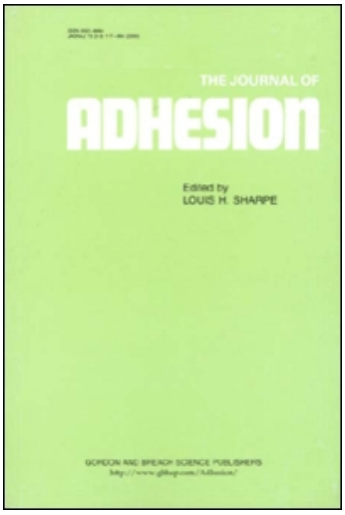

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I. Stangel[a]; C. Young[a]; E. Sacher[b]; S. Hanley[c]
[a] Faculty of Dentistry, McGill University, Quebec, Canada [b] Department of Engineering Physics, Ecole Polytechnique, Quebec, Canada [c] McGill University, Pulp and Paper Institute, Quebec, Canada

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The Effect of Conditioning on Adhesion to Human Dentin*

I. STANGEL** AND C. YOUNG

McGill University, Faculty of Dentistry, 740 Doctor Penfield, Montreal, Quebec H3A 1A4, Canada

E. SACHER

Ecole Polytechnique, Department of Engineering Physics, Montreal, Quebec, Canada

S. HANLEY

McGill University, Pulp and Paper Institute, Montreal, Quebec, Canada

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The effect of conditioning dentin was investigated using ethyleneglycol bis(aminoethylether) tetraacetic acid (EGTA) and three proprietary agents containing ethylenediamine tetraacetic acid (EDTA), maleic acid and dipentaerythritol pentaacrylate phsophoric acid ester (PENTA). Ground dentin was treated with EGTA or one of the three proprietary agents. After adhering composite resin to treated surfaces, the shear bond strength (SBS) was determined with and without thermal stress. Scanning electron and atomic force microscopies were used to assess morphological effects of each of the agents, while low resolution X-ray photoelectron spectroscopy (XPS) was employed to evaluate elemental changes due to treatment. Mean bond strength was greatest for the PENTA-conditioned surfaces. EDTA and maleic acid demineralized the dentin surface while the agent containing PENTA produced an adherent surface film. The XPS survey showed a reduction in Ca and an increase in N for agents containing EGTA, EDTA and maleic acid, while a simultaneous reduction in both these species was observed for PENTA. EGTA did not improve adhesion for systems which were based on smear layer removal and substrate demineralization. For the PENTA-based system, which relied on the development of a molecular overlayer, EGTA degraded bond strength.

KEY WORDS dentin; bonding; adhesion; interface; bond strength; scanning electron microscopy; atomic force microscopy; conditioning; X-ray photoelectron spectroscopy (XPS).

INTRODUCTION

Human dentin is a multiphasic substrate consisting of 69% (w/w) polycrystalline calcium hydroxyapatite (HA), 18% proteins (primarily in the form of type I collagen) and 13% water. Structurally, it consists of a solid (circumpulpal) phase

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**Corresponding author.

surrounding a network of tubules containing organic cell processes. The primary constituent of the solid phase consists of mineral crystals deposited between, and in association with, a network of collagen fibers. This region is termed intertubular dentin. A more highly mineralized sheath largely devoid of collagen (peritubular dentin) immediately surrounds the tubules.

Adhesion to dentin requires surface conditioning followed by the interpositioning of an adhesion promoter, a material capable of bonding to both the dentin and a resin overlayer. Commercial adhesive systems consist of conditioners and primers applied separately or in combination. Conditioning agents structurally alter cut dentin to optimize the surface for chemical adhesion or micromechanical bonding. The latter can result from resin infiltration into decalcified intertubular dentin[1] or from penetration of tubules by resin tags after removal of the smear layer[2] (the superficial, adherent layer created by the cutting of dentin). Chemical adhesion can occur *via* hydrogen bonding, complexation or covalent bonding.[3,4]

For certain proprietary adhesive systems, smear layer removal followed by surface demineralization are important precursors for establishing bonds to dentin.[1,5,6,7,8] The primary effect of these actions is to expose collagen for either micromechanical or chemical interaction, although tubular tags also arise. Thus, for these materials, the use of agents that enhance demineralization and the availability of collagen would be useful for propagating good adhesion. Acids and chelating agents have been used for this purpose.[9,10]

Ethylenediamine tetraacetic acid (EDTA), buffered to a pH of 7.4, has been successfully used as a conditioner in a dentin adhesive system containing the hydrophilic monomer 2-hydroxyethyl methacrylate (HEMA).[11] We were interested in employing a more powerful chelating agent, ethyleneglycol bis)aminoethylether) tetraacetic acid (EGTA), believing it would be more effective in exposing collagen for either mechanical or chemical interaction with adhesive monomers. Here, we evaluate EGTA as a dentin conditioner across three HEMA-containing adhesive systems. Its effect on adhesion is assessed by bond strength measurements and surface analysis, both of which are contrasted against proprietary materials.

EXPERIMENTAL

Materials and Methods

The occlusal enamel of 240 extracted human teeth stored in Sorenson's buffer was removed with a rotating diamond blade using a copious water spray. Dentin surfaces were thus exposed as close to 90 degrees to the mid-axis of the tooth and the dentinoenamel junction as possible. The sectioned teeth were mounted in PVC rings using polymethylmethacrylate so that the dentin surface was exposed 0.5 mm above the edge of the ring. The mounted teeth were initially ground using 600-grit silicon carbide paper in a Buehler Metaserv Grinder (Buehler LTD, U.K.) at 150 rpm and 15 psi using a water coolant. The surfaces were then ground a second time using 1200-grit paper at 150 rpm and 5 psi, one minute clockwise and one minute counter-clockwise. All samples were screened for the presence of a uniformly reflective, smooth, flat surface, and the absence of enamel, caries and

perforated pulp chambers. This process yielded 216 samples for the experiment. Samples were returned to the water bath after the screening.

Teeth were randomly assigned to three groups based on one of three proprietary HEMA-based adhesive systems. These included Gluma (Bayer, Dormagen, Germany), Scotchbond 2® (SB2), (3M, St. Paul, MN, USA) and Prisma Universal Bond 2® (PUB2), (L.D. Caulk, Milford, DE, USA). Group sizes were 71, 74 and 71, respectively. Each of these was further divided into two groups, one being conditioned with EGTA and the other with the proprietary agent provided in the systems. A 0.5 M solution of EGTA was prepared by dissolving crystals in sodium hydroxide and adjusting the pH to 7.2 with hydrochloric acid. Two of the proprietary agents had a conditioner and adhesion promoter in solution. (For convenience, the term "conditioner" will be used to describe either single or dual component agents). Half of the specimens received no further treatment while the other half was submitted to a thermal stress test prior to shear bond testing. The major components by application step of each proprietary system are listed in Table I. The concentrations of the acid components of each of the systems are 0.5 M for EDTA, 0.18 M for maleic acid and 0.10 M for PENTA.

Teeth were assigned numbers and were randomly selected for preparation according to a schedule generated from a random numbers table.[12] The surface of each sample was dried with a gentle stream of air and treated with either EGTA or the proprietary conditioner of each of the adhesive systems. Subsequent components of the proprietary adhesive system, which included interfacial low viscosity resins, were then applied per manufacturers' instructions. For Gluma, the resin was not polymerized at this stage while it was polymerized for the other two materials. Polymerization was initiated by exposure to a visible light source in the frequency range of 480 nanometers (Translux, Kulzer, Germany). Gelatin capsules were loaded by syrine with a standard dental composite resin (Herculite XR,

TABLE I
Major adhesive system components

	Component		
System	1	2	3
Gluma	EDTA[1]	Glutaraldehyde,[2] HEMA[2]	[a]TEGDMA,[3] [b]BIS-GMA[3]
SB2	Maleic Acid,[1] HEMA	HERMA, BIS-GMA	
PUB2	PENTA,[1] HEMA	PENTA, HEMA, Glutaraldehyde,[2] TEGDMA, [c]UDMA[3]	

[1]conditioner [2]adhesion promoter [3]low viscosity resin
[a]TEGDMA—triethyleneglycol dimethacrylate
[b]BIS-GMA—bisphenol glycidyl methacrylate
[c]UDMA—urethane dimethacrylate

Kerr, Romulus, MI, USA) and were perpendicularly positioned to the surface using a jig mounted on the tooth. The composite was polymerized by exposure to the light source for 20 seconds on each of five axes. These included an initial cure obtained by positioning the light over the end of the capsule followed by a cure at each of four points 90 degrees apart around the circumference of the capsule. After storage in water at 37°C for seven days, samples to be subjected to thermal stress were place in a separate water bath at 90°C for eight minutes. They were replaced in the previous water bath and thermally stabilized prior to mounting in an universal testing machine (Instron, Canton, MS, USA). All samples were subjected to a continuous shear load at a cross-head speed of 2 mm/minute using a wire loop placed at the interface. The load at the point of failure was recorded and analyzed. Samples that debonded prior to being mounted for testing were not aggregated into the results.

Scanning electron microscopy (SEM) was used to examine morphological effects of conditioners on dentin and to provide supplemental data on the characteristics of the interface for select specimens. For the latter, samples demonstrating high and low bond strength within each of the groups were selected for analysis. The percent of intertubular dentin for these samples was estimated by subtracting the sum of the areas of the tubules from the overall area in the micrograph. This value was then correlated to bond strength. Samples undergoing SEM analysis were coated with a 12 nm layer of gold and examined in a Hitachi S2500 SEM (Hitachi, Japan) at an accelerating voltage of 15 KV.

Post-hoc evaluation of surfaces treated by the EDTA, maleic acid and PENTA conditioners was made with atomic force microscopy using a Nanoscope II instrument (Digital Instruments, Santa Barbara, CA, USA). Samples were glued to steel discs which were mounted onto an xyz piezo translator with a maximum range of 75 μm. The samples were raster scanned under a sharp tip mounted on a 100 μm long Si_3N_2 cantilever (Digital Instruments) with a spring constant of 0.6 nN. The samples were scanned in air at room temperature. The scans used varied from 1.02 Hz to 8.6 Hz. Both the force and height mode were used to record 400 × 400 pixel images.

Elemental analysis for controls, the maleic acid and PENTA conditioners was undertaken with X-ray photoelectron spectroscopy (XPS) using a Leybold LH Max 200 (Hanua, Germany) instrument. A second instrument (VG ESCALAB 3 MK II, East Grinstead, England) was used to evaluate a separate control and EDTA-conditioned dentin due to a positioning error that occurred with the first instrument. For the analyses, the occlusal enamel of each of two teeth was removed to expose a dentin plane. The surfaces were abraded to a 1200 grit finish using silicon carbide paper. A second cut was made parallel to the first to obtain a dentin wafer measuring approximately 1 mm thick. Each wafer was fractured into three segments. One was used as a control while the other two were treated with one of the conditioners. The samples were carefully handled during preparation to avoid contact with the surface. XPS surveys were undertaken using monochromatized Mg Kα radiation at a resolution of 0.7 electron volts (eV) with an energy accuracy of 0.01 eV. The instruments were operated at 12 kv and 25 μa using a spot size of 1000 μm. Low resolution survey spectra were made using a pass energy of 192 eV. Peak areas were converted into relative concentrations using sensitivity factors determined for each instrument and normalized to 100%.

Statistical Methods

Data values exceeding the 95% bound of the Studentized range were identified as outliers.[13] Those affecting the data analysis were removed. This procedure resulted in one of 216 data points being removed. A two-way analysis of variance (ANOVA) was performed to examine the effect of EGTA and the thermal stress test on the bond strength within each of the adhesive systems used. For the purposes of this paper, significant is defined as $p<0.05$ and highly significant as $p<0.01$.

RESULTS

Bond Strength

The mean values and 95% confidence intervals for each of the groups are shown in Figure 1. For the Gluma groups, the method of surface conditioning was not significant while thermal treatment was highly significant. There was no interaction between factors. For the Scotchbond groups, neither the surface condition-

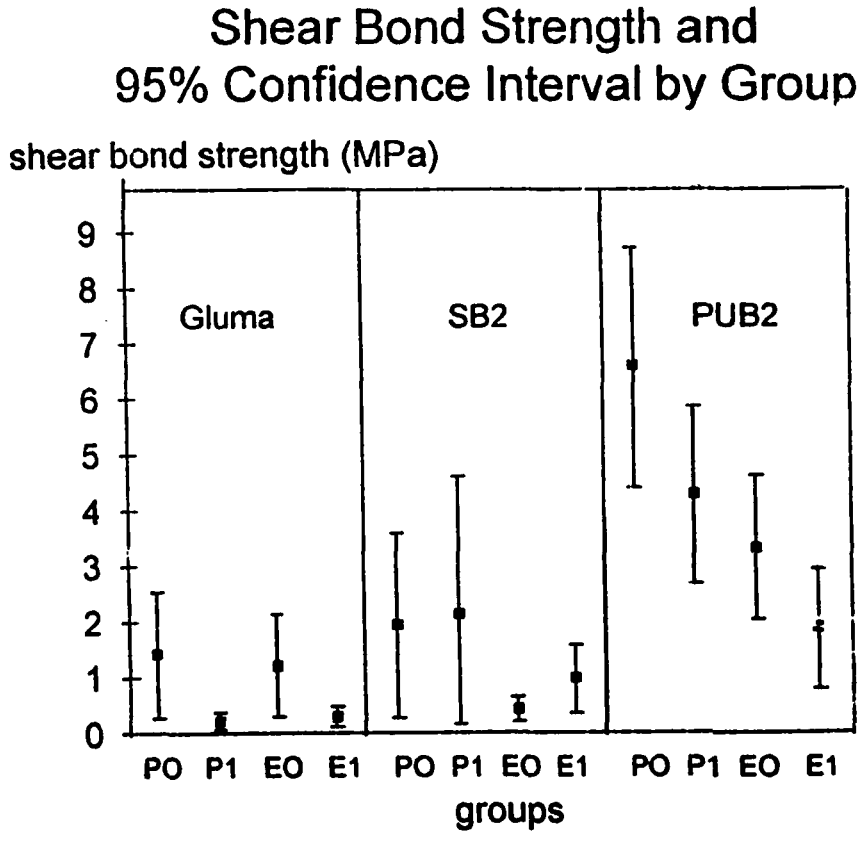

FIGURE 1 Means and 95% confidence intervals for shear bond strength for each of three proprietary groups. Group codes: P—proprietary conditioner; E—experimental conditioner; 0—no thermal treatment; 1—thermal stress applied.

ing, heat treatment or their interaction was significant. For the Prisma Universal Bond 2 groups, the effect of surface conditioning was highly significant; the thermal treatment was significant. Interaction between factors was not significant. Ten percent of non-thermally stressed and 18% of thermally stressed samples debonded prior to the testing procedure.

Surface Morphology

SEM examination of ground dentin (Figure 2) showed a characteristic amorphous surface. Although tubular apertures were obliterated by the smear layer, their outlines were faintly visible due to the thinness of the smear produced by a 1200-grit finish. A three-dimensional view of smeared dentin (120,000 × magnification) is shown in the atomic force topograph (AFT) in Figure 3. The image displayed amorphous irregularly-shaped surface structures. Their layered, often elongated appearance was consistent with a conclusion that the surface had undergone plastic deformation, a phenomenon inherent in the dynamics of abrasion. The orien-

FIGURE 2 Surface of ground dentin showing smear layer covering surface (viewed by scanning electron microscopy, 3,000 ×).

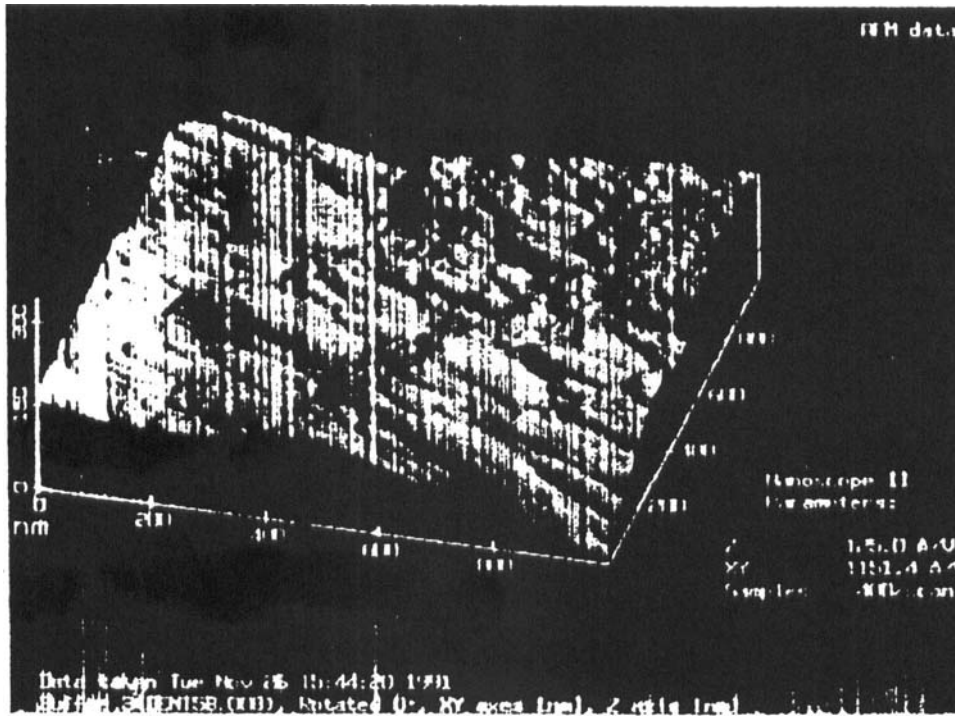

FIGURE 3 Topograph of a three-dimensional view of smear layer (viewed by atomic force microscopy, 120,000 ×) depicting amorphous structures produced by plastic deformation of surface by grinding particles. See Color Plate VI.

tation of the elongated structures was uni-directional and likely in line with the directional movement of the grinding particles.

Three of four surface conditioners (the exception being the PUB2 agent) dissolved the smear layer and revealed tubular apertures (Figures 4–6). Based on varying levels of surface smoothness and aperture diameters, differences in demineralization could be detected. Maleic acid thus produced the greatest degree of demineralization. Compared with dentin reacted with EDTA, the tubular diameter of maleic acid-treated dentin increased by an approximate factor of two due to acid dissolution of the peritubular dentin. AFM examination of intertubular regions revealed that micromorphologies of dentin treated by either EDTA or the maleic acid and HEMA were similar. An AFM topograph of the latter can be seen in Figure 7. At a scale of 3000 nm (40,000 × magnification), the surface appeared to have been etched. An array of structures protruding from the surface was revealed. Cross-sectional imaging of a similarly-treated surface by transmission electron microscopy[14] showed that the uppermost region of the interphase consisted of a collagenous matrix devoid of hydroxyapatite crystals. Thus, the structures imaged in this topograph are likely demineralized collagen bundles exposed due to the acid etching treatment. The detection of HEMA at scales to 1000 nm was not possible.

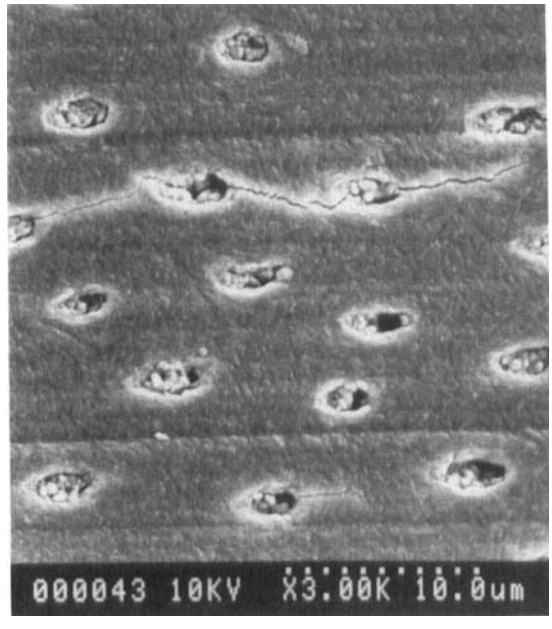

FIGURE 4 Surface of ground dentin treated with EGTA (SEM, 3,000×). Tubular apertures containing granular particles can be observed.

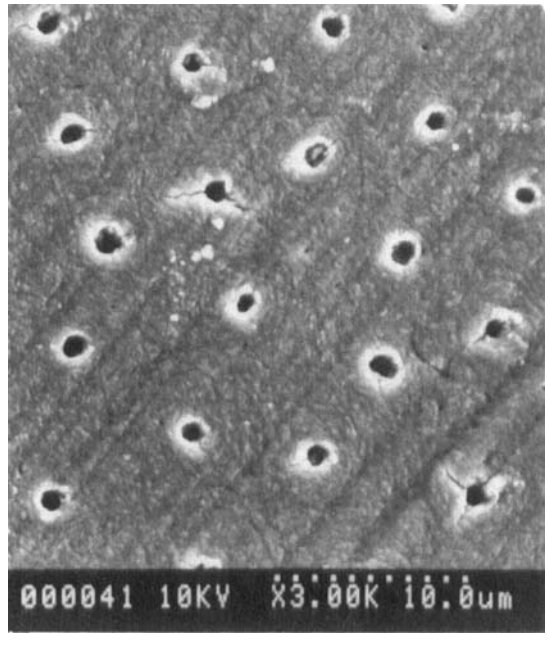

FIGURE 5 Surface of ground dentin treated with EDTA (SEM, 3,000×). Tubular apertures show minimum enlargement as a result of treatment.

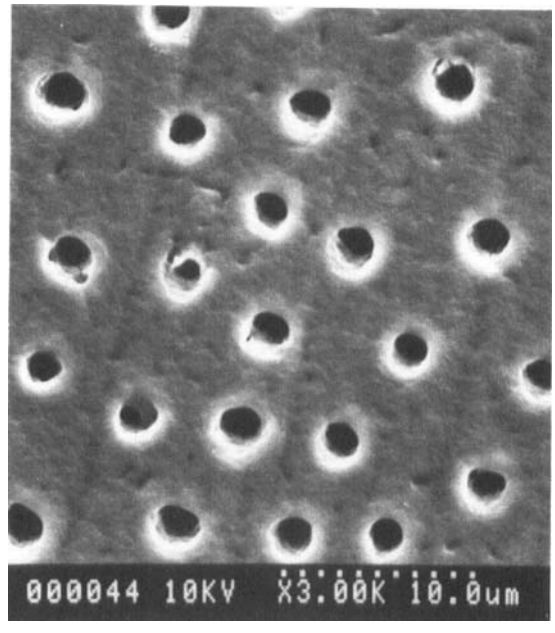

FIGURE 6 Surface of ground dentin treated with maleic acid/HEMA (SEM, 3,000×). The tubular apertures have been enlarged due to acidic dissolution.

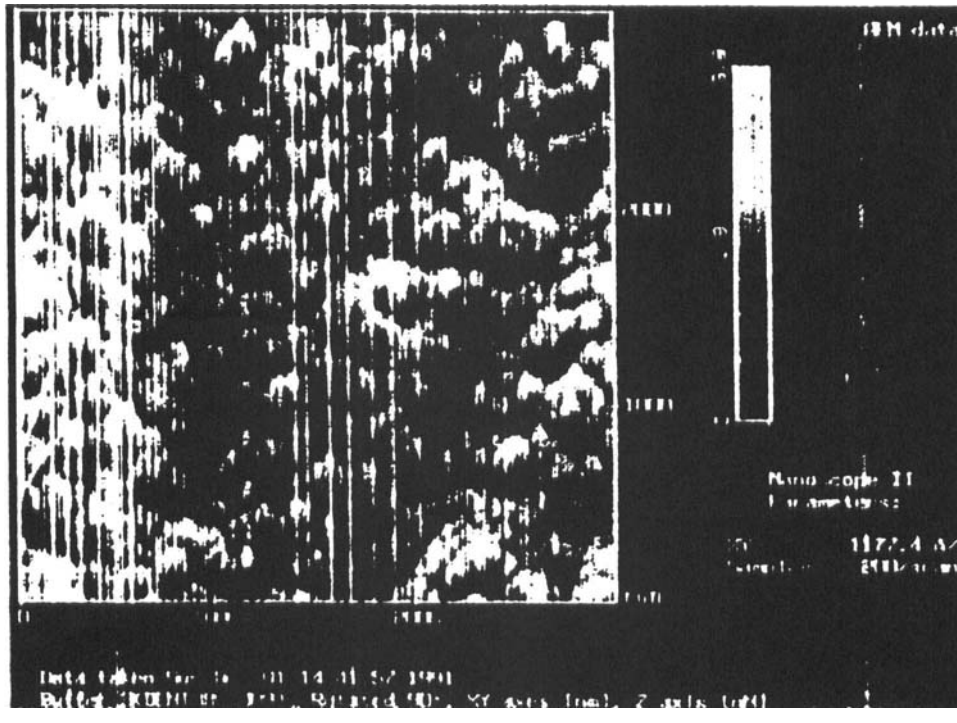

FIGURE 7 A top view of ground dentin treated by maleic acid/HEMA (AFM, 40,000×). The surface has been decalcified likely revealing the morphology of collagenous bundles.
See Color Plate VII.

For dentin treated with the agent containing PENTA (Figure 8), a surface film similar to the smear layer in morphologic characteristics was observed when viewed by SEM. Tubules remained largely obliterated. However, the contents of several of their apertures were visible. Smear debris appeared to have remained engorged within the tubules, suggesting that the demineralizing action, if any, of PENTA was relatively mild. Examination of the dentin side of a PUB2-dentin interface (exposed by an adhesive failure between the surface film and the underlying dentin) in Figure 9 provides morphological confirmation of minimal, if any, subsurface demineralization due to the PENTA-containing primer. Peritubular dentin remained intact and surface scratches produced by the grinding procedure remained marked in appearance. Also, virtually no resin tags were present in the tubules.

An AFT of the surface seen in Figure 8 at a scale of 1000 nm (120,000 ×) (Figure 10) revealed that dentin treated with the PENTA conditioner was, in fact, uniquely distinct from smear layer. In comparison with clusters of amorphous structures seen for the latter, the AFT here showed that the surface consisted of spheroidal structures having well organized interfacial boundaries. The spheroids ranged in size from approximately 50 to 150 nanometers. In contrast to the AFT of the smear layer, and with the understanding that a surface film was being imaged, this AFT showed that new molecular complexes had been formed on the dentin surface due to its treatment with the PENTA-containing conditioner.

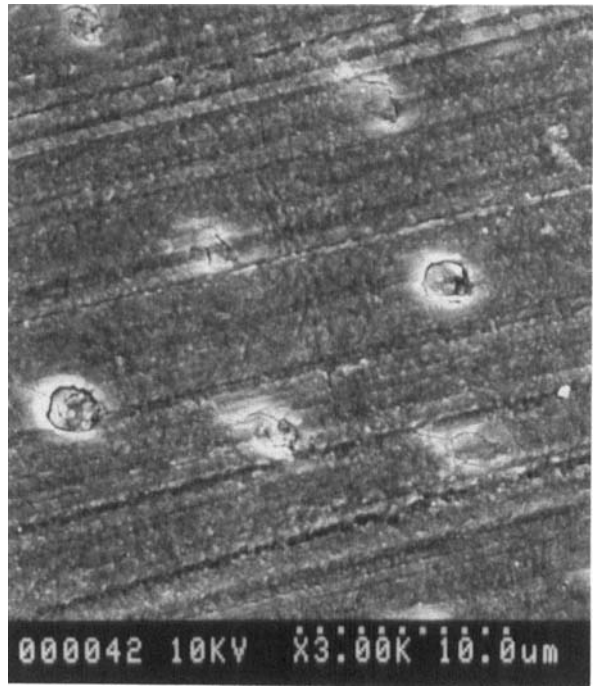

FIGURE 8 Surface of ground dentin treated with PENTA/HEMA (SEM, 3,000 ×). A layer largely obliterating tubules remains on the surface.

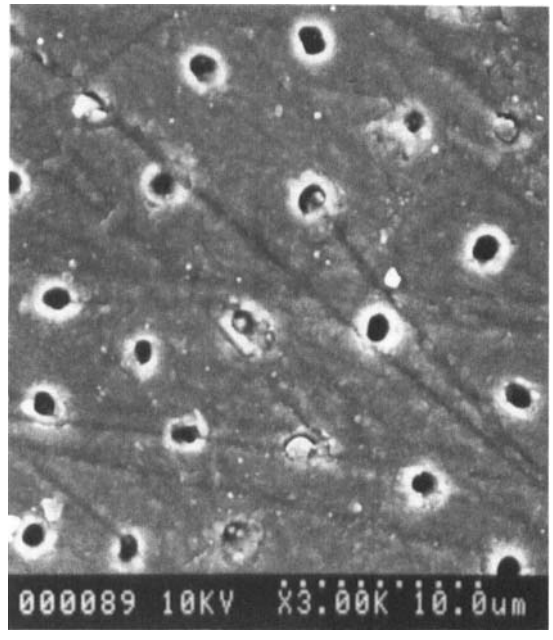

FIGURE 9 The dentin side of a bond failure between dentin and the PENTA/HEMA layer. The surface subjacent to the layer shows minimal, if any, tubular enlargement. Surface scratches from the grinding procedure are evident.

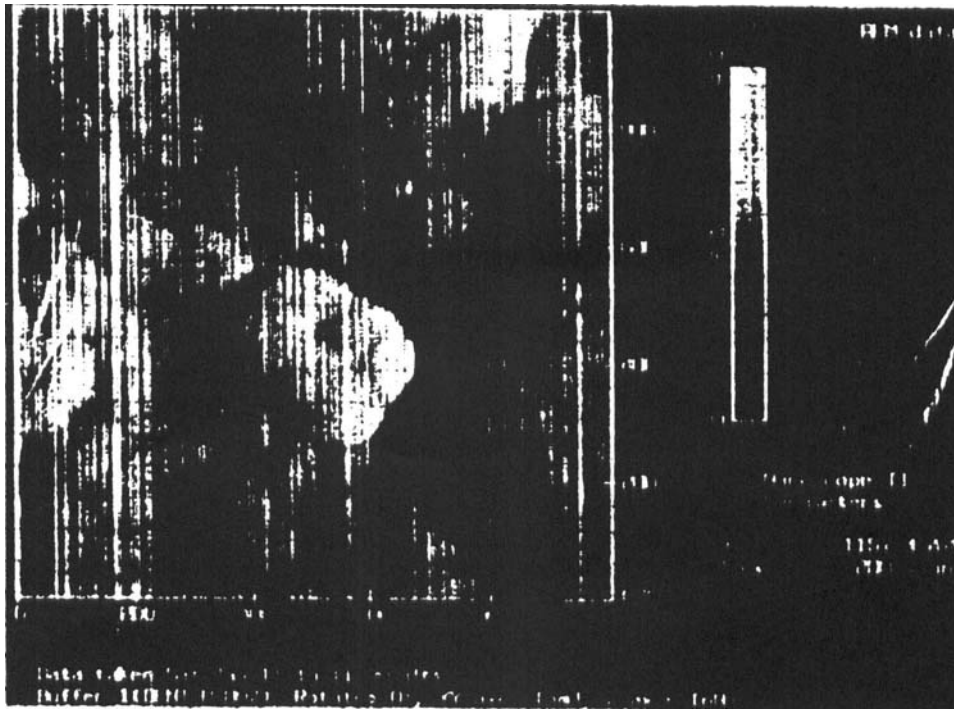

FIGURE 10 A top view of ground dentin treated with PENTA/HEMA (AFM, 120,000×). The surface layer produced by the PENTA/HEMA treatment consists of globular structures which vary in dimension from approximately 50 to 150 nanometers. See Color Plate VIII.

Failure Modes

SEM analysis of high and low bond strength within-group samples revealed no systematic pattern of fracture, although the preponderance of failures appeared to be adhesive in nature. Failure within the same sample was often bi-modal (adhesive-cohesive). Similarly, a variety of tag patterns within tubules was observed during post-failure analysis. For agents that removed the smear layer, tags either sheared at the dentinal plane or were partially displaced prior to fracture. Concomitantly, few, if any, tags were observed when the smear layer was not removed (PENTA-treated dentin).

Tags were generally not well adapted to the tubular walls when present. Given the relatively low bond strength of samples having a high density of tags remaining in tubules, their micromechanical contribution to bond strength was minor. Clearly, high bond strength was contingent on the appropriate interaction of conditioners and adhesive monomers with circumpulpal dentin. Further evidence for this finding is found in the PENTA-treated sample in Figure 11. This sample, which failed by cohesive fracture in dentin, had the highest overall bond strength.

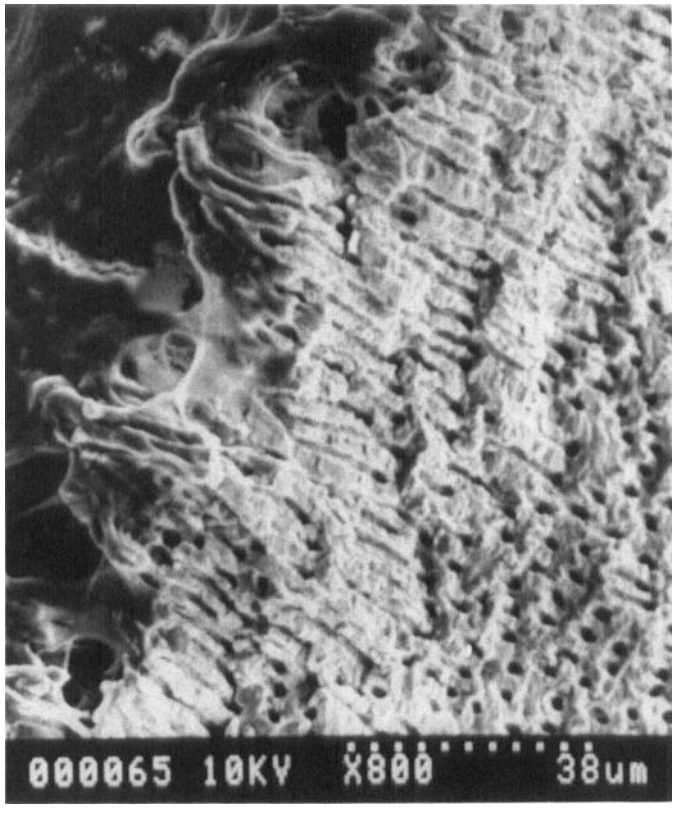

FIGURE 11 The adhesive interface of a PENTA/HEMA specimen after cohesive failure in dentin. The fractured dentin has remained attached to the composite resin (left upper corner of micrograph).

Consistent with previously reported data,[15] no tubular tags were observed at the tooth-resin interface for this specimen.

The area measurements of circumpulpal dentin (CPD) for the selected high and low strength specimens were in the range of 70 to 95% of the region examined. Differences in area were accounted for by tubular density variation and the degree of peritubular demineralization. When the bond strength data for the subset of high and low samples were pooled, a threshold effect for area was noted (Figure 12), with an area of 89% CPD appearing to be the minimum required for improving bond strength. It should be noted, however, that both high and low strengths were observed above this point. Differences in CPD area within and between experimental groups vastly exceeded discrepancies in shear bond strength. The data plotted in Figure 12 were based on pooling a subset of high and low values within each group. Thus, as a result of a non-parametric distribution, individual regressions lines were fit to the group of values above and below the 89% cutpoint. The slopes of the lines were, respectively, $Y=92.7-4.2\times10^{-2}X$ and $Y=74.1+20.4X$.

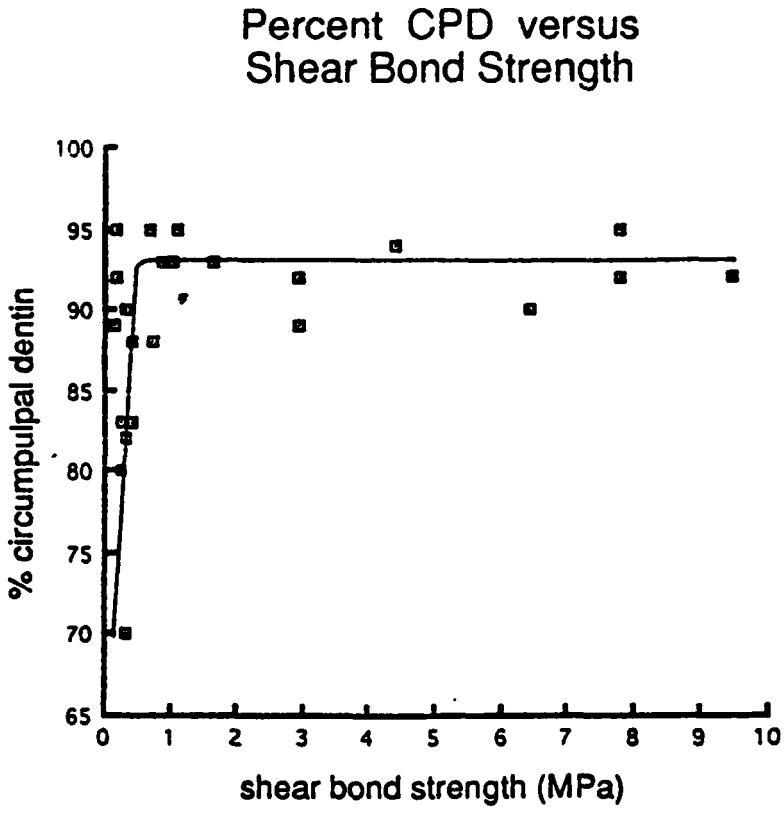

FIGURE 12 The percent area of circumpulpal dentin plotted against bond strength for high-low bond strength specimens within each of the groups.

X-ray Photoelectron Spectroscopy

As calcium to phosphate ratios were relatively constant, only Ca2p and N1s binding energies were followed to assess the effects of conditioning agents on either the mineral or protein phase of dentin. For facilitating comparisons relative intensity values were expressed as a percent shift in relation to a control surface. The results of this analysis can be seen in Figure 13.

All conditioners decreased Ca at the dentin interface. The greatest loss occurred with the agent containing maleic acid, followed by the experimental conditioner EGTA. The stronger chelating action of EGTA compared with EDTA was confirmed. A concomitant increase in N was observed for all groups with the exception of the PUB2-conditioned dentin, which had a decrease compared to its control.

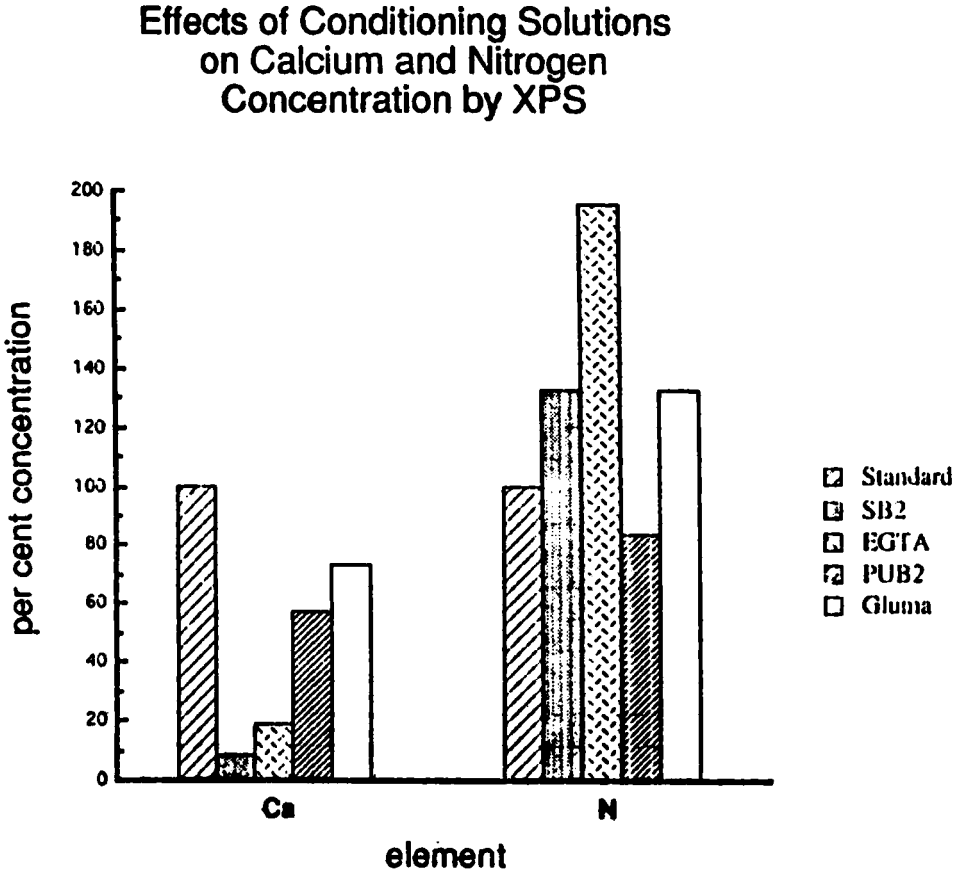

FIGURE 13 Results of XPS surveys showing percent elemental increase or decrease of calcium and nitrogen compared with a standard.

DISCUSSION

The purpose of this study was to evaluate EGTA as a conditioner for bonding to dentin. EGTA, along with EDTA an maleic acid, removed the smear layer and extracted calcium from subsurface dentin while PENTA produced an adherent overlayer that largely obliterated tubules. Thus, it is not surprising that EGTA had no effect on bond strength when smear removal and demineralization were an integral part of the adhesive mechanism of a bonding system. When the adhesive bond relied, instead, on the formation of a new, overlaying surface complex, the use of EGTA as a conditioner decreased bond strength.

The nature of the PENTA/HEMA bond was not investigated in this study. However, given the high strengths obtained for the PUB2 groups, the complex formed by the PENTA/HEMA conditioner was strongly adhered to subsurface (below the smear) dentin for many of the samples evaluated. We previously studied the effect of the PENTA/HEMA conditioner on the chemical states of hydroxyapatite powder and collagen, the two major components of dentin. Using photoacoustic Fourier transform infrared spectroscopy, we found that this agent was capable of forming chemical complexes with each of these substrates.[16] Cabasso and Sahni[17] have also suggested that phosphonated esters, such as PENTA, can react with both divalent calcium in hydroxyapatite and amide groups in protein. Thus, it would appear likely that the PENTA/HEMA overlayer is chemisorbed to subsurface dentin, one mechanism possibly involving complexation of the phosphate moiety in PENTA with Ca^{2+} in intact hydroxyapatite crystals in the bulk.

The XPS evaluation indicated that each of the conditioners produced alterations in the dentin surface. As only survey spectra were obtained these changes were interpreted in general terms with respect to agent effects on the concentration of calcium hydroxyapatite and the collagenous and non-collagenous proteins in dentin. For the latter two, N has been attributed to amino groups in the protein phase.[18] Thus, a concentration shift of either of the dentin phases was followed using Ca2p and N1s. The Ca and N atomic percentages for ground dentin found in this study were in general agreement with previously published data.[19] As the elemental composition of the smear layer and native dentin are similar,[16,17] the baseline reference for Ca and N obtained for the ground dentin control study were taken as the reference for bulk dentin. Thus, the relative changes in surface concentrations of these elements were contrued to be indicative of shifts within the bulk.

In addition to the expected detection of various elements, silica was found in trace amounts in several samples and was likely a contaminant from the abrading procedure. Fluorine was uniformly detected, with concentrations ranging from 0.13 to 0.99%. Fluorine was most likely present in the form of fluoroapatite, which is less prone to acidic dissolution than its calcium form. Although this may have implications for bonding with respect to the effects of acid conditioners, fluoroapatite constituted a relatively minor component of dentin. Thus, the varying fluorine concentrations detected in this study did not likely contribute to variance in bond strengths observed.

The thermal stress test was empirically derived to assess the adhesive bonds for

durability and non-hydrolizability. It was devised to be a relatively rapid means of thermally stressing the adhesive joint without inducing the turbulence associated with boiling water. Although the raising of the water temperature to 90°C may have approached the glass transition temperature,[20] the delay between the thermal stress and shear test allowed for thermal restabilization, and thus should not have been a factor in the results. The effect of temperature elevation may have, however, increased the degree of conversion of either the thin film, low viscosity resin overlayer or the composite resin itself. Thus, the modulus of either of these components may have been changed, producing more brittle components in the adhesive joint. This effect on bond strength measurement has not been determined.

The mean values for bond strength, for the Gluma, and SB2 groups, were generally lower than those obtained in prior studies in our laboratory.[21] However, the upper limits of individual values for Gluma and SB2 were consistent with these previous results while the upper limits of values for the PUB2 system were relatively high. Nonetheless, any factor that may have contributed to lower bond strength was equally distributed within all groups as a result of the randomized block design. In addition, the relative mark order of bond strength obtained, for each of the three proprietary groups, were in agreement with a previously published evaluation.[22] The value for the PUB2 group was greater than for either the Gluma or SB2 groups, both of whose values approached each other.

SUMMARY AND CONCLUSIONS

The effect of EGTA as a conditioner on dentin was similar to EDTA and maleic acid, both of which removed the smear layer and demineralized the surface. EGTA had no effect on bond strength for two adhesive systems which depended on these events, while it decreased bond strength for one which relied on the formation of a surface overlayer. Thus, no benefits were derived from the use of EGTA.

Differences in bond strength between conditioners may be due, in part, to their effect on the structure of the interface and the interaction of the subsequently-placed interfacial resin with that structure. Three of the agents produced a weakened interphase consisting of the demineralized, collagenous fraction of dentin. Its reinforcement relied on subsequent resin infiltration into spaces vacated by mineral crystals. The fourth agent appeared to preserve the integrity of the interface and to complex with it.

Within the limits of this investigation, we concluded that adhesion to dentin can be optimized by using agents that interact with an interface that remains structurally intact after conditioning. Based on the finding that the PENTA-treated dentin, in conjunction with its resin overlayer, had the highest bond strength, it would appear that the nature of the interaction is preferably one that primarily relies on chemical rather than micromechanical linkages.

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