## 1961

Adhesion Mechanisms of Resin to Etched-Dentin Studied by $^{13}C$ NMR. N.NISHIYAMA*, K.KOMATSU, S.MATSUKAWA, K.NEMOTO (Nihon University School of Dentistry at Matsudo, Chiba, JAPAN), and K.SUZUKI (Okayama University School of Dentistry)

Previously, we reported that the application of the N-methacryloyl glycine, NMαA primer to etched-dentin effectively increased the bond strength of resin (*J.Biomed.Mater.Res.*, 31, 379-384, 1996). However, the adhesion mechanisms of resin to etched-dentin through the primer is not clarified yet. In this study, in order to understand how the NMαA primer improves the adhesiveness at the resin-dentin interface, the details of the interaction between the NMαA primer and the dentin were investigated by using the $^{13}C$ NMR. The dentin of the bovine teeth, which was frozen by liquid nitrogen, was reduced to powder by using a ball mill. After this, the dentin particles were demineralized by using 40 wt% $H_3PO_4$ for 15 m, and then were rinsed with distilled water. The insoluble dentin particles were then collected. Next, 0.070 g of the demineralized dentin was suspended into 0.600 g of $D_2O$ containing NMαA, $6.73 \times 10^{-5}$ mol. The pH of the suspension was 1.7. The $^{13}C$ NMR spin-lattice relaxation time, $T_1$ observation of the NMαA was conducted in the presence of the demineralized dentin by using a EX 270 spectrometer (JEOL). In this case, only the NMαA species, which is dissolved in an aqueous solution, is detected in the $^{13}C$ NMR spectrum. When the dentin was added to the NMαA solution, the peak intensity and the $T_1$ values of all of carbons attributed to NMαA were reduced (Scheffe's multiple comparison test, $p<0.01$). This is due to the decrease in the mobility of the NMαA species. This data clearly demonstrated that the NMαA species directly interacted with the dentin. Probably, the un-ionized NMαA species adsorbed on the dentin would promote the adhesiveness at the interface.

Table 1 $T_1$ value (s) of carbons of the NMαA species in the absence or presence of demineralized dentin

| | $CH_2$= | -C- | $-CH_3$ | -CONH- | α-$CH_2$ | -COOH |
|---|---|---|---|---|---|---|
| Absence | 1.1 | 21.6 | 4.1 | 33.0 | 1.3 | 23.4 |
| Presence | 0.6* | 10.9* | 2.9* | 17.8* | 0.7* | 14.9* |

*: Significant difference corresponded to the $T_1$ value of the presence to the $T_1$ value of the absence

## 1962

A PA-FTIR Investigation of the Interactions of PENTA with Dentin. J. XU[1]*, T. ELLIS[1], E. SACHER[2], I. STANGEL[3], (Biomaterials Interfaces Group: [1] Dept. of Chemistry, Univ. de Montréal; [2]Engin. Physics, École Polytechnique; [3]Fac. of Dentistry, McGill Univ.)

Adhesion promoters containing dipentaerythritol pentaacrylate phosphoric acid ester (PENTA) have been shown to form bonds to dentin without first developing a typical hybrid zone. This may be explained by previous FT-Raman and NMR studies (Xu *et al.*, 1996) which have shown that the interactions of PENTA with dentin, collagen and hydroxyapatite mainly occur between PENTA and hydroxyapatite. The purpose of this study was to further explore the reactive mechanism of PENTA with dentin by photoacoustic Fourier transform infrared spectroscopy (PA-FTIR). PENTA was dissolved in acetone to make a solution having a 6% concentration. Several dentin specimens (prepared as disks), type I collagen and hydroxyapatite powder were separately placed in the PENTA solution and left to stand for 2 h. The solution was then filtered off and the samples divided into two parts. The first was allowed to dry in air before recording PA-FTIR spectra. The second was washed at different times with acetone and dried in air prior to recording the spectra. All spectra were recorded on an FTIR spectrometer equipped with an MTEC model 300 photoacoustic detector. The spectrum of collagen washed six times with acetone showed that the PENTA was completely removed from the collagen surface by the washing. However, the spectra of dentin and hydroxyapatite showed that PENTA still remained on the surface, even when washed up to 10 times with acetone. The spectra further showed that the interaction of PENTA with dentin and hydroxyapatite did not seem to involve the carbonyl or carbon-carbon double bonds. These results are consistent with those of previous studies. Hence, we confirm that the interactions of PENTA with dentin mainly occur between PENTA and hydroxyapatite. Supported by the Natural Sciences and Engineering Research Council of Canada.

## 1963

A Field Emission SEM Study of Enamel and Dentin. L. BRESCHI[1]*, I. STANGEL[2], P.GOBBI[1], G.MAZZOTTI[1], T. ELLIS[3], E. SACHER[4]. ([1] Universita di Bologna, Italy; [2]McGill University, [3] Université de Montréal, [4] École Polytechnique, Canada)

The microscopic analysis of surfaces constitutes an important method of elucidating acid effects on teeth. Here, we investigate the first use of a Field Emission in Lens Scanning Electron Microscope (FEISEM) in evaluating acid-conditioning of enamel and dentin. This type of SEM has a resolution power of up to 0.7 nm (7Å), and can work at a very low accelerating voltage to allow better preservation of biological samples. Dentin disks having an intact enamel border were gently dried in air and exposed to phosphoric acid (pH=1.0) for 30 s. After washing and drying, samples were mounted and coated with a 1.5 µm Pt-C film. Observations were made using a FEISEM (Jeol JSM 890) at 7 kV and 1x10-11 amp probe current. For enamel, the repetitive pattern of prisms was clearly detectable in all samples. Both interprismatic and intraprismatic crystals were also clearly recognizable, with the interprismatic crystals showing a longitudinal and parallel orientation to the long axis of the prisms. For dentin, low magnification frontal sections showed an amorphous intertubular (IT) substance not previously observed by SEM. In addition, pores were routinely present in this region. Tubules contained ring-like structures which, at higher magnification, appeared to consist of a fibrous network. Typical collagen banding could be observed on these structures. The fibrous network as well as small orifices of side canals could be observed on the tubular walls of fractured dentin, while the IT dentin appeared to be a compact structure consisting both of crystals without orientation and a non-crystalline amorphous aggregate. We conclude that FEISEM can routinely provide high resolution images of enamel and dentin, and that it has the capability of revealing the defined distribution of crystals and collagen fibers in dental tissues. Supported by ISS 1% Ministero Sanità, Italy and NSERC, Canada.

## 1964

Effect of a Self-etching Primer System on Resin-Dentin Interfacial Ultrastructure. S.H.Y.WEI* A.J.GWINNETT[1], F.R.TAY (The University of Hong Kong, [1]SUNY at Stony Brook, New York)

This study investigated the ultrastructural features of the resin-dentin interface using a self-etching primer system (Clearfil Liner Bond II, Kuraray). TEM features were compared with a dentin adhesive system (All-Bond 2, Bisco) which may be used either with the smear layer intact (no-etch technique) or with the smear layer removed after acid conditioning of dentin (all-etch technique). Eighteen 1 mm dentin discs prepared from recently extracted third molars and were randomly divided into three groups a) All-Bond 2 (no-etch),b) Clearfil Liner Bond II, & c) All-Bond 2 (all-etch). Following the application of the respective dentin primer, discs in each group were bonded together to form disc-pairs using the bonding resin supplied with that system. They were completely demineralized in EDTA and processed for TEM examination. Application of All-Bond 2 directly to smear layer covered dentin resulted in the preservation of an electron-dense smear layer of about 0.2 µm thick within the dentin primer. The underlying intertubular and peritubular dentin was not altered and smear plugs within the dentinal tubules were preserved. With Clearfil Liner II, a hybrid layer was observed that consisted of remnants of the smear layer as well as 1 to 1.5 µm of the underlying demineralized intertubular dentin. Smear plugs were partially preserved within the dentinal tubules. Application of All-Bond 2 following acid conditioning resulted in the total removal of the smear layer and smear plugs and the formation of a hybrid layer that consisted entirely of the intertubular dentin matrix. It was concluded that application of Clearfil Liner Bond II to dentin resulted in a form of hybridization that is intermediate between the hybridized smear layer observed in the All-Bond 2 no etch technique and the hybridized intertubular matrix observed in the All-Bond 2 all-etch technique.

## 1965

Chemical Modifications of Dentin Studied by Photoacoustic FTIR. M. DI RENZO[1]*, T. ELLIS[1], E. SACHER[2], I. STANGEL[3] (Biomaterials Interfaces Group: [1]Chemistry Dept., Univ. de Montréal, [2]Engin. Physics, École Polytechnique, [3]Fac. of Dentistry, McGill Univ.)

We are interested in following the surface modifications caused by chemical agents on dentin using various spectroscopies and microscopies. To determine the effects of acids and a bleaching agent, we studied surface modifications of dentin as a function of time using photoacoustic FTIR spectroscopy. Dentin surfaces were either exposed to a) citric, maleic or phosphoric acid (pH=1.0), b) sodium hypochlorite (12% w/v), or c) both acid and hypochlorite. Spectra of each of the treated surfaces were obtained at different times. For the acids, spectra were obtained at t = 0, 10 and 30 seconds, and 1, 2, 5, 11 and 15 minutes); for the sodium hypochlorite, samples were evaluated at 1 and 2 hours, 1, 2 and 6 days (the spectral changes being more gradual). Samples treated with both acid (maleic acid, 2 minutes) and hypochlorite were evaluated at t = 0, 30 seconds, 1, 2, 5 and 15 minutes after exposure to bleach. Samples were analyzed with an FTIR spectrometer equipped with an MTEC model 300 photoacoustic detector. The results indicated that all acids caused the continuous removal of the mineral phase of dentin as indicated by the reduction of peaks assigned to both calcium hydroxyapatite and carbonate-apatite. The rate of change of spectral features was greatest during the first 2 minutes of exposure, decreasing thereafter with time. Spectra of dentin treated with sodium hypochlorite showed the removal of the organic phase of dentin. The spectra of etched dentin treated with sodium hypochlorite for 2 minutes resembled that of untreated dentin. Further treatment (up to 15 minutes) induced no additional change. We concluded that acid effects on dentin can be followed spectroscopically, and that sodium hypochlorite is an effective agent for dissolving collagen exposed by acid etching. Supported by the Natural Sciences and Engineering Research Council of Canada.

## 1966

Effect of Curing Method on the Amount of Residual Monomer. T. Yucel*, E. Yildiz, and B.Güvener (University of Istanbul, Faculty of Dentistry and Institute of Experimental Medical, Çapa, Istanbul, TURKEY)

The aim of this study was to evaluate the amount of residual monomer of a resin composite (Brilliant, Coltene) cured with visible light and heat techniques. Prior to polymerization, 8 samples per group of composite resin was placed into a Teflon mold (Ø 5 x 2 mm) and cured with a visible light (VL)(Celalux II, Coltene) for exposure times 20 and 40 sec, and distances 1mm and 1cm from the resin surface. Another group of samples with 20 sec curing time from 1mm distance was heat treated in the oven (DI 500, Coltene). After all samples had been generated, they were pulverized and weighed and the unpolymerized resin remaining was extracted with methanol. The TEGDMA and Bis-GMA standard calibration solutions were analyzed by HPLC and peak heights were identified. The mean values of HPLC analysis for each group were as follows:

| | Distance | VL 20 sec | VL 40 sec | Heat |
|---|---|---|---|---|
| Bis-GMA | 1mm | 20.93 ± 9.80 | 10.16 ± 2.06 | 7.96 ± 1.82 |
| | 1cm | 32.47 ± 4.99 | 9.67 ± 3.55 | |
| TEGDMA | 1mm | 12.10 ± 2.60 | 3.40 ± 1.83 | 1.59 ± 0.41 |
| | 1cm | 14.43 ± 2.16 | 5.22 ± 1.23 | |

A one way ANOVA was performed on the polymerization data. It was determined that a significantly greater degree of microhybrid resin polymerization was achievable following heat curing compared to conventional VL curing technique. According our data, we can conclude that the heat curing should be considered a potentially advantageous polymerization method for composite resins. This study supported by Research Foundation of Istanbul University.

## 1967

Nanomechanically Coupled Inorganic/organic Composites With Improved Toughness. J. LUO, J.J. LANNUTTI and R.R. SEGHI* (The Ohio State University, Columbus, Ohio, USA).

The fabrication of composites by impregnation of monomers into acid-catalyzed nanoporous silica gels and its subsequent polymerization *in-situ* has been previously reported. The negative effect of silane coupling and the influence of filler porosity on composite wear resistance for some fillers have been established. We report here the preparation, and toughness evaluation of TEGDMA based nanocomposites reinforced with silica (Snf) and alumina (Alc) based porous precipitates. The precipitates were prepared through hydrolysis and condensation of metal alkoxides. The two experimental composites were formed without coupling agents through standard *in-situ* photopolymerization. Specimens of pure TEGDMA (Tp) and TEGDMA reinforced with silanated (Bs) and unsilanated (Bns) $BaSiO_3$ particles (avg. 0.6 µm, Kerr) acted as the positive and negative controls. Toughness ($K_{Ic}$) was evaluated after one week storage in water using miniature compact specimens in tensile-opening mode. The mean $K_{Ic}$ (sd) of composites Bs and Snf were 1.42 (0.26) and 1.24 (0.18) respectively and were not significantly different (Tukey-Kramer, $p>0.05$). Composite Alc resulted in an intermediate toughness of 1.08 (0.09) and was not significantly different than Snf. Both the experimental nanocomposites resulted in significantly greater toughness than materials Bns and Tp with mean values of 0.82 (0.17) and 0.55 (0.13). The fractured surfaces were examined by SEM. The nature and durability of these unique interfaces are under further investigation. Novel inorganic/organic nanostructured hybrids having good toughness have been produced from porous, unsilanated silica and alumina precipitates. (Support from NIH/NIDR DE11306-01).

## 1968

Wear Resistance of Layered Composites. B.B. HUTSON, V.A. MARKER*, S.L. WENDT, and J.P. FORD (Baylor College of Dentistry – Texas A&M University System, Dallas, Texas, USA).

This study was conducted to determine if there is a synergistic effect on the occlusal contact wear resistance of composites when a microfill is layered over a hybrid. Disks (2 mm thick) were made from four hybrid composites: two traditional (P50, 3M and Clearfil Photo Posterior, Kuraray) and two submicron (Z100, 3M and AP-X, Kuraray). A 1 mm layer of Silux (3M) was then added to each disk. Control specimens consisted of 3 mm thick disks of each hybrid and the microfill. The specimens were exposed to a cyclic high-impact wear force for 5 min. Replicas were made at 0 time, 2 min and 5 min. To access the wear, surface roughness measurements were made using a Surftest 402 (Mitutoyo). $R_a$ and $R_{max}$ results were analyzed by ANOVA and Scheffé's tests ($p<0.05$). All layered specimens showed significantly less wear than the Silux specimens ($R_{max}$=19.7±8.9 µm). P-50 and Clearfil layered specimens exhibited significantly less wear (2.7±0.8 µm and 5.9±3.3 µm, respectively) than the controls (22.9±5.5 µm and 17.2 ± 6.0 µm, respectively). There was no difference in the amount of wear for the layered or control submicron-hybrid specimens. For the control specimens, the differences among materials were similar to results found in other wear studies. The amount of wear produced with this test method was comparable to 3 year clinical results for P-50 and Clearfil. As expected, Silux performed poorly under impact loading but, when backed with a hybrid composite, the microfill surface was as resistant as submicron hybrids and more resistant than traditional hybrids to forces simulating occlusal contact wear. We wish to thank the manufacturers for supplying the materials.