

**ETCHANT/PRIMER COMPOSITION,
ETCHANT/PRIMER/ADHESIVE MONOMER
COMPOSITION, KITS AND METHODS
USING THE SAME FOR IMPROVED
BONDING TO DENTAL STRUCTURES**

FIELD OF THE INVENTION

The present invention is directed to an etchant/primer composition, an etchant/primer/adhesive monomer composition, kits comprising the same and methods using the same for dental restorative applications. More particularly, the present invention is directed to an etchant/primer composition, an etchant/primer/adhesive monomer composition, kits comprising the same and methods using the same for improving the bond strength of adhesive resins bonded to dentin, enamel, bone, or other such dental structures.

BACKGROUND OF THE INVENTION

The restoration of decayed dental structures including caries, decayed dentin or decayed enamel, is often accomplished by the application of polymer based adhesives to the relevant dental structures. However, typically, polymer-based adhesive resins alone do not form strong bonds with dentin or enamel. To improve the adhesion of polymer-based resins to dentin or enamel, various pre-treatment steps are undertaken. Ordinary pre-treatment steps include an etching step followed by a priming step. Typically, after priming, the adhesive resin is applied as a polymeric adhesive resin or as polymer-forming monomer(s) polymerized on the dental structure in question.

During the etching step, an aqueous solution of inorganic or organic acids is applied to the relevant dental structure, e.g., dentin or enamel. The acid etches the enamel layer and removes the "smear layer" from dentin and demineralizes a surface layer of dentin. The "smear layer" is a coating of debris that forms on the dentin surface as a result of the cutting and grinding processes of, for example, cavity preparation. After etching, a "primer" is applied during the priming pre-treatment step. The "primer" improves the bonding between the subject dentin, enamel, or bone structure and the yet to be applied adhesive resin (or monomer(s) thereof).

The above-noted etchants, primers, resins and monomers are typically applied in a step-wise fashion. In addition to the step-wise etching, priming and polymerizing (applying and curing adhesive resins or monomers) steps, between these steps, one or more rinsing, drying, and rinsing/drying steps may be required. As a result, dental restoration involves using complex, technique-intensive, multi-step restorative procedures.

To simplify these complicated restorative procedures, it would be beneficial to provide a single composition that accomplishes at least both etching and priming. Thus, separate etching and priming steps desirably could be combined into a single step by applying a suitable combination etchant/primer composition. Additionally, it would be desirable to provide a single composition comprising an etchant, a primer, and an adhesive resin monomer. Finally, it would be desirable to provide a kit comprising the same and methods for using the same.

In an effort to formulate multi-component compositions, it was undertaken to investigate whether the addition of an acid to a primer such as N-phenyliminodiacetic acid (PIDAA) might improve the shear bond strength (SBS) of an

adhesive resin such as PMDM (the reaction product of 2-hydroxyethyl methacrylate (HEMA) and pyromellitic acid dianhydride) or PMDGM (reaction product of glyceroldimethacrylate and pyromellitic acid dianhydride) bonded to dentin. A study was conducted to determine the effect on adhesive resin-dentin SBS by incorporating various acidic additives into a primer such as PIDAA.

In particular, various acids (10% w/w H_3PO_4 , 5% w/w ascorbic acid (AA), or 2.8% w/w CPIDAA) added to 0.3M PIDAA (dissolved in acetone:H₂O (1:1 v/v) solution) were evaluated for their effect on SBS. Additionally, a 0.6M PIDAA (dissolved in acetone:H₂O (1:1 v/v)) solution was evaluated as a control for its effect on SBS. The bonding protocol utilized a two-step procedure: the first step was to apply a test self-etching primer (e.g., PIDAA with 10% w/w H_3PO_4 , 5% w/w ascorbic acid or 2.8% w/w CPIDAA, respectively) to a dentin surface for 60 seconds which was then dried with a stream of air. The H_3PO_4 acid and ascorbic acid containing test specimens were rinsed with water and air dried. Thereafter, a 20% w/w adhesive resin of PMDGM (in acetone activated with 0.07% w/w camphorquinone (CQ; visible light photoinitiator)) was applied and light cured (LC) for 20 seconds. The light activated resin composite was then applied to the dentin previously treated with the acid modified or experimental self-etching primers and cured for 60 seconds. After 24 hours storage in H₂O at 23° C., SBS values were measured. SBS values were measured in MPa units (SD, n=10). The results were as follows (MPa (SD)): H_3PO_4 , 5.5 (7.9); AA, 9.1 (6.3); CPIDAA, 13.9 (6.2); and PIDAA (control), 16.9 (5.6). ANOVA indicated significant differences existed between the SBS values measured. Dunnett's multiple comparison test (p<0.05) showed that the SBS values compared as follows: $H_3PO_4 \approx AA < CPIDAA \approx PIDAA$.

These results indicated that adding an acid to an iminodiacetic acid primer such as PIDAA weakened the shear bond strength of the adhesive resin-dentin bond. See "1997 IADR ABSTRACT FOR—ORLANDO" submitted by G. E. Shumacher and J. M. Antonucci entitled "Etchant-Modified N-phenyliminodiacetic Acid as a Self-etching Primer for Dentin Bonding" (submitted September 20, 1996).

Accordingly, one of ordinary skill in the art would have been led to believe that the addition of an acid to an iminodiacetic acid primer yields a self-etching primer that weakens (rather than strengthens) the shear bond strength of an adhesive resin bonded to dental structures such as dentin. Thus, one of ordinary skill would not have been motivated to combine acid etchants with iminodiacetic acid primers to yield a single etchant/primer composition. Consequently, until now, the need for a single self-etching primer composition (e.g., etchant/primer composition or an etchant/primer/adhesive monomer composition) remained unfulfilled.

Accordingly, there is a need in the art for a single self-etching primer composition which does not weaken the SBS between an adhesive resin and the underlying dental structure being restored.

SUMMARY OF THE INVENTION

Thus, it is an object of the present invention to provide a single composition which is a self-etching primer composition (e.g., an etchant/primer composition or an etchant/primer/adhesive monomer composition) for dental restorative purposes that does not sacrifice the SBS between the subject dental structure and the adhesive resin bonded thereto. It is a further object of the present invention to provide a kit and a method for using the same.