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Strategies to stabilise dentine-bonded interfaces through remineralising operative approaches – State of The Art

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ABSTRACT

Dental adhesive systems have improved considerably over the last ten years, although shortcomings such as post-operative sensitivity, premature reductions in bond strength, interface and marginal degradation, and biocompatibility are still considered important issues with such materials. Enzymatic degradation of collagen fibrils within the hybrid layer and hydrolysis of polymers are the major factors thought to destabilise the resin-dentine interface. However, "smart" resin-based materials that can interact therapeutically with dental hard tissues and reduce the degradation of the resin-dentine interface via remineralisation of the mineral-depleted dental hard tissues can improve the durability of resin-dentine bonds. Moreover, as the resin-dentine interfaces produced by contemporary adhesives are characterised by low mechanical properties, therapeutic remineralising bonding approaches may also contribute to strengthening of hybrid layers, producing more gradual gradients of stiffness that prevents localised stress concentrations. This review attempted to bring together a number of seemingly unrelated events, to show how they may contribute to improvements in the durability of resin-dentine bonds. Innovative new approaches to remineralise the resin-dentine interface may protect hybrid layers from different types of degradations over time, and have a therapeutic role in caries prevention. Recent investigations have revealed that the air-abrasion technique performed with bioactive glass 45S5 (BAG) is capable of creating a therapeutic bioactive smear-layer-covered surface for bonding procedures. BAG can react with body fluids, evoking hydroxyapatite (HAP) precipitation and remineralisation of dentine at the bonded interface, especially when used in combination with fluoride-releasing materials such as glass ionomer cements (GIC) and resin-modified glass ionomer cements (RMGIC). The remineralising potential of these therapeutic approaches is potentiated in the presence of a calcium-sequestering agent such as poly (acrylic acid). However, GIC-based materials as well as calcium silicate cements are not able to restore the mechanical properties of dentine. Thus, experimental adhesive systems containing (30–50 wt%) ion-releasing fillers with advanced remineralising properties and matrix metallo-proteinases (MMP) inhibitors have been developed and used in combination with resin primers containing Ca-sequestering polyanion acids such as poly(aspartic acid) (PASA) or poly(acrylic acid) (PAA) and biomimetic analogues of collagen phosphoproteins such as sodium trimetaphosphate to remineralise resin-dentine interfaces. This biomimetic approach is able to evoke a "bottom-up" remineralisation that restores the original stiffness (i.e. Young's Modulus) of water-rich/resin-poor dentine-bonded interfaces. The next step will be the commercialisation of resin-based materials such as flowable composites and "smart" adhesive systems containing biomimetic reagents that can remineralise and prevent degradation of resin-dentine bonds to enhance their clinical longevity.

Contents

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1. Overview and basic coverage

It is important to define the terms that will be used in this review. Remineralisation is meant to describe a process of restoring the biomechanical properties of dental hard tissues (i.e. enamel and dentine) that have lost mineral and then, later, regained that mineral. A good example would be remineralisation of acid-etched enamel. The common use of 32–37% phosphoric acid on enamel solubilises several microns of enamel crystallites in a non-uniform manner. This roughened enamel surface contains millions of nano- and micro-sized irregularities that can create mechanical retention when bonded with adhesive resins. The "chalky" appearance of non-resin-infiltrated acid-etched enamel slowly disappear over days to weeks as salivary ionised calcium and phosphates remineralise enamel by epitaxial crystals deposition using the residual apatite seed crystallites to grow more "enamel" layer by layer [1].

Remineralisation of completely demineralised dentine collagen fibrils is far more difficult because the original demineralising event often removes all of extra-fibrillar and intra-fibrillar apatite crystallites. If one demineralise dentine using ethylenediaminetetraacetic acid (EDTA) for a short time, only some, but not all, of the extra-fibrillar apatite crystallites are removed. When exposed to appropriate level of ionised calcium and trivalent phosphates, those surfaces may regain mineral by epitaxial deposition [2].

The use of 32–37% phosphoric acid to demineralise dentine, removes all crystallites from dentine collagen; no extra-fibrillar or intra-fibrillar apatite minerals remain to serve as residue patterns for nucleation of new crystals. If one exposes such dentine to supersaturated solution of Ca^{++} and PO_4^{3-}, the structure will take up mineral, but the mineral will be on the collagen fibrils rather than "in" them. This is usually due to the Ca/P crystals growing too rapidly. In order to reinstate the mechanical properties of dentine collagen fibrils, specific Ca/P compounds such as amorphous calcium phosphate must fill the nanometric-sized gap regions in demineralised dentine collagen [3].

Most authorities agree that these crystals begin in the gap region of the fibrils that are only 40 nm long. If any Ca/P crystals are larger than 40 nm, they may not "fit" into demineralised collagen. This is the case of most contemporary remineralising techniques used to remineralise dentine collagen at the bonding interface (i.e. glass ionomer cements and calcium silicate cements) [4]. Conversely, the most recent research suggests that amorphous (non-crystalline) calcium phosphate enters collagen fibrils in a biomimetically stabilised "fluidic" state. The biomimetic substances that can restrict the size of the Ca/P are generally polyanionic compounds such as PAA, PASA and other poly(carboxylic acids). These all bind ionised calcium to lower its functional concentration and size, while it slowly infiltrates nanometre-sized water-filled spaces within the collagen fibrils.

The presence of nanometre-sized apatite crystallites inside collagen fibrils can only be observed by high-resolution transmission electron microscopy (TEM). Measurements of mineral density using technique such as X-ray density or energy-dispersive X-ray spectroscopy (EDX) only show mineral deposition; too often, that mineral is on and not in collagen fibrils. Such remineralisation cannot re-establish the stiffness of mineralised dentine back to its original values (18-22 GPa). Nano-indentation of resin-dentine interfaces provides important, quantitative information of local hardness and stiffness [5,6]. In multilayer composites, when layers have very different degree of stiffness, application of stress to those composites creates high stress concentrations where the difference in stiffness are greatest. When dentine surfaces are acid-etched to completely demineralise them, the stiffness of the mineral-free water-saturated demineralised dentine matrix was reported to be as lower as 134 KPa [7]. However, even if water-saturated dentine matrix could be perfectly infiltrated with adhesive resins, the stiffness of these polymerised resins is only 3–4 GPa [6]. Thus, one would expect stresses to concentrate at the top of the adhesive and hybrid layer covered with stiff resin composite (10–15 GPa) and at the bottom of the hybrid layer were water-filled demineralised matrices meet the underlying mineralised dentine (18–21 GPa).

Ideal multi-layered composites exhibit a "smooth" gradient of stiffness that precludes localised stress concentrations. When resin-bonded dentine has been "back-filled" with apatite minerals, those regions of the hybrid layers have stiffness values close to 18 GPa, while resin infiltrated regions only 3–4 GPa [5,6]. The ideal dentine hybrid layer would be 2–3 μm of partially demineralised collagen fibrils, held open by infiltration of a 3–4 GPa adhesive resins covered by a flowable resin-based composite that contains calcium and phosphates, along with biomimetic molecules like polyanions acid. The ion-releasing flowable composite would slowly release polyanion-stabilised-calcium and phosphate ions (i.e. amorphous calcium-phosphate), that would slowly replace water in the resin-infiltrated collagen with apatite crystals [8]. This would increase the stiffness of the resin-infiltrated dentine to 10–15 GPa. As the therapeutic resin composite releases its filler contents, the resin-dentine interface would ultimately become filled with apatite crystals so that the stiffness of the completely remineralised dentine can reach values of 18–20 GPa [5,6]. The end result would be collagen fibrils that regained their original stiffness and were re-fossilised so that even their endogenous proteases would be inactive due to remineralisation of the collagen to which they are bound [9].

2. Background and introduction

Dr. Buonocore [10] introduced the first fundamental concepts for the adhesion of resin-based materials to hard dental substrates such as enamel. Essentially, he recommended the use of 85% ortho-phosphoric acid to chemically condition the enamel, thereby forming microporosities in which liquid resin would permeate, creating nano- and micro-resin projections into enamel