

617 Micro-structure Evaluation of the Resin Dentin Interface. *J. TAGAMI¹, N. INAI and T. TAKATSU. (Ohtu Univ., Sch. of Dent., Koriyama, Fukushima, & Tokyo Med. & Dent. Univ., Tokyo, Japan).

Previous studies have shown the existence of a resin impregnated layer of dentin, the so-called hybrid layer, at the interface between adhesive resin and dentin. However, the fine, ultrastructural characteristics of this layer are still unclear. The purpose of this study was to investigate the micro-structure of the resin-dentin interface using a field emission electron probe surface roughness analyzer (ERA-8000FE, Elionix, Tokyo, Japan) which also enables observations at extremely high magnification. The surface roughness analysis of the polished specimens indicated that the resin impregnated layer was depressed below the surface compared to the layer of bonding resin and underlying dentin in all materials evaluated in this study (Clearfil Liner Bond 2, Kuraray; All Bond 2, Bisco; Super Bond D-Liner, Sun Medical; Scotchbond Multi-Purpose, 3M). When polished or fractured specimens were observed under high magnification of more than x20,000, micro-spaces were found in and under the resin impregnated layer in all of the bonding systems evaluated. A structure similar to the resin impregnated layer was also observed to be created when only resin composite was applied to the primed dentin without application of bonding resin. It was concluded that bonding resin did not fully penetrate into the superficially decalcified dentin making a porous, weak resin-impregnated layer. This was true of all of the bonding systems tested. This indicates that most hybrid layers are more porous than is commonly thought and may contribute to hydrolytic degradation of both resin and collagen components of resin-infiltrated layers.

619 An Atomic Absorption Study on the Effect of Concentration on Dentin Demineralization. M. DI RENZO¹, J. GIRGIS², E. SACHER³, I. STANGEL² and T. ELLIS¹. (Univ. of Montreal, ² McGill Univ., ³ Ecole Polytechnique)

The etching of dentin using dilute acids or chelating agents is an inherent first step in most dentin bonding systems. Many of these acids have been shown to remove the smear layer as well as decalcify the surface dentin. However, the rates and mechanisms involved in these treatments are not well understood. In this study, we use atomic absorption spectroscopy (AAS) to study the decalcification rates of dentin at several concentrations of several aqueous acids. The purpose is to qualify and quantify the initial rate of dissolution of calcium from human dentin. Dentin wafers were prepared from human teeth for this experiment. The samples were coated with nail polish, leaving a 5mm diameter circle of exposed dentin. Each sample was immersed in 100 ml of an aqueous acid solution. A control was immersed in water only. The solutions were evaluated using AAS at the wavelength of calcium absorption (424 nm) for the first two minute interval. For samples immersed in maleic acid in the concentration range of 0.2 to 2M, the initial results show that slopes of plots of log calcium intensity vs. log time vary between 0.69 and 0.93, with standard deviations ranging from ± 0.08 to 0.21. An analysis of variance indicated that there are no significant differences among slopes for the different concentrations. The control samples had trace amount signals for calcium. The slope values obtained are consistent with predicted diffusion-controlled reactions, expected to have theoretical slopes of 0.5 for homogeneous materials. The higher values for diffusion rates obtained here may be explained by the heterogeneity of dentin with respect to composition and morphology. We concluded that the various acid concentrations had little effect on the time constant of the initial step of the demineralization, which is diffusion controlled.

621 FTIR Curing Study of Three Dental Adhesive Primers: BPDM, PMGDM, and PMDM. X.J. Qian¹ and B.I. Suh (BISCO, Inc., Itasca, IL, USA).

The clinical performance as well as *in-vitro* bonding efficacy of any dental adhesive depends, among other factors, largely on the degree of cure or crosslinking of the adhesive. FTIR spectroscopy was employed to study the curing characteristics of three commercial dual-curing dental adhesive primers at room temperature: BPDM (All-Bond), PMGDM (Mirage ABC) and PMDM (Tenure S). The effects of self-cure (S/C), light-cure (L/C), and dual-cure (D/C) on the degree of conversion (D.C.) of primers were studied using two different curing Modes: (I) S/C for 620s and then L/C for 10s; and (II) S/C for 180s, L/C for 10s, and then further S/C to 600s of total S/C time. The increases in D.C. (Δ(D.C.)) in each step and total D.C.'s were:

Adhesive System	Mode I			Mode II		
	Δ(D.C.), % S/C 620s	L/C 10s	Total D.C., %	Δ(D.C.), % S/C 180s	L/C 10s	Total D.C., %
All-Bond 2	35.1(2.1)	10.8(2.3)	45.7(3.0)	20.3(1.6)	32.0(1.1)	7.0(0.5)
Mirage ABC	12.5(1.3)	1.1(0.2)	13.8(1.1)	5.1(0.8)	7.1(1.8)	3.8(1.0)
Tenure S	7.5(0.8)	0.0(2.0)	7.5(1.8)	7.1(1.5)	6.2(1.5)	1.1(1.0)

One way ANOVA revealed that BPDM (All-Bond 2) has significantly larger increases (p<0.05) in D.C. than the other two primers in both S/C and L/C situations, and therefore achieves significantly higher total D.C. at the end of Mode I or Mode II curing (Dual-cure). Higher D.C.'s were obtained when the primers were light-cured at an earlier time (after 180s of S/C in Mode II curing), as compared to those when light-cured at a later time (after 620s of S/C in Mode I curing).

623 Relation Between Composite Matrix Molecular Structure and Properties. D. TAYLOR¹, S. KALACHANDRA^{1,2}, Q. XU² and J. MCGRATH². (1) UNIV. OF NORTH CAROLINA, Chapel Hill, NC, and (2) VIRGINIA TECH, Blacksburg, VA.

Dental composite materials based on BIS-GMA require the addition of a diluent monomer to adjust the viscosity of the composite pastes to a useful range. Increasing the content of the commonly used diluent TEGDMA causes an increase in both polymerization shrinkage and water sorption, thus modifications of the base monomer which reduce the need for dilution offer a potential means of improving composites. This project investigated modifications of the bis-phenol in the BIS-GMA core by substitution with phosphate and fluoride containing groups, and replacement of the pendant -OH groups in the glycidyl moiety with -CH₃ and -H. Properties measured include viscosity using a Beckman cone and plate viscometer, wetting by contact angle measurement using a sessile drop technique, and curing shrinkage measured gravimetrically. The required dilutions and resultant shrinkages are shown below. Significant improvements in these properties were found among the experimental monomers.

TEGDMA (%) TO 1000cp VISCOSITY and RESULTANT SHRINKAGE (%)

PENDANT	CORE	BIS-A	CF ₃	PO ₄	CF ₆
-OH	34	8.3		23	8.0
-H	17	5.7	28	7.3	15
-CH ₃	0.0	7.5	14	6.3	2.8

For each core group, substitution of -H and -CH₃ for -OH resulted in progressive reductions in required diluent and shrinkage. At 1000cp all experimental monomers needed less dilution and shrank less than BIS-GMA. Supported by NIH-NIDR grant DE 10156.

618 Acid and Surface Condition Effects on Dentin Bond Strength and Micromorphology. S. DICKENS¹ (ADAHF PRC, NIST, Gaithersburg, MD).

It has been reported that bonding with a carboxylic adhesive to wet dentin treated with H₃PO₄ resulted in higher shear bond strength (SBS). Here, the effect of 4 different acids on bonding to dry or wet dentin and on the surface morphology was studied by means of SBS and transmission electron microscopy (TEM). The acids were chosen because they differed in pK_a, ionic strength, osmolality and chelating potential, and were expected to show different effects under dry or wet conditions from those seen with H₃PO₄. Exposed dentin surfaces were treated with 2.5% HNO₃, 10% citric acid/3% FeCl₃ (10-3), 1.28% (isotonic) formic acid (FA) for 1 min or 10% H₃PO₄ for 30s. After rinsing the surfaces, they were thoroughly dried or kept wet and bonded to a composite via the activated carboxylic adhesive PMGDM and an unfilled resin. SBS after 24 h in MPa ± sd in the order of Duncan's grouping were: H₃PO₄/wet 21.0±1.8^a; 10-3/dry 20.5±6.0^a; 10-3/wet 20.0±6.1^a; HNO₃/dry 17.5±4.3^{ab}; HNO₃/wet 17.0±2.2^{ab}; FA/dry 15.7±3.9^{ab}; FA/wet 13.7±4.1^b; H₃PO₄/dry 12.7±3.7^b (unequal letters indicate significant differences; p<0.05). For TEM the treated specimens were cut into small blocks, subjected to a fixation/dehydration/embedding process and cut into 70 nm-thick sections. TEM showed that all 4 acids removed mineral from a several μm-thick layer adjacent to the surface. On dry dentin TEM revealed distinct differences of the interfaces for the 4 acids: with HNO₃, frequently collapsed, fused collagen fibers were found, while conditioning with 10-3 and FA seemed to have prevented the superficial fusing. Treatment with H₃PO₄ showed crystalline deposits after drying of the dentin surface. Wet conditions for HNO₃ showed collagen bundles oriented towards the surface and for H₃PO₄-treated dentin cavitation at the surface, but no crystalline deposits. 2-way ANOVA, which showed significant differences (p<0.05) for the acids and the interaction between acid and dry/wet surface conditions, indicated that bonding to wet surfaces is important with H₃PO₄. The other acids tested here did not show a similar trend; they bonded equally well to desiccated and to wet surfaces. The sensitive reaction to desiccation of H₃PO₄-treated dentin may be due to the crystalline deposits, detected by TEM, that coat the surface, thereby reducing SBS. Supported by NIDR grant DE05129, ADAHF and NIST.

620 Ultrastructure of wet and dry total-etched resin/dentin interfaces in *Elitebond* S.H.Y. WEI¹, F.R. TAY, A.J. GWINNETT², K.M. PANG (Faculty of Dentistry, University of Hong Kong, ²SUNY at Stony Brook, New York)

Preservation of the morphological integrity of demineralized dentin collagen in their hydrated status may account for success observed in wet bonding procedures (Gwinnett, 1994; Titley *et al.*, 1994). This study investigated the micromorphological differences between a wet and dry total etch bonding technique with the use of *Elitebond*, an alcohol-base, single component dentin adhesive primer system containing diarylsulfonatedimethacrylate (Bisco, Itasca, IL). Twelve 1 mm dentin discs were divided into two groups. They were etched with 10% H₃PO₄ without benzalkonium chloride (All-Eich semigel, Bisco) for 20 seconds and rinsed for 20 seconds. In the wet group, etched dentin surfaces were blotted so that they remained visibly moist prior to bonding. In the dry group, dentin surfaces were intensively air-dried for 30 seconds. *Elitebond* primer and bonding agent were applied individually according to manufacturer's instructions and light cured for 20 seconds. Discs in each group were then bonded together using a chemical cure resin. Each bonded disc-pair was sectioned into two halves. In one half, the resin-dentin interfaces were polished, etched for 3 minutes with plasmarized argon (Plasmatic Systems, Inc., North Brunswick, NJ) and prepared for SEM observation. The other half was completely demineralized in EDTA, stained en bloc and post-fixed together with 0.1% ruthenium red and 1% OsO₄, and processed for TEM examination. Conditioning with 10% H₃PO₄ for 20 seconds did not result in a "partially demineralized zone" within the resin impregnated dentin. The hybrid layer in the wet group was characterized by presence of banded collagen right to the dentin surface, while that in the dry group was covered with an electron dense crust on the surface, along the walls of the tubules and along the course of their lateral branches. (Supported by the CRCG grant, the University of Hong Kong)

622 Thermal and Mechanical Characterization of Composite Materials. D. W. JONES¹, A. S. RIZKALLA, S. BERMINGHAM, E. J. SUTOW & G. C. HALL. (Dalhousie University, Halifax, N.S., Canada).

Objective: To compare thermal expansion (α) and transition temperature (T) for 6 commercial composites. Specimens (discs 6 X 3 mm) were tested (n = 3) in three conditions: i) dry(D) ii) wet(w) and iii) wet-boiled(WB). Prior to testing dry specimens were aged for 4 days in air, hydrated specimens for 2 weeks in distilled water at 37 ± 1°C. The WB specimens were further held for 60 min in water @ 100°C. Thermal analysis (TMA) involved heating from 20 to 100°C at a scanning rate of 10°C/min. The measuring probe applied a force of 100 mN. Modulus values (E) were obtained using an ultrasonic test method. The T values for D ranged from 57.69 to 67.59°C, for W from 60.13 to 69.66°C, and for WB from 52.09 to 60.31°C. Correlations were found for α D < T vs. filler (wt%), α W < T vs. filler (wt%), α WB < T vs. filler (wt%), (P < 0.01). Correlations were also found between filler (wt%) and α values of D, W and WB > T (P < 0.01). The T values for D, W and WB all correlated with filler (wt%) (P < 0.05). Correlations were obtained for T W vs. E W (P < 0.001) and for T WB vs. E WB (P < 0.001). Correlations were found for α W < T vs. E W (P < 0.001), α W > T vs. E W (P < 0.01), α WB < T vs. E WB (P < 0.01) and α WB > T vs. E WB (P < 0.01). No significant difference was found between E W and E WB (P = 0.05). Thermal expansion (α above and below T) and T values of all eight composite materials were significantly affected by both storage and boiling in water (P < 0.01). Surprisingly, boiling the previously stored wet specimens did not significantly affect elastic modulus values for any of the 8 materials (P = 0.05).

624 Dynamic Contact Analysis of Three Dental Restorative Materials. (D.A. SAVETT¹, C. SHEN and K.J. ANUSAVICE, Department of Dental Biomaterials, University of Florida, Gainesville, FL, USA)

Surface modifications brought on by interactions between the liquid media and the material can result in time-dependent changes in contact angle measurement. The purpose of this study was to investigate the influence of liquid media on the dynamic contact angle of a high-copper dental amalgam and two dental composites with different filler contents. A Dynamic Contact Analyzer (DCA 312, Cahn Instruments Inc., Cerritos, CA) was used to measure 1) the advancing and receding contact angles in HPLC grade water and formamide, and 2) the hysteresis relaxation behavior over a prolonged immersion (30-45 min) in HPLC grade water, artificial saliva (pH 6.5) and 0.9% saline solutions (pH 4.5, 5.8 and 7.0). The resin surfaces were polished to a 1200 grit finish while those of the amalgam were finished through 1.0 μm Al₂O₃ powders. Four specimens (15x7.5x1 mm) for each composite and two of amalgam were prepared for contact angle determination. Each specimen was cleaned in a 1:1 ethanol-water ultrasonic bath followed by a four-cycle measurement. Two-way ANOVA indicated that material and liquid media significantly affected the advancing contact angle (p<0.0001), but not the receding contact angle. The hysteresis relaxation profiles (changes of wetting force with time) of the composites in water exhibit an initial repulsive force, during the first 8-12 sec, followed by a logarithmic increase. When placed in artificial saliva or saline, the initial repulsive force increased significantly (p<0.0001) and represents approximately 0.25% to 0.35% of the dry mass. This repulsive force was observed with amalgam in all media and represents 0.15% to 0.58% of the dry amalgam mass. Hysteresis relaxation reflects the surface modifications caused by the chemical and physical heterogeneity of the surface and its interaction with the media. This is exemplified by the lack of significant variation in the receding contact angle. The advancing contact angle values, which were significantly affected by the material and the media, were based on a fresh surface, reflecting the heterogeneity of a non-modified surface. In conclusion, surface modification as shown by the hysteresis relaxation significantly affects the contact angle measurement and is important in understanding the dynamic behavior of the surface. This study was supported by NIH-NIDR Grant T32 DE07234-02.