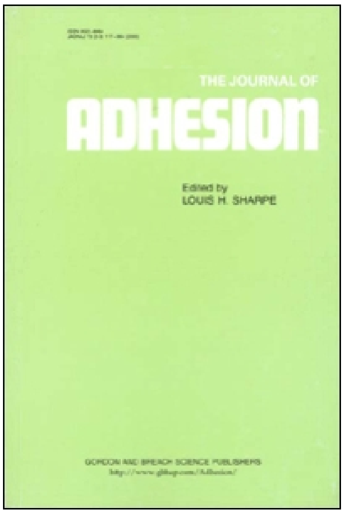

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XPS Characterization of Dentin and Dentin Treated with Bonding Conditioners*

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Samples of smear layer dentin prepared with #600 grit paper and treated with various conditioners (Gluma Conditioner, Scotchprep or Tenure Dentin Conditioner) were analyzed using XPS to determine the changes in surface composition as compared with controls of the smear layer or fractured dentin. Dentin treated with phosphoric acid liquid or gel was also analyzed. All of the conditioners lowered the Ca and P on the dentin. While phosphoric acid treated dentin exhibited similar reduction in Ca and P, Si was adsorbed onto the dentin when phosphoric acid etching gels were employed. Surface behavior diagrams were used to illustrate these changes. Micro ATR FTIR was used to confirm both the loss of Ca and P from the phosphoric-acid-etched dentin and the adsorption of the silica from the etching gel. These data are compared with other XPS studies of dentin conditioners and primers.

KEY WORDS dentin bonding; fractured dentin; smear layer; phosphoric acid etching; XPS; FTIR; surface behavior diagrams.

INTRODUCTION

Bonding of resins to the enamel and dentin of tooth structure is of major concern in dentistry. Consistent bonding of resin to phosphoric-acid-etched tooth enamel is routinely possible and is the basis of many of the restorative techniques used by the dentist. Bonding of resin to dentin has been an elusive undertaking because of the complex nature of the substrate. Dentin is approximately 54% by volume protein, ninety percent of which is collagen, 33% by volume apatite structures and the remainder water.[1] This composition represents a challenge for the adhesive chemist[2] and is further compounded by the complex three-dimensional organization of the dentin. Dentin is organized from the pulp to the dentino-enamel junction (DEJ) in

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*One of a Collection of papers honoring John D. Venables, the recipient in February 1991 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

a radial direction with tubules of roughly 2.0–2.9 microns in diameter. These tubules extend the entire width of the dentin and narrow in diameter only slightly as they approach the DEJ. Within these tubules are the long cellular processes of the odontoblasts whose cell bodies line the inner aspect of the dentin in the pulp tissue. This vital tissue is comprised of intratubular dentin, arranged circumferentially around the lumen of the tubules and intertubular dentin where the collagen fibers are arranged more laterally connecting the intratubular structures. The degree of calcification of the intratubular dentin is higher than that of the intertubular dentin. The relative amount of these subcomponents changes as the cross-sectional area of dentin occupied by the dentin tubules increases near the pulp.

Increasing the difficulty in bonding to the dentin surface is the dentin smear layer, an adherent layer of collagen, broken apatite crystals, and cellular components, which is created by any grinding or cutting of the surface. The dentin smear layer has been found to vary in thickness from 2–5 microns and forms plugs in the dentinal tubules. Detailed investigations of the structure of dentin and dentin smear layers have been conducted since the advent of the SEM.[3] However, progress in development of systems to condition, prime and bond to the dentin surface have suffered from lack of a definitive understanding of the interaction of the components of these systems. There has been variation of the approach to the dentin smear layer, some systems seeking to modify it while others remove the smear layer with acids or chelating agents.[4] Progress in this area depends upon surface characterization of the dentin substrate before and during the stages of the bonding procedures. It is the objective of this research to investigate by X-ray photoelectron spectroscopy (XPS) the nature of the dentin surface in its native state and when prepared for bonding.

XPS is a valuable tool for biological surface analysis[5] but until recently has found little application in deciphering the bonding mechanism(s) of resin systems to dentin. Hercules and Craig[6] utilized XPS to determine enamel surface concentrations of Ca, P, and F, following treatment with an acid phosphate-fluoride gel. Bowen[7] employed XPS to determine which of various cations were adsorbed by enamel when incorporated in a phosphoric acid etching solution. Until recently there was little published on the surface composition of dentin.

Eliades *et al.*[8] attempted to use XPS of dentin surfaces treated with several dentin bonding agents to investigate the mechanism of bond formation. Ion sputtering to determine the changes in concentration and bond status of various atomic species with depth was employed. They found no definitive evidence of chemical bond formation. More recently, Ruse and Smith[9] have investigated the surfaces of bovine dentin treated with a chlorophosphate-based dentin adhesive, Scotchbond® (3M), or with phosphoric acid, hydrochloric acid or hydrogen peroxide. They found evidence for the removal of surface calcium and phosphate along with the dentin smear layer after the use of the acid solutions. The XPS spectrum of peroxide-treated dentin was similar to that of ground dentin. They also found, as previously noted,[10] that silicon remained on the dentin surface following etching with phosphoric acid gels, in which silicon dioxide in the form of fumed silica is used as a thickening agent. Williams and Williams[11] have also investigated dentin surfaces with XPS.

Our preliminary studies,[10] along with the recent studies cited above, suggest that XPS can be used to establish a baseline molecular composition of the dentin surface and can monitor surface molecular changes following treatment with various primers and etchants. In this study we sought to determine the effect of various dentin bonding conditioners or primers on the dentin with the intention of establishing a basis for the mechanism of adhesion of these dentin bonding systems. This also represents base line data for our studies of bonding to carious dentin.[12]

MATERIALS AND METHODS

The following methods were employed in order to provide control and test surfaces. Freshly extracted human third molar teeth that had been stored in 4°C saline for no more than three weeks were used to generate dentin samples. Samples were obtained by making horizontal cuts through the crown below the DEJ and above the roof of the pulp chamber. The samples were of approximately 1.5 mm thickness and were wet ground flat on fresh #600 grit SiC paper. The occlusal surface was troughed with a No. 33 inverted cone bur in a high speed handpiece to subdivide the dentin surface into buccal and lingual regions (Fig. 1). The sample was further cut from buccal to lingual in three sections perpendicular to the trough with a diamond saw. Each section was then divided by the trough which was intended to confine the surface treatment to a specific area or create a site to initiate a fracture through the dentin section. Fractured specimens were further cut to 2 mm in height from the fracture surface to the surface to be in contact with the XPS mounting stud. The remaining trough-divided sections were treated on the occlusal surface with the various conditioners, primers, etchants or left as a control smear layer. Thus, *each dentin coronal section had one fractured surface, a control surface (smear layer), and four other surfaces available for treatment.* The method of preparation of the samples from the molar teeth, shown in Figure 1, minimizes the variation from tooth to tooth but does not allow for the variation in dentin composition across the surface of the dentin.

Various solutions for conditioning or priming the dentin surface were employed (Table I). The following solutions were applied to the dentin: Gluma® cleanser (0.1 M ethylene diamine tetra-acetic acid (EDTA) at pH 7.4), 30 sec and rinsed; Scotchbond 2® primer, Scotchprep® (5% maleic acid and 35% 2-hydroxyethylmethacrylate (HEMA)) 60 sec with scrubbing then dried (no rinsing); Tenure® conditioner (Den-mat Corp., Santa Maria, CA, USA) (3.5% Al oxalate, 2.5% nitric and 0.5% phosphoric acid), 30 sec and rinsed. Subsequent samples were prepared to determine the effects of phosphoric acid gels (Enamel Etching Gel, LD Caulk, Milford, DE, USA); Scotchbond Etching gel (3M, St Paul, MN, USA), as compared with commercial phosphoric acid liquids (Etching Liquid, SS White, now Kerr/Sybron, Romulus, MI, USA; Kura-etch, Kuraray Co. Ltd, Osaka, Japan), or 40% phosphoric acid (Fisher Scientific, ACS grade). The etch time was varied as either 30 or 60 sec.

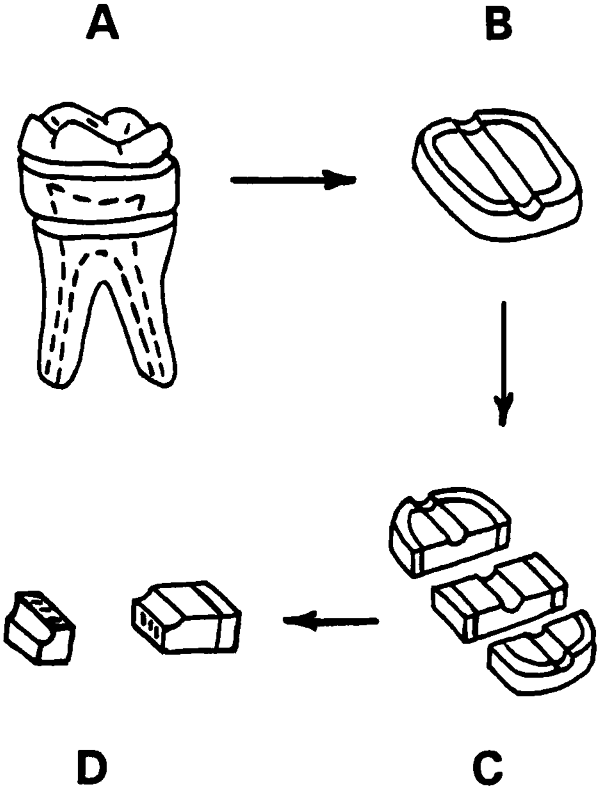

FIGURE 1 Specimen preparation for four treatment areas, one control smear layer and one fractured surface from one tooth section: A = sectioning of third molar tooth parallel to the occlusal plane, B = following finishing the occlusal face to #600 grit preparation of mesial to distal trough in disk surface to separate treatment areas, C = cutting of disk for 3 treatment slices, D = fracturing of middle slice and reorienting one fractured face for analysis after reduction in height.

TABLE I
Materials used

Gluma Cleanser® (GLUMA Adhesive System)	Columbus Dental	St. Louis, MO, USA
Phosphoric Acid (40%)	Fisher Scientific	Fair Lawn, NJ, USA
Enamel Etching Gel (50% Phosphoric Acid)	L D Caulk	Milford, DE, USA
Scotchbond Etching Gel® (Scotchbond 2 Adhesive System)	3M	St. Paul, MN, USA
Etching Liquid (37% Phosphoric Acid)	Kerr/Sybron	Romulus, MI, USA
Kura-etch® (37% Phosphoric Acid)	Kuraray Co. Ltd.	Osaka, Japan
Scotch Prep® (Scotchbond 2 Adhesive System)	3M	St. Paul, MN, USA
Tenure Conditioner® (Tenure Dentin Bonding System)	Den-Mat	Santa Maria, CA, USA

All samples were handled with tweezers or hemostats by the enamel periphery to avoid contamination. Atmospheric contamination of low energy surfaces such as organics and ceramics are not a problem in comparison with high energy metal surfaces. In addition, we allowed for this factor in having all treatments applied to the subdivided dentin coronal section from one tooth. All sections were exposed in the same manner prior to analysis.

Treated sections were then attached to the mounting stud of an SSX100-03 Surface Science Instrument XPS Spectrometer with double-sided adhesive tape. The mounting stud was placed under vacuum overnight in order to remove water from the sample. The spectrometer employed monochromatized Al Kα X-rays focused to either 300 or 600 micron spot size. A 3 ev flood gun provided charge neutralization. The emission angle of the photoelectrons was 60° with respect to the surface normal. After XPS, all data were normalized to the aliphatic C1s peak (284.6 ev) and the curve-fitted peaks assigned based upon Wagner *et al.*[13] SEM inspection (JEOL SX1200) of each sample at magnifications to 1500× was conducted in order to verify surface condition, the condition of the smear layer and, as was found later, to verify that the dentin slice was finished to a sufficient depth that no islands of enamel were present in the XPS analyzed area.

The XPS software expressed surface composition in atomic concentration based upon manufacturer supplied sensitivity factors; however, it is easier to evaluate surface changes by observing elemental ratio changes as we had noted earlier.[10] The ratio results from three or more samples of each test condition were averaged, analyzed by ANOVA and Newman-Keuls multiple comparisons applied and evaluated at 0.05 level of significance.

Samples for micro ATR-FTIR were prepared from coronal sections of extracted third molars cut parallel to the occlusal plane as described above. The samples were cut with a diamond saw to remove all enamel and then finished on SiC paper to #600 grit to yield a section of dentin 10×5×1 mm. The sections were maintained in 4°C water until IR observation. Samples were treated just prior to mounting in a micro ATR attachment (Wilks Scientific, Vineland, N.J., USA) against a 0.5 mm thick KBr crystal allowing 10 reflections from one crystal face. Samples were lightly dried with N_2 just prior to mounting. It was necessary to compress the dentin tightly against the metal-holder-backed KBr crystal to obtain reasonable transmission of the IR beam. Spectra were obtained with an Analect 6160 FTIR employing an MCT detector. All spectra were referenced to Al foil against the KBr crystal as the background using 32 or 64 scans. Smear layer spectra were obtained as well as spectra of dentin etched with phosphoric acid liquid and gel. Etching times were either 30 or 60 seconds. Only one dentin section was analyzed at a time. The smear layer spectra was then recorded following a 5 minute CO_2- and H_2O-free air purge of the instrument sample chamber. For each test spectrum at least 64 scans was employed. Following each spectrum, the slice was removed and re-etched, washed for 30 sec, dried with N_2 and remounted and a second spectrum was recorded to verify conditions. The second spectrum in each instance was essentially equivalent to the original save for slight differences in intensity. ATR-FTIR spectra for smear layer dentin treated with Scotchbond 2 primer as well as GLUMA and Tenure conditioners have been obtained[14] but are reported elsewhere.

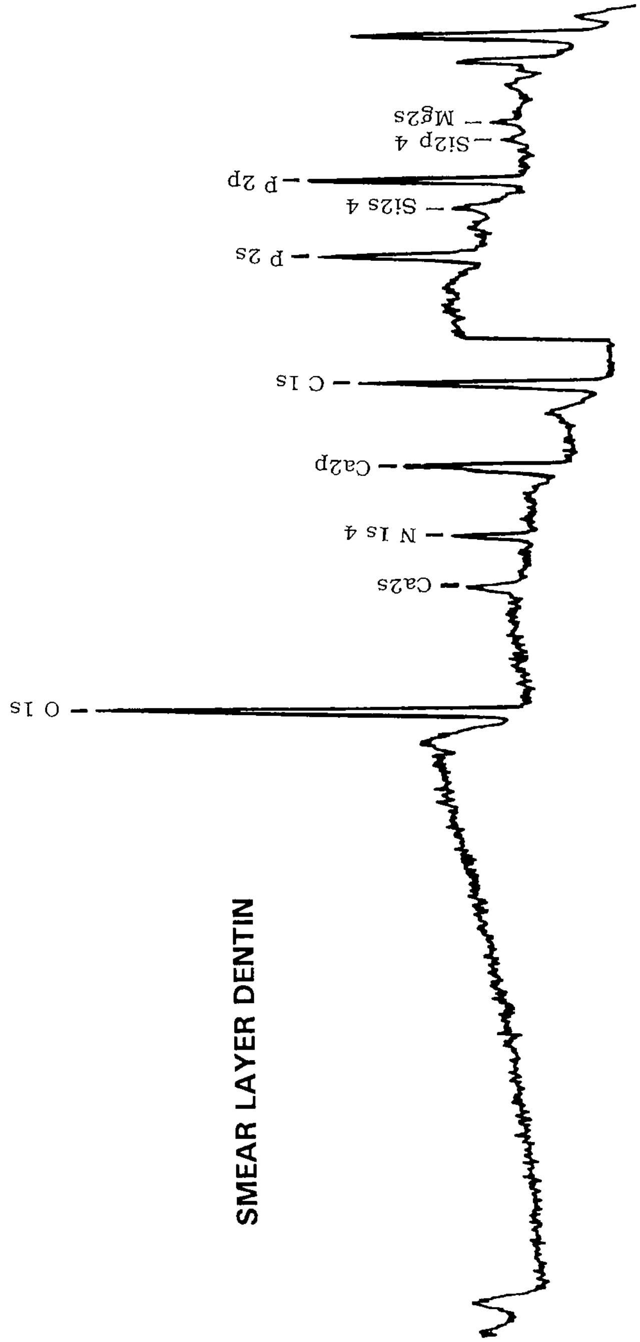

FIGURE 2 XPS spectra of smear layer dentin prepared with #600 grit paper as compared with fractured dentin of the same tooth. Note in this instance that both the smear layer and fractured dentin exhibit a small concentration of silicon on the surface.

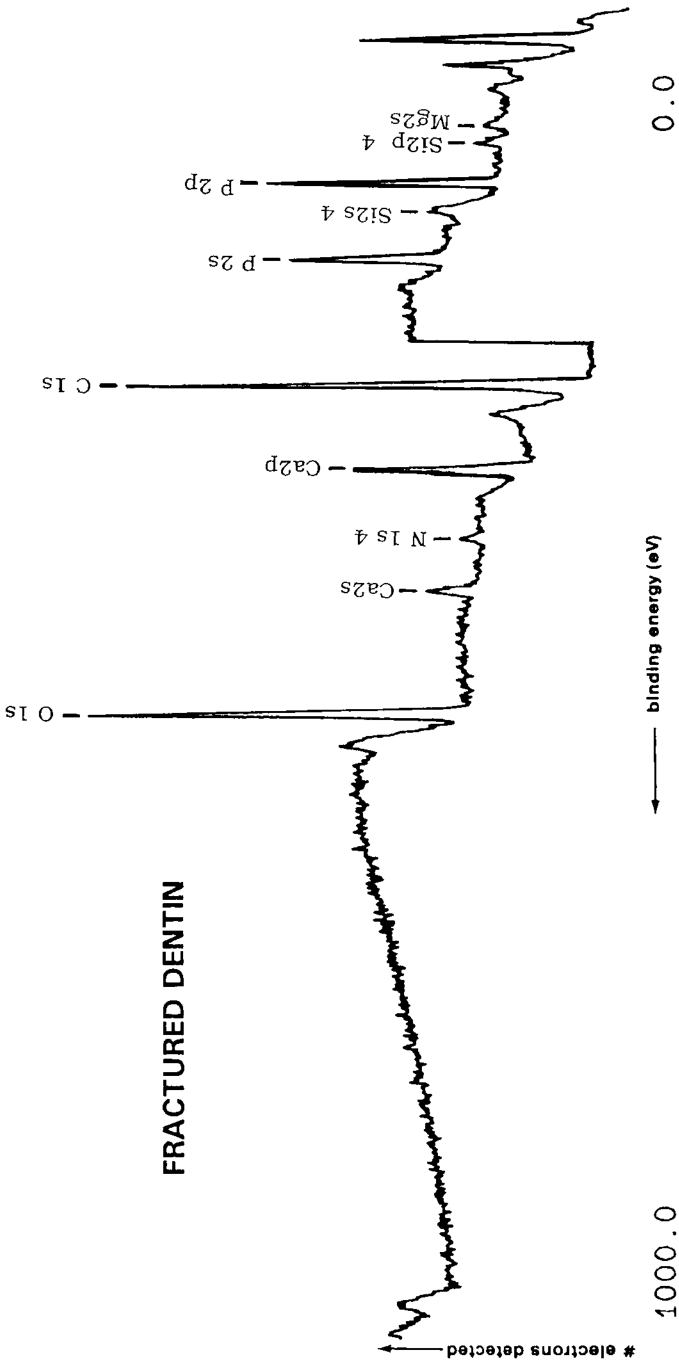

FIGURE 2 *(Cont.)*

RESULTS

Typical XPS spectra for smear layer and fracture specimens are shown in Figure 2. Depending upon the tooth, there were minor amounts of Al, Zn or Si present in some tooth samples, but these were consistent between sections from the same tooth and were ignored unless greater than 0.5%, except for Si. Silicon was noted at about the 1% level in dentin smear layers and is likely the result of transfer of abrasive particles from the SiC paper.

A comparison between the XPS-determined compositions for smear layer dentin as compared with a fracture surface from the same specimen is shown in Table II. Smear layers were uniformly reduced in Ca and P as compared with the fractured surface. The fractured surface was analyzed parallel to the dentin tubule direction and was by the nature of the preparation deeper in the dentin and correspondingly closer to the pulp. This increases the relative cross-sectional area occupied by the tubules and of the intertubular as compared with the intratubular dentin. The Ca/P ratio is 1.37 for the fractured surface and 1.64 for the smear layer for this tooth slice. This ratio difference was consistent for all dentin samples analyzed.

The relative ratio of the principal atomic species present on the dentin surface following a variety of treatments is shown in Table III. Here it can be noted that all of the treatments reduce the Ca and P on the surface as shown by the Ca/C ratio while the Ca/P ratio does not change radically. The C/N ratio varied widely for the fractured dentin but was relatively consistent for the smear layer as well as for conditioned dentin.

Gluma conditioner (EDTA, pH 7.4) effectively removed about 90% of the surface Ca but maintained a Ca/P ratio (1.31 ± 0.16) statistically equivalent to fractured (1.32 ± 0.01) and smear layer (1.51 ± 0.16) dentin. For the acidic conditioners Scotchprep and Tenure Conditioner the Ca/P ratio was statistically significantly reduced to 0.93 ± 0.30 and 0.86 ± 0.25, respectively.

Pretreatment of the dentin surface with Gluma cleanser (EDTA) yielded consistent increases in the C/O ratios. The fact that the C/N ratio remained relatively constant suggests that there is no increase in carbon but a decrease in oxygen. This oxygen loss is associated with P in the form of PO_4 which, in turn, is lost secondarily to the Ca. A decrease in the Ca/C ratio occurred as expected with EDTA treatment.

The effect of phosphoric acid in liquid and gel form on dentin for several different treatment times is shown in Table IV. The atomic ratios presented were determined on surfaces that had a fresh smear layer created with #600 grit silicon carbide paper just prior to final sectioning and etching. An XPS spectrum of a control smear layer was taken for each tooth section subjected to the various acid treatments.

These above data can be more easily understood when plotted on a surface behavior diagram (SBD). This involves a matrix normalization of the surface-sensitivity data on the surface from atomic concentrations to molar concentrations.[15] The data for several teeth are plotted in the SBD format in Figure 3. The view in Figure 3A is down the Si axis while in the other, Figure 3B, the view is along the nitrogen axis in order to see the Si adsorption from the etching gels. The data for Caulk etching gel are compared with those for the etching liquid. The grouping of all of the dentin conditioners/primers near the N vertex is consistent with the reduc-

TABLE II
Relative atomic % of major elements on dentin surfaces by XPS

Treatment	C	O	N	Ca	P	Si
Fractured	45.5	31.8	6.0	9.2	6.7	—
Smear Layer	59.0	25.5	5.8	5.4	3.3	1.0

TABLE III
Ratio of surface atomic % for dentin treatments

Treatment	C/O	C/N	Ca/P	Ca/C
Fracture	1.78	11.76	1.32	0.17
(n=3)	±0.80	±9.75	±0.10	±0.06
Smear Layer	1.63	7.2	1.51	0.19
(n=5)	±0.82	±1.60	±0.16	±0.07
Scotchprep	3.17	6.07	0.93	0.022
(n=3)	±0.07	±1.46	±0.30	±0.002
Gluma Conditioner	4.06	6.00	1.31	0.025
(n=2)	±0.33	±0.42	±0.16	±0.007
Tenure Conditioner	3.89	6.27	0.86	0.006
(n=3)	±0.29	±1.97	±0.25	±0.004

TABLE IV
Ratio of surface atomic % for phosphoric acid treated dentin

Treatment	C/O	C/N	Ca/P	Ca/C	Si/C	Si%
H_3PO_4 (Caulk)						
1 min gel	1.2	10.3	—	—	0.38	16.1
1 min liq	3.5	3.8	—	—	0.002	0.2
1 min liq	4.2	4.4	—	—	0.002	0.2
H_3PO_4 (liquid)						
30 sec (SSW)	1.7	9.7	0.36	0.06	0.003	0.1
30 sec (Kuraetch)	1.7	10.6	0.32	0.06	—	—
H_3PO_4 (gel)						
30 sec (Caulk)	2.0	33.3	0.39	0.07	0.23	9.3
30 sec (Scotchbond)	1.2	36.0	0.44	0.08	0.15	6.6
1 min (Caulk)	1.2	10.3	—	—	0.38	16.1
Smear Layer Control						
#600 Grit	1.6	7.2	1.51	0.19	0.03	0.8

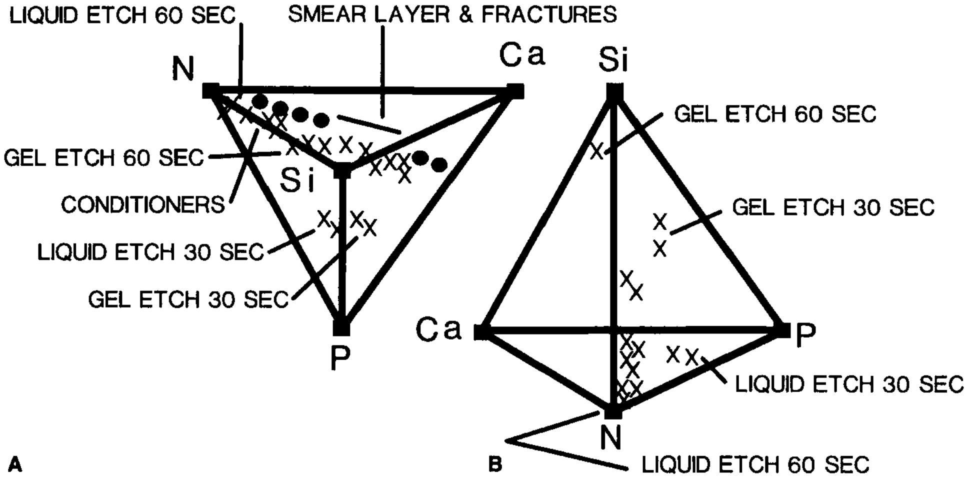

FIGURE 3 XPS results converted to a Surface Behavior Diagram including N, Ca, P, and Si. In 3A the dotted line extending from the Ca-P concentration line to the N vertex is the Ca/P ratio for dentin (1.58). In 3B the rotation to view the Si vertex shows the changes in Si concentration with gel etching time.

tion in Ca and P expected from acid or EDTA treatment. The cluster of points near the middle of the Ca-P-N plane represents the fracture and smear layer surfaces. The smear layer surfaces tend to be closer to the N vertex indicating the greater concentration of organic phase, while the fracture surfaces are closer to the hydroxyapatite point along the Ca-P axis. The further depletion of the mineral phase in the treated samples is indicated by the cluster of points near the N vertex. Finally, the residual fused silica left by the gel treatments is reflected by the points above the Ca-P-N plane.

The ATR FTIR spectra for smear-layer-covered dentin as compared with the same dentin surface treated with phosphoric acid etching liquid is shown in Figure 4. The following peaks can be assigned based upon FTIR investigations of collagen assembly in solution.[16] Amide I is a non-symmetric peak present at this limited resolution (4 cm^{-1}), and is likely a doublet with peaks at 1655 and 1640 cm^{-1}. The Amide II band is present as one peak at about 1556–1551 cm^{-1}. The Amide III peak is consistently present at 1240 cm^{-1} and for the smear layer does not have distinct side bands. There are symmetric side bands found at 1278–1283 and 1205–1206 cm^{-1} that are distinct when the smear layer is modified or removed. The broad N-H stretch at 3300 cm^{-1} is present but contributions from bound water and CH are also present.

The phosphate peaks of smear layer dentin are found as a broad strong peak at about 1010 with another at 955 cm^{-1}. The phosphate peak is more closely similar to the transmission spectrum for amorphous calcium phosphate than for hydroxyapatite, according to the recent review by Bailey and Holt.[17] The peaks assigned the HAP are sharp and at 1040 and 1092 cm^{-1} while those present in the smear layer are broad and diffuse in comparison.

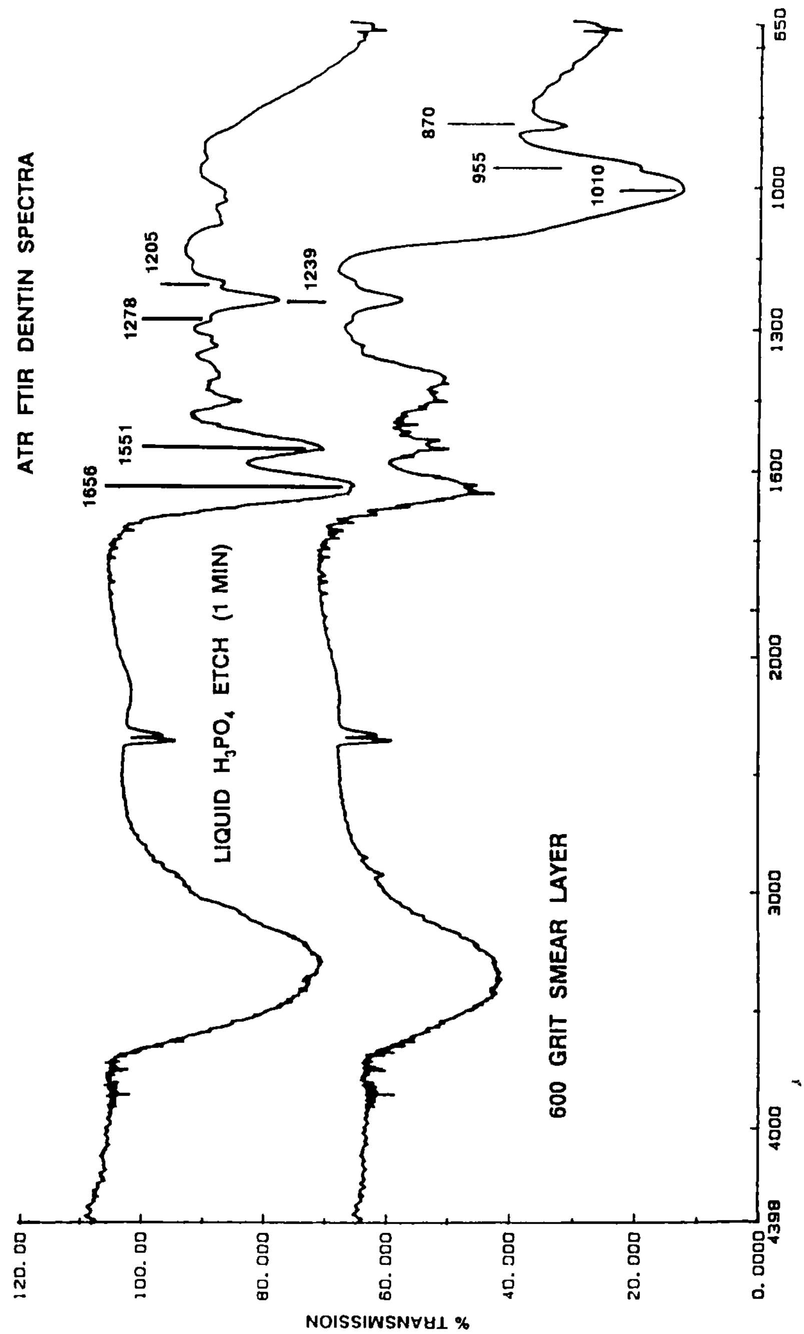

FIGURE 4 The micro ATR FTIR transmission spectra of smear layer dentin as a reference is compared with the same sample after phosphoric acid (37%) etching for 60 seconds. The Amide I peak at 1640–1655 cm^{-1} is strong along with the Amide II at 1551–1556 cm^{-1} while the Amide III is present at 1240 with side bands at 1278–1280 and 1205–1206 cm^{-1}. The amide bands are more defined on the etched surface but absent are the phosphate peaks at 1010, 955 and 870 cm^{-1}.

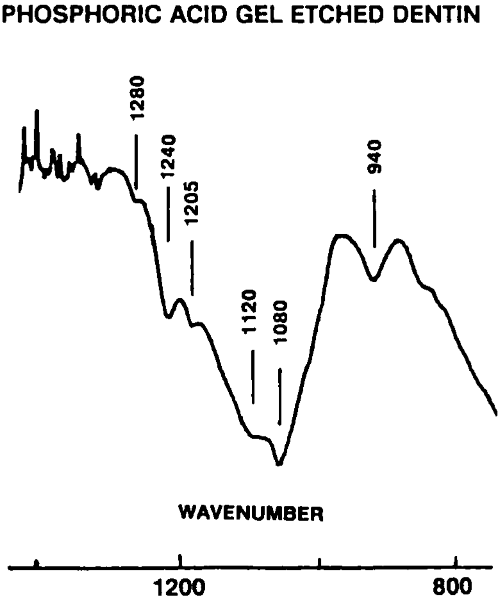

FIGURE 5 A micro ATR FTIR transmission spectrum of a 60 sec phosphoric acid gel (LD Caulk) etched dentin surface in the 800–1400 cm^{-1} region. The 1120, 1080 and 940 cm^{-1} peaks correspond to SiO_2 with the Amide III peaks present as shoulders at 1280, 1240 and 1205 cm^{-1}.

The calcium phosphate peaks are removed with acid treatment of the dentin surface (Fig. 4). ATR spectra of dentin where the surface has been etched with 37% phosphoric acid gel (Scotchbond Etching Gel®, 3M) for one minute is shown in Figure 5. The similarity of this spectrum to that of Figure 4 confirms that the acid removes the mineral phase of the smear layer, leaving the collagen spectrum. However, in Figure 5 the effect of the etching gel is seen. In place of the phosphate peaks of smear layer dentin are other broad transmission peaks that extend from about 1300–850 cm^{-1}. The Amide III peaks centered at 1240 cm^{-1} are superimposed on this band. The peaks for this broad band are found at 1120, the strongest at 1080 and another at 940 cm^{-1}. These correspond to SiO_2 with the Si-O-Si stretch at 1080 and the Si-OH at 960–940 cm^{-1}.[18] SiO_2 adsorption from etching gels onto the surface of dentin appears to be confirmed by the ATR FTIR and XPS data. The ATR data suggest that the Si absorbs into the dentin as the IR sampling depth in this wavenumber region is approximately 7–10 microns.[19]

DISCUSSION

The pretreatments with Gluma, Scotchprep and Tenure conditioners all effectively lowered the surface Ca and phosphate concentrations as determined by XPS analysis. This mineral depletion suggests that organic bonding or micromechanical retention within the remaining collagen structure may be responsible for a major portion of the bond strengths recorded for these systems rather than inorganic bonding or chelation. This possibility is strongly suggested by the ATR-FTIR data where the mineral phase is removed to a depth of 7–10 microns (based upon ATR sampling depth) by treatment with the above conditioners.[14]

Scotchprep treatment of the smear layer resulted in a consistent removal of Ca from the surface according to the XPS analysis. This was unanticipated as this primer is not rinsed from the surface, as for the others, but air dried on the surface. It is conceivable that some of the Ca is lost in the excess solution and that some has infiltrated into the dentin tubules and aggregates or complexes there at some depth from the surface. The decrease is far more than can be explained by dilution on the surface from the maleic acid and HEMA. Alternatively, the dried solution could create a maleate and HEMA layer on the surface overlaying the dentin hydroxyapatite. However, because this layer would cause an increase in C/O and C/N ratios, the constant or slightly lower C/N ratio argues against this surface layer.

Of the three propietary conditioners, Tenure Dentin Conditioner was the most aggressive in its ability to remove Ca from the dentin surface. XPS indicates less than 4% of the Ca remains on the surface as compared with the smear layer. The resulting surface has a high C and O concentration indicating bound oxalate but apparently not bound to Ca. Bowen[20] had suggested that NTG-GMA forms ionic bonds to Ca on the surface. This may occur further within the surface. Given the low Ca concentration at the surface the concentration of NTG-GMA at the surface would be small if it chelates on a one-to-one molar basis with Ca. This might be sufficient for wetting and bonding.

Phosphoric acid etching for 1 min. removes Ca and P from the surface. Phosphoric acid etching for 30 secs leaves Ca and P on the surface at less than 30% the normal concentration. Etching of dentin with phosphoric acid gels results in significant surface adsorption of Si in the form of SiO_2 as was also found by Ruse and Smith.[9] This adsorbed SiO_2 might interfere with subsequent bonding or, alternatively, it suggests that the etched surface has an affinity for multivalent cationic oxides even at low pH. This bears further investigation for alternative bonding modalities to acid-preparation dentin.

These preliminary data illustrate the capability of XPS for determining the concentration of atomic species on the dentin surface and the possibility of determining the bond state of the atoms present. Eliades *et al.*[8] have analyzed the surface of dentin after conditioning with several different commercial dentin bonding systems. There is reasonable agreement between their data and ours. They analyzed the dentin after application of GLUMA, Scotchbond 2 and Tenure resins. However, in their work the dentin was argon-ion sputtered through the first 2.0 nm at 0.5 nm increments and, from the resulting high resolution XPS spectra, bonding states were inferred from standard spectra and relative concentrations assigned for given bonding states. Unfortunately, the authors have failed to note that ion milling of proteins or resins can result in damage and fragmentation of the molecules. This altered surface layer can cause erroneous chemical state assignments. A nondestructive way to analyze changes in concentration with depth from the surface is to vary the take-off angle of the photoelectrons which changes the probing depth. Without verification, by this method, that no beam damage occurs, the resulting concentration with depth profiling is highly suspect. In addition, the authors have failed to note the number of samples analyzed and it appears from their materials and methods section that several sites were measured on one specimen for each bonding agent with one section from the same tooth as a control. There is no indication of the number of total specimens used for the reference dentin which was treated with 3% hydrogen peroxide. We have noted a variation in the C/N ratio for fractured dentin as compared with the smear layer. The C/N ratio we have found (Table III) is 7.2 ± 1.6 while they find 11.7 ± 2.2. The value for Ca/P for reference dentin given by Eliades *et al.*[8] is 1.0 ± 0.3 while we find for five samples an average of 1.5 ± 0.2. The Ca/P ratio for fractured dentin is 1.3 ± 0.1. Our values are much closer to the literature values for whole dentin which is 1.58.[21]

We noted a doubling or more in the C/O ratio for Scotchprep, Gluma and Tenure Cleansers while Eliades *et al.*[8] found an increase for Gluma and Tenure and a reduction as compared with the control for Scotchprep. Their result for Scotchprep is surprising as the solution is dried on the surface and a high concentration of maleic acid and HEMA are anticipated to remain on the dentin which could be expected to increase the C/O ratio, particularly as the Ca/P and Ca/C ratios for all treatments were found to decrease significantly. A lowering of the oxygen concentration with loss of phosphate is expected but this could be compensated to varying degrees by the remaining maleate-HEMA, EDTA, or oxalate depending on the conditioner.

CONCLUSIONS

1. Phosphoric acid etching for one minute removes detectable levels of Ca or P.
2. Phosphoric acid etching for 30 seconds leaves Ca and P on the surface, at less than 30% of the normal concentration.
3. Etching of dentin with phosphoric acid gels results in surface adsorption of Si in the form of SiO_2 as observed by both XPS and ATR FTIR.
4. All dentin conditioners significantly lowered the amount of Ca and P on the surface.
5. The Ca and P depletion of the surface suggests that organic bonding or infiltration of the collagen with resin is likely responsible for the major portion of the bond strengths recorded for these systems.

References

1. A. Linde, "Dentin: structure, chemistry and formation" in *Dentine and Dentine Reactions in the Oral Cavity,* A. Thylstrup, S. A. Leach and V. Qvist, Eds. (IRL Press, Washington, D.C., 1987), pp. 17–26.
2. H. J. Busscher, H. M. Uyen and J. Arends, "Physio-chemical properties of the dentin surface relevant for adhesion" in *Dentine and Dentine Reactions in the Oral Cavity,* A. Thylstrup, S. A. Leach and V. Qvist, Eds. (IRL Press, Washington, D.C., 1987), pp. 225–234.
3. R. Dippel, D. C. Broggreven and A. R. Hoppenbrouwers, "Morphology and permeability of the dentinal smear," *J. Prosth. Dent.* **52,** 651–662 (1984).
4. S. Kubo, W. J. Finger, M. Muller and W. Podszun, "Principles and mechanisms of bonding with dentin adhesive materials," *J. Esthet. Dent.* **3,** 62–69 (1991).
5. D. B. Ratner, P. K. Weathersby, A. S. Hoffman, M. A. Kelley and L. H. Scharpen, "Radiation

grafted hyrogels for biomedical applications as studied by ESCA technique," *J. Appl. Polym. Sci.* **22,** 643–664 (1978).

6. D. M. Hercules and R. L. Craig, "Composition of fluoridated dental enamel studied by photoelectron spectroscopy (ESCA)," *J. Dent. Res.* **55,** 829–835 (1976).
7. R. L. Bowen, "Adhesive bonding of various materials to hard tooth tissues. XIV, Enamel mordant selection assisted by ESCA (XPS)," *J. Dent. Res.* **57,** 551–556 (1978).
8. G. Eliades, G. Palaghias and G. Vougiouklalis, "Surface reactions of adhesives on dentin," *Dent. Mater* **6,** 208–216 (1990).
9. N. D. Ruse and D. C. Smith, "Adhesion to bovine dentin-surface characterization," *J. Dent. Res.* **70,** 1002–1008 (1991).
10. V. P. Thompson, T. L. Edler and G. D. Davis, "XPS characterization of dentin and dentin treated with bonding primers," *J. Dent. Res.* **68 (Special Iss),** 958, Abst. No. 733 (1989).
11. R. L. Williams and D. F. Williams, "X-ray photoelectron spectroscopy (XPS) of dentin surfaces." *J. Dent. Res.* **67 (Div Abst),** 673, Abst. No. 269 (1988).
12. V. P. Thompson, A. L. Delisle and S. Sato, "Tensile bonds to artificial caries prepared dentin," *J. Dent. Res.* **71,** Abstract No. 1510 (1992).
13. C. D. Wagner, W. Riggs M., L. E. Davis, J. F. Moulder and G. E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer, Eden Prairie, MN, 1979).
14. T. L. Edler, E. Krikorian and V. P. Thompson, "FTIR surface analysis of dentin and dentin bonding agents," *J. Dent. Res.* **69,** Abstract No. 1534 (1991).
15. G. D. Davis, "Use of surface behavior diagrams to study surface and interfacial reactions," *Surf. and Interface Anal.* **9,** 421–429 (1986).
16. R. J. Jakobsen, L. L. Brown, S. Winters, T. B. Hetson, D. J. Fink and A. Veis, "Interactions in collagen self-assembly as revealed by fourier transform infrared spectroscopy," *Science* **220,** 1288–1290 (1983).
17. R. T. Bailey and C. Holt, "Fourier transform infrared spectroscopy and characterization of biological phosphates" in *Calcified Tissue,* D. L. W. Hukins, Ed. (CRC Press, Boca Raton, FL, 1989), pp. 93–120.
18. M. Yamane, "Monolith formation from the sol-gel process" in *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes,* L. C. Klein, Ed. (Noyes Publications, Park Ridge, NJ, 1988), pp. 200–222.
19. N. J. Harrick, *Internal Reflection Spectroscopy* (Interscience, New York, NY, 1967).
20. R. L. Bowen and E. N. Cobb, "A method of bonding to dentin and enamel," *J. Am. Dent. Assoc.* **107,** 734–736 (1983).
21. F. C. M. Driessens, "Formation and stability of calcium phosphates in relation to the phase composition of the mineral in calcified tissues" in *Bioceramics of Calcium Phosphates,* K. de Groot, Ed. (CRC Press, Boca Raton, FL, 1983), pp. 1–32.