

EXAMPLE 1

As a first step, one drop of 2.5% nitric acid solution was applied to the dentin surface. The surface was rubbed with a cotton pellet wetted with the same acid solution for 60 seconds and then excess liquid was blown off using a stream of air; care was taken so that the surface was not dried excessively. One drop of a 5% acetone solution of the magnesium salt or complex of NTG-GMA, an adhesion-promoting agent, was then applied to the surface. The surface was kept wet with this solution for 30 s, and then excess solvent was allowed to evaporate and the surface blown dry for 60 s. To the surface was then applied one drop of a 10% acetone solution of PMDM, an adhesive resin monomer, and the surface was kept wet with this solution for 30 s, after which time excess solvent was allowed to evaporate and the surface blown dry for 60 s. Finally, an unfilled light-cure resin was applied to the surface for 30 s, then blown thin with air and light cured for 30 s. An amount of conventional self-curing composite restorative material was then applied, and the average tensile adhesive bond strength tested after soaking in water for 1 day. The average adhesive bond strength to dentin with this testing protocol was 2,160 psi (pounds per square inch; 14.9 MPa, $s=4.6$, $n=10$), a result significantly higher than that of the first comparative control described in Example 2.

COMPARATIVE EXAMPLE 2

The adhesive bonding of tooth surfaces to conventional self-curing composite restorative material using the methods of this invention as described herein was compared with a method as disclosed in U.S. Pat. No. 4,964,911 in order to assess the differences in adhesive bonding and tensile adhesive strength between the present invention, employing di- or polyvalent cations, and a method employing monovalent cations.

Commercial samples of the adhesive bonding materials described in U.S. Pat. No. 4,964,911 were used according to the manufacturer's instructions. First, an aqueous solution of phosphoric acid or a mixture of phosphoric and nitric acids along with aluminum oxalate, or phosphoric acid alone, as supplied by the manufacturer, was applied to the surface to be bonded, following the manufacturer's directions. The surface was then rinsed thoroughly with water and dried under a stream of compressed air. Next, a solution comprising a solvent and a mixture of the adduct of N(p-tolyl)glycine and glycidyl methacrylate with its alkali metal salt and a solution of PMDM was applied to the surface, as supplied and directed by the manufacturer's directions. Finally, the same manufacturer's unfilled, light-curing resin was applied and light cured, as directed. Adhesive bond strengths of the resulting bonded surfaces were tested as described in Example 1. Using this method, a lower ranking average bond strength, compared with the methods of the present invention, was obtained: 680 psi (4.7 MPa, $s=3.9$, $n=10$). Because these results were lower than expected, the same protocol was repeated, except that the containers were shaken before dispensing; in this case the average bond strength was 1,400 psi (9.7 MPa, $s=4.4$, $n=9$). These results support the concept of this invention, that polyvalent cations can promote stronger bonding than monovalent cations to cleansed, superficially demineralized surfaces.

EXAMPLE 3

Another alternative embodiment of the present inventive method contains a step calling for treatment of the surface to be adhesively bonded with the lithium salt of p-toluene sulfinate. In the first step of this embodiment of the invention, one drop of 2.5% nitric acid solution was applied to the surface. The surface was rubbed with a cotton pellet wetted with the same acid solution for 60 s and then excess liquid was blown off using a stream of air; care was taken so that the surface was not dried excessively. One drop of a freshly-prepared solution of 2.5% lithium-p-toluene sulfinate in acetone/water (1:1) was then applied to the surface and allowed to stand undisturbed for 60 s before being dried gently with a stream of air. One drop of a 5% acetone solution of the magnesium salt or complex of NTG-GMA was then applied to the surface and let stand for 60 s then dried under a stream of compressed air. To the surface was then applied one drop of a solution of 15% PMGDM (the reaction product of pyromellitic dianhydride and glycerol dimethacrylate), 0.2% camphorquinone and 1.3% N,N-dimethylaminoethylbenzoate in acetone; the solvent allowed to evaporate for 50-60 s, the surface blown dry and light cured for 10 s. An amount of conventional self-curing composite restorative material was then applied, and the average tensile adhesive bond strength was tested in the usual manner after soaking in water for 1 day. Even without the use of an unfilled light-cured resin, which usually results in higher bond strengths, the average strength was 1,580 psi (10.9 MPa, $s=2.0$, $n=10$).

EXAMPLE 4

Additional di- and polyvalent salts or complexes of NTG-GMA were evaluated as adhesion-promoting agents in the same manner as in Example 1. The average tensile bond strengths obtained using these compounds were as follows: aluminum, 2,160 psi (14.9 MPa, $s=6.1$, $n=10$); zinc, 1,970 psi (13.6 MPa, $s=4.9$, $n=9$); calcium, 1,740 psi (12.0 MPa, $s=5.3$, $n=10$); and strontium, 1,540 psi (10.6 MPa, $s=4.1$, $n=10$). As can be seen from these results, using the methods of the present invention results in greater adhesive bond strengths than are obtained using methods employing monovalent cations of these adhesion-promoting agents.

EXAMPLE 5

In another set of comparative evaluations, after aqueous acidic cleansing, dentin was impregnated with acidic (zwitterionic) NTG-GMA or its Na, Mg, or other salt solutions in acetone and then with a PMDM (the adduct of pyromellitic dianhydride and hydroxyethyl methacrylate) acetone solution, followed by application of a composite resin. Mean ($n=10$) tensile bond strengths (see Bowen, *J. Dent Res* 71:615 abstract #796, 1992) were: acidic NTG-GMA, 11.4 MPa ($s=3.4$); Na NTG-GMA, 12.9 ($s=4.6$); and Mg NTG-GMA, 14.9 ($s=4.6$). Average bond strength rankings and storage stability of solutions suggest further development and utilization of divalent and polyvalent cation salts or complexes of NTG-GMA.

It should be understood that the foregoing disclosure emphasizes certain specific embodiments of the invention and that all modifications or alternatives equivalent thereto are within the spirit and scope of the invention as set forth in the appended claims.

I claim: