



Nano-controlled molecular interaction at adhesive interfaces for hard tissue reconstruction

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ABSTRACT

Although decayed/fractured teeth can be reconstructed minimally invasively and nearly invisibly using adhesive technology, the clinical longevity of dental composite restorations is still too short. Water sorption is thought to be the principal cause of destabilization of the biomaterial–tooth bond. However, the actual mechanisms of interfacial degradation are far from understood. Here we report how nano-controlled molecular interaction at the biomaterial–hard tissue interface can improve bond durability. The use of functional monomers with a strong chemical affinity for the calcium in hydroxyapatite is essential for long-term durability. Correlative X-ray diffraction and solid-state nuclear magnetic resonance disclosed a time-dependent molecular interaction at the interface with stable ionic bond formation of the monomer to hydroxyapatite competing in time with the deposition of less stable calcium phosphate salts. The advanced tooth–biomaterial interaction model gives not only an insight into the mechanisms of bond degradation, but also provides a basis to develop functional monomers for more durable tooth reconstruction.

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1. Introduction

Since 2008 the use of dental amalgam to restore teeth has been forbidden in Norway [1] and since 1 June 2009 in Sweden also [2], mainly because of environmental issues and potential health risks related to its mercury content. Other countries may soon follow [3], so that composites are definitely the materials of choice to directly restore teeth in the least invasive way (Fig. 1). Although decayed/fractured teeth can be reconstructed minimally invasively and nearly invisibly using adhesive technology, the clinical longevity of composite restorations is still too short [4,5]. Bonding is also indispensable in the treatment of root caries lesions (Fig. 1c), the current worldwide prevalence of which increases dramatically with age [6]. However, tooth bonding in the relatively aggressive oral environment is far from perfect. Within a time frame of 3–5 years adhesive restorations lose their marginal seal, leading first to unaesthetic discoloration and eventually caries recurrence

(Fig. 1d–f). This forces dentists to replace restorations too often, leading with each new intervention to further weakening of the patient's tooth and, naturally, also to higher public health costs.

Also in orthopedic medicine, one of the main causes of aseptic loosening of cemented hip replacements is the lack of a compound stable against hydrolysis between the hydrophobic bone cement and the hydrophilic acetabular bone stock [7]. Current hydrophobic bone cements cannot chemically bond to the hydrophilic osseous surface and thus undergo long-term hydrolytic degradation processes, causing the bone–bone cement interface to de-bond. Bone bonding cements containing functional monomers that can directly adhere to bone and thus can complement the current purely mechanical stabilization of orthopedic implants would, therefore, be of great benefit in orthopedic surgery [8,9].

Further improvements in (dental) adhesive technology have been shown to be achievable by synthesis of functional monomers tailored to exhibit good chemical bonding potential to hydroxyapatite (HAp) that remains available within the submicron hybrid layer of so-called 'mild' self-etch adhesives [10–12]. The monomer 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) ap-

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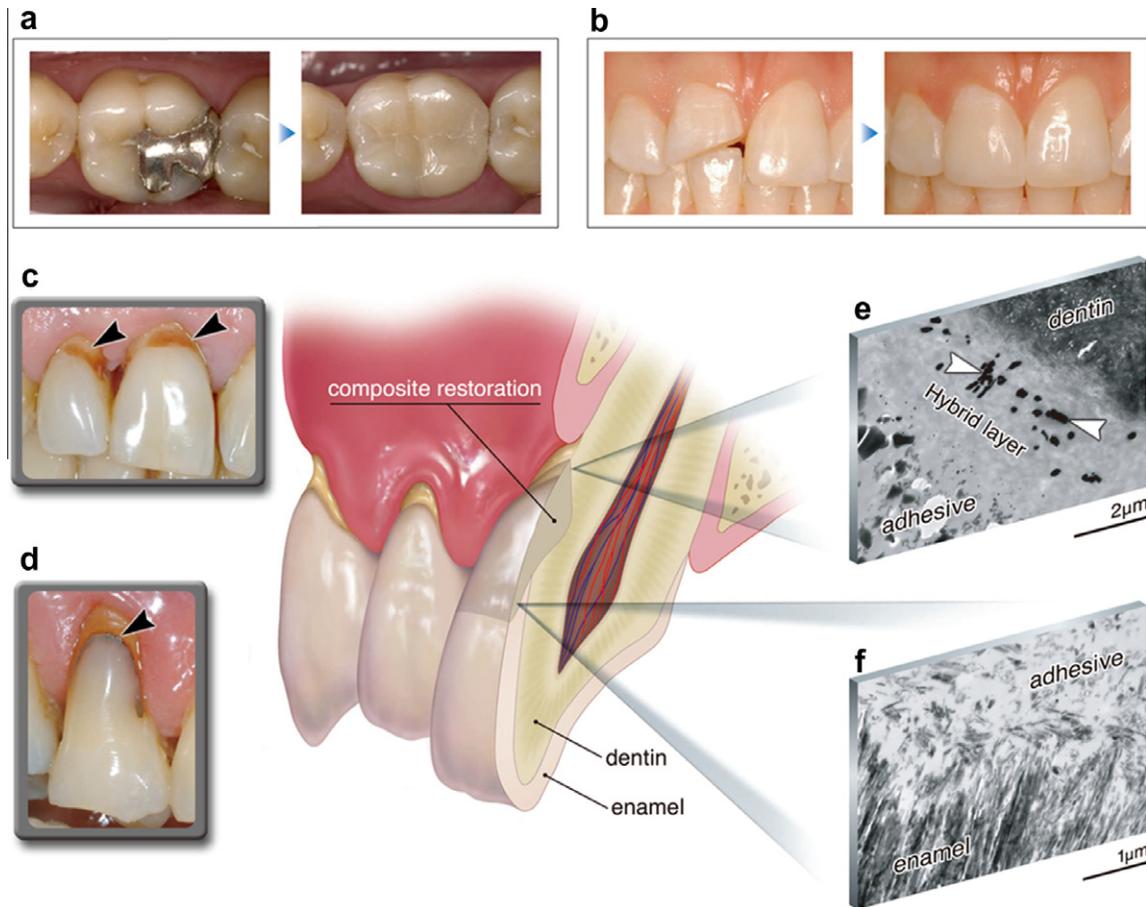


Fig. 1. Potential and limitations of current dental bonding technology. Clinical photographs illustrating the potential of adhesive dentistry (a) to minimally invasively replace amalgam restoration of a molar tooth with a tooth colored composite restoration and (b) to nearly invisibly restore a fractured incisor with composite. (c) Elderly patients present more often with root caries lesions (arrows) that can most effectively be restored using adhesive technology. (d) The clinical longevity of adhesive restorations is still limited, like this cervical composite restoration that failed at its dentin margin (arrow) after 5 years of clinical service. The heavily discolored and leaking restoration margin will, in the long term, develop into a new caries lesion. While the adhesive–enamel bond effectively seals the restoration margin against water sorption through nano-sized channels (commonly referred to as nano-leakage), the bond to dentin is much more vulnerable to nano-leakage. TEM of adhesive–tooth interfaces revealed that silver as a tracer of nano-leakage was clearly omnipresent (arrows) within the hybrid layer on dentin (e), while no silver was deposited at the interface with enamel (f).

pears to not only interact intensively with HAp, its ionic bond with calcium appears to be hydrolytically stable, as compared with 4-methacryloyloxyethyl trimellitic acid (4-MET) and 2-methacryloyloxyethyl phenyl hydrogen phosphate (phenyl-P) [11]. Thus, out of three self-etch adhesives containing one of the three functional monomers, the 10-MDP-based self-etch adhesive appeared most hydrolytically stable in terms of micro-tensile bond strength after long-term thermocycling, with the less favorably performing 4-MET-based adhesive still being more hydrolytically resistant than the phenyl-P-based adhesive [13]. For the latter adhesive clear changes in interfacial ultrastructure indicative of bond degradation were observed by transmission electron microscopy (TEM) after long-term thermocycling, while this was less evident for the 4-MET-based adhesive and non-existent for the 10-MDP-based adhesive. Likewise, an experimental 10-MDP-based luting agent showed a better bonding performance to dentin than three other experimental luting agents that differed only in the functional monomer [12]. Again, high bond strength of the adhesive cement corresponded to a low dissolution rate of the calcium salt of the respective functional monomer, as measured by atomic absorption spectroscopy (AAS) [12]. The latter is, according to the adhesion/decalcification (AD) concept, suggestive of a high chemical bonding capacity [14,15]. All the above data indicate that the durability of tooth bonding is related, in part, to chemical interaction of specific functional monomers with inorganic substrate components.

Intimate intermolecular contact may help to prevent nano-leakage [16] and thus prolong the intra-oral lifetime of adhesive restorations [4,5,17]. Chemical interaction of functional monomers with the organic dentin component has also been demonstrated [18,19]. However, it mainly involves hydrogen bonding and possibly van der Waals forces that may, however, be too weak to contribute much to bond durability.

Despite adhesive–hard tissue interfaces having been thoroughly studied ultra-morphologically using diverse techniques such as scanning electron microscopy (SEM) [20,21], TEM [21–23], confocal microscopy [24,25] and even atomic force microscopy [26,27], the complex molecular interactions at the interface have hardly been investigated and are far from understood. Currently, many studies on adhesive technology are, therefore, empirical, with a limited understanding of the mechanisms involved, which has delayed the development of theoretically designed materials with long-lasting adhesive potential. For instance, currently one does not yet understand why, as mentioned above, certain functional monomers have a higher chemical bonding potential than others, why ‘mild’ self-etch adhesives bond less favorably to enamel despite enamel being mainly constituted of HAp (that thus is abundantly available for chemical bonding) and what effect the calcium phosphates that are produced at the interface during self-etching and are embedded in the hybrid layer (since they are not rinsed off using the self-etch approach) may have on bond durability.

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