

Enhancement of the physical properties of the cement by addition of monomer and glass may result from the establishment of an interpenetrating network of the cement embedded in the glass reinforced resin. The improved packing of the cement and better matrix adhesion to residual powder and resin particles may also contribute to the increase in mechanical properties.

Variations in compressive strength were observed with different batches of ingredients. Thus, careful quality control of raw materials is required. Greatest strength was obtained with compositions containing a high percentage of monomer and glass. Strength of the most useful compositions is much superior to that of presently available intermediate restorative resins with the increase in compressive strength ranging from 40% to over 100% and a 200% to 300% improvement in tensile strength. The excellent biocompatibility of the monomer-free cement may be reduced by the addition of methacrylate or glass, especially in high concentrations. Efforts in this study were therefore directed to optimize properties of formulations containing not more than equal parts of the resin and cement components.

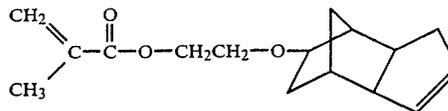
Dimethacrylate monomers yield stronger cements than those prepared with monomethacrylate ingredients. However, when dissolved in hexyl vanillate, EBA and amine, the dimethacrylates have poor storage stability and partially polymerize at room temperature within days. Separate storage of the HV-EBA and the inhibited dimethacrylate and accelerator prior to mixing the ingredients overcomes this problem.

Cements-composites with the best overall characteristics have been obtained with monomethacrylates. The commercialization of a clinically useful product requires a long shelf life of its ingredients. Therefore, somewhat lower strength is compensated for by the much improved storage stability. Methyl methacrylate is too volatile and when used as cement ingredient may yield dry mixes in which a portion of the powder does not form a cohesive mass. Cements incorporating dicyclopentadienyloxyethyl methacrylate (QM-657) either as the only monomeric ingredient or partially diluted with methyl methacrylate have excellent properties. A 70% QM-657, 30% methyl methacrylate (by weight) solution to which HV-EBA has been added mixes well with the powder and yields cements with strength not attainable with similar intermediate restoratives. Excellent properties, especially tensile strength are also obtained on using cyclohexyl methacrylate as monomer.

A big advantage of the cement-composites over the commercial intermediate restoratives which have minimal adhesion is their excellent bonding to various substrates even in an aqueous environment. Tensile strength of the cement-substrate bond reaches as high as 9.9 MPa (1435 psi) to composites and 15.6 MPa (2262 psi) to stainless steel. Failure occurs cohesively within the material in the range of the tensile strength of the intermediate restorative cement-composite. This strong adhesion may have clinical applications in the repair of fractured porcelain or porcelain to metal crown and bridges, to which the cement strongly adheres.

No adhesion of the material to untreated enamel or dentin has been observed in the presence of water. Using HV-EBA-ZnO cement significant adhesion of stainless steel to acid etched enamel has been obtained. Future studies should establish if on pretreatment of dental surfaces the cement bonds to this substrate. The HV-EBA-ZnO cement elicits pulp reactions similar to intermediate restoratives based on eugenol. The

most promising properties for cement-composite restorations were obtained with solutions containing the high molecular weight, commercially available dicyclopentenyloxyethyl methacrylate (QM-657)



without or with and methyl methacrylate as diluent or cyclohexyl methacrylates as monomers. The former monomer according to the manufacturer's fact sheet has low volatility, low odor, low viscosity, low curing shrinkage and is non-mutagenic. Its acute oral toxicity in rats and acute dermal toxicity in rabbits are both greater than 5 g/kg. Acute toxicity screening tests on rabbits are reported to have shown only slight irritation of the eyes and a primary skin irritation index of 2.5. Guinea pigs were not sensitized on exposure.

Hexyl vanillate-EBA-ZnO cements are compatible with acrylic monomers (e.g. dicyclopentenyloxyethyl methacrylate, cyclohexyl methacrylate). Such solutions mixed with powder, made up from silanized glass reinforcing agent and zinc oxide and containing suitable initiator/accelerator systems, have good working properties and harden in a few minutes. The cured materials have compressive and tensile strength one and a half to three times that of eugenol based intermediate restoratives. These cement-composites adhere strongly to composites, non-precious metals or porcelain. Rupture of the bond occurs as the result of cohesive failure.

The foregoing description of the specific embodiments will so fully reveal the general nature of the invention that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phrasing or terminology employed herein is for the purpose of description and not of limitation.

What is claimed is:

1. In a cementitious dental composition comprising a solid phase which includes a metal oxide or hydroxide of a Group II metal or tin and a liquid phase which includes a chelating compound, said chelating compound comprising an ester containing at least one vanillyl group, said ester being the product of a reaction of an alcohol and at least one of a member selected from the group consisting of vanillic acid, isomers of vanillic acid, and homologs of vanillic acid, or other molecules containing vanillyl groups, the improvement comprising a syringic acid ester in an amount sufficient to inhibit caries formation.
2. The cementitious dental composition of claim 1, further comprising a solvent.
3. The cementitious dental composition of claim 1, further comprising a silanized glass powder as filler.
4. The cementitious dental composition of claim 1, wherein the alcohol moiety of the syringic acid ester is n-hexyl or 2-ethylhexyl.
5. The cementitious dental composition of claim 2, wherein said solvent is a chelating agent.