The adhesive monomer systems of the present invention may also include free-radical initiator and accelerators. These may either include chemical type (redox systems) in which a peroxide initiator and a polymerization accelerator react at ambient temperatures to initiate the polymerization of the monomer system or a photoinitiator system in which light, such as ultraviolet light, but preferably the visual portion of the spectrum is employed as the energy source to stimulate free-radical initiation. Examples of such chemical initiators include hydroperoxides, peresters or diacyl peroxides, such as benzoyl peroxide. Examples of amine accelerators include tertiary aromatic amines, such as N,N-dimethyl-p-toluidine. Suitable photoinitiators include benzyl-2,3-butanedione, phenyl-1,2-propandione, and camphorquinone (CQ).

Chemical and photo-initiated bonding resins, both with and without a carboxylic acid monomer, such as PMDM, provide significant shear bond strengths between the polymeric composite and dentin. In various experiments, the highest average shear bond strength of 27±5.3 MPa was obtained with a monomer system of PMDM (10% w/w) in acetone activated with camphorquinone on a previously PIDAA treated dentin.

While such monomer systems, including both a single monomeric compound or a plurality thereof and an initiator, optionally including an activator, may be employed in the present invention, it is frequently unnecessary to include an initiator or accelerator of the type commonly used with typical adhesive monomer systems. Thus, when the iminodiacetic acids or their salts used as the etchant/primer compounds of the present invention are applied to a substrate, such as dentin, with only light rinsing or without rinsing the substrate thereafter, it is unnecessary to include a separate initiator and optional accelerator. Because of such behavior, the etchant/primer compositions of the present invention may also be combined with the adhesive monomer systems of the present invention shortly before use, and thereby used in a single component system. Such modes of use result from the fact that the etchant/primer compositions of the present invention function not only as etchants, but also as polymerization activator/co-initiators when combined with ethylenically unsaturated monomers. It is preferred to use the highly effective monomeric bonding agents with surface-active functional groups, discussed above, such as PMDM, when clinically preferred reaction rates are desired. They also behave as polymerization accelerators for certain initiators, including diacyl peroxides, such as benzoyl peroxide, and peroxyesters, such as t-butylperoxymaleic acid. The iminodiacetic acid etchant/primer compositions of the present invention are also effective as photoinitiators/co-activators with vicinal diketones, such as CQ.

While the etchant/primer/adhesive monomer systems of the present invention provide very high shear bond strengths, the mechanical strength between the etchant/primer composition treated dentin and the adhesive polymer composite formed thereafter may be further strengthened by inclusion of catalytic amounts of redox metal compounds in the system. These are typically mixed with the monomer adhesive system when later applied. Such redox metal compounds may be inorganic or organic metal compounds. Exemplary of such redox metal compounds are iron compounds in both oxidation states, such as ferrous sulfate, ferric sulfate, ferrous oxalate, ferric oxalate, ferrous and ferric chloride; copper salts, such as cuprous and cupric sulfate; titanium (III) and (IV) salts; such as titanyl acetylacetonate; cerium (III) and (IV) salts, ammonium nitrate; silver compounds such as silver nitrate, silver citrate and silver benzoate, etc.

The adhesive monomer compositions used in the present invention may be employed in the same manner as they are conventionally employed in conjunction with separate etchant and primer treatments. That is, the etchant/primer composition of the present invention may be applied to the surface of the substrate, such as a dentin surface, and either lightly rinsed with water or the rinsing step eliminated altogether. Thereafter, the adhesive monomer composition may be applied to the substrate surface which has just undergone treatment with the etchant/primer composition.

## Etchant/Primer/Adhesive Monomer

## Compositions and Kits

Because of the properties described above for the etchant/primer compounds of the present invention, various types of systems or kits may be used to form high shear strength bonds between a polymeric material and a substrate, particularly dentin and particularly in a dental procedure. Thus, either a one step or two step procedure may be employed using one of several two-composition systems according to the present invention. Both systems include the etchant/primer composition of the present invention, described above. The systems differ, however, in the second component and the manner in which the systems are employed.

The first system, designated as system (A), includes as a first component, an etchant/primer composition (A1), which may be placed in a separate container or separately packaged or at least maintained separate from the second composition until it is ready to be used. The second component of etchant/primer/adhesive monomer system (A) corresponds to an adhesive monomer system (A2) described above, which includes not only one or more monomeric compounds, but also an initiator and optionally an activator. Like the first component of system (A), (A1), the adhesive monomer composition may be preferably separately packaged or at least kept separate from the etchant/primer compound or composition that corresponds to the first component (A1) until it is to be used.

The etchant/primer/adhesive monomer system (A) of the present invention may be used as described above. That is, a suitable amount of etchant/primer composition (A1) may be removed from its container and applied to the substrate surface and allowed to remain for a period of about 15 to about 180 seconds. Thereafter, either with light rinsing with water or without any rinsing, a suitable amount of the solution of adhesive monomer composition (A2) to form a polymeric matrix and anchor to the substrate, may be removed from its container and applied to the etchant/primer treated substrate. Due to the function of the initiator, the subsequently applied adhesive monomer system will cure and form mechanically strong bonds to the substrate surface.

The second etchant/primer/adhesive monomer system (B), like the aforementioned system (A), includes an etchant/primer composition (B1) as a first component which is, in most instances, the same or substantially the same as the etchant/primer composition (A1) of the system (A) described above. The most significant difference between the two systems is in the second component, the adhesive monomer component or composition (B2). The adhesive monomer composition (B2) of the second etchant/primer/adhesive monomer system (B) differs from (A2) in that it contains a monomer system without the conventional free-