Interfacial Mineralization and Antibacterial Mechanisms of a Calcium Salt–Functionalized Universal Adhesive

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Abstract

Objective: To investigate the interfacial physicochemical mechanisms underlying mineral induction, demineralization resistance, and antibacterial activity of a universal adhesive functionalized with calcium 4-methacryloxyethyl trimellitate (CMET).

Materials and Methods: A CMET-containing adhesive (Bioactive Universal Bond; BA, Sun Medical, Japan) was evaluated alongside three commercial universal adhesives lacking calcium salt monomers: Clearfil Universal Bond Quick (CU, Kuraray Noritake, Japan), Prime & Bond Universal (PB, Dentsply Sirona, USA), and Scotchbond Universal Plus Adhesive (SUB, 3M ESPE, USA).

To elucidate mineral nucleation behavior, polymerized BA specimens were immersed in simulated body fluid (ISO 23317, 37 °C). Surface phase formation was analyzed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) to determine crystal morphology and Ca/P ratios.

Interfacial stability under acidic challenge was examined using a dynamic pH-cycling model (pH 6.8–4.5). Adhesives were applied to polished bovine dentin substrates, and mineral distribution across the adhesive–dentin interface was quantified by transverse microradiography (TMR), with integrated mineral loss (IML) serving as a measure of demineralization resistance.

To explore antibacterial mechanisms mediated by soluble components, eluates were prepared from cured specimens after seven-day aqueous storage and serially diluted. After 24 h incubation with *Streptococcus mutans*, *Actinomyces viscosus*, and *Lactobacillus casei*, viable bacterial counts were quantified using propidium monoazide–quantitative PCR (PMA-qPCR), enabling discrimination of membrane-compromised cells.

Results: Immersion in simulated body fluid resulted in the formation of plate-like calcium phosphate precipitates on BA surfaces. EDS revealed Ca/P ratios consistent with octacalcium phosphate–like intermediates, suggesting that CMET provides localized calcium ion availability and negatively charged carboxylate coordination sites that facilitate heterogeneous nucleation and subsequent apatite maturation.

Under cyclic acidic stress, BA exhibited significantly reduced interfacial mineral loss compared with the control adhesives. The reduced IML is presumed to arise from sustained calcium ion release and potential in situ mineral reprecipitation at the hybrid layer, thereby buffering local acidity and stabilizing the adhesive–dentin interface.

Eluate analysis demonstrated concentration-dependent antibacterial activity of BA against *S. mutans* and *A. viscosus*, with detectable inhibition of *L. casei* at higher concentrations. This effect may be attributed to calcium-mediated alterations in local ionic equilibrium and/or monomer-derived interactions affecting bacterial membrane integrity, as reflected by PMA-qPCR results.

Conclusions: Functionalization of a universal adhesive with a calcium salt monomer promotes interfacial mineral nucleation, enhances resistance to acid-induced mineral loss, and exerts concentration-dependent antibacterial effects. These findings indicate that calcium-coordinating methacrylate monomers can serve as active interfacial modifiers, transforming adhesive systems from passive bonding agents into dynamic biointeractive materials.