

Adhesive system self-etch functional monomer interactions with hydroxyapatite

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INTRODUCTION: Self-etch adhesives with intermediate pH (between 1 and 2) partly demineralise dentine and do not completely remove all the hydroxylapatite from the collagen fibers. In addition to micromechanical bonding, functional monomers could interact chemically with residual hydroxylapatite surfaces¹ and contribute to the overall adhesive performance of the self-etch systems. The functional monomer of AdheSE (Ivoclar Vivadent, Schaan, Liechtenstein) has two ionisable protons on the phosphonate group. Only the most acidic proton (pKa=1.82) participates in demineralization^{2,3}. The neutralization of this phosphonate charge by divalent calcium cations produces crosslinks in the polymer structure. Our aim was to characterize by ³¹P NMR the products of the reaction between dental hydroxylapatite and the phosphonate group of AdheSE.

METHODS: Dentin particles were prepared from sound molars extracted from patients with eruptive problems. Dentin disks were cut from crown segments parallel to the occlusal surface at the top of the pulp chamber with an Isomet saw. Occlusal enamel was removed by means of a second cut parallel to the sectioned dentin. Peripheral enamel was removed under water irrigation with a diamond burr. Dentin blocks were fragmented in a hydraulic press at 50 GPa pressure (Weber, Remshalden, Germany). The dentin particles collected were sieved to retain fragments smaller than 100 µm.

³¹P NMR spectra were obtained in the solid state with a Bruker 400 MHz spectrometer (Bruker France, Wissembourg, France). The samples were studied pure and in three mixture ratios.

RESULTS: Table 1. NMR table of results showing peak assignments.

Products	NMR		
	Type	Spectra	Chemical shift, ppm
Dentin powder	hpec { ¹ H}	³¹ P	3.86 a
AdheSE primer + Dentin	hpec { ¹ H}	³¹ P	22.85 – 3.91 – 2.37
	CP	³¹ P- ¹ H	22.71 – 3.91 – 2.31
AdheSE + Dentin 1 / 1	hpec { ¹ H}	³¹ P	24.50 – 3.93 – 2.32
	CP	³¹ P	23.74 – 3.92 – 2.30 b
AdheSE + Dentin 2 / 1	hpec { ¹ H}	³¹ P	23.67 – 3.94 – 2.46
	CP	³¹ P- ¹ H	24.01 – 3.94 – 2.33 c

Fig. 1 ³¹P NMR spectra
AdheSE/dentin ratios : 0 in a, 1 in b and 2 in c

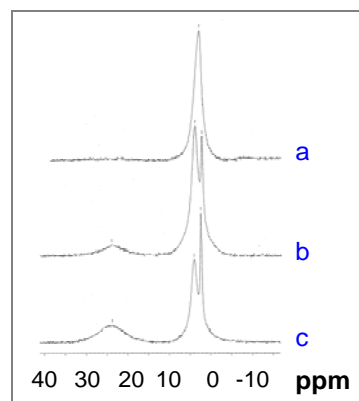


Figure 1 illustrates the NMR spectra. The analysis results is presented in Table 1. The chemical shift for hydroxyapatite is at 3.9 ppm while that of the phosphonate is at 23 ppm. The broad absorption corresponds to the average signal of protonated and deprotonated phosphonates. When AdheSE reacts with the hydroxyapatite, the hydroxyapatite peak decreases in intensity as a function of the acid proportion and a new peak appears centered at 2.3 ppm. This absorption is identified as a new mineral phase: Brushite.

DISCUSSION & CONCLUSIONS: The results show that part of the hydroxyapatite is dissolved by the acidic monomer to yield brushite, a calcium phosphate with a lower Ca/P ratio than that of hydroxyapatite. The rest of the calcium ions dissolved neutralize the phosphonate groups according to the balanced reaction: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 8 \text{RPO}_3\text{H}_2 \rightarrow 6 [\text{CaHPO}_4] + 4 [\text{Ca}(\text{RHPO}_3)_2] + 2 \text{H}_2\text{O}$.

Thus the phosphonate acid groups of AdheSE react with hydroxyapatite, are neutralized by the dissolved calcium ions and lead to the formation of a brushite precipitate. This new metastable phase present in the hybrid layer may evolve with time.

REFERENCES: ¹Yoshida Y et al (2004) *J Dent Res* **83**:454-58. ²Moszner N et al (2005) *Dent Mater* **21**:895-910. ³Nishiyama N et al (2005) *Biomaterials* **26**:2653-2661.

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