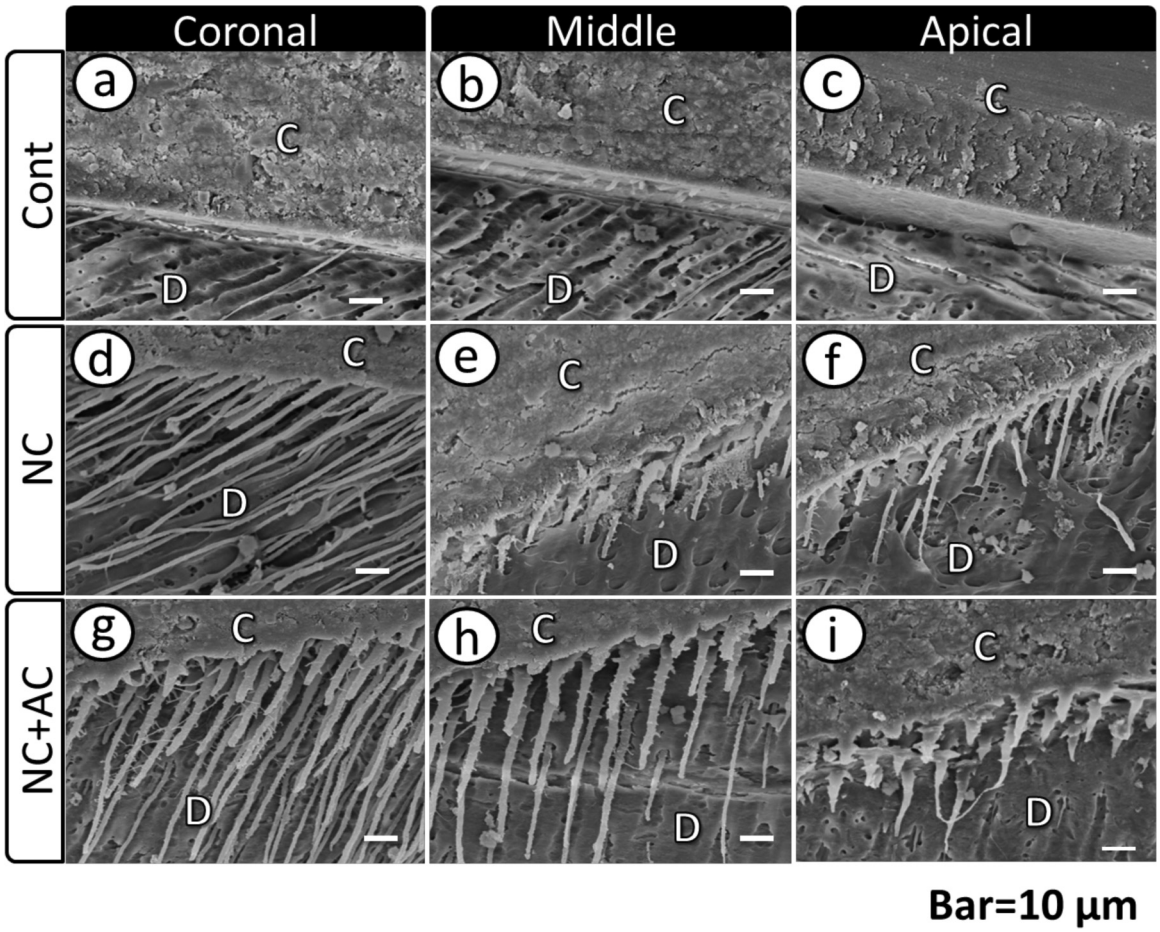

Fig. 6. SEM photographs of adhesive interfaces.
Cont: Resin tags are not observed in the dentin tubules. NC: (d) A resin tag with a length over 50 μm is observed in a dentin tubule. (f) A resin tag with a length over 10 μm is observed in a dentin tubule. NC+AC: (g) A resin tag with a length over 50 μm is observed, (h) A 10 to 50 μm length resin tag is observed, (i) A resin tag with a length over 10 μm is observed. C: Composite, D: Dentin.

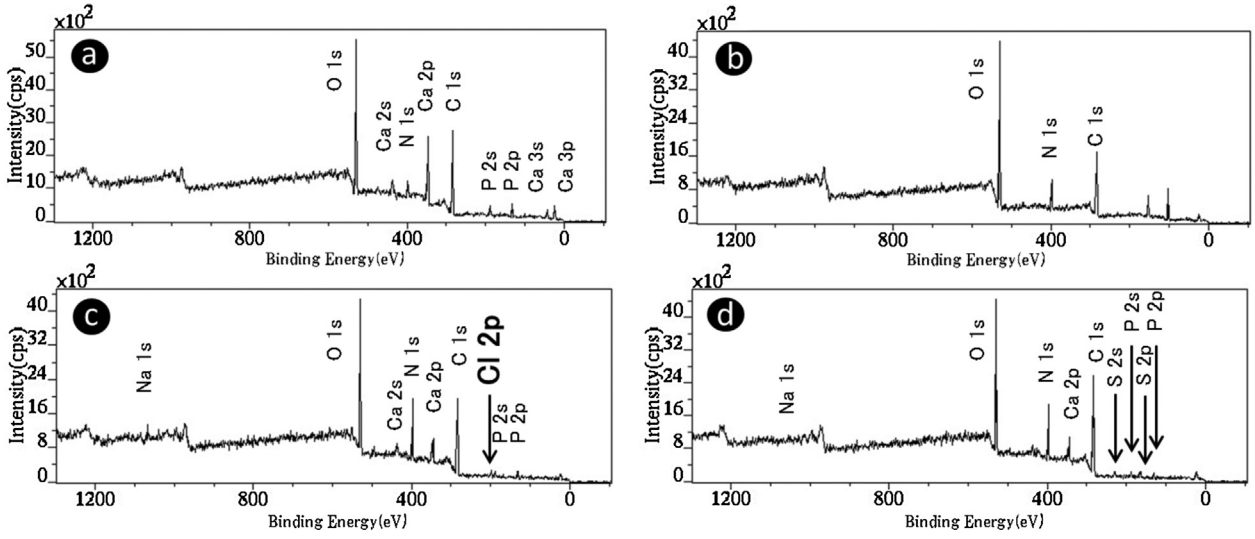

Fig. 7. Wide-scan XPS data.
(a) Cont: C, N, O, P and Ca are observed. (b) Etching: C, N and O are observed. (c) NC: C, N, O, Na, P, Cl and Ca are observed. (d) NC + AC: C, N, O, Na, P, Ca and S are observed.

those involving the use of EDTA). SEM observations also demonstrated that the adhesive interface was markedly different between the Cont and NC groups. It is known that applying a NaOCl gel after phosphoric acid treatment can remove the smear layer, as well as exposed collagen fibrils [18–21]. As a result, resin tags were observed in the NC and NC + AC groups (Fig. 6). In the case of the NC + AC group, ethanol contained in the Accel evidently dried the root canal, such that resin tags were observed in the collateral dentin

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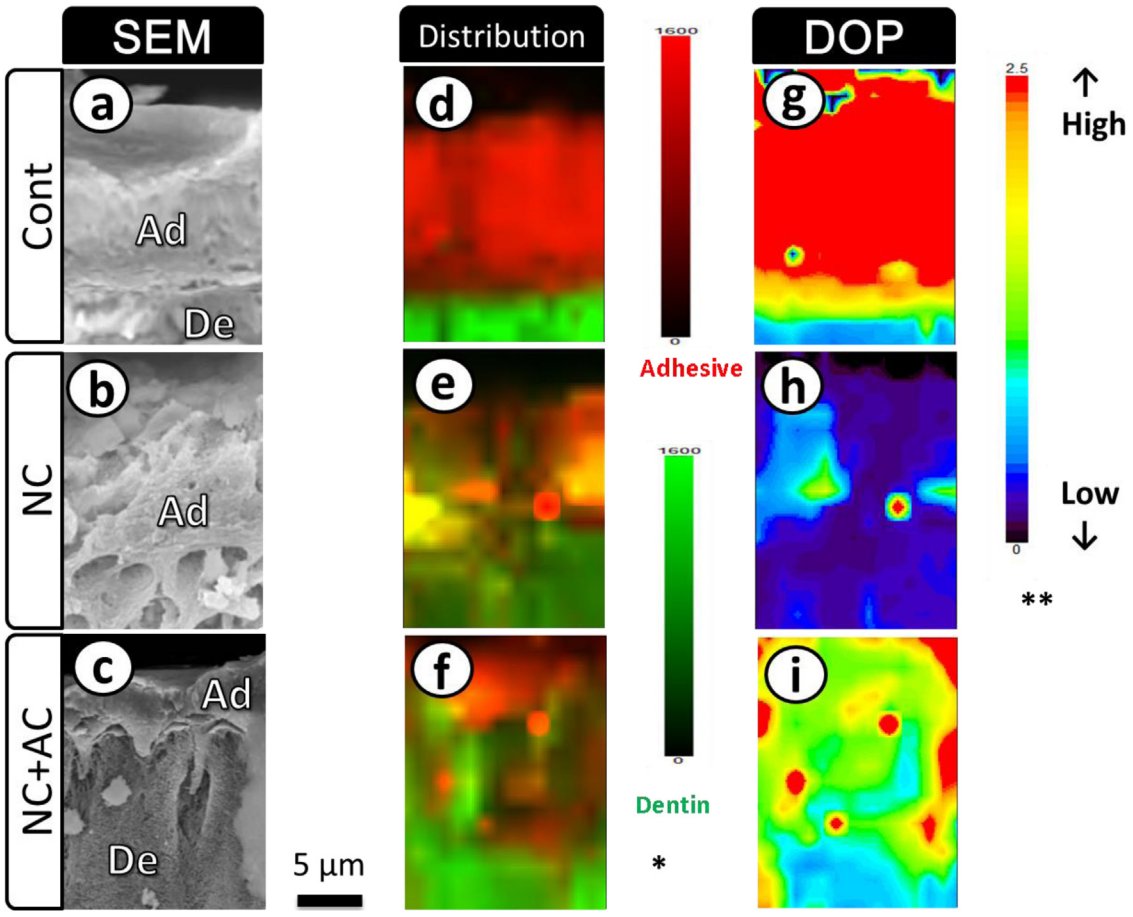

Fig. 8. Results of Raman analysis.
Each SEM image and Raman analysis are from a single tooth.
(a) An SEM photomicrograph of the Cont sample. Resin tags are not observed in the dentin tubules. (b) An SEM photomicrograph of the NC sample. Resin tags are not observed in the dentin tubules. (c) An SEM photomicrograph of the NC + AC sample. Resin tags are not observed in the dentin tubules. *Red = a greater amount of adhesive resin was present, green = a greater amount of dentin was present. (d) Distribution map of the Cont sample, in which the adhesive resin and dentin are well defined. (e) Distribution map of the NC sample, in which the boundary between adhesive and resin is unclear. (f) Distribution map of the NC + AC sample, in which the boundary between adhesive and resin is unclear. **Red = higher degree of polymerization, blue = lower degree of polymerization. (g) Degree of polymerization of the Cont sample, in which the adhesive resin layer exhibits a high degree of polymerization. (h) Degree of polymerization of the NC sample, in which the adhesive resin layer exhibits a low degree of polymerization. (i) Degree of polymerization of the NC + AC sample, in which the adhesive resin layer exhibits a comparatively high degree of polymerization. Ad: adhesive resin, De: dentin.

tubules. Moreover, sulfinic acid sodium salt application following NC treatment improved the bond strength between the root canal dentin and the adhesive. This result is in agreement with some previous studies [18–21]. Specifically, Taniguchi et al. reported that applying Accel improved the bond strength of self-etching adhesives to NaOCl-treated dentin [27], while Prasansuttiporn et al. found that applying Accel or rosmarinic acid improved the bond strength between self-etching adhesives and NaOCl-treated dentin [28]. These authors proposed that the reducing activity of the sulfinic acid sodium salt reversed the residual oxidizing effect on the NaOCl-treated dentin, which in turn had a positive effect on polymerization of the resin monomer [27,28]. However, it is not clear whether the DOP of the monomer was actually increased in these prior studies.

The second purpose of this study was to evaluate the DOP of one-step self-etching adhesives on dentin treated with NC and sulfinic acid sodium salt. XPS analyses were used to determine the elements present on the dentin surfaces with high sensitivity, while Raman spectroscopy was employed to examine the DOP of the adhesive resin. The data confirmed that Na and Cl remained on the dentin surface after NC treatment, and that the DOP was decreased as a result, although the DOP was recovered in the NC + AC group. Therefore, the second null hypothesis, that NC treatment followed by sulfinic acid sodium salt application does not affect the DOP of one-step self-etching adhesives, was rejected.

XPS analyses did not show the presence of P and Ca (both of which are inorganic components of dentin) after treatment with phosphoric acid. However, both elements were found following NC treatment in conjunction with phosphoric acid because organic material was removed. In addition, Na and Cl (which are constituents of sodium hypochlorite) were detected despite copious rinsing with water after the NC treatment. Sodium hypochlorite is more likely to remain in the root canal dentin because the treated surface has a complex morphology involving deep internal cavities. Therefore, rinsing tends to be insufficient for such surfaces as compared to smooth surfaces. Narrow scan XPS analyses found peaks related to each component, but shifts in these peaks after the various treatments or due to differences in the chemical bonding state could not be identified.

Mapping using Raman spectral analysis clearly demonstrated that the DOP of the adhesive resin was inhibited by the application of sodium hypochlorite and subsequently restored by applying sulfinic acid sodium salt. Prior work has confirmed that the spectra of adhesive resin and resin composite are very similar, and thus it is difficult to distinguish the two. Therefore, when preparing specimens for Raman spectral analysis in this study, an aluminum

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bar was attached to the dentin instead of the composite resin. However, even using aluminum, it was not possible to accurately determine the location of the interface solely by a single linear measurement, because resin tags were formed at the adhesion interface. In addition, the interface had a complex morphology in the case of the NC and NC + AC groups. Adequate information could be obtained by performing repeated linear measurements with a 1 μm shift between each measurement (Fig. 8). Additionally, the distributions of the adhesive resin and dentin could be visually examined by mapping. By comparing the distributions of the adhesive resin and dentin based on mapping of the peak at 1640 cm^{-1}, it was possible to determine the DOP of the adhesive layer based on multiple measurement points.

The bond strength of the NC treatment group did not improve in this study. Based on the results of the surface elemental analysis and the DOP measurements, it appears that even though the smear layer was removed (as was also the case for the NC + AC treatment group), the residual sodium hypochlorite inhibited the polymerization of the adhesive resin by acting as an oxidizing agent, such that the adhesive layer became weaker. In contrast, although the DOP of the adhesive layer in the NC group was low, the bond strength did not decrease compared to the Cont group. This result is believed to have occurred because the mechanical interactions were improved by the formation of resin tags after the removal of the smear layer and collagen (Fig. 6).

New adhesive systems tend to be promoted as reducing the number of steps required, and have shown success rates similar to those of composite resin restoration in the crown area [31]. However, the extent of adhesion between root canal dentin and resin composites may be inhibited for many reasons, such as a high C-factor and the difficulty in reaching the treatment area with instruments, such that it can be challenging to obtain suitable adhesion compared to the adhesion between coronal dentin and resin composites [29,30]. In addition, XPS and Raman spectral analysis provide evidence that sodium hypochlorite remains on the adherent surface and lowers the DOP of the resin. However, the present study demonstrates a method consisting of the application of a phosphoric acid conditioner together with a NaOCl gel to remove the smear layer and expose collagen fibrils, along with the application of a sulfinic acid sodium salt solution followed by NC treatment to prevent polymerization inhibition due to residual sodium hypochlorite. This series of treatments effectively improves adhesion to root canal dentin. Applying sulfinic acid sodium salt in addition to phosphoric acid and sodium hypochlorite treatments was also expected to improve the durability of resin-dentin specimens. The results of long-term durability tests from trials using phosphoric acid, sodium hypochlorite and sulfinic acid sodium salt during coronal flat dentin-resin bonding have been reported in a prior publication [32]. However, further research is required to confirm long-term durability in conjunction with root canal dentin.

5. Conclusion

This work demonstrated that initial adhesion to root canal dentin was improved by applying sulfinic acid sodium salt in addition to phosphoric acid and sodium hypochlorite treatments when using a mild one-step adhesive system. The data also confirm that both Na and Cl remain on the dentin surfaces following treatment with sodium hypochlorite, even after rinsing with water. The DOP of the adhesive resin is inhibited by treatment with sodium hypochlorite and restored by applying sulfinic acid sodium salt.

Conflicts of interest

None.

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