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Analysis of Chemical Interaction of 4-MET with Hydroxyapatite Using XPS

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Each dental adhesive contains a specific functional monomer that determines its actual adhesive performance to tooth tissue. 4-methacryloxyethyl trimellitic acid (4-MET) is well-known as one of the functional monomers mostly available and consequently widely used in commercial adhesives. We therefore characterized the chemical interaction of 4-MET with hydroxyapatite (HAp) using X-ray Photoelectron Spectroscopy (XPS). XPS revealed that the peak representing -COO- of 4-MET shifted to a lower binding energy, when 4-MET was adsorbed onto HAp. Deconvolution of this shifted peak disclosed two components with a peak representing unreacted carboxyl groups and ester groups, and a peak suggesting chemical bonding of other carboxyl groups to Ca of HAp. XPS spectra of HAp treated with 4-MET also disclosed the surface to be enriched in calcium and decreased in phosphorus, indicating that phosphorus was extracted at a relatively higher rate than calcium. It can thus be concluded that true chemical bonding of 4-MET with calcium present in HAp occurred, as it was proven using XPS.

Key words: Adhesion, 4-MET, XPS

INTRODUCTION

During the last three decades, aesthetic dentistry has undergone a remarkble progress thanks to continuous and rapidly evolving tooth-bonding technology[1−4]. Currently, adhesive techniques combined with tooth-colored restorative materials are frequently used by clinicians. They restore patients' teeth not only anatomically and functionally, but also esthetically. Furthermore, adhesive technology is also widely used in resin cements for the cementation of in- and onlays, crowns, bridges and posts, and for the bonding of orthodontic brackets. For all these indications, numerous adhesive materials have been developed, and overwhelmed clinicians in a continuous and fairly rapid turnover.

Each dental adhesive contains a specific functional monomer that is commonly an ester originating from the reaction of a bivalent alcohol with methacrylic acid and phosphoric/carboxylic acid derivatives. To a large extent the functional monomer determines the actual adhesive performance. Among functional monomers used in commercially available adhesives, 4-methacryloxyethyl trimellitate anhydrate (4-META) or 4-methacryloxyethyl trimellitic acid (4-MET) is well-known as one of mostly used acidic functional monomers. 4-META/MMA-TBB resin has for instance been widely used in orthopedic and prosthetic dentistry. It also suits well for use in periodontal tissues, such as for retrograde root[5] sealing and for treatment of vertically fractured roots[6−8]. 4-MET thanks its wide indication area to its good adhesive durability to dentin[9,10] and cementum[11], and to its high biocompatibility[12].

4-MET is the active ingredient of many currently available self-etch adhesives[13−16]. In contrast to etch-and-rinse adhesives that involve phosphoric-acid etching, self-etch adhesives containing 4-MET only partially demineralize dentin, leaving HAp partially attached to collagen within a submicron hybrid layer[14,16]. It has been suggested that this residual HAp may serve as receptor for chemical interaction with the functional monomer, subsequently contributing to the eventual adhesive performance in addition to micro-mechanical hybridization.

However, the interaction of 4-MET with dental tissues has not been fully characterized using chemical analytical techniques. The aim of this study is

therefore to characterize chemically the interaction of a 4-MET with synthetic HAp. X-ray Photoelectron Spectroscopy (XPS) was used to study potential chemical bonding of 4-MET with apatitic hard tissue.

MATERIAL AND METHODS

The functional monomer 4-MET (4-methacryloxyethyl trimellitic acid) and its calcium salt 4-METCa were provided by GC (Tokyo, Japan). From 4-MET, a 15% (w/w) solution including 45% (w/w) ethanol and 40% (w/w) water was prepared. HAp plates (APP-101, Pentax, Tokyo, Japan) were treated with the 15% (w/w) 4-MET solution at 37℃ for 30 min, followed by ultrasonic rinsing twice in 52.9% (w/w) ethanol for 20 min. Then, the specimens were chemically analyzed using X-ray Photoelectron Spectroscopy (XPS, AXIS-HS, Kratos, Manchester, UK) *in vacuo* of less than 10^{-7} Pa. Al-Kα monochromatic X-ray with a source power of 150 W was utilized. Wide and narrow scans were measured at a pass energy of respectively 80 and 40 eV. Quantitative data were obtained from peak areas, and identification of chemical states was made from detailed measurement of peak positions and separations. The average binding energy per functional group or atom was statistically analyzed for significant differences using a Student t test at a significance level of 0.01.

RESULTS

Fig. 1 shows XPS wide-scan spectra of untreated HAp and of HAp treated with 4-MET for 30 min, respectively. Both spectra are alike, except for the C 1s peak at a binding energy of approximately 285 eV that appeared when HAp was exposed to 4-MET. The intensity of the weak C 1s peak of untreated HAp, representing common carbon contamination of the surface (Fig. 1a), considerably increased when HAp was treated for 30 min with 4-MET (Fig. 1b).

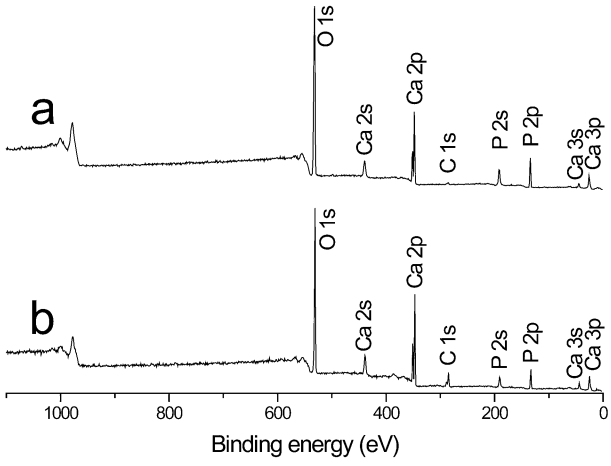

Fig. 1 XPS wide-scan spectra of untreated HAp in (a),and of HAp treated with 15% (w/w) 4-MET for 30 min in (b).

Application of 4-MET on HAp resulted in a significant shift of the peak representing carboxyl groups and esters to a lower binding energy and an increase of its FWHM (full width at half maximum) (Fig. 2). Deconvolution of the shifted peak disclosed two components, representing either esters and unreacted carboxyl groups, and carboxyl groups that reacted with Ca of HAp (Fig. 3).

Comparison with XPS data of $CaHPO_4$, $Ca(H_2PO_4)_2$. H_2O and of 4-METCa suggests that 4-

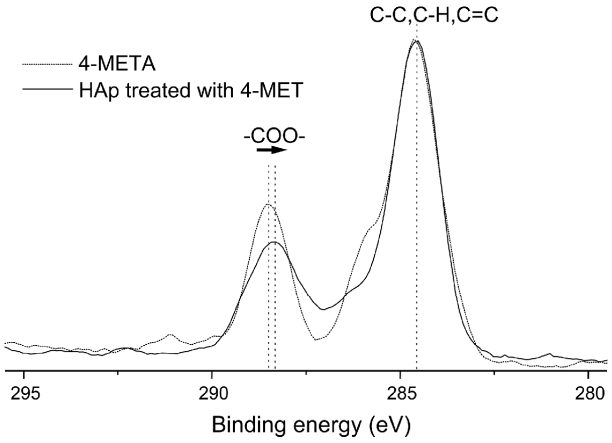

Fig. 2 XPS narrow-scan spectra of the C 1s region of 4-META (4-methacryloxyethyl trimellitate anhydride) powder (top spectrum) and of HAp treated with 15% (w/w) 4-MET for 30 min (bottom spectrum). As compared to 4-META powder, the carboxyl peak had shifted to a lower binding energy.

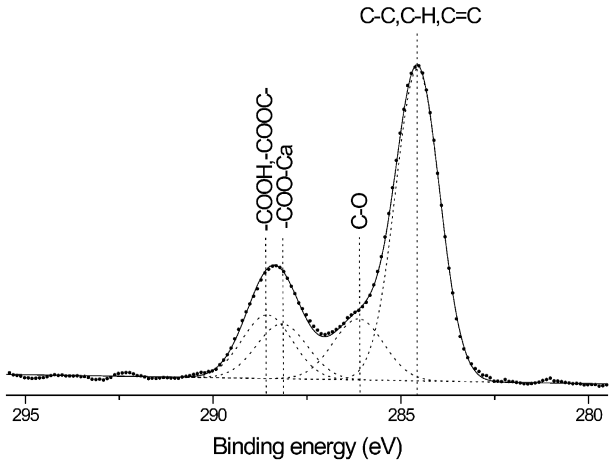

Fig. 3 XPS narrow-scan spectra of the C 1s region of HAp treated with 15% (w/w) 4-MET for 30 min. Peak deconvolution revealed that almost all carbon originated from 4-MET with a peak at 284.6 eV representing C-C, C-H and C=C bindings, a peak at 286.1 eV representing C-O bindings, and a peak representing ester and carboxyl groups.

Table Average binding energy in eV.

	C 1s	Ca 2p	P 2p	Δ (Ca 2p, P 2p)
4-MET	284.60*	----	----	----
Hydroxyapatite (HAp)	284.60*	346.67 (0.19)	132.70 (0.14)	213.97 (0.16)
4-MET on HAp	284.60*	346.78 (0.04)	132.72 (0.06)	214.06 (0.05)
$CaHPO_4$	284.60*	347.24 (0.16)	133.44 (0.17)	213.80 (0.05)
$Ca(H_2PO_4)_2 . H_2O$	284.60*	347.74 (0.23)	134.38 (0.36)	213.28 (0.03)
4-METCa	284.60*	347.13 (0.07)	----	----

*Binding energy taken from literature and used as calibration reference;
Values connected by line are not statistically different (*t*-Test: $P>0.01$);
$n>5$ for $CaHPO_4$ and $Ca(H_2PO_4)_2 . H_2O$; $n>10$ for the other measurements (n=number of samples studied).

MET bonded to HAp through its carboxylic groups that ionically bonded to calcium of HAp (Table).

DISCUSSION

Although retention of adhesive tooth restorations for a reasonable time is no longer a clinical problem, maintaining the margins of adhesive restorations sealed against leakage phenomena remains the major factor that shortens clinical longevity. The fundamental principle of adhesion to tooth substrate is based upon an exchange process by which inorganic tooth material is exchanged for synthetic resin[1−3]. This process involves two phases. One phase consists of removing calcium phosphates, by which microporosities are exposed at both the enamel and dentin tooth surface. The subsequent so-called hybridization phase involves infiltration and subsequent *in situ* polymerization of resin within the produced surface micro-porosities. The resultant micro-mechanical interlocking is primarily based on mechanisms of diffusion. While micro-mechanical interlocking is believed to be a prerequisite to achieve good bonding within clinical circumstances, the potential benefit of additional chemical interaction between functional monomers and tooth substrate components has recently regained attention.

Among several chemical analytical tools, infrared (IR) spectroscopy has most frequently been used in an attempt to demonstrate chemical bonding[17−19]. However, IR could never reveal indisputable evidence of chemical bonding[20−22]. While the reaction of carboxyl groups with calcium can be detected using IR, it is not possible to distinguish between carboxyl groups of the acidic monomer that chemically interacted with calcium at the HAp interface and those that merely participated in gelation through reaction with calcium extracted from HAp. To detect true chemical bonding at the interface, chemical information must be gathered exclusively from the bonded layer within a few nm at the interface. Indeed, one of the most difficult problems in material science is to study the chemistry at interfaces. XPS is a highly selective and specific method of surface analysis[20,21]. The method allows the upper 1 to 10 atomic layers (0.5 to 5 nm) to be investigated with a detection limit of 0.1-1 at%. However, XPS is only capable to acquire detailed chemical information of the interaction between the two materials at an atomic scale on the condition that an ultra-thin film of the molecule with chemical bonding potential is present on top of the substrate.

Based on the chemical interaction of 4-MET with HAp, the obtained XPS data clearly indicate that the carboxyl groups of 4-MET bonded chemically to calcium of HAp, based on the following:

(i) As can be derived theoretically from the chemical formula of 4-MET, the ratio of C-C/C-H/C=C bindings to C-O bindings and to -COO- bindings is 9 to 2 to 4. Peak area analysis of the peak that appeared upon interaction of 4-MET with HAp, revealed areas of respectively 9.1 ± 0.2 for the C-C/C-H/C=C peak, and of 2.0 ± 0.0 for the C-O peak, when the area of the -COO- bindings was taken as 4. The theoretical and measured peak ratios are alike, thus indicating that the recorded C 1s peak represented 4-MET that was attached to HAp. This C 1s peak cannot represent any carbon contamination, as it would have resulted in totally different peak area ratios (Fig. 3).

(ii) Carboxyl groups of 4-MET were detected to have ionically bonded to calcium of HAp, as was demonstrated by a significant shift of the -COO- peak to a lower binding energy. This is indicative for the formation of an ionic bond between the carboxyl groups of 4-MET and Ca of HAp (Fig. 2)[21−24].

(iii) Calcium salts, such as $CaHPO_4$ and $Ca(H_2PO_4)_2$, were not detected at the treated surface, because the binding energies of Ca 2p and P 2p of treated HAp and the difference between the binding energies of Ca 2p and P 2p, Δ (Ca 2p, P 2p), are significantly different from those of $CaHPO_4$ and $Ca(H_2PO_4)_2$ (Table). Consequently, any phosphate detected in the spectra of HAp treated with 4-MET must be attributed to HAp, and cannot originate from PO_4^{3-} extracted by 4-MET.

(iv) The binding energies of Ca 2p for HAp treated with 4-MET (Table: 346.78 eV) are significantly different from the binding energy of Ca 2p in the

control calcium salt of 4-MET (Table: 347.13 eV). Therefore, the XPS-spectra of HAp treated with 4-MET could only have been recorded from an ultra-thin layer that was bonded to the substrate. Carboxyl groups that merely participated in 4-METCa through reaction with calcium extracted from HAp did not remain on the surface (see also (v)).

(v) The FWHM of Ca 2p of HAp treated with 4-MET (1.32 ± 0.01 eV) was smaller than that of untreated HAp (1.38 ± 0.06 eV). In addition, deconvolution of the Ca 2p peak of HAp treated with 4-MET did not show a peak at 347.1eV, which would have represented 4-METCa (Table). This excludes the final possibility that the Ca 2p peak of HAp treated with 4-MET could have represented partial bonding of a multi-layer 4-METCa to HAp with areas of attachment interspersed with areas of non-attachment. In the latter case, the FWHM of the Ca 2p peak would have been expected to be larger, because it would then originate from both 4-METCa and pure HAp.

(vi) XPS of HAp treated with 4-MET disclosed surfaces enriched in Ca and reduced in P, indicating that P was extracted at a relatively higher rate than Ca. The Ca/P ratio of HAp significantly increased from 1.30 ($+/-0.02$) to 1.46 ($+/-0.03$) when treated with 4-MET. All these XPS results support the proposed mechanism in which carboxylic groups replace PO_4^{3-} ions of the substrate and make ionic bonds with Ca ions of HAp.

The fact that these effects were detected after thorough ultrasonic cleaning suggests that 4-MET has a strong chemical bonding potential to calcium-containing substrates, such as tooth and bone tissues. In summary, true chemical bonding of 4-MET to calcium present in HAp has been positively demonstrated using XPS.

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