

## Adhesion in Dental Applications

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### 1. Adhesion to calcified tissue

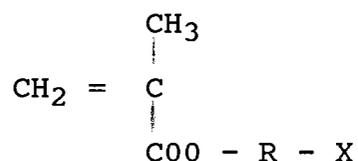
Most dental filling materials shrink on setting, leaving a gap between the restoration and the tooth, with the consequent potential for secondary caries. This problem has become particularly acute with the development of polymeric based composite filling materials, and the shrinkage consequent on the polymerisation of the monomeric component. Clearly if the restorative material can be made to adhere to the cavity wall, then the problem is solved, albeit at the expense of stress development.

The first method used for adhesion to enamel, was to acid etch it (e.g. with citric acid) and rely on mechanical interlocking; this has been surprisingly successful. Achieving adhesion to dentine, which has far less calcified tissue than enamel, is a much more difficult problem.

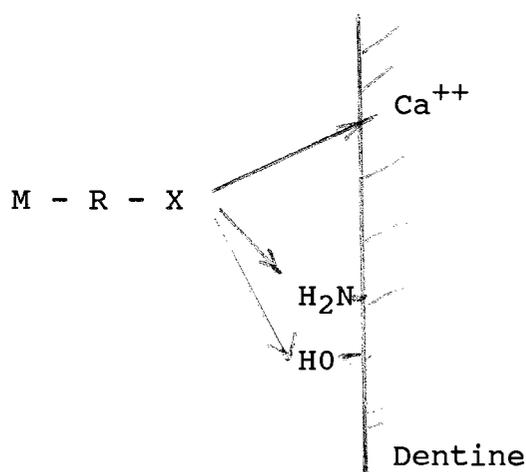
The principle of adhesion is simple enough, produce a molecule with dual functionality, i.e. a methacrylate functionality to copolymerise with the monomer in the filling material, and a functionality either to react with the hydroxyapatite of the dentine, or the amine groups in the collagen or both! (The real difficulty lies in

producing chemical bonds with hydrolytic stability - The mouth is at 37°C with p.H values down to 4).

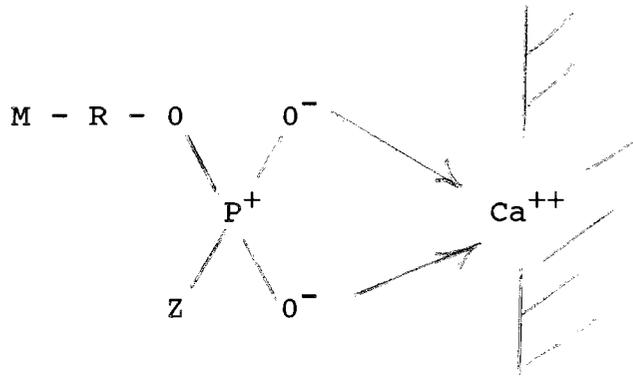
The general structure of a dentine bonding agent is:



Group X can bond to dentine by two different methods namely, to the inorganic part (hydroxyapatite) represented by  $\text{Ca}^{++}$  ions or to the organic part (collagen) represented by amino or hydroxy groups.

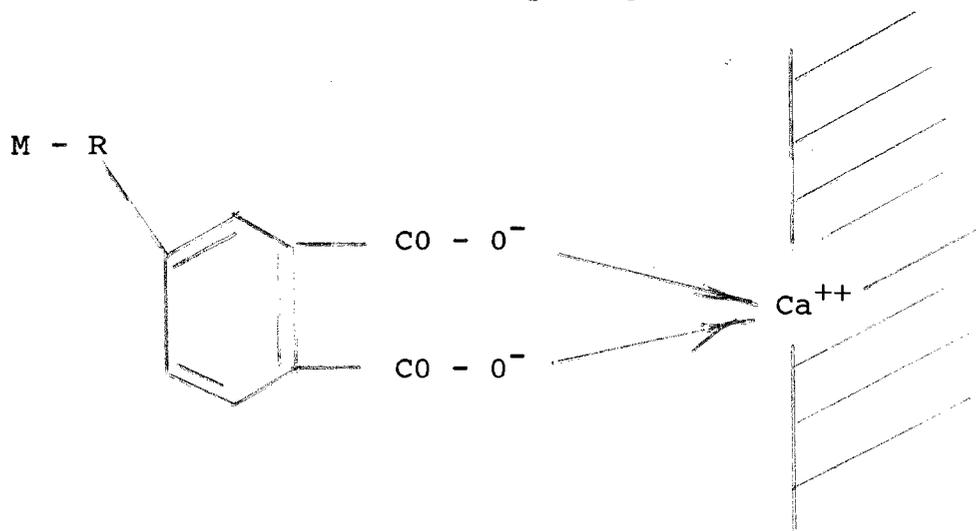


Bonding to the inorganic part of dentine involves ionic interaction between the positive  $\text{Ca}^{++}$  ions in the surface of dentine and negative charges on the group X of the dentine adhesive. In several proprietary dentine adhesives the negative charges of the adhesive molecule are supplied by a phosphate group.



Substituent  $Z$  varies with the adhesive and may be for example a hydroxy group. In 1956 Buonocore et al reported the adhesive properties of a dimethacrylate with glycerophosphoric acid. Bond strengths of 3 MPa were obtained but diminished in water due to hydrolysis of phosphate-calcium bond. Alternatively, a phenyl-phosphate ester has been used with a bond strength of 5 MPa. Adhesion involves electrostatic attraction between  $P^-$  and  $Ca^{++}$  ions. Halogenated phosphates have also been used.

Chelating agents have also been used, such as 4-methacryloxyethyl trimellitic acid anhydride (4-META). Results in improved bonding to dentine when 5% is added to methylmethacrylate systems. The bond is claimed to resist prolonged immersion in water and thermal cycling.



The bond strength can be significantly increased by pre-treatment with certain mordent ions such as Aluminium oxalate (Bowen, Cobb and Rapson, 1982).

Bonding to the organic part of dentine (collagen) has also been attempted. The predominant groups available for specific bonding reactions are amino ( $\text{NH}_2$ ), hydroxy ( $\text{OH}$ ), carboxylic ( $\text{COOH}$ ) and amido ( $\text{CONH}_2$ ). Since dentine collagen is not very reactive, fairly vigorous chemical conditions are needed for grafting.

Masuhara (1969) developed a tributyl borane activated methyl methacrylate (TBB-MMA) resin which bonded to the collagen backbone via  $\text{NH}_2$  groups but the retention was not durable.

Polyfunctional isocyanates which form chemical bonds to the  $\text{NH}_2$  and  $\text{OH}$  groups of collagen have been used. Bond strengths of  $\sim 3\text{MPa}$  were obtained.

The previously mentioned adhesive to collagen gave poor bonding due to dentinal surface water. Consequently adhesives in aqueous solution, such as aldehydes, are of interest e.g., Gluma (Glutaraldehyde methacrylate) supposedly the bonding is initiated by aldehyde attack on the amino group which forms a complex. This reacts with the hydroxy group of the methacrylate monomer (shown as  $\text{RH}$  in diagram), linking  $\text{M}$  to dentine. Bond strengths of  $14\text{MPa}$  were obtained.



These materials have excellent adhesion to calcified tissue which does not deteriorate with time and the G.I. cements make excellent aesthetic filling materials for anterior teeth. Unfortunately they have relatively poor mechanical properties, so cannot be used in load bearing situations.

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## Bond Durability Under Stress in Hostile Service Environments

(A. Maddison, Stoke Golding Applied Research Lab.)

The many advantages of structural adhesive bonding are widely recognised, but doubts concerning service durability persist, particularly when surface treatment options are limited by economic or production constraints.

Bond durability as a function of Adherend pretreatment or other variables is most frequently assessed by measurement of the residual mechanical properties of unstressed specimens after periods of exposure to laboratory-based test conditions. Whilst such strategies are undoubtedly useful for initial screening purposes, more realistic test procedures require the simultaneous application of stress. Improved discrimination of surface treatment effects may be obtained, (1) though care must be exercised in the selection of stress levels, since, for example, artificially high test loads may induce creep failure rather than reproduce the interfacial effects observed in service. It is also important that test media relevant to the intended application are used, and that temperatures approximate to service limits and never approach the  $T_g$  of the adhesive.

Very long period of exposure to static outdoor conditions may be required in order to observe the influence of surface treatment and adhesive type on the durability of standard lap shear joints (2,3). In the absence of space and weight constraints conventional stressing techniques may be considered for use under these conditions.

For use in more confined test environments however, a range of miniature stress tubes has been developed. For example, in studies of the durability of candidate bonding systems for automotive applications, a large number of instrumented versions, each containing a single short diffusion-path bonded joint, with additional unstressed controls, are currently deployed on a long distance heavy goods vehicle in Australia.

Complex cycles of aggressive conditions are encountered, i.e. in addition to daily and seasonal variations, the route includes passage through arid, mountainous, rain forest and marine regions. The remote detection of spontaneous bond failures facilitates early intervention and specimen recovery, and temperature and humidity data are continually recorded. The results obtained will be compared to those generated under laboratory conditions. This dual approach to bond durability evaluation is recommended when the prediction of the mechanisms and kinetics of bond degradation remains uncertain.

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