Compliant Phase Reduces Polymerization Shrinkage in Dental Composite Resin

Valerie A. Lee and H. Ralph Rawls

Health Science Center, University of Texas, San Antonio, Texas

ABSTRACT: Commercially available dental composite resins undergo polymerization shrinkage during curing, setting up internal stress that can result in debonding at the tooth-composite interface, tooth fracture and composite failure. Debonding can also lead to marginal leakage and recurrent decay. The presence of a compliant phase, in this case polybutadiene in aggregate form with fumed silica, is shown to reduce polymerization shrinkage in the *bis*-GMA/TEGDMA resin system. The addition of a small amount of the plasticizer triphenylethylene promoted additional reduction in cure shrinkage by reducing the glass transition temperature, T_g. A trend toward reduced cure shrinkage was noted as the polybutadiene : silica ratio decreased within each molecular weight of polybutadiene tested. The optimal formulation tested was determined to be 0.25 wt. % triphenylethylene in *bis*-GMA with aggregates formed from polybutadiene of molecular weight 2–3 million, in a polybutadiene : silica ratio of 0.005. Shrinkage reduction in this system was ~ 42% without loss of Knoop hardness. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2306–2310, 2005

Key words: polymer; polybutadiene; polymerization shrinkage; plasticizer; composite resins

INTRODUCTION

Polymerization shrinkage during curing of dental composite resins often leads to debonding at the tooth–composite interface, marginal leakage, and recurrent decay. Stresses at the bonded interface are known to cause fracture of tooth structure.[1] The production during shrinkage of internal stresses in the composite may also promote mechanical failure of the material.[2] The present generation of nonflowable and flowable light-activated resin composites undergo volumetric shrinkage in the range of 2–9%.[3–6]

Current clinical approaches to reducing the deleterious effects of polymerization shrinkage include placing the restorative material in small increments,[7] resulting in reduced overall absolute shrinkage of the composite, or the application of an elastic liner to the cavity walls,[8] which allows the composite some freedom of movement and thereby reduces stresses at the composite–tooth interface.

Much research is currently underway to produce a nonshrinking or an expanding matrix polymer through modification or replacement of the traditional bisphenol-A and glycidyl methacrylate reaction product (*bis*-GMA). Spiro-orthocarbonates (SOCs) are bicyclic monomers that, upon polymerization, undergo opening of the rings, resulting in expansion. When incorporated into *bis*-GMA/triethylene glycol dimethacrylate (TEGDMA) systems, the presence of SOCs results in decreased shrinkage. The presence of SOCs, however, also results in decreased molecular conversion in the composite, and therefore, decreased mechanical properties, and are not marketed because of these difficulties and other limitations.[9–10]

Epoxy-based monomers have been developed which have a significantly reduced volumetric shrinkage either alone or in comonomer form with SOCs, but slow reaction rates of the epoxy monomer have so far rendered them unsuitable for use as a direct filling material.[11–12]

Liquid crystal monomers, which are in a compact arrangement before curing, show little shrinkage after curing. In addition, polymerization shrinkage in these materials has been shown to be offset by expansion of the nematic-to-isotropic transformation during curing. Shrinkage decreased from 5% for 100% *bis*-GMA/TEGDMA (unfilled) to 2% for 100% liquid crystal. Continuing research into these promising materials is currently underway.[13]

Condon and Ferracane[14] have added silanated, nonfunctional silanated, and unsilanated microfillers to dental resins and tested the contraction stress generated by these materials during curing. The addition of nonfunctional silanated microfillers resulted in a 50%
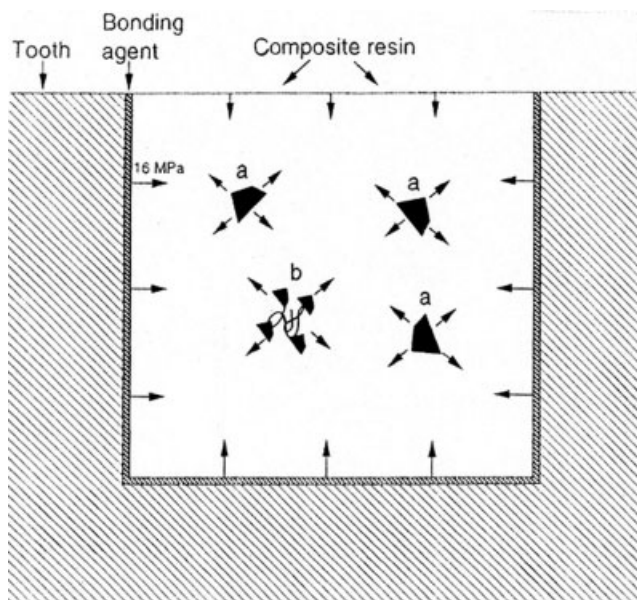
Figure 1 Cross-sectional drawing of prepared cavity with bonding agent and composite resin restoration. Arrows indicate tensile forces generated during curing. Particle sizes are greatly exaggerated. (a) Conventional filler particle; (b) expandable polybutadiene/silica aggregate.

decrease in polymerization stress, whereas unsilanated microfillers, when added to small-particle composite, produced a 30% reduction in contraction stress compared to composite containing silanated microfillers. They proposed that the decrease in contraction stress observed is due to relief of internal stresses at microfiller particle surfaces that are not bonded to the resin matrix.

At present, there is no commercially available solution to polymerization shrinkage other than to increase the volume fraction of the dispersed phase. We describe here a novel means of reducing shrinkage that entails only two simple modifications of existing technology. In the first, a compliant phase material, polybutadiene, in aggregate form with fumed silica, replaces the reinforcing filler. These homogeneously dispersed, compliant aggregates yield under the hydrostatic tensile stress state generated by polymerization and allow expansion, or compliance, of the aggregates, thereby offsetting cure shrinkage and reducing stress at the bonded interfaces (Fig. 1). The second modification is the introduction of a small amount of plasticizer into the matrix monomer. Plasticizers are relatively small molecules that operate by increasing the free volume among polymer chains and allowing the chains to slide past one another more easily. This allows greater molecular accommodation in the developing *bis*-GMA matrix as the degree of cure progresses. This, in turn, allows the developing strain to be more easily translated to the compliant phase, thus further reducing shrinkage.

EXPERIMENTAL

The polymer matrix was formulated as follows: *bis*-GMA, an aromatic dimethacrylate (3*M*), 70 parts by weight; TEGDMA (3*M*; St. Paul, MN), a diluent monomer, 30 parts by weight; 0.2 wt % camphorquinone, a photosensitive initiator (Sigma, St. Louis, MO); 0.27 wt % *N,N*-dimethylaminoethyl methacrylate, an accelerator (Sigma); and triphenylethylene, a plasticizer, wt % ranging from 0.0 to 1.0 (Aldrich, Milwaukee, WI). These ingredients were mixed by hand to a uniform consistency.

Experimental filler was fumed silica (Degussa, 300 m^2/g; Parsippany, NJ) or fumed silica in aggregate form with polybutadiene (Scientific Polymer Products; MW, 5000, 420,000, and 2–3 million). Aggregates were formed by allowing adsorption of polybutadiene of varying molecular weights onto fumed silica from carbon tetrachloride while stirring. After evaporation of solvent, the dried powder was ground and sifted to particle size < 20 μm. Aggregates of polybutadiene/silica ratios of 0.005, 0.05, and 0.5 by weight were produced. Silica or polybutadiene/silica was added to the *bis*-GMA matrix at 10 vol % and mixed in by hand by using a spatula and a glass slab.

A water dilatometer (Fig. 2) was used to measure shrinkage during polymerization. Water for use in the dilatometer was maintained at a temperature of 23.0 ± 0.2°C. Sample holders were stainless steel rings, 3 mm in height by 9 mm outside diameter, to which a layer of plastic wrap was glued to one open side. No bonding agent was applied to the sample holders, so
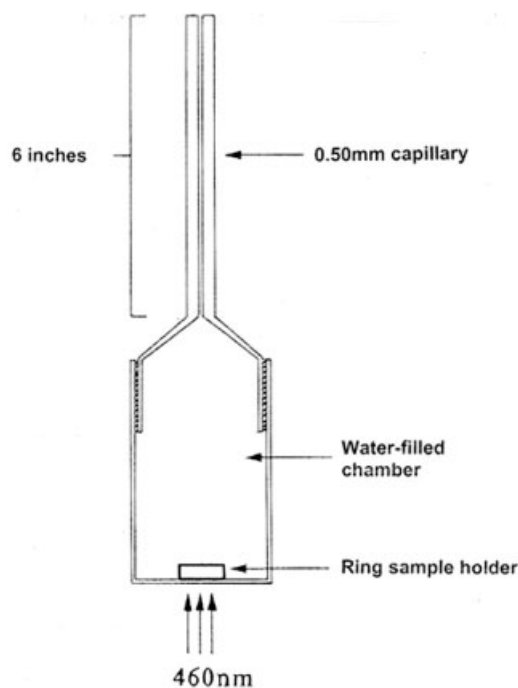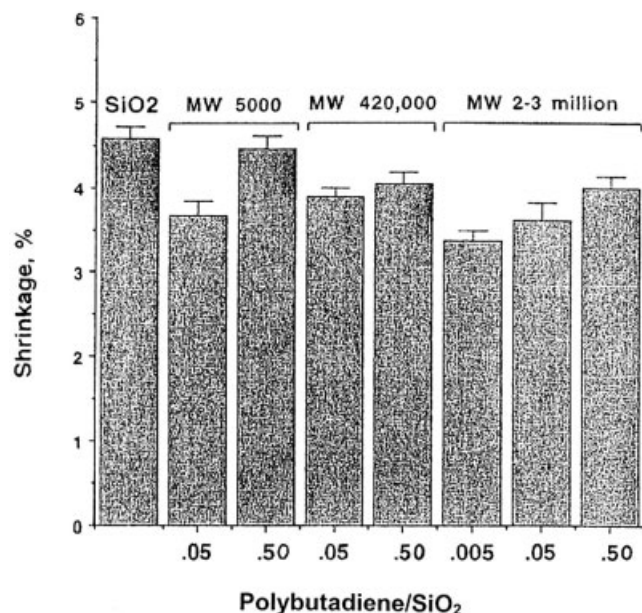

Figure 2 Water dilatometer.

Figure 3 Volumetric % shrinkage versus molecular weight and polybutadiene/silica ratio in *bis*-GMA with 10 vol % silica or aggregate.

the shrinkage measurements were essentially volumetric. Composite samples were filled level with the top of the sample rings and were exposed to a curing light of wavelength 460 nm for 1 min. The drop in water level in the dilatometer capillary was measured to calculate shrinkage. Three samples of each experimental formulation were tested.

A correction for expansion resulting from heat buildup in the water in the dilatometer during exposure was made as follows. Glass plates were glued to both open sides of three sample rings and the rings were exposed to the curing light as described above. The rise of water in the dilatometer capillary was measured and used to correct the shrinkage measurements.

Knoop hardness was measured from the smooth bottom surface of the composite sample, the side oriented toward the curing light and in contact with the plastic wrap. Five hardness measurements were made on each sample.

RESULTS

All aggregate formulations tested resulted in decreased shrinkage when compared to the silica-filled control, ranging from 3 to 26% (Fig. 3). Within each molecular weight tested, shrinkage was reduced as the polybutadiene/silica ratio decreased. A weak trend toward decreasing shrinkage with increasing polybutadiene molecular weight can also be seen in Figure 3. Thus, the largest reduction in shrinkage occurred with aggregates having the highest molecular weight

polybutadiene (2–3 million) and at the smallest polybutadiene/silica ratio (0.005). Shrinkage in this formulation is significantly different than that of the silica-filled control at the $P < 0.05$ level.

Addition of the plasticizer triphenylethylene in weight concentrations ranging from 0.1 to 1.0% to samples containing aggregates (MW, 2–3 million; polybutadiene/silica ratio, 0.005) resulted in additional reduction of shrinkage by 1–24% (Fig. 4).

Because a material's hardness correlates with most mechanical properties, hardness can be used as an estimate of the effect of the two modifications on those properties. Figure 5 shows the effect of increasing triphenylethylene on Knoop hardness of samples containing aggregates (MW, 2–3 million; polybutadiene/silica ratio, 0.005) compared to the fumed silica-filled control. Samples containing up to 0.25 wt % triphenylethylene show no significant difference in Knoop hardness compared to the silica-filled control ($P \gg 0.05$). Above 0.25 wt % triphenylethylene, hardness drops off dramatically.

Of these, so far the optimal system investigated appears to be 0.25 wt % triphenylethylene in *bis*-GMA with aggregates formed from polybutadiene of molecular weight 2–3 million, in a polybutadiene/silica ratio of 0.005. Shrinkage reduction in this system is ~ 42%, producing a final volumetric shrinkage of 2.5%.

Figure 6 shows that a further reduction in shrinkage is realized by increasing the volume fraction of aggregates (MW, 2–3 million; polybutadiene/silica ratio, 0.005; 0.25 wt % triphenylethylene). An increase from 10 to 15% produces a small but significant ($P < 0.05$)
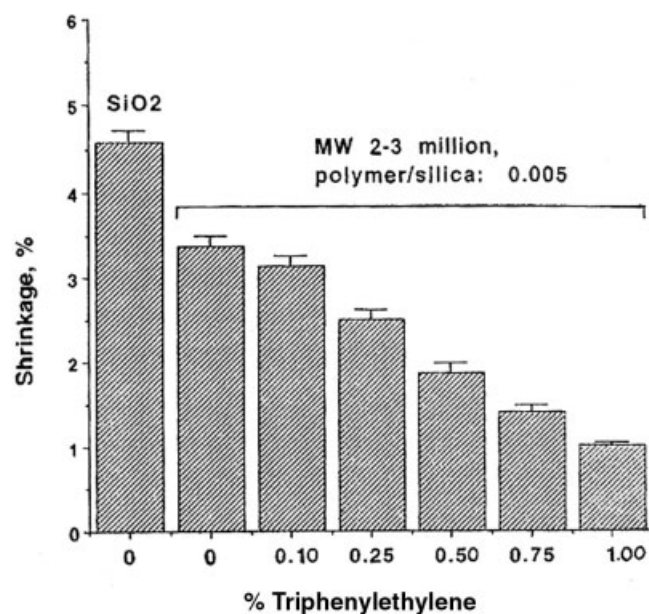

Figure 4 Volumetric % shrinkage versus wt % triphenylethylene in *bis*-GMA with 10 vol % silica or aggregate.
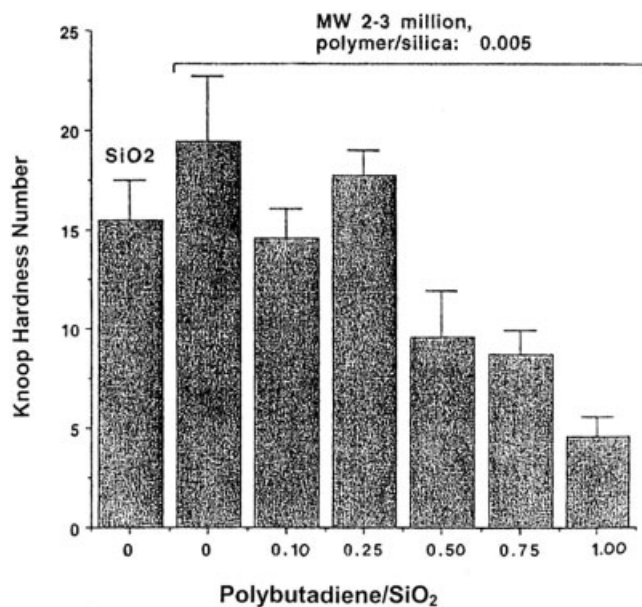
Figure 5 Knoop hardness number versus wt % triphenyl-ethylene in *bis*-GMA with 10 vol % silica or aggregate.

additional reduction in volumetric shrinkage, to 2.0%. Volume fractions above 15% were not easily obtainable by hand mixing.

DISCUSSION

Polybutadiene is a rubber that yields under very low stresses and appears to function well as a compliant material in the *bis*-GMA/TEGDMA system. High molecular weight rubbers exhibit greater ductility because of their larger number of entanglements, which were able to unfold under tensile stress. It was expected that increased ductility would be reflected as reduced cure shrinkage with increasing molecular weight of the polybutadiene at a constant polybutadiene/silica ratio. Although there is some evidence for such a trend in Figure 3, it could not be demonstrated statistically. Molecular weights above 2–3 million were not tested in this work, and their usefulness may be limited by their insolubility in carbon tetrachloride and otherwise suitable solvents.

The trend within each molecular weight of decreased cure shrinkage as polybutadiene/silica ratio decreases is probably due to a larger number of small aggregates produced during grinding, and the consequent larger exposure of polybutadiene surface area to the matrix (Fig. 3). All particles of <20 μm were collected, but the particle size distribution was not determined. Polybutadiene/silica ratios of <0.005 were not tested in this work, but the clear trend within each molecular weight suggests that such work might be fruitful.

The plasticizer triphenylethylene reduces the glass transition temperature (T_g) during curing such that chain mobility remains high for a longer time during the course of the crosslinking and chain extension reaction. Once T_g exceeds the ambient temperature, the matrix becomes glassy and is no longer compliant. Thus, retarding the rate of increase in T_g allows greater compliant offset of cure shrinkage as monomer conversion to polymer progresses (Fig. 4). Figure 5 shows that the plasticizer did not alter hardness at 0.25% or less, but at higher concentrations the composites were rubbery or spongy after curing. The softening effects of a small amount of plasticizer can be offset by the increase in conversion due to retardation of T_g, as discussed above.[15] However, beyond a certain point (>0.25% in this case), the softening effect is no longer offset. As shown in Figure 5, Knoop hardness values indicate that the best compromise between increased molecular accommodation and reduced mechanical properties occurs at a triphenylethylene concentration somewhere between 0.25 and 0.50 wt %.

It is necessary for a bond to exist between the polybutadiene and the polymer matrix in order for expansion of aggregates to occur. It appears that a bond to some extent does exist. It is possible that a chemical modification of the polybutadiene at the aggregate surface would produce a stronger bond with the matrix, perhaps by forming an interpenetrating network, and result in an additional reduction of shrinkage without loss in other properties.

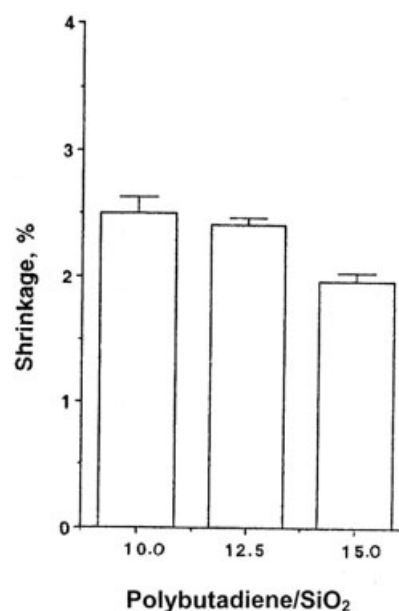Shrinkage values in composite systems are much affected by volume fraction of filler. Higher volume

Figure 6 % Volumetric shrinkage versus vol % aggregate filler, 0.25 wt % triphenylethylene and aggregate of MW 2–3 million, polybutadiene/silica: 0.005.

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fractions displace matrix polymer and reduce the potential for shrinkage. We were not able to incorporate more than a 15% volume loading by using hand-mixing techniques; however, this additional loading reduced cure shrinkage to 2.0 vol % (Fig. 6). It is expected that higher fractions typically found in commercial composites (>50 vol %) would result in still greater reductions in shrinkage. Future studies will explore the upper limits of this approach by using mechanical mixing techniques.

A potential benefit of the use of polybutadiene/silica aggregates as a component of the reinforcing filler is increased fracture toughness of the cured composite. Molecular accommodation, either with or without plasticizer, reduces residual stresses after curing. Crack propagation would therefore not proceed so readily, a very desirable effect in a relatively brittle material. Rubber particles are typically used in crosslinked epoxy resins to increase fracture toughness, although with a significant decrease in elastic modulus. Under applied stress, the rubber particles produce voids, which are effective in crosslinked materials where the molecular weight between crosslinks is large enough to permit shear deformation processes.[16-17] Such a mechanism may well be operative in the highly crosslinked structures of the acrylic resins used in dentistry.

Future work will involve placing polybutadiene on individual silica or zirconia particles, instead of in aggregate form with silica. In the case of nanosized particles, a very large compliant surface area would be exposed to the matrix polymer. Fracture toughness, modulus, and ultimate strength will also be investigated. It is expected that such a system would exhibit improved shrinkage and toughness without loss of mechanical properties. Eventually, attention will also have to be given to ensuring that esthetic properties are maintained.

CONCLUSIONS

These results demonstrate the potential and promise for the incorporation of compliant silica aggregates in place of conventional fumed silica, in whole or in part. Such compliant phases, if optimized, could well reach the goal of near-zero cure shrinkage without significant compromise—or perhaps enhancement—of other properties.

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